Newark Bay Study Area

Fish Sampling and Analysis

Quality Assurance Project Plan

Baseline Human Health and
Ecological Risk Assessment

Tierra Solutions, Inc.

East Brunswick, New Jersey

October 2014

Revision 2

Figure

Appendices

Acronyms and Abbreviations

ABS	Aquatic Biological Survey
AOC	Administrative Order on Consent
BERA	baseline ecological risk assessment
BHHERA	baseline human health and ecological risk assessment
BHHRA	baseline human health risk assessment
CARP	Contaminant Assessment and Reduction Project
CBR	critical body residue
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COPC	constituent of potential concern
COPEC	constituent of potential ecological concern
CPG	Cooperating Parties Group
CV	coefficient of variation
LPRRP	Lower Passaic River Restoration Project
NBSA	Newark Bay Study Area
NOAA	National Oceanic and Atmospheric Administration
QAPP	Quality Assurance Project Plan
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin (dioxin)
PCDF	polychlorinated dibenzofuran (furan)
Problem Formulation	Newark Bay Study Area Problem Formulation (Tierra 2013a)
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
SOP	standard operating procedure
SVOC	semivolatile organic compound
Tierra	Tierra Solutions, Inc.
TRV	toxicity reference value
USEPA	U.S. Environmental Protection Agency

1. Introduction

This document presents the Fish Sampling and Analysis Quality Assurance Project Plan (QAPP) for the proposed sampling and analysis of fish tissue in the Newark Bay Study Area (NBSA). Fish tissue collection is being conducted as part of sampling activities for the baseline human health and ecological risk assessment (BHHERA) which is under Phase III of the Remedial Investigation (RI) for the NBSA. The BHHERA will address the goal "*to determine the primary human and ecological receptors (endpoints) of PCDDs, PCDFs, PCBs, PAHs, pesticides, and metals contaminated sediments in the NBSA*" (U.S. Environmental Protection Agency [USEPA] 2004).

Agreements made during the June 28 to 29, 2011 BHHERA Workshop among USEPA, its Partner Agencies[1] and Tierra Solutions, Inc. (Tierra) resulted in the development of the Problem Formulation for the NBSA (Problem Formulation; Tierra 2013a). Following approval of the Problem Formulation, this QAPP is one of several documents being developed for sampling associated with the BHHERA. The additional planning documents will provide details regarding the collection of shellfish and sediment:

- Crab and Clam Sampling and Analysis QAPP (Crab and Clam QAPP; Tierra 2014)
- Sediment Quality Triad Sampling and Analysis QAPP (SQT QAPP, *to be developed*).

Additional details regarding the proposed sampling program for the BHHERA can be found in the draft technical memorandum entitled *Proposed Risk Assessment Field Sampling and Analysis Program – Newark Bay Study Area* (ARCADIS 2013; Draft, not approved by USEPA).

Specifically, fish tissue data collected under this QAPP will support the following objectives of the BHHERA:

1. Evaluate whether exposure to site-related constituents of potential ecological concern (COPECs) in the NBSA poses unacceptable risks to fish.
2. Evaluate whether the consumption of fish from the NBSA poses unacceptable risks to human and ecological receptors (e.g., birds, mammals).

[1] The Partner Agencies include the U.S. Army Corps of Engineers (USACE), New Jersey Department of Environmental Protection (NJDEP), New Jersey Department of Transportation (NJDOT), National Oceanic and Atmospheric Administration (NOAA), and U.S. Fish and Wildlife Service (USFWS).

2. Background Information

The NBSA is identified as Newark Bay and portions of the Hackensack River, Kill van Kull, and Arthur Kill. Pursuant to the Administrative Order on Consent (AOC) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA Index 02-2004-2010; USEPA 2004), a Remedial Investigation/Feasibility Study (RI/FS) is being conducted by Tierra, on behalf of Occidental Chemical Corporation (the successor to Diamond Shamrock Chemicals Company [formerly known as Diamond Alkali Company]), for the NBSA.

The NBSA is situated within one of the most urbanized and industrialized areas in the United States and is known to be contaminated with a number of chemicals including, but not limited to, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, herbicides, volatile and semivolatile organic compounds (VOCs and SVOCs, respectively), polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs), and metals (NOAA 1995; USEPA 1998).

The majority of the shoreline of the NBSA consists of commercial, developed, or abandoned properties. Information from the Reconnaissance Survey in September 2013 indicates that the majority of shoreline (66 percent) consists of bulkhead and riprap (Tierra 2013b; Draft, not approved by USEPA). Residential and recreational areas are located along the waterfront in many of these bulkhead and riprap areas, particularly along the eastern shoreline. Four new residential areas have been proposed for development (Tierra 2013a).

Due to the size and complexity of the NBSA, USEPA and Tierra agreed in 2005 that the RI would be implemented in multiple phases. Collectively, the Phase I and Phase II investigations gathered information on NBSA sediment, as described in the *Phase I and Phase II Sediment Deposition Report, Revision 1* (Tierra 2011) and the *Draft Phase I and Phase II Data Evaluation and Analysis Report, Revision 1* (Tierra 2013c). Other activities under the RI have included work related to the risk assessments (e.g., *Draft Pathways Analysis Report* [USEPA 2006] and *Screening-Level Ecological Risk Assessment* [USEPA 2008]). As part of the baseline risk assessment process, the Problem Formulation (Tierra 2013a) was developed to document the goals and focus of the baseline risk assessments, and define the questions to be addressed during these evaluations. Additional history and background information on the NBSA can be found in the aforementioned documents.

3. Data Use

The primary objective of this sampling event is to analyze fish tissue samples collected from the NBSA for chemical parameters. Fish sampling is anticipated to occur in the fall (September-October) 2014. Fish community observations (i.e., species of non-target fish) will be recorded during fish sampling to supplement the substantial existing community data for the NBSA. These data will be used to provide general information regarding the relative abundance and structure of the fish community during the time of sampling. In addition, a subset of the fish collected for tissue analysis will be examined by a fish pathologist to provide qualitative information on the overall health of the fish collected from the NBSA. The examination will include overall morphology, gonad condition, presence/absence of lesions, gonadosomatic index, and internal and external physical conditions/abnormalities. Section 5.2 provides additional information regarding the evaluation of fish health.

3.1 Baseline Ecological Risk Assessment

The fish data collected as described in this QAPP, in conjunction with additional data anticipated to be collected under Phase III of the RI, will collectively support the baseline ecological risk assessment (BERA) in evaluating the assessment endpoints for fish, bird, and mammal populations as presented in the Problem Formulation (Tierra 2013a) and summarized below:

Assessment Endpoint No. 4 - Survival, growth, and/or reproduction of fish.

Fish data collected as part of this sampling event will be used as a measurement endpoint to evaluate risks to fish by answering the following risk question: **Are COPEC concentrations in fish tissues from the NBSA greater than critical body residue (CBRs) for the survival, growth, and/or reproduction of fish?** To do this, whole-body COPEC concentrations in fish tissue will be compared to literature-based CBR data.

To aid in the evaluation of potential effects on fish reproduction, individual fish health data will be collected as ancillary information during the collection of tissue for analysis. Further, information on the fish community (species counts) will also be collected to supplement the existing NBSA fish community data (refer to Section 5.3 and ARCADIS [2014]).

Assessment Endpoints No. 5 and 6 - Survival, growth, and/or reproduction of birds and mammals, respectively.

Tissue chemistry data collected as part of this sampling event will be used as input parameters for a food web model to estimate dietary intakes for select bird and mammal receptors by answering the following risk question: **Does the daily dose of COPECs received by birds and mammals from consumption of the tissues of prey species and from other media in the NBSA exceed the toxicity reference values (TRVs) for survival, growth, and/or reproduction of birds and mammals? If yes, what are the probabilities of effects of differing magnitude for survival, growth, and/or reproduction of birds and mammals?** To do this, measured chemical concentrations in fish tissue will be incorporated into the food

web model to estimate a daily dietary ingestion of chemicals. The estimated dosage will then be compared to the literature-based TRV to evaluate potential risks. If potential risks are evident (i.e., the resulting hazard quotient is greater than 1), a probabilistic food web model will be run to estimate the range of possible risks, following work plan approval by USEPA.

3.2 Baseline Human Health Risk Assessment

The tissue data collected during this sampling effort, combined with additional data anticipated to be collected under Phase III of the RI (including sediment and blue crab tissue data), will collectively be used to support the baseline human health risk assessment (BHHRA) by estimating potential human exposures and assessing the potential impact of constituents of potential concern (COPCs) on human health via consumption of fish and shellfish from the NBSA. Potential consumption scenarios are presented in the human health conceptual site model included in the Problem Formulation (Tierra 2013a). Potential risks and health hazards will be evaluated using chemistry data from individual or composite fish fillet samples. The BHHRA will use these data as the basis for quantitatively evaluating the exposure of individuals under current and future scenarios for both cancer and non-cancer health effects following USEPA Superfund guidance, guidelines, and policies.

4. Overview of Sampling Design and Locations

The overall sampling design is a simple, stratified random approach for collecting fish data from within known or likely habitat areas of the NBSA. For simplicity and consistency with the screening level ecological risk assessment and other planning documents and to ensure that the large spatial area of the NBSA is adequately sampled, it has been divided into three zones for planning purposes: Newark Bay North, Newark Bay Central, and Newark Bay South. In addition, the NBSA contains several geomorphic areas, three of which are important for sampling discussions: Subtidal Flats, Transitional Slopes, and Intertidal Areas[2]. While the Navigation and Port Channels may provide overwintering habitat for aquatic organisms (e.g., blue crabs), these areas are regularly dredged for maintenance purposes. As such, the focus of the proposed sampling program is on the shallower Subtidal Flats, Transitional Slopes, and Intertidal Areas of the NBSA. Areas that were historically dredged but are no longer maintained are also included in the sampling program. These include the former Navigation Channel areas in Newark Bay North and south of Shooters Island.

A single sampling event during the fall will be conducted. Field efforts will continue until the required number of fish has been captured or until a 10-day field effort has been expended, whichever comes first. If, after 10 days of sampling, the sample size has not been achieved, sampling may either be continued or postponed until a second field effort is conducted based on consultation between Tierra, USEPA and its Partner Agencies.

At present, Tierra anticipates using regional reference data for biological tissues from the New York/New Jersey Harbor Estuary and elsewhere to evaluate background conditions. This is similar to the approach being used for the LPRRP. The same background datasets are anticipated to be utilized as those used for the LPRRP, with the addition of information for some species that were not found or sampled in the Passaic River.

4.1 Fish Species

The tissue sampling and analysis program proposed for the NBSA targets several fish species that were identified during the BHHERA Workshop and in the Problem Formulation (Tierra 2013a). These target species were chosen to represent key trophic levels and feeding guilds in the NBSA. Species selection was based on their seasonal relative abundance in the NBSA, as determined from more than 10 years of seasonal surveys, and their known importance in terms of being a key forage species, predator species, species of special interest, sport fish, and other considerations, as described in the Problem Formulation (Tierra 2013a).

[2] Refer to the Conceptual Site Model (Tierra 2013d) for detailed descriptions of the geographic and geomorphic areas.

Several species of finfish will be collected from each of the three zones within the NBSA, each from a specific feeding guild. Fish tissue samples composed of forage fish, benthic/demersal fish, and pelagic predatory fish will be collected to characterize tissue COPEC concentrations from different trophic levels. Target receptors will be collected to represent species consumed by humans and key ecological feeding guilds:

Forage fish:

- Mummichog (*Fundulus heteroclitus*) or striped killifish (*Fundulus majalis*)
- Atlantic menhaden (*Brevoortia tyrannus*)
- Bay anchovy (*Anchoa mitchilli*) or Atlantic silverside (*Menidia menidia*)

Benthic demersal flatfish:

- Flounder or hake (e.g., *Pseudopleuronectes americanus, Paralichthys dentatus, Scophthalmus aquosus*)

Pelagic predatory fish:

- White perch (*Morone americana*)
- American eel (*Anguilla rostrata*)

Sport fish[3]:

- Striped bass (*Morone saxatilis*)
- Bluefish or weakfish (*Pomatomus saltatrix* or *Cynoscion regalis*)

4.2 Estimates of Sample Size

When sampling an aquatic system the size of the NBSA, reasonable estimates of the distributions of chemical concentrations in fish tissue are needed to estimate potential risks to the wildlife and humans that may consume them. To determine the number of samples sufficient to conduct the risk assessments, Tierra conducted statistical evaluations using the existing (albeit limited) fish tissue data available for the NBSA, and also considered the sample numbers that were agreed upon for the LPRRP and for the 1999-2000 Ecological Sampling Plan conducted by Tierra in the Passaic River. The sample size needed to estimate the average concentration in a given species/matrix is defined by the precision and confidence required and the expected variance of the population being sampled. Precision is defined by the minimum difference of the estimate from true mean that is considered acceptable with the desired confidence, generally 95 percent. As the minimum difference gets smaller (i.e., greater precision), the required sample size becomes larger. The

[3] Sport fish are defined as fish species targeted for human consumption and may also include fish from other trophic feeding guilds (e.g., white perch, American eel, flounder).

variance is a measure of the variability of the population. Heterogeneous populations, characterized by large variance, require large sample sizes for a given precision.

Available fish tissue data from the Contaminant Assessment and Reduction Project (CARP) database were used to estimate tissue sample sizes. Because the sample variance is an unbiased estimate of the true variance of a population, sample variances for the tissue data from the CARP database (Newark Bay samples only) were calculated as an estimate for tissue sample variance in the NBSA. To ease calculations, all sample variances were converted to a standardized measure of variation, the coefficient of variation (CV). The sample CV is calculated as the ratio of the sample standard deviation to the sample mean. CVs were calculated for all species and all chemicals with a sample size of at least five and a frequency of detection of 100 percent. It should be noted that the ability to utilize the CARP data to calculate appropriate site-specific sample sizes is limited because of the low overall number of samples and species collected in Newark Bay for this program.

The ranges and 80th percentile of CVs for various species were calculated using the Sample Size for Estimation of Mean Module in the USEPA ProUCL software (Version 4.00.05) and are presented in Exhibit 1, below. Sample size estimates assumed a required precision for the mean estimate to be within 50% of the true mean with 95 percent confidence and assumed the CV equal to the 80th percentile of the populations of CVs for each species. Because of the variability in CVs among various chemicals, the ultimate precision attainable for each sample size varies. The range of sample sizes required for various CVs and precision requirements are presented in Exhibit 2, below. The sample sizes and locations were chosen to provide the best precision for most species and chemicals, in consideration of spatial and seasonal representativeness of the fish community. Fish community data collected under USACE's Aquatic Biological Survey (ABS) program (refer to the Problem Formulation [Tierra 2013a]) were reviewed as well as species home/foraging ranges. In addition, the sample numbers are based on chemical tissue data collected under the CARP as well as agreements on sample numbers under the LPRRP sampling program and 1999-2000 Ecological Sampling Plan.

Exhibit 1. Fish Tissue Sample Size Estimates

Species	Tissue Type	Coefficient of Variation (CV)[a]		Sample Size[b]
		Range	80th Percentile	
Mummichog	Whole organism	0.3 - 1.0	0.8	12
Striped bass	Standard fillets	0.4 - 1.4	1	17
White perch	Whole body, fillets	0.1 - 0.9	0.7	9

Notes:
a. Based on CARP tissue dataset for Newark Bay.
b. Calculated using ProUCL Version 4.00.05, Sample Size for Estimation of Mean Module, based on estimating the mean within 50 percent of the true mean with 95 percent confidence.

Exhibit 2. ProUCL Sample Size Using Various Percentages of the Mean with 95% Confidence

Precision (Percent of True Mean)		Coefficient of Variation						
		0.5	0.7	0.8	0.9	1	1.2	1.5
	25%	17	32	41	52	63	90	140
	50%	6	9	12	14	17	24	36
	75%	4	5	6	7	9	12	17
	100%	3	4	4	5	6	7	11

Note:
Calculated using ProUCL Version 4.00.05, Sample Size for Estimation of Mean Module.

Based on the statistical evaluation, a summary of the total number of fish samples is summarized below in Exhibit 3.

Exhibit 3. Recommended Fish Species, Matrices, and Numbers for Tissue Analysis

Species	Sample Preparation	Individual/Composite[a]	Number of Samples	Minimum Target Size
Forage Fish				
Mummichog/striped killifish	Whole body	Composite	16 to19 total[b]	NA
Bay anchovy/Atlantic silverside/menhaden	Whole body	Composite	3 per zone[c], 9 total	NA
Benthic/Demersal				
Flounder/hake (bottom flatfish)	Whole body	Individual	6 per zone, 18 total	NA
Pelagic Predatory				
White perch	Whole body[d]	Individual or Composite (depending on size)	9 per zone, 27 total	NA
White perch	Liver	Composite	3 per zone, 9 total	NA
American eel	Whole body[d]	Individual or Composite (depending on size)	6 per zone,18 total	NA
Sport Fish				
Striped bass	Skin-on, scales-off fillet	Individual or Composite (depending on size)	18 total	28 inches
Bluefish/weakfish	Skin-on, scales-off fillet	Individual or Composite (depending on size)	18 total	Bluefish = no minimum size; Weakfish = 13 inches
White perch	Skin-on, scales-off fillet	Composite (due to size)	6 per zone, 18 total	No minimum size
American eel	Skinless fillet	Individual or Composite (depending on size)	6 per zone,18 total	9 inches
Flounder/hake (bottom flatfish)	Skin-on, scales-off fillet	Individual or Composite (depending on size)	6 per zone, 18 total	Winter flounder = 12 inches; Summer flounder (fluke) = 18 inches

Notes:

a. Composite samples will consist of similar-sized organisms of the same species.
b. Mummichog sampling locations correspond to softshell clam sampling locations (see Section 4.3).
c. Zones defined as Newark Bay North, Newark Bay Central, and Newark Bay South (as depicted on Figure 1).
d. Whole body samples are targeted, but reconstituted whole body samples may be required if insufficient fish are available.

NA = not applicable; recreational size limits only necessary for sport fish fillets.

Several species of fish will be collected from the NBSA, each from specific feeding guilds (i.e., forage fish, benthic/demersal fish, and pelagic predatory). Tissue types include whole-body, liver only, and edible fillets (skin-on and skin-off). Each whole body composite sample will consist of individual fish of the same species and similar sizes collected from the same location. The lengths of all organisms in a composite should be within 25% of the mean length for that composite. Other fish species will be analyzed as whole-body individual samples unless an individual fish does not meet the mass requirements, in which case, two or more individuals will be composited. Large sport fish species will be analyzed individually as fillets. If sufficient tissue to meet analytical mass requirements cannot be collected from a single fish, then additional fish will be added to the sample as necessary. Fish will be collected using gill nets, seines, traps, and trawls, as appropriate. More than one fishing attempt may be made at each sampling location, but each location will be fished for at least one day.

4.3 Sample Locations

Fish samples will be collected from various locations along the Subtidal Flats and Transitional Slopes throughout each of the three zones in the NBSA. The exact sample locations will be determined in the field based on habitat and availability of the target species. Fish will be collected from each of the different geographic areas to provide spatial coverage of the entire NBSA. Collection efforts will include seining, otter trawls, fish traps and gill nets. If the initial collection attempts are unsuccessful, sampling equipment will be moved to other areas within the zone with appropriate habitat. The three geographic zones are depicted on Figure 1 and used for planning purposes only. Each zone will be sampled until the sample size is filled or for a reasonable level of effort (e.g., 10 days of active sampling). If after 10 days of sampling the sample size has not been achieved, sampling may either be continued or postponed until a second field effort is conducted, based on consultation between Tierra, USEPA and its Partner Agencies.

Twelve intertidal areas will be targeted for up to 19 mummichog samples (Figure 1). These areas are consistent with the intertidal areas selected for bivalve clam and sediment sampling (refer to the Crab and Clam QAPP; Tierra 2014). In these shallow water areas, mummichog collection activities will be conducted primarily with seine nets, and mummichog and eel traps. Mummichogs will be collected at 16 sampling locations and 3 supplemental sampling locations (Intertidal Areas 124, 125, and 126). If mummichogs are not found at the supplemental locations, these samples will not be redistributed. The sample location design placed more samples in larger Intertidal Areas (e.g., Intertidal Area 122). Tierra will confirm the locations and sample numbers for each Intertidal Area with USEPA.

5. Fish Data

5.1 Chemical Analysis

The analyte list for fish tissue collected under this sampling event is based on available data collected under the LPRRP RI/FS Cooperating Parties Group (CPG) Fish and Decapod Crustacean Tissue Collection (Windward 2009). Matrices for chemical analysis include whole body fish, fillets, and a subset of fish livers.

The target chemical groups for tissue analysis are provided in Worksheets No. 10, 15-1 and 15-2 and are consistent with the parameters analyzed for in tissue under the CPG LPRRP and Crab and Clam QAPP (Tierra 2014), and include the following: PCDD/PCDF, PCBs (as congeners and Aroclors), metals (including methylmercury, mercury, and titanium), SVOCs (including phthalates and alkylated PAHs), lipids, percent moisture, pesticides (excluding toxaphene), and butyltins. Fish will not be depurated prior to analysis.

5.2 Fish Health

During fish tissue sampling, non-forage fish will be externally examined, and any gross physical abnormalities, lesions, or anomalies will be documented. For the forage fish, a subset of individual fish will be externally examined. In addition, a representative sample of individual non-forage fish – up to at least 20 individuals for each of two different species – will be submitted for internal pathological examination. Both target and non-target species will be sampled, but preference will be on resident and benthic species with sufficient abundance (e.g., white perch, flounder, hake). Fish pathology evaluations will be conducted on the first five fish of each species collected during the fish sampling effort. The internal examination will be conducted by a fish pathologist within hours of capture and will include overall morphology, gonad condition, presence of lesions, gonadosomatic index, and internal physical conditions/abnormalities. These data will be used to provide general qualitative information about the health of fish found within the NBSA. Fish will be examined following pathology-specific laboratory protocol, USGS (2002), or similar guidance. Retaining target species for tissue chemistry analysis is prioritized over sacrificing the fish for pathology evaluation.

5.3 Fish Population

During fish tissue sampling, in addition to collecting fish for chemical and health analyses, the numbers of captured fish (both target and non-target species) will be recorded and tallied. The fish counts and species data will be used to provide general information about the relative abundance and structure of the fish community at the time of sampling. The data will be compared to the existing ABS community data for the fall months to evaluate consistency of the types and relative abundance of fish captured under both programs (ARCADIS 2014).

6. Document Organization

This document was prepared using the Uniform Federal Policy for Quality Assurance Project Plans guidance (USEPA et al. 2005). Worksheet No. 2 identifies the location of each element of this QAPP. A brief summary of the information provided in this document is presented below.

Information about personnel and project organization related specifically to this QAPP, including personnel responsibilities, qualifications, and special training; as well as project organization, distribution, and communications pathways, are presented in Worksheet Nos. 3 through 8. A summary of the scoping sessions conducted for the development of this QAPP is presented in Worksheet No. 9.

The problem definition, project quality objectives, a summary of project tasks, and the project schedule and timeline for this QAPP are summarized in Worksheet Nos. 10, 11, 14, and 16, respectively. A summary of secondary data that may be used for the completion of this QAPP is provided in Worksheet No. 13. The field sampling design, rationale, and a list of proposed sampling locations are provided in Worksheet Nos. 17 and 18.

Information related to laboratory analyses, including performance criteria; reference limits and evaluations; analytical standard operating procedure (SOP) requirements; SOP references; instrument calibration, maintenance, testing, and inspection; quality control samples; and analytical services are presented in Worksheet Nos. 12, 15, 19, 23, 24, 25, 28, and 30, respectively.

Field quality control samples are summarized in Worksheet No. 20. Field sampling SOPs are presented in Appendix A of this document, and the location of each SOP is identified in Worksheet No. 21. Procedures for the calibration and maintenance of field equipment are presented in Worksheet No. 22. Field sample handling and custody procedures are provided in Worksheet Nos. 26 and 27, respectively.

A summary of the documents and records associated with this QAPP, from field sampling effort to the delivery of the data report, is presented in Worksheet No. 29. Internal and external assessments of the field activities, map preparation, laboratory analytical method compliance, data usability, and document review are described in Worksheet No. 31. Types of findings and corrective action responses are outlined in Worksheet No. 32. A summary of quality assurance management reports for this QAPP is provided in Worksheet No. 33. Verification of field sampling data, validation of laboratory analytical data, and an assessment of data usability are presented in Worksheet Nos. 34 through 37.

7. References

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QAPP Worksheets

QAPP Worksheet #1 (UFP-QAPP Manual Section 2.1): Title and Approval Page

Document Title: Fish Sampling and Analysis Quality Assurance Project Plan

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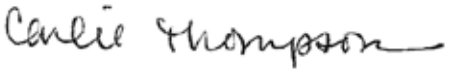

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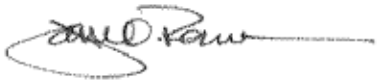

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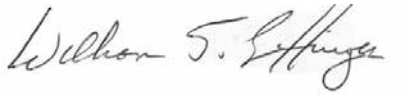

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Investigative Organization's Project Quality Assurance Officer:

Jane Rowan/Normandeau Associates, Inc.

QAPP Worksheet #2 (UFP-QAPP Manual Section 2.2.4): QAPP Identifying Information

Site Name/Project Name:	Newark Bay Study Area/Fish Sampling and Analysis Quality Assurance Project Plan (Fish QAPP)
Site Location:	Newark Bay, New Jersey
Site Number/Code:	Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Document No. 02-2004-2010
Operable Unit:	003
Contractor Name:	ARCADIS/Normandeau Associates
Contractor Number:	Not Applicable (NA)
Contract Title:	NA
Work Assignment Number:	NA

1. Identify guidance used to prepare QAPP:

   - U.S. Environmental Protection Agency (USEPA), U.S. Department of Defense, and U.S. Department of Energy. 2005. Intergovernmental Data Quality Task Force. Uniform Federal Policy for Quality Assurance Project Plans. Evaluating, Assessing, and Documenting Environmental Data Collection and Use Programs. Part 1: UFP-QAPP Manual. USEPA 505-B-04-900A. Final Version 1. March.

2. Identify regulatory program: CERCLA

3. Identify approval entity: USEPA Region 2

4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one)

5. List dates of scoping sessions that were held:

   - February 22, 2013
   - July 22 and 29, 2013

6. List dates and titles of QAPP and Field Sampling Plan documents written for previous site work, if applicable:

Tierra Solutions, Inc. (Tierra). 2005. Newark Bay Study Area Remedial Investigation Work Plan. Sediment Sampling and Source Identification Program, Newark Bay, New Jersey. Phase I. Revision 1. Volumes 1-3. September.
Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan. Sediment Sampling and Source Identification Program, Newark Bay, New Jersey. Phase II. Revision 2, Amendment 1. November.
Tierra. 2011. Final Waste Characterization Quality Assurance Project Plan, Diamond Alkali Superfund Site, Operable Unit 1/CERCLA Non-Time-Critical Removal Action – Lower Passaic River Study Area and Newark Bay Study Area, Revision 1, December 2011.
Tierra. 2012. Quality Assurance Project Plan for Newark Bay Study Area: Multi-beam and Single-beam Bathymetric Survey. Revision 1. December.

Tierra. 2013a. Final Newark Bay Study Area Problem Formulation. Baseline Human Health and Ecological Risk Assessment. June.
Tierra. 2013b. Newark Bay Study Area Draft Reconnaissance Survey Report. Baseline Human Health and Ecological Risk Assessment. December. Not approved by USEPA.
Tierra. 2014. Newark Bay Study Area Crab and Clam Sampling Quality Assurance Project Plan. Final. Revision 3. August.

Additionally, the following QAPPs and documents were written for similar work on an adjacent site (Lower Passaic River) and were used to guide the scope of this QAPP:

Tierra Solutions. 1999. Passaic River Study Area Ecological Sampling Plan. Quality Assurance Project Plan. Volume 2 of 6. Tierra Solutions, Inc. Newark, New Jersey.
Windward. 2009a. Lower Passaic River Restoration Project. Quality Assurance Project Plan. Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey. Final. August 6.
Windward. 2009b. Lower Passaic River Restoration Project. Quality Assurance Project Plan. Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation and Tissue Testing. Final. October 8.
Windward. 2011. 2009 Fish and Blue Crab Tissue Chemistry Data for the Lower Passaic River Study Area. Prepared for Cooperating Parties Group, Newark, NJ. September.

7. List organizational partners (stakeholders) and connection with lead organization:

   This work will be performed under the requirements of the Administrative Order on Consent (CERCLA-02-2004-2010) (USEPA 2004) for the NBSA, with oversight conducted by USEPA and its partner agencies (New Jersey Department Environmental Protection, National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, U.S. Army Corps of Engineers, New Jersey Department of Transportation). Tierra (acting as Facility Coordinator), has engaged ARCADIS/Normandeau to prepare this document on its behalf.

8. List data user: see Worksheet #11.

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

QAPP Worksheet #2 (UFP-QAPP Manual Section 2.2.4): QAPP Identifying Information (continued)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information Relevant to Collection of Fish Tissue Data	Crosswalk to QAPP Worksheet No. or Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	1
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	 2
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	3 4
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	5 6 7 8
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps	9 9 10 Figure 1
2.6 Project Quality Objectives (PQOs) and Measurement Performance Criteria 2.6.1 Development of PQOs Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	11 12
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	13
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	14 15 16

QAPP Worksheet #2 (UFP-QAPP Manual Section 2.2.4): QAPP Identifying Information (continued)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information Relevant to Collection of Fish Tissue Data	Crosswalk to QAPP Worksheet No. or Related Documents
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale/Sample Location Map - Sample Locations and Methods/Standard Operating Procedure (SOP) Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control (QC) Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	17 18 19 20 20 21 22
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	23 24 25
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flo Diagram - Example Chain-of-Custody Form and Seal	26 26 27 27
3.4 QC Samples 3.4.1 Sampling QC Samples 3.4.2 Analytical QC Samples	- QC Sample Tables - Screening/Confirmatory Analysis Decision Tree	28 28
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table	29 30

QAPP Worksheet #2 (UFP-QAPP Manual Section 2.2.4): QAPP Identifying Information (continued)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information Relevant to Collection of Bird Egg Tissue Data	Crosswalk to QAPP Worksheet No. or Related Documents
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessment and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses	31 31 32
4.2 Quality Assurance Management Reports	- Quality Assurance Management Reports Table	33
4.3 Final Project Report		
Data Review		
5.1 Overview 5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	 - Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation Guidance Summary Table - Usability Assessment	 34 35 36 37

QAPP Worksheet #3 (UFP-QAPP Manual Section 2.3.1): Distribution List

QAPP Recipients	Title	Organization	Telephone Number	Email Address
Eugenia Naranjo	Remedial Project Manager	USEPA Region 2	212.637.3467	naranjo.eugenia@epamail.epa.gov
William Sy	USEPA Project Quality Assurance Officer	USEPA Region 2	732.321.6648	sy.william@epa.gov
Marc Greenberg	Environmental Toxicologist	USEPA Headquarters	732.452.6413	greenberg.marc@epa.gov
Jay Nickerson	Site Remediation Manager	NJDEP	609.633.1448	jay.nickerson@dep.state.nj.us
Clay Stern	Team Leader	USFWS	609.646.9310, ext. 27	clay_stern@fws.gov
Bryce Wisemiller	Project Manager	USACE NY District	917.790.8307	bryce.w.wisemiller@usace.army.mil
Reyhan Mehran	Coastal Resource Coordinator	NOAA	212.637.3257	reyhan.mehran@noaa.gov
Carlie Thompson	Facility Coordinator	Tierra	732.246.5849	carlie.thompson@tierra-inc.com
Clifford Firstenberg	Project Director	Tierra	757.258.7720	clifford.firstenberg@tierra-inc.com
Bryan Lees	Field Supervisor	Normandeau Associates	484.945.2578	blees@normandeau.com
William Ettinger	Project Manager	Normandeau Associates	302.945.3567	wettinger@normandeau.com
William Ettinger	Technical Expert	Normandeau Associates	302.945.3567	wettinger@normandeau.com
Jane Rowan	Principal-in-Charge	Normandeau Associates	484.945.2500	jrowan@normandeau.com
Richard Kling	Health and Safety Manager	Normandeau Associates	484.945.2575	rkling@normandeau.com
Jane Rowan	Quality Assurance Officer	Normandeau Associates	484.945.2500	jrowan@normandeau.com
Angela Gatchie	Quality Assurance Coordinator	Field & Technical Services	412.428.9411	agatchie.2006@f-ts.com
Martha Maier	Laboratory Project Manager	Vista Analytical Laboratory	916.673.1520	mmaier@vista-analytical.com
Wendy Kozma	Laboratory Project Manager	eurofins/Lancaster Laboratories	717.556.7257	wendykozma@eurofinsus.com
Amy Goodall	Laboratory Project Manager	eurofins/Frontier Global Sciences	425.686.3557	amygoodall@eurofinsus.com
Kirk Young	Laboratory Project Manager	Test America Burlington, VT	802.660.1990	kirk.young@testamericainc.com

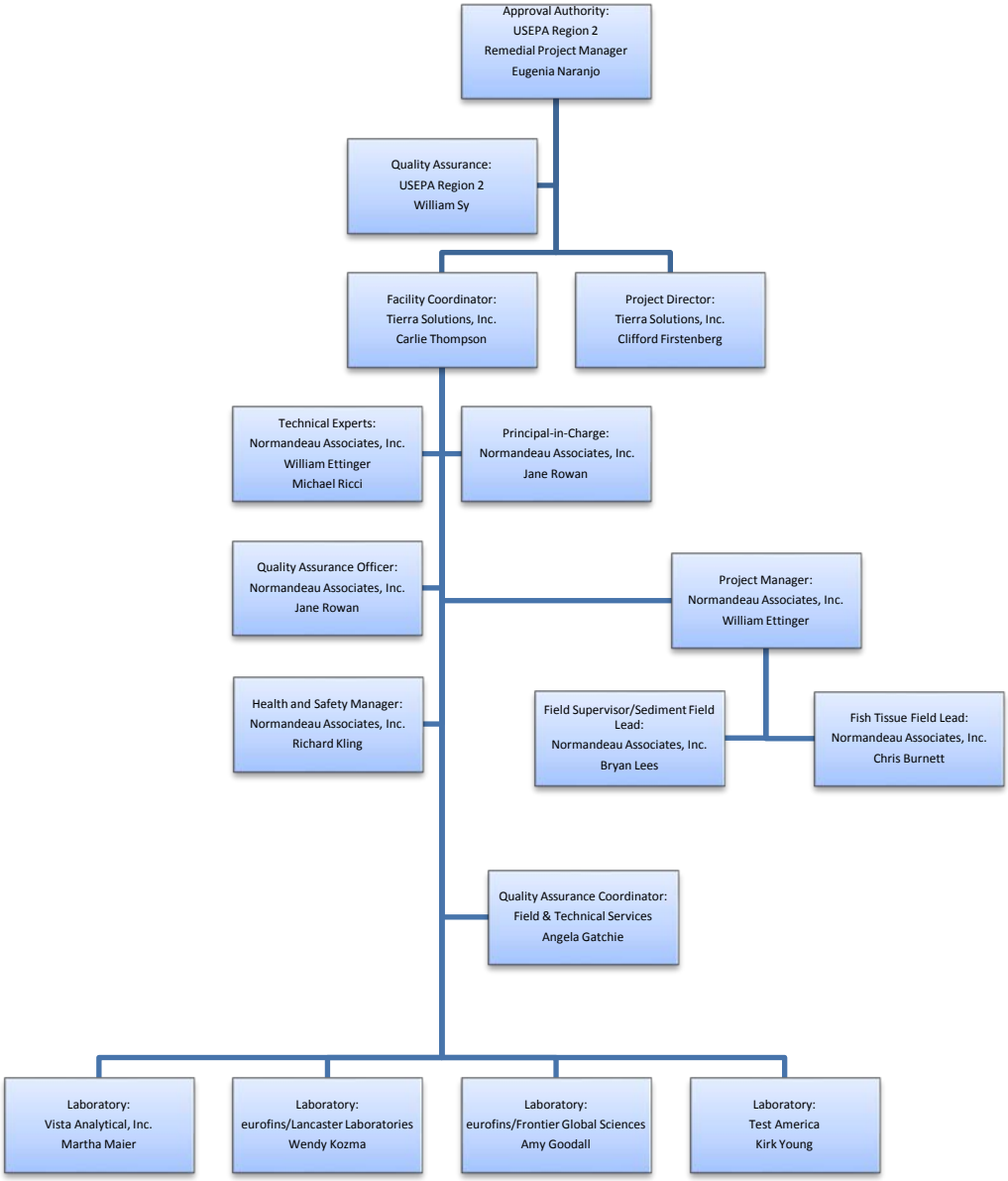
Notes:
NJDEP = New Jersey Department of Environmental Protection
NOAA = National Oceanic and Atmospheric Administration
Tierra = Tierra Solutions, Inc.
USACE = U.S. Army Corps of Engineers
USEPA = U.S. Environmental Protection Agency
USFWS = U.S. Fish and Wildlife Service

QAPP Worksheet #4 (UFP-QAPP Manual Section 2.3.2): Project Personnel Sign-Off Sheet

Project Personnel	Title	Organization	Telephone Number	Signature	Date QAPP Read

Note:
*Signature indicates that personnel have read the applicable QAPP sections and will perform the tasks as described.

QAPP Worksheet #5 (UFP-QAPP Manual Section 2.4.1): Project Organizational Chart



QAPP Worksheet #6 (UFP-QAPP Manual Section 2.4.2): Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (e.g., timing, pathways)
Field Sampling Communication	Field Supervisor	Bryan Lees	484.945.2578	Communicate daily, or as needed, with field personnel, Investigative Organization Project Manager, and QA Coordinator directly or via email or phone.
Communication with Investigative Organization Project Manager				
Communication with QA Coordinator				
Health and Safety Communication	Site Health and Safety Manager	Richard King	484.945.2575	Communicate daily, or as needed, with field personnel directly, or via email or phone, on matters regarding health and safety.
Communication with Investigative Organization Project Manager	Facility Coordinator	Carlie Thompson	732.246.5849	Communicate daily, or as needed, with Investigative Organization Project Manager, and QA Coordinator directly or via email or phone.
Communication with Investigative Organization QA/QC Manager				
Communication with Facility Coordinator	Investigative Organization Project Manager	William Ettinger	302.945.3567	Communicate daily, or as needed, with Facility Coordinator via email or phone, including recommendations regarding sample size and composites.
	QA Coordinator	Angela Gatchie	412.428.9411	
Communication with Analytical Laboratories	Investigative Organization Project Manager	William Ettinger	302.945.3567	Communicate, as needed, with Laboratory Project Managers regarding laboratory and analysis issues.
	QA Coordinator	Angela Gatchie	412.428.9411	
	Investigative Organization Biological Laboratory Coordinator	Bryan Lees	484.945.2578	
Communication with USEPA	Facility Coordinator	Carlie Thompson	732.246.5849	Communicate with USEPA Project Manager, as needed, via email or phone. USEPA will review and approve final sampling locations (as needed to adjust for field conditions) and final compositing scheme for tissue samples.
Quality Status and Issues	QA Coordinator	Angela Gatchie	412.428.9411	Communicate with Facility Coordinator, as needed, via email or phone.
Sampling Vessel Operations	Field Supervisor	Bryan Lees	484.945.2578	Communicate with vessel captain regarding safety issues.

Notes:
QA = quality assurance
QC = quality control
USEPA = U.S. Environmental Protection Agency

QAPP Worksheet #7 (UFP-QAPP Manual Section 2.4.3): Personnel Responsibilities and Qualifications Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications[a]
Carlie Thompson	Facility Coordinator	Tierra Solutions, Inc.	Program Manager	BS Chemical Engineering/ 9 years
Cliff Firstenberg	Project Director	Tierra Solutions, Inc.	Environmental Sciences Manager	MS Physical Oceanography, BA Earth and Planetary Sciences/30 years
Jane Rowan	Senior Principal Scientist	Normandeau Associates, Inc.	Principal-in-Charge	MS Environmental Science BS Biology/32 years
William Ettinger	Principal Aquatic Ecologist	Normandeau Associates, Inc.	Senior Technical Expert/Program Manager	MS Entomology, BS Fundamental Sciences/40 years
Michael Ricci	Program Manager	Normandeau Associates, Inc.	Technical Expert	AAS Marine Science /40 years
Bryan Lees	Aquatic Ecologist	Normandeau Associates, Inc.	Field Supervisor	MS Wildlife and Fisheries Science, BS Wildlife and Fisheries Sciences, BS Environmental Resource Management/13 years
Chris Burnett	Senior Field Crew Leader	Normandeau Associates, Inc.	Fish Tissue Field Lead	23 years
Richard Kling	Principal Environmental Scientist	Normandeau Associates, Inc.	Health and Safety Manager	BA Biology/29 years
Ryan Bauman	Field Technician	Normandeau Associates, Inc.	Field Scientist/Technician	5 years
Charles Dix	Field Technician	Normandeau Associates, Inc.	Field Scientist/Technician	BS Fisheries Science/27 years
Keith Marburger	Field Technician	Normandeau Associates, Inc.	Field Scientist/Technician	BS Environmental Science/3 years
Jayme Schaeffer	Field Technician	Normandeau Associates, Inc.	Field Scientist/Technician	BS Wildlife and Fisheries Science/9 years
Michael Mettler	Field Technician	Normandeau Associates, Inc.	Field Scientist/Technician	BS Marine Science/18 years
Angela Gatchie	Data Manager	Field & Technical Services	Quality Assurance Coordinator	BS Chemistry/12 years
Kendra Chintella	Database Analyst	Field & Technical Services	Quality Assurance Assistant	BS Chemistry/5 years
Martha Maier	Laboratory Manager	Vista Analytical, Inc.	Laboratory Project Manager	BS Chemistry/23 years
Wendy Kozma	Project Manager	eurofins/Lancaster Laboratories	Laboratory Project Manager	BS Environmental Science/21 years
Amy Goodall	Project Manager	eurofins/Frontier Global Sciences	Laboratory Project Manager	BS Chemistry/11 years
Kirk Young	Project Manager	Test America, Burlington, VT.	Laboratory Project Manager	BS Civil Engineering/33 years

Note:
[a] Resumes of all individuals are available upon request.

QAPP Worksheet #8 (UFP-QAPP Manual Section 2.4.4): Special Personnel Training Requirements Table

All field personnel assigned to the site must have successfully completed 40 hours of training for hazardous site work in accordance with Occupational Safety and Health Administration (OSHA) 29 Code of Federal Regulations (CFR) 1910.120(e)(3) and be current with their 8-hour refresher training in accordance with OSHA 29 CFR 1910.120(e)(8). Documentation of OSHA training is required prior to personnel being permitted to work on site.

Personnel managing or supervising work on site will also have successfully completed 8 hours of Manager/Supervisor Training in accordance with OSHA 29 CFR 1910.120(e)(4).

Personnel assigned to the site must be enrolled in a medical surveillance program, which meets the requirements of OSHA 29 CFR 1910.120(f). Personnel must have successfully passed a periodic occupational physical and be medically cleared to work on a hazardous waste site and capable of wearing appropriate personal protective equipment. For employees potentially exposed more than 30 days per year, the frequency of periodic examinations will be annual. For employees potentially exposed less than 30 days per year, the frequency for periodic examinations will be once every 24 months.

It is the responsibility of the site worker's employer to provide their employees with the required training and medical monitoring prior to assigning them to work at the site. Each employer will be responsible for providing documentation of training and monitoring to the Field Supervisor prior to sending their employees to the site to work.

Additional health and safety information and records documentation information are detailed in the site-specific Health and Safety Plan.

QAPP Worksheet #9 (UFP-QAPP Manual Section 2.5.1): Project Scoping Session Participants Sheet, February 22, 2013

Project Name: Fish Sampling **Projected Date(s) of Sampling:** Summer 2014 **Project Managers:** Carlie Thompson (Tierra) /Melissa Beauchemin (ARCADIS)	**Site Name:** NBSA **Site Location:** Newark Bay, New Jersey
Date of Session: February 22, 2013 **Scoping Session Purpose:** To discuss measurement endpoints for the upcoming baseline ecological risk assessment of the NBSA	

Name	Affiliation	Phone #	Email Address	Project Role
Melissa Beauchemin	ARCADIS	978-322-4551	melissa.beauchemin@arcadis-us.com	Project Manager
Carlie Thompson	Tierra	732-246-5849	carlie.thompson@tierra-inc.com	Facility Coordinator
Cliff Firstenberg	Tierra	757-258-7720	clifford.firstenberg@tierra-inc.com	Project Director
Eugenia Naranjo	USEPA Reg 2	212-637-3467	naranjo.eugenia@epa.gov	Remedial Project Manager
Chuck Nace	USEPA Reg 2	212-637-4164	nace.charles@epa.gov	Ecological Risk Assessor
Marc Greenberg	USEPA Headquarters	732-452-6413	greenberg.marc@epa.gov	Ecological Risk Assessor
Norman Richardson	Battelle	781-869-1417	richardsonn@battelle.org	Contractor
Len Warner	Louis Berger Group	914-798-3721	lwarner@louisberger.com	Contractor
Tim Iannuzzi	ARCADIS	410-991-9754	tim.iannuzzi@arcadis-us.com	Technical Expert

Comments/Decisions:

A summary of the Meeting Minutes as they pertain to the evaluation of fish in the NBSA is provided below:

Assessment Endpoint 3: Fish

The primary focus for this endpoint is tissue analysis.

- The data use objective will be revised to indicate a more quantitative analysis as opposed to "general information" as stated in Table 4-3 of the Problem Formulation Document.
- The organ histopathology/analysis was included as a candidate ME for the Passaic River but was not a final ME. The reason for this is that a large sample size/dataset is required (~50 fish of same species) to be statistically robust. USEPA does not consider deformities, erosions, lesions, or tumors in ecological risk assessment; it is supplemental information.
- Tierra will likely include some sort of analysis of fish bile to assess exposure to PAHs. Tierra will modify text in Table 4-3; the first "Description of Measurement Endpoint" in AE 3 will read "liver and other tissue (including bile)" rather than "liver tissue."[a]
- It was agreed that there is enough fish community information (including seasonal data) from multiple historical surveys (1993-2009, potentially beyond?) that additional fish community surveys are not necessary.
- Fish reproductive health was not included as an ME in the Passaic River, but mummichog eggs were collected.
  - There are unlikely to be as many mummichogs in the bay due to the lack of large intertidal areas.
  - There are no known Early Life Stage studies on estuarine species.
  - Few fish species actually spawn in the bay (notably bay anchovy) based on historical fish community data presented in the Problem Formulation (Tierra 2013; citations will be provided).
  - It was agreed to evaluate fish reproductive health based on the following:
    - Overall morphology, gonadosomatic index, gonad condition, external/internal physical observations.
    - Historical fish community data from over a decade of fish community studies in the bay.
    - Possible limited ichthyoplankton sampling collected during trawls for fish tissue collection.
    - Tierra will remove reference to "biomarkers" from Table 4-3 in the related "Description of Measurement Endpoint."
  - Norm mentioned comment #94, which discusses incorporating text about photo-induced toxicity of PAHs. Marc clarified that he is simply looking for a sentence noting the possibility of photo-induced toxicity and to provide a citation in the toxicity profile section of the Problem Formulation.

a. Although bile was discussed during project scoping sessions, it has been eliminated from analysis and is not discussed further in this QAPP.

QAPP Worksheet #9 (UFP-QAPP Manual Section 2.5.1): Project Scoping Session Participants Sheet, July 22, 2013

Project Name: Fish Sampling **Projected Date(s) of Sampling:** Summer 2014 **Project Managers:** Carlie Thompson (Tierra)/Melissa Beauchemin (ARCADIS)	**Site Name:** NBSA **Site Location:** Newark Bay, New Jersey
Date of Session: July 22, 2013 **Scoping Session Purpose:** Discuss sampling and analytical methods.	

Name	Affiliation	Phone #	Email Address	Project Role
Melissa Beauchemin	ARCADIS	978-322-4551	melissa.beauchemin@arcadis-us.com	Project Manager
David Rigg	ARCADIS	518-250-7379	david.rigg@arcadis-us.com	Field Supervisor
Tim Iannuzzi	ARCADIS	410-295-1205	tim.iannuzzi@arcadis-us.com	Technical Expert
Carlie Thompson	Tierra	732-246-5849	carlie.thompson@tierra-inc.com	Facility Coordinator
Cliff Firstenberg	Tierra	757-258-7720	clifford.firstenberg@tierra-inc.com	Project Director
Diane Waldschmidt	EDS	412-486-6989	dwaldschmidt@eds-us.net	QA Coordinator
Mark Harris	ToxStrategies	281-394-1567	mharris@toxstrategies.com	Human Health Risk Assessor

Comments/Decisions:

- Laboratories: decision to use Tierra laboratories (likely two or three laboratories).
- Analyte list: decision to keep in everything (include herbicides, Aroclors, and butyltins).
- VOCs do not accumulate in tissue, can eliminate from tissue.
- Tissue processing may need to be done in laboratory with oversight by a biologist from the investigative organization (TBD).
- Discussed numbers of organisms to make composite to get enough tissue for all analyses (base on a memorandum written for the Lower Passaic River).

See the last page of Worksheet #9 for a description of footnotes.

QAPP Worksheet #9 (UFP-QAPP Manual Section 2.5.1): Project Scoping Session Participants Sheet, July 29, 2013

Project Name: Fish Sampling **Projected Date(s) of Sampling:** Spring 2014 **Project Managers:** Carlie Thompson (Tierra) /Melissa Beauchemin (ARCADIS)	**Site Name:** NBSA **Site Location:** Newark Bay, New Jersey
Date of Session: July 29, 2013 **Scoping Session Purpose:** Discuss sampling and analytical methods	

Name	Affiliation	Phone #	Email Address	Project Role
Melissa Beauchemin	ARCADIS	978-322-4551	melissa.beauchemin@arcadis-us.com	Project Manager
Carlie Thompson	Tierra	732-246-5849	carlie.thompson@tierra-inc.com	Facility Coordinator
Cliff Firstenberg	Tierra	757-258-7720	clifford.firstenberg@tierra-inc.com	Project Director
Paul Bluestein	Tierra	732-246-3091	pjbluestein@tierra-inc.com	Alternate Facility Coordinator
Mark Harris	ToxStrategies	281-394-1567	mharris@toxstrategies.com	Human Health Risk Assessor
Diane Waldschmidt	EDS	412-486-6989	dwaldschmidt@eds-us.net	QA Coordinator
Elise Francken	EDS	412-486-6989	efrancken@eds-us.net	Data Validator/QA Assistant

Comments/Decisions:

- Estimated sample size for tissue for each analysis – total is approximately 200 grams.
- Need to prioritize analyte list (develop hierarchy).
  - Remove VOCs and total petroleum hydrocarbons from tissue.
  - Remove herbicides from tissue (lack of methods).
  - Remove hexavalent chromium from tissue.
- The need for Aroclors was discussed. ARCADIS recommends keeping them in the analyte list for trends analysis, but as in the lower Passaic River, they will not be used in the risk assessment (polychlorinated biphenyl congener data are better for use in risk assessment). They were maintained in the lower Passaic River; however, few data have been collected in the NBSA for trend analysis.

Reference:
Tierra. 2013. Final Newark Bay Study Area Problem Formulation. Baseline Human Health and Ecological Risk Assessment. Tierra Solutions, Inc., East Brunswick, NJ. June.

Notes:
ARCADIS = ARCADIS U.S., Inc.
EDS = Environmental Data Services, Ltd.
ME = measurement endpoint
NBSA = Newark Bay Study Area
PAH = polycyclic aromatic hydrocarbon
QA = quality assurance
Tierra = Tierra Solutions, Inc.
USEPA = U.S. Environmental Protection Agency
VOC = volatile organic compound

QAPP Worksheet #10 (UFP-QAPP Manual Section 2.5.2): Problem Definition

The problem to be addressed by the project:

An understanding of the concentration of COPECs/COPCs in fish tissue.

The environmental questions being asked:

The overall question is

Does exposure to site-related COPECs/COPCs in the NBSA pose unacceptable risks to fish and to organisms and unacceptable risks and hazards to humans that consume fish?

Specifically, the following questions are being asked for the BERA:

- Are COPEC concentrations in fish tissues from the NBSA greater than critical body residues (CBRs) for the survival, growth, and/or reproduction of fish?
- Does the daily dose of COPECs received by birds and mammals from consumption of tissues of prey species and from other media in the NBSA exceed the toxicity reference values (TRVs) for survival, growth, and reproduction of birds and mammals? If yes, what are the probabilities of effects of differing magnitude for survival, growth, and/or reproduction of birds and mammals?

Specifically, the following question is being asked for the BHHRA:

- Do COPCs in fish and shellfish consumed by humans from the NBSA pose potentially unacceptable cancer risks or non-cancer hazards?

Observations from any site reconnaissance reports:

A Reconnaissance Survey occurred in September 2013, the results of which are draft and, although it has not been approved by USEPA, guided the preparation of this Quality Assurance Project Plan (QAPP).

A synopsis of secondary data or information from site reports:

The basis for the fish tissue sample size is from the Contaminant Assessment and Reduction Project (CARP) Data collected from one sampling location in the NBSA. The following species were collected under CARP and analyzed for chemical contaminants: mummichog, white perch, American eel, and striped bass.

The classes of contaminants and the affected matrices:

There are several different classes of organic and inorganic contaminants in the NBSA, many of which may accumulate in fish and be transferred through the food web to upper-trophic level wildlife. Fish tissue samples will be analyzed for the following analytes: polychlorinated biphenyl congeners, PCB Aroclors, PCDDs/PCDFs, pesticides (excluding toxaphene), PAHs (including alkylated PAHs), semivolatile organic compounds (including phthalates), metals (including total mercury, methylmercury, and titanium), butyltins, lipid content, and percent moisture. Worksheet #15 lists the specific analytes in each of these chemical classes that will be analyzed. Although VOCs and herbicides are identified as possible COPECs/COPCs, VOCs were not identified as bioaccumulative chemicals by USEPA (2000). Therefore, VOCs will not be analyzed in tissue samples. Herbicides are not included for analysis in tissue for the following reasons: 1) there are no published methods for herbicides in tissue, 2) herbicides are infrequently detected in recent studies, and 3) the bioaccumulation potential is low.

The analysis of PCB Aroclors is being conducted to provide data comparable to historical PCB Aroclor data for the purposes of trend analysis on the basis of PCB Aroclors. The PCB Aroclor data will not be used in either the human health risk assessment or baseline ecological risk assessment due to the superior accuracy and precision of the PCB congener data. Total PCB concentrations will be calculated as the sum of PCB congeners and not the sum of PCB Aroclors.

See the last page of Worksheet #10 for a description of footnotes.

QAPP Worksheet #10 (UFP-QAPP Manual Section 2.5.2): Problem Definition (continued)

The rationale for inclusion of chemical and non-chemical analyses:

Fish tissue COPEC and COPC concentrations will provide valuable information that will be used to perform the baseline ecological risk assessment (BERA) and baseline human health risk assessment (BHHRA) for the NBSA.

Project decision conditions:

The conditions for project decisions (i.e., those decisions that may require communication between Normandeau, Tierra Solutions, Inc., and USEPA and the Partner Agencies during the field event include the decision to continue sampling if sample size has not been filled at the end of the first 10 day sampling event, prioritization of chemical analyses if insufficient fish tissue is collected, and the prioritization for submitting samples as composites or individuals within a given sampling area.

A pre-homogenization minimum tissue mass of 194 g and a post-homogenization mass of 169 g is needed, per sample, for analysis of all proposed chemical groups. A mass of 25 g was added to the sum of the minimum mass requirements for chemical analyses (169 g) to account for tissue lost during processing and homogenization, for a total pre-homogenization minimum mass of 194 g. The minimum mass requirements per analytical group are provided in the priority list below. Mass requirements have been optimized with each analytical laboratory, such that they are the lowest required to achieve the detection limits presented in Worksheet #15. The minimum mass does not include enough mass for re-extractions or matrix-specific quality control samples. If the pre-homogenization minimum tissue mass (194 g) for chemistry analysis cannot be obtained for a given species/location, the available tissue collected will be analyzed according to the priority chemical list provided below. If a post-homogenization minimum mass of 169 g is not obtained, the following priority list for the chemical analyses of tissue samples will be considered:

1. PCDDs/PCDFs including percent lipids (30-g minimum mass)
2. PCB congeners (20-g minimum mass)
3. Methylmercury (1-g minimum mass)
4. Mercury (1-g minimum mass)
5. TAL metals including titanium (1-g minimum mass)
6. Pesticides (20-g minimum mass)
7. Percent moisture (1-g minimum mass)
8. Semivolatile organics (15-g minimum mass)
9. Semivolatile organics SIM (15-g minimum mass)
10. Butyltins (50-g minimum mass)
11. PCB Aroclors (15-g minimum mass)

Reference:
USEPA. 2000. Bioaccumulation Testing and Interpretation for the Purpose of Sediment Quality Assessment Status and Needs. EPA 823-R-00-001. February.

Notes:
COPC = constituent of potential concern
COPEC = constituent of potential ecological concern
g = gram
NBSA = Newark Bay Study Area
PAH = polycyclic aromatic hydrocarbon
Partner Agencies = U.S. Army Corps of Engineers, New Jersey Department of Environmental Protection, New Jersey Department of Transportation, National Oceanic and Atmospheric Administration, and U.S. Fish and Wildlife Service.
PCB = polychlorinated biphenyl
PCDD = polychlorinated dibenzo-*p*-dioxin (dioxin)
PCDF = polychlorinated dibenzofuran (furan)
USEPA = U.S. Environmental Protection Agency
VOC = volatile organic compound

QAPP Worksheet #11 (UFP-QAPP Manual Section 2.6.1): Project Quality Objectives/Systematic Planning Process Statements

Who will use the data?

The data collected under this QAPP will be used by Tierra and USEPA for CERCLA-related decisions, specifically for the BERA and BHHRA, and by other interested parties (e.g., U.S. Army Corps of Engineers, New Jersey Department of Environmental Protection, U.S. Fish and Wildlife Service, New Jersey Department of Transportation, National Oceanic and Atmospheric Administration) for other purposes, such as restoration planning.

What will the data be used for?

The data collected during this sampling effort will be used in risk-based decision-making for the Remedial Investigation/Feasibility Study in the NBSA. Specifically, the data will be used to evaluate whether exposure to site-related COPECs in the NBSA pose unacceptable risks to fish and whether consumption of, and COPCs in, fish and shellfish (refer to the Crab/Clam QAPP [Tierra 2014]) from the NBSA poses unacceptable risks and hazards to human and ecological receptors (e.g., birds and mammals). The results of the BERA and BHHRA will be used to inform remedial decision-making under CERCLA/National Contingency Plan and other appropriate regulations and future restoration planning.

BERA Assessment Endpoints:

Assessment Endpoint No. 4 – Survival, growth, and/or reproduction of fish

Fish tissue data collected as part of this sampling event will be used as a measurement endpoint to evaluate risks to fish by answering the following risk question: **Are COPEC concentrations in fish tissues from the NBSA greater than CBRs for the survival, growth, and/or reproduction of fish?** To do this, whole body COPEC concentrations in fish tissue will be compared to literature-based CBR data.

To aid in the evaluation of potential effects on fish reproduction, individual fish health metrics will be collected as ancillary information during the collection of tissue for analysis. Further, information on the fish community (species counts) will also be collected to supplement the existing community data that exists for the NBSA (refer to Section 5.3).

Assessment Endpoints No. 5 and 6 – Survival, growth, and/or reproduction of birds and mammals, respectively.

Tissue chemistry data collected as part of this sampling event will be used as input parameters for a food web model to estimate dietary intakes for select bird and mammal receptors by answering the following risk question: **Does the daily dose of COPECs received by birds and mammals from consumption of fish tissue and from other media in the NBSA exceed the toxicity reference values (TRVs) for survival, growth, and/or reproduction of birds and mammals? If yes, what are the probabilities of effects of differing magnitude for survival, growth, and/or reproduction of birds and mammals?** To do this, measured chemical concentrations in fish tissue will be incorporated into the food web model to estimate a daily dietary ingestion of chemicals. The estimated dose is compared to the literature-based TRV to evaluate potential risks. If potential risks are evident (i.e., the resulting hazard quotient is greater than 1), a probabilistic food web model will be run to estimate the range of possible risks, following work plan approval by USEPA.

BHHRA Endpoints

The data collected during this sampling effort will also be used to support the BHHRA. In addition to the BERA risk questions outlined above, the BHHRA risk question relevant to this project is as follows:

- What are the potential adverse effects of chemicals in the NBSA to human health under current and future exposure scenarios for both cancer and non-cancer health effects via fish and shellfish consumption from the NBSA?

See the last page of Worksheet #11 for a description of footnotes

QAPP Worksheet #11 (UFP-QAPP Manual Section 2.6.1): Project Quality Objectives/Systematic Planning Process Statements (continued)

The tissue data collected during this sampling effort, combined with additional data anticipated to be collected under Phase III of the Remedial Investigation, will collectively be used to support the BHHRA by estimating potential human exposures and assessing the potential impact of chemicals on human health via consumption of fish and shellfish from the NBSA. Potential consumption scenarios are presented in the human health conceptual site model included in the Problem Formulation (Tierra 2013). Potential risks will be evaluated using fish tissue fillets from individual or composite fish tissue samples and blue crab data (refer to the Crab/Clam QAPP [Tierra 2014]). The BHHRA will use these data as the basis for quantitatively evaluating the exposure of individuals under current and future scenarios for both cancer and non-cancer health effects following USEPA Superfund guidance, guidelines, and policies. Human health risks will be evaluated for young children, adolescents, and adults.

What type of data are needed (matrix, target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques)?

Several different types of fish tissue samples will be collected as part of this sampling including whole-body, liver only, and edible fillet samples. Fish will not be depurated prior to analysis. The number of fish in each sample will vary depending on sample type and to meet the anticipated minimum sample mass requirements (194 grams pre-homogenization, 169 grams post-homogenization. The types of samples and sample numbers are presented in the table below.

Species	Sample Preparation	Individual/Composite[a]	Number of Samples	Minimum Target Size
Forage Fish				
Mummichog/striped killifish	Whole body	Composite	16 to 19 total[b]	NA
Bay anchovy/Atlantic silverside/menhaden	Whole body	Composite	3 per zone[c], 9 total	NA
Benthic/Demersal				
Flounder/hake (bottom flatfish)	Whole body[d]	Individual	6 per zone, 18 total	NA
Pelagic Predatory				
White perch	Whole body[d]	Individual or Composite (depending on size)	9 per zone, 27 total	NA
White perch	Liver	Composite	3 per zone, 9 total	NA
American eel	Whole body[d]	Individual or Composite (depending on size)	6 per zone,18 total	NA
Sport Fish[e]				
Striped bass	Skin-on, scales-off fillet	Individual or Composite (depending on size)	18 total	28 inches
Bluefish/weakfish	Skin-on, scales-off fillet	Individual or Composite (depending on size)	18 total	Bluefish = no minimum size; Weakfish = 13 inches
White perch	Skin-on, scales-off fillet	Composite (due to size)	6 per zone, 18 total	No minimum size

See the last page of Worksheet #11 for a description of footnotes.

QAPP Worksheet #11 (UFP-QAPP Manual Section 2.6.1): Project Quality Objectives/Systematic Planning Process Statements (continued)

Species	Sample Preparation	Individual/Composite[a]	Number of Samples	Minimum Target Size
American eel	Skinless fillet	Individual or Composite (depending on size)	6 per zone,18 total	9 inches
Flounder/hake (bottom flatfish)	Skin-on, scales-off fillet	Individual or Composite (depending on size)	6 per zone, 18 total	Winter flounder = 12 inches; Summer flounder (fluke) = 18 inches

Notes:
a. Composite samples will consist of similar-sized organisms of the same species.
b. Mummichog sampling locations correspond to softshell clam sampling locations.
c. Zones defined as Newark Bay North, Central, and South (as depicted on Figure 1) are provided for planning purposes only.
d. Whole body samples are targeted, but reconstituted whole body samples may be required if insufficient fish are available.
e. Sport fish are defined as fish species targeted for human consumption and may include fish from various trophic feeding guilds (e.g., white perch, American eel, flounder)
NA = not applicable; recreational size limits only necessary for sport fish fillets.

How "good" do the data need to be in order to support the environmental decision?

The data will be used to support decisions about the magnitude and spatial distribution of potential risks to fish in the NBSA, as well as mammalian and avian ecological receptors and human receptors. The data will be used to better define risk decisions for discrete endpoints. The data may also be used to support initial investigations of potential remedial options. Consequently, the data need to be collected with a design that specifically addresses the questions that are being posed (see above, "What will the data be used for?").

It is inevitable that biological data may be highly variable. However, if the data have been collected with a logical design to cover the range of variation in the controlling physical factors at the site, the interpretation of the results is more straightforward, even when the variance of relationships is high. Because a number of assumptions will be made when assessing potential risks, the data must be collected in a way that makes the evaluation of assumptions possible and allows assessments of the remaining uncertainty to be conducted in a way that enables decision makers to weigh the costs and benefits of proceeding with remedial action decisions.

How much data are needed (number of samples for each analytical group, matrix, and concentration)?

The overall target number of the different types of fish samples was identified based on the ability to statistically evaluate the data while minimizing potential impacts to the fish population. In addition, the number of samples is adequate to cover the large spatial area of the NBSA. The numbers of each type of sample are shown in the table above. While this table presents the ideal targeted number of samples per species, the abundance of aquatic organisms is highly variable. As such, fishing may cease after 10 days, in consultation with USEPA, if targeted numbers of species have not been collected.

Where, when, and how should the data be collected/generated?

Fish samples will be collected during late summer/early fall 2014 using a variety of techniques including gill nets, trawls, seines, and fish traps as described in SOP No. 4 - Fish Collection and Tissue Sampling.

Who will collect and generate the data?

As described in Worksheet No. 7, Normandeau will provide the field sampling coordination and personnel required to conduct the tissue and sediment collection efforts. FTS will provide laboratory coordination and support.

QAPP Worksheet #11 (UFP-QAPP Manual Section 2.6.1): Project Quality Objectives/Systematic Planning Process Statements (continued)

How will the data be reported?

Daily activities will be communicated (e.g., telephone conversation, email) to Project Managers and the Facility Coordinator, as described in Worksheet #6.

An electronic database that includes the coordinates for the location of each sample area will be provided. The database will be maintained to include the following:

- Target species: counts, weights, lengths, and sample IDs.
  - For small forage fish (e.g., mummichog), if large numbers are caught, a subset will be weighed and measured and counts and weight of the total catch will be developed. This decision will be made in the field in coordination with the USEPA observer.
- Non-Target species:
  - If fish are intact, species counts, weights, and lengths will be recorded. Fish will then be returned to the water.
  - If fish are not intact, only fish species and counts will be recorded.
  - If large numbers of a species are caught, a subset will be weighed and measured; this will be a field decision in coordination with the USEPA observer.

A data report(s) summarizing the fish tissue collection and analysis results will be provided 90 days after receipt of all Phase III validated chemical data. In addition, this report will include maps that present the sampling locations.

How will the data be archived?

Data records, forms, and notes will be scanned and stored electronically in a project file. Hard copies will be archived in Tierra's main office in East Brunswick, New Jersey. Similarly, the data reports will be issued and then archived electronically and as hard copies. The analytical results will also be provided, as electronic data deliverables, to the project database. Multimedia electronic data deliverables (MEDD) will be provided to USEPA Region 2 by FTS in their required format.

Notes:
BERA = baseline ecological risk assessment
BHHRA = baseline human health risk assessment
CBR = critical body residue
CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act
COPC = constituent of potential concern
COPEC = constituent of potential ecological concern
Crab/Clam QAPP = Crab and Clam Sampling and Analysis Quality Assurance Project Plan
MEDD = multimedia electronic data deliverable
NBSA = Newark Bay Study Area
QAPP = Fish Sampling and Analysis Quality Assurance Project Plan
SOP = standard operating procedure
Tierra = Tierra Solutions, Inc.
TRV = toxicity reference value
USEPA = U.S. Environmental Protection Agency

References:

Tierra. 2013. Final Newark Bay Study Area Problem Formulation. Baseline Human Health and Ecological Risk Assessment. Tierra Solutions, Inc., East Brunswick, NJ. June.

Tierra. 2014. Crab and Clam Sampling and Analysis Quality Assurance Project Plan. Tierra Solutions, Inc., East Brunswick, NJ. Rev 3. August.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank

Matrix	Rinse/Field Blank
Analytical Group[a]	PCDDs/PCDFs
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-1	Accuracy/Bias	All target compound concentrations must fall within range provided in Table 6 of L-1	Ongoing Precision and Recovery	A
		Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Accuracy/Bias	Per L-1	Initial Calibration	A
		Accuracy/Bias	Per L-1	Calibration Verification	A
		Accuracy/Bias	Per L-1	Labeled Compound Spike	A
		Accuracy/Bias	Per L-1	Labeled Internal Standards	A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	PCB Congeners
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-2	Accuracy/Bias	All target compound analytes contained in the OPR must have observed concentration values that fall within the acceptance ranges provided in Table 6 of L-2	Ongoing Precision and Recovery	A
		Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Accuracy/Bias	Per L-2	Initial Calibration	A
		Accuracy/Bias	Per L-2	Calibration Verification	A
		Accuracy/Bias	Per L-2	Labeled Compound Spike	A
		Accuracy/Bias	Per L-2	Labeled Internal Standards	A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	TAL Metals, Titanium
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-3, L-29	Accuracy/Bias	**Compound** All target analyes	**% Recovery** 80-120	Laboratory Control Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks and Instrument Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field/Trip Blank
Analytical Group[a]	Mercury
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-4	Accuracy/Bias	**% Recovery** 77-123	Ongoing Precision and Recovery	A
		Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks,Trip Blanks[d] and Instrument Blanks	A
		Accuracy/Bias	Per L-4	Initial Precision and Recovery	A
		Accuracy/Bias	Per L-4	Initial Calibration	A
		Accuracy/Bias	Per L-4	Calibration Verification	A
		Accuracy/Bias	**% Recovery** 50-150	Quality Control Sample	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field/Trip Blank
Analytical Group[a]	Methylmercury
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-5	Accuracy/Bias	**% Recovery** 67-133	Ongoing Precision and Recovery	A
		Accuracy/Bias	Per L-5	Initial Precision and Recovery	A
		Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks, Trip Blanks[d] and Instrument Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Accuracy/Bias	Per L-5	Initial Calibration	A
		Accuracy/Bias	Per L-5	Calibration Verification	A
		Accuracy/Bias	**% Recovery** 50-150	Quality Control Sample	A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	Butyltins
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-6	Accuracy/Bias	**Surrogate Compounds**	**% Recovery**	Surrogate Spikes	A
			Tripentyltin	15-150		
		Accuracy/Bias	**Compound**	**% Recovery**	Laboratory Control Sample	A
			Monobutyltin	10-48		
			Dibutyltin	30-150		
			Tributyltin	30-150		
			Tetrabutyltin	30-150		
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	Semivolatile Organics
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-8	Accuracy/Bias	**Surrogate Compounds** Phenol-d_5 2-Fluorobiphenyl 2-Fluorophenol 2,4,6-Tribromophenol Nitrobenzene-d_5 p-Terphenyl-d_{14}	**% Recovery** Per L-8	Surrogate Spikes	A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** 20-150	Laboratory Control Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	Semivolatile Organics (SIM)
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-9	Accuracy/Bias	**Surrogate Compounds**	**% Recovery**	Surrogate Spikes	A
			Fluoranthene-d_{10}	64-120		
			Benzo(a)pyrene-d_{12}	62-141		
			1-Methylnaphthalene-d_{10}	58-134		
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	Aroclor PCBs
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-10	Accuracy/Bias	**Surrogate Compound** Tetrachloro-m-xylene Decachlorobiphenyl	**% Recovery** 43-144 43-144	Surrogate Spikes	A
		Accuracy/Bias	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130	Laboratory Control Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks and Instrument Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blanks (continued)

Matrix	Rinse/Field Blank
Analytical Group[a]	Pesticides
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-3	L-11	Accuracy/Bias	All target compound percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11		Ongoing Precision and Recovery	A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** 70-130	Secondary Source Standard	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks and Instrument Blanks	A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Accuracy/Bias	Per L-11		Initial Calibration	A
		Accuracy/Bias	Per L-11		Calibration Verfication	A
		Accuracy/Bias	Per L-11		Labeled Compound Spike	A
		Accuracy/Bias	Per L-11		Labeled Internal Standards	A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Rinse/Field Blank (continued)

Notes:

[a] If information varies within an analytical group, separate by individual analyte.
[b] Reference number from Worksheet #21.
[c] Reference number from Worksheet #23.
[d] Trip blanks will be collected, travel with environmental samples, and be submitted for analysis in association with any samples collected for volatile organics, mercury or methylmercury analysis.

Definitions of Terms:

Rinse Blank = Blank sample collected by pouring de-ionized water or solvent, whichever is appropriate to the contaminants of interest, over the homogenization sampling equipment after it has been cleaned in the laboratory. Rinse blanks are submitted for testing at the event of 1 per 20 samples, not to exceed more than one per day. Rinse blanks check for sample contamination caused by reuse of decontaminated homogenization equipment, as well as the sampling process and transportation.

Trip Blank = Sample matrices that are as free of volatile analytes as possible and transported with the samples to the laboratory without being opened. These serve as a check on sample contamination during transport, shipping, and storage before analysis.

Field Blank = Blank samples collected by pouring de-ionized water or solvent through the filleting equipment in the field. Field blanks serve as a check on contamination prior to sample processing.

DCAA = 2,4-dichlorophenylacetic acid
PCBs = polychlorinated biphenyls
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans
PQL = project quantitation limit
QC = quality control
RPD = relative percent difference
SIM = selective ion monitoring
SOP = Standard Operating Procedure
TAL = Target Analyte List
USEPA = U.S. Environmental Protection Agency
% = percent

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue

Matrix	Tissue
Analytical Group[a]	PCDDs/PCDFs
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP -5	L-1	Precision - Lab	**Compound** All target analytes	**RPD** <50	Matrix Spike Duplicate	A
		Accuracy/Bias	**Compound** All analytes	**% Recovery** 60-140	Matrix Spike	A
		Accuracy/Bias	All target compound concentrations must fall within the acceptance ranges provided in Table 6 of L-1		Ongoing Precision and Recovery	A
		Accuracy/Bias	All certified target compound concentrations must be within ± 25% of certified value when concentrations fall within the range of the initial calibration		Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks and Rinse Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicate	S & A
		Accuracy/Bias	Per L-1		Initial Calibration	A
		Accuracy/Bias	Per L-1		Calibration Verification	A
		Accuracy/Bias	Per L-1		Labeled Compound Spike	A
		Accuracy/Bias	Per L-1		Labeled Internal Standards	A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	PCB Congeners
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-2	Precision - Lab	**Compound** 86 target analytes	**RPD** <50	Matrix Spike Duplicate	A
		Accuracy/Bias	**Compound** 86 target analytes	**% Recovery** 60-140	Matrix Spike	A
		Accuracy/Bias	All target compound concentrations must fall within the acceptance ranges provided in Table 6 of L-2		Ongoing Precision and Recovery	A
		Accuracy/Bias	All certified target compound concentrations must be within ± 25% of certified value when concentrations fall within the range of the initial calibration		Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥ PQL		Method Blanks, Field Blanks and Rinse Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	PCB Congeners
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-2	Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples	Field Duplicate	S & A
		Accuracy/Bias	Per L-2	Initial Calibration	A
		Accuracy/Bias	Per L-2	Calibration Verification	A
		Accuracy/Bias	Per L-2	Labeled Compound Spike	A
		Accuracy/Bias	Per L-2	Labeled Internal Standards	A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	TAL Metals, Titanium
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-3, L-29	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 75-125	Matrix Spike	A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** 80-120	Laboratory Control Sample	A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** **70-130**	Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks, Rinse Blanks, Instrument Blanks, and Calibration Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Precision-Lab	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Laboratory Duplicate	A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicate	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Mercury
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-4	Accuracy/Bias	**% Recovery** 71-125	Matrix Spike	A
		Accuracy/Bias	**% Recovery** 77-123	Ongoing Precision and Recovery	A
		Accuracy/Bias	Per L-4	Initial Precision and Recovery	A
		Accuracy/Bias	**% Recovery** 75-125	Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks, Trip Blanks[d], Field Blanks, Rinse Blanks, and Instrument Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Precision - Lab	RPD ≤24%	Matrix Spike Duplicate	A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples	Field Duplicate	S & A
		Accuracy/Bias	Per L-4	Initial Calibration	A
		Accuracy/Bias	Per L-4	Calibration Verification	A
		Accuracy/Bias	Per L-4	Quality Control Sample	A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Methylmercury
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-5	Precision - Lab	RPD ≤35%	Matrix Spike Duplicate	A
		Accuracy/Bias	**% Recovery** 65-135	Matrix Spike	A
		Accuracy/Bias	**% Recovery** 67-133	Ongoing Precision and Recovery	A
		Accuracy/Bias	Per L-5	Initial Precision and Recovery	A
		Accuracy/Bias	Target compound concentration must be within ± 35% of certified value.	Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks, Field Blanks, Rinse Blanks, Trip Blanks[d] and Instrument Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples	Field Duplicate	S & A
		Accuracy/Bias	Per L-5	Initial Calibration	A
		Accuracy/Bias	Per L-5	Calibration Verification	A
		Accuracy/Bias	**% Recovery** 50-150	Quality Control Sample	A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Butyltins
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-6	Precision - Lab	RPD <30%		Matrix Spike Duplicate	A
		Accuracy/Bias	**Analyte** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-160 30-160 30-160	Matrix Spike	A
		Accuracy/Bias	**Analyte** Tripentyltin	**% Recovery** 30-120	Surrogate Spikes	A
		Accuracy/Bias	**Analyte** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-160 30-160 30-160	Laboratory Control Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks and Rinse Blanks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicate	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Semivolatile Organics
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-8, L-30 and L-32	Precision - Lab	RPD <30%		Matrix Spike Duplicate	A
		Accuracy/Bias	**Compound** All target compounds	**% Recovery** 20-150	Matrix Spike	A
		Accuracy/Bias	**Surrogate Compounds** Phenol-d_5 2-Fluorobiphenyl 2-Fluorophenol 2,4,6-Tribromphenol Nitrobenzene-d_5 p-Terphenyl-d_{14}	**% Recovery** Per L-8	Surrogate Spikes	A
		Accuracy/Bias	**Compound** All target compounds	**% Recovery** 20-150	Laboratory Control Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks and Rinse Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicate	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Semivolatile Organics (SIM)
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-9, L-30, L-31 and L-32	Precision - Lab	**Compound** All target analytes	**RPD** <40	Matrix Spike Duplicate	A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** 60-140	Matrix Spike	A
		Accuracy/Bias	**Surrogate Compounds** Fluoranthene-d_{10} Benzo(a)pyrene-d_{12} 1-Methylnaphthalene-d_{10}	**% Recovery** 50-150	Surrogate Spikes	A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** Recovery within limits set by performance evaluation sample vendor.	Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks and Rinse Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicate	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Aroclor PCBs
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-10	Precision - Lab	**Compound** Aroclor-1016 Aroclor-1260	**RPD** <15 <20	Matrix Spike Duplicate	A
		Accuracy/Bias	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130	Matrix Spike	A
		Accuracy/Bias	**Surrogate Compound** Tetrachloro-m-xylene Decachlorobiphenyl	**% Recovery** 30-150 30-150	Surrogate Spikes	A
		Accuracy/Bias	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130	Laboratory Control Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks, Rinse Blanks, and Instrument Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicates	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	Pesticides
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria		QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-11	Precision - Lab	RPD < 25%		Matrix Spike Duplicate	A
		Accuracy/Bias	**Compound** All spiking compounds	**% Recovery** 50-150	Matrix Spike	A
		Accuracy/Bias	**Compounds** All target analytes	**% Recovery** 70-130	Secondary Source Standard	A
		Accuracy/Bias	All target analyte percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11		Ongoing Precision and Recovery	A
		Accuracy/Bias	All target analyte percent recoveries must fall within the acceptance criteria provided by the vendor		Performance Evaluation Sample	A
		Accuracy/Bias Contamination	No target compounds ≥PQL		Method Blanks, Field Blanks, and Rinse Blanks	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Checks	S & A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples		Field Duplicate	S & A
		Accuracy/Bias	Per L-11		Initial Calibration	A
		Accuracy/Bias	Per L-11		Calibration Verification	A
		Accuracy/Bias	Per L-11		Labeled Compound Spike	A
		Accuracy/Bias	Per L-11		Labeled Internal Standards	A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	% Lipids
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-1	Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks	A
		Accuracy/Bias	The % lipids percent recovery must fall within the acceptance criteria provided by the vendor	Performance Evaluation Sample	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Precision - Lab	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples	Laboratory Duplicate	A
		Precision - Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples	Field Duplicate	S & A

See the last page of Worksheet #12-2 for a description of footnotes.

QAPP Worksheet #12-2 (UFP-QAPP Manual Section 2.6): Measurement Performance Criteria – Tissue (continued)

Matrix	Tissue
Analytical Group[a]	% Moisture
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-4 and SOP-5	L-21	Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Precision - Lab	RPD ≤20%	Laboratory Duplicate	A

Notes:

[a] If information varies within an analytical group, separate by individual analyte.
[b] Reference number from Worksheet #21.
[c] Reference number from Worksheet #23.
[d] Trip blanks will be collected, travel with environmental samples, and be submitted for analysis in association with any samples collected for volatile organics, mercury, or methylmercury analysis.

PCBs = polychlorinated biphenyls
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans
PQL = project quantitation limit
QC = quality control
RPD = relative percent difference
SIM = selective ion monitoring
TAL = Target Analyte List
SOP = Standard Operating Procedure
USEPA = U.S. Environmental Protection Agency
% = percent

QAPP Worksheet #13 (UFP-QAPP Manual Section 2.7): Secondary Data Criteria and Limitations Table

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s)	Data Use	Limitations on Data Use
NBSA Sampling Performed by Others				
Tissue Data	Contaminant Assessment and Reduction Program, available online at (http://www.carpweb.org/main.html)	Fish tissue data collected by the New Jersey Department of Environmental Protection and New York State Department of Environmental Conservation between 2000 and 2004.	• Tissue chemistry data were used to select the species appropriate for tissue-residue analysis. • Statistical evaluations were conducted on the data to determine the number of fish tissue samples needed.	Limited sample numbers collected from only one station in Newark Bay.
Fish Community Data	USACE's Aquatic Biological Survey Program	Fish community data (species counts collected as catch per unit effort) collected on a monthly basis from 1999 to 2011.	• Qualitative evaluations regarding any potential temporal or spatial changes in the fish community in the NBSA.	Data not associated with chemicals in fish tissue therefore cannot be linked to changes in tissue concentrations.

QAPP Worksheet #14 (UFP-QAPP Manual Section 2.8.1): Summary of Project Tasks

Sampling Tasks:

Fish samples will be collected from three zones within the NBSA to characterize concentrations of constituents of potential ecological concern in fish tissue. The following types and numbers of fish tissue samples will be targeted for collection and analysis:

Trophic Level	Target Species	Sample Preparation	Type of Sample	Number of Samples per Zone	Total Number of Samples
Forage Fish	Mummichog/striped killifish	Whole body	Composite	--	16 - 19
	Bay anchovy/ Atlantic silverside/menhaden	Whole body	Composite	3	9
Benthic/ Demersal	Flounder/hake	Whole body	Individual	6	18
Pelagic Predatory	White perch	Whole body	Individual or Composite	9	27
	White perch	Liver	Composite	3	9
	American eel	Whole body	Individual or Composite	6	18
Sport Fish[c]	Striped bass	Skin-on, scales off fillet	Individual or Composite[a]	--	18
	Bluefish/weakfish	Skin-on, scales off fillet	Individual or Composite[a]	--	18
	White perch	Skin-on, scales off fillet	Composite	6	18
	American eel	Skinless fillet	Individual or Composite[a]	6	18
	Flounder/hake	Skin-on, scales off fillet	Individual or Composite[a]	6	18
Total					**196[b]**

Notes:

Zones defined as Newark Bay North, Central, and South (Figure 1)

a. Individual preferred but fillet composites may be required to fulfill analytical mass.
b. Assumes a total of 16 mummichog samples.
c. Sport fish are defined as fish species targeted for human consumption and may also include fish from other trophic feeding guilds (e.g., white perch, American eel, flounder).

Fish samples will be collected using gill nets, seines, trawls, and fish traps as described in SOP No. 4 - Fish Collection and Tissue Sampling. Following collection, fish will be observed for external anomalies, and processed following the procedures in SOP No. 5 – Fish Tissue Sample Processing.

See the last page of Worksheet #14 for a description of footnotes

QAPP Worksheet #14 (UFP-QAPP Manual Section 2.8.1): Summary of Project Tasks (continued)

Analysis Tasks:

Following fish sample collection, samples will be processed (i.e., weighed, measured, and filleted or composited as necessary) in the field at the 80 Lister Avenue Field Facility, and shipped frozen to the analytical laboratory (Refer to SOP-5). In the laboratory, samples will be homogenized and submitted for chemical analysis. The homogenate from the tissue samples will be shipped to subcontracted laboratories if necessary. Fish tissue samples will be submitted for laboratory analysis of the chemicals listed in Worksheet #15-2.

Additionally, Tierra will submit performance evaluation (PE) samples to the laboratories for analysis initially (pre-program), and on an on-going basis throughout the sample collection phase.

Planned PE samples include the following:

Analytical Group	Matrix
Polychlorinated Dibenzo-p-dioxins / Polychlorinated Dibenzofurans	Sediment and Tissue
Polychlorinated Biphenyl Congeners	Sediment and Tissue
Organochlorine Pesticides	Sediment and Tissue
Semivolatile Organics SIM	Sediment and Tissue
Mercury	Sediment and Tissue
Methylmercury	Sediment and Tissue
Target Analyte List Metals	Sediment and Tissue
Percent Lipids	Tissue only

Per agreement between Tierra and USEPA Region 2, ongoing PE samples will be submitted to the appropriate laboratory for analysis at the following frequency: one PE sample (as described in the table above) for each sample delivery group (SDG) that contains samples that are split for analysis by both Tierra's laboratory and USEPA's laboratory. In the case of remaining SDGs (those that do not contain samples split between Tierra and USEPA laboratories) one PE sample (as described in the table above) will be submitted to Tierra laboratories for every 40 field samples collected.

Quality Control Tasks:

Field notes and forms completed during the field sampling task will be checked daily by the Field Supervisor. The Field Supervisor will also communicate daily with the Task QA/QC Manager to confirm objectives are being met. As part of the QC process to assess the accuracy of species identification, specimens of each captured species will be collected and independently verified by a biologist who is not associated with the field task. Fish measurements and weights will be compiled in a table and reviewed as a QC step. Any lengths and weights that appear to be anomalous will be verified by a second team member by re-measuring. Sample identifications will be similarly verified.

Electronic sampling equipment (e.g., scale, GPS units) will be calibrated, maintained, tested, and inspected according to manufacturers' specifications, as necessary, to confirm they are functioning properly (refer to Worksheet #22).

Laboratory procedures will be carried out per the SOPs and analytical methodologies provided in the appendices of this document. In addition, field and laboratory quality control samples will be processed as indicated in Worksheets #28-1 and 28-2. Project quality objectives and measurement performance criteria will be monitored throughout project implementation and at the conclusion of field and analytical activities. Data produced will undergo data validation steps specified in Worksheets #34, 35, and 36. These data evaluation steps will be performed by the QA Coordinator, from an organization independent from those generating the data.

See the last page of Worksheet #14 for a description of footnotes.

QAPP Worksheet #14 (UFP-QAPP Manual Section 2.8.1): Summary of Project Tasks (continued)

Secondary Data:

Other tissue and chemistry data that are summarized in Worksheet #13 will also be reviewed and potentially used qualitatively to accomplish project objectives.

Data Management Tasks:

The data management task will include keeping accurate records of field activities and observations so that project team members using the data will have accurate and appropriate documentation. Field data will be stored in their native format and in the project sampling database. GPS data will also be downloaded and stored electronically in a project file. Laboratory analytical data will be loaded into the project sampling database, verified against the laboratory reports, merged with corresponding field data, and updated based on validation. Subsequently, the spatial data will be mapped for the data report.

Documentation and Records:

It is important that field activities be documented in an organized, chronologically accurate manner. Field activities will be recorded in a field notebook maintained by the Field Supervisor. The field notebook is intended to provide sufficient data and observations to enable participants to reconstruct events that occurred during the sampling period. Procedures for documentation are presented in SOP No. 8. Relevant forms and records are presented in Worksheet #29-1. In general, the following information will be recorded:

- The identities and affiliation of the personnel conducting field activities.
- Model numbers and serial numbers of instruments and/or equipment being used, will, to the extent available, be recorded in the field notebook.
- A description of the type of field work being conducted and the equipment used.
- The date and time the field activities were initiated and completed, with specific temporal information for each task (e.g., record the time activities commenced at each individual location, if applicable).
- The site where the field activities were conducted and also any locations within that site where work was performed (e.g., specific sampling sites, coordinates).
- The general methodology used to conduct the activities.
- Communications with Project Managers and personnel regarding field activities.
- Field collected data (e.g., GPS measurements, collection totals).
- Daily health and safety briefings.
- Deviations from this Fish Sampling QAPP, SOPs, or project HASP, reason for change, and any corrective actions taken. Corrective actions will be electronically documented on the Protocol Modification Form (Appendix D).
- Photographs will be taken of the fish samples collected and any anomalies noted. When photos associated with sampling locations, field activities, or samples are taken, they will be documented in the field notebook, including the date, time, photographer, and brief description.

The Location Data Form and Specimen Tally Form (Appendix D) will be completed electronically by field personnel to document sampling location information and gross external observations of collected fish. A daily tally of all species that are caught will also be recorded in the Specimen Tally Form and Non-Target Species Tally Form (Appendix D).Fish samples that will be analyzed will be recorded electronically in the Sample Processing Form (Appendix D) by field laboratory personnel or the project chemist.

A record of personnel briefed on the HASP will be maintained by the Field Supervisor, Site Safety and Health Officer, or designee. The record will be archived at Tierra Solutions, Inc.'s office upon completion of the sampling efforts.

Laboratories will provide complete hard copy analytical data packages, as outlined in Worksheets #29-2 and 29-3. Specifications for electronic laboratory data deliverables are located in Worksheet #29-4.

See the last page of Worksheet #14 for a description of footnotes.

QAPP Worksheet #14 (UFP-QAPP Manual Section 2.8.1): Summary of Project Tasks (continued)

Assessment/Audit Tasks:

Assessment/audit tasks will be conducted, as summarized below:

1. Laboratory Technical Systems Audit (one audit of each laboratory prior to use or again after period of inactivity associated with Tierra Solutions, Inc. exceeding 2 years).
2. Field Readiness Review. Refer to Worksheets #31 and 32.
3. Laboratory Readiness Review. Refer to Worksheets #31 and 32.
4. Data Validation.
5. Data Usability Assessment Report.

Data Review Tasks:

All field records will be reviewed by the Field Supervisor for completeness and accuracy and verified by the Task QA/QC Manager or a designee.

Contract laboratories will verify that all data are complete for samples received. All data package deliverable requirements will be met. Data will be validated by FTS per the requirements specified in Worksheets #34, 35 and 36. A Data Validation Report will be produced for each sample delivery group and each analytical group.

Validated data and all related field logs/notes/records will be reviewed to assess total measurement error and determine overall usability of the data for project purposes. Data limitations will be determined and data will be compared to project quality objectives and required action limits. Corrective action will be initiated, as necessary. Final data will be placed in the database, with necessary qualifiers.

As part of data report preparation, chemical data will be reviewed to determine if differences related to species and/or location are evident. In addition, the data report will also undergo a senior and peer review process before the final draft is submitted to USEPA (see Worksheets #34 through 37 for relevant procedures).

A tissue chemistry data report will be prepared once all of the tissue chemistry results (including all Phase III data) have been validated. This data report will be provided to USEPA after 90 days of receipt of validated data and will include validation results.

Notes:

FTS = Field & Technical Services
GPS = global positioning system
HASP = health and safety plan
NBSA = Newark Bay Study Area
QA/QC = quality assurance/quality control
QAPP = Quality Assurance Project Plan
SOP = standard operating procedure
USEPA = U.S. Environmental Protection Agency

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank

Matrix: Rinse/Field Blank
Analytical Group: PCDDs/PCDFs
Concentration Level: Low
Analytical Method/SOP Reference: L-1

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
2,3,7,8-TCDD	1746-01-6	---	2.00	Not provided in method	10	1.0	2.00
1,2,3,7,8-PeCDD	40321-76-4	---	10.0	Not provided in method	50	3.0	10.0
1,2,3,6,7,8-HxCDD	57653-85-7	---	10.0	Not provided in method	50	3.0	10.0
1,2,3,4,7,8-HxCDD	39227-28-6	---	10.0	Not provided in method	50	4.0	10.0
1,2,3,7,8,9-HxCDD	19408-74-3	---	10.0	Not provided in method	50	4.0	10.0
1,2,3,4,6,7,8-HpCDD	35822-46-9	---	10.0	Not provided in method	50	6.0	10.0
OCDD	3268-87-9	---	20.0	Not provided in method	100	10.0	20.0
2,3,7,8-TCDF	51207-31-9	---	2.00	Not provided in method	10	1.0	2.00
1,2,3,7,8-PeCDF	57117-41-6	---	10.0	Not provided in method	50	2.0	10.0
2,3,4,7,8-PeCDF	57117-31-4	---	10.0	Not provided in method	50	3.0	10.0
1,2,3,6,7,8-HxCDF	57117-44-9	---	10.0	Not provided in method	50	3.0	10.0
1,2,3,7,8,9-HxCDF	72918-21-9	---	10.0	Not provided in method	50	4.0	10.0
1,2,3,4,7,8-HxCDF	70648-26-9	---	10.0	Not provided in method	50	3.0	10.0
2,3,4,6,7,8-HxCDF	60851-34-5	---	10.0	Not provided in method	50	3.0	10.0
1,2,3,4,6,7,8-HpCDF	67562-39-4	---	10.0	Not provided in method	50	4.0	10.0
1,2,3,4,7,8,9-HpCDF	55673-89-7	---	10.0	Not provided in method	50	3.0	10.0
OCDF	39001-02-0	---	20.0	Not provided in method	100	6.0	20.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB1	2051-60-7	---	20.0	82	200	10.0	20.0
PCB2	2051-61-8	---	20.0	4	10	7.0	20.0
PCB3	2051-62-9	---	50.0	88	200	11.0	50.0
PCB4/10	13029-08-8/33146-45-1	---	50.0	Not provided in method	Not provided in method	13.0	50.0
PCB6	25569-80-6	---	20.0	13	50	7.0	20.0
PCB5/8	16605-91-7/34883-43-7	---	20.0	Not provided in method	Not provided in method	8.0	20.0
PCB7/9	33284-50-3/34883-39-1	---	20.0	Not provided in method	Not provided in method	7.0	20.0
PCB11	2050-67-1	---	100	105	200	34.0	100
PCB12/13	2974-92-7/2974-90-5	---	50.0	28	100	19.0	50.0
PCB14	34883-41-5	---	20.0	31	100	8.0	20.0
PCB15	2050-68-2	---	50.0	183	500	16.0	50.0
PCB16/32	38444-78-9/38444-77-8	---	20.0	Not provided in method	Not provided in method	9.0	20.0
PCB17	37680-66-3	---	20.0	86	200	9.0	20.0
PCB18	37680-65-2	---	50.0	175	500	16.0	50.0
PCB19	38444-73-4	---	20.0	42	100	8.0	20.0
PCB20/21/33	38444-84-7/ 55702-46-0/38444-86-9	---	50.0	Not provided in method	Not provided in method	22.0	50.0
PCB22	38444-85-8	---	20.0	90	200	9.0	20.0
PCB23	55720-44-0	---	20.0	50	200	7.0	20.0
PCB24/27	55702-45-9/38444-76-7	---	20.0	Not provided in method	Not provided in method	10.0	20.0
PCB25	55712-37-3	---	20.0	55	200	8.0	20.0
PCB26	38444-81-4	---	50.0	83	200	12.0	50.0
PCB28	7012-37-5	---	50.0	192	500	22.0	50.0
PCB29	15862-07-4	---	50.0	83	200	12.0	50.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB30	35693-92-6	---	50.0	175	500	16.0	50.0
PCB31	16606-02-3	---	50.0	152	500	18.0	50.0
PCB34	37680-68-5	---	20.0	74	200	7.0	20.0
PCB35	37680-69-6	---	20.0	77	200	9.0	20.0
PCB36	38444-87-0	---	20.0	79	200	8.0	20.0
PCB37	38444-90-5	---	20.0	132	500	10.0	20.0
PCB38	53555-66-1	---	20.0	83	200	7.0	20.0
PCB39	38444-88-1	---	20.0	85	200	8.0	20.0
PCB40	38444-93-8	---	100.0	119	500	42.0	100.0
PCB41/64/71/ 72	52663-59-9/52663-58-8/ 41464-46-4/41464-42-0	---	100.0	Not provided in method	Not provided in method	42.0	100.0
PCB42/59	36559-22-5/74472-33-6	---	50.0	Not provided in method	Not provided in method	16.0	50.0
PCB43/49	70362-46-8/41464-40-8	---	50.0	Not provided in method	Not provided in method	14.0	50.0
PCB44	41464-39-5	---	100.0	195	500	40.0	100.0
PCB45	70362-45-7	---	50.0	51	200	22.0	50.0
PCB46	41464-47-5	---	20.0	101	200	10.0	20.0
PCB47	2437-79-8	---	100.0	195	500	40.0	100.0
PCB48/75	70362-47-9/32598-12-2	---	50.0	Not provided in method	Not provided in method	14.0	50.0
PCB50	62796-65-0	---	100.0	58	200	25.0	100.0
PCB51	68194-04-7	---	50.0	51	200	22.0	50.0
PCB52/69	35693-99-3/60233-24-1	---	50.0	Not provided in method	Not provided in method	15.0	50.0
PCB53	41464-41-9	---	100.0	58	200	25.0	100.0
PCB54	15968-05-5	---	50.0	118	500	14.0	50.0
PCB55	74338-24-2	---	50.0	120	500	12.0	50.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB56/60	41464-43-1/33025-41-1	---	50.0	Not provided in method	Not provided in method	15.0	50.0
PCB57	70424-67-8	---	50.0	125	500	11.0	50.0
PCB58	41464-49-7	---	50.0	127	500	14.0	50.0
PCB61/70	33284-53-6/32598-11-1	---	200.0	171	500	59.0	200.0
PCB62	54230-22-7	---	100.0	57	200	37.0	100.0
PCB63	74472-34-7	---	50.0	138	500	12.0	50.0
PCB65	33284-54-7	---	100.0	195	500	40.0	100.0
PCB67	73575-53-8	---	50.0	147	500	12.0	50.0
PCB68	73575-52-7	---	50.0	149	500	14.0	50.0
PCB73	74338-23-1	---	50.0	160	500	14.0	50.0
PCB74	32690-93-0	---	200.0	171	500	59.0	200.0
PCB76/66	70362-48-0/32598-10-0	---	200.0	Not provided in method	Not provided in method	59.0	200.0
PCB77	32598-13-3	---	50.0	169	500	14.0	50.0
PCB78	70362-49-1	---	50.0	171	500	16.0	50.0
PCB79	41464-48-6	---	50.0	173	500	13.0	50.0
PCB80	33284-52-5	---	50.0	175	500	11.0	50.0
PCB81	70362-50-4	---	50.0	177	500	18.0	50.0
PCB82	52663-62-4	---	50.0	133	500	15.0	50.0
PCB83	60145-20-2	---	100.0	217	500	29.0	100.0
PCB84/92	52663-60-2/52663-61-3	---	20.0	Not provided in method	Not provided in method	11.0	20.0
PCB85/116	65510-45-4/18259-05-7	---	100.0	104	200	38.0	100.0
PCB86	55312-69-1	---	200.0	149	500	74.0	200.0
PCB87/117/125	38380-02-8/ 68194-11-6/74472-39-2	---	200.0	Not provided in method	Not provided in method	74.0	200.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB88/91	55215-17-3/68194-05-8	---	50.0	118	500	22.0	50.0
PCB89	73575-57-2	---	50.0	195	500	13.0	50.0
PCB90/101	68194-07-0/37680-73-2	---	200.0	241	1000	47.0	200.0
PCB93	73575-56-1	---	200.0	221	500	77.0	200.0
PCB94	73575-55-0	---	50.0	121	500	13.0	50.0
PCB95/98/102	38379-99-6/ 60233-25-2/68194-06-9	---	200.0	221	500	77.0	200.0
PCB96	73575-54-9	---	50.0	210	500	15.0	50.0
PCB97	41464-51-1	---	200.0	149	500	74.0	200.0
PCB99	38380-01-7	---	100.0	217	500	29.0	100.0
PCB100	39485-83-1	---	200.0	221	500	77.0	200.0
PCB103	60145-21-3	---	50.0	225	500	11.0	50.0
PCB104	56558-16-8	---	50.0	228	500	14.0	50.0
PCB105	32598-14-4	---	50.0	109	200	17.0	50.0
PCB106/118	70424-69-0/31508-00-6	---	50.0	Not provided in method	Not provided in method	17.0	50.0
PCB107/109	70424-68-9/74472-35-8	---	50.0	Not provided in method	Not provided in method	17.0	50.0
PCB108/112	70362-41-3/74472-36-9	---	100.0	Not provided in method	Not provided in method	29.0	100.0
PCB110	38380-03-9	---	100.0	243	1000	39.0	100.0
PCB111/115	39635-32-0/74472-38-1	---	50.0	243	1000	14.0	50.0
PCB113	68194-10-5	---	200.0	241	1000	47.0	200.0
PCB114	74472-37-0	---	50.0	120	500	15.0	50.0
PCB119	56558-17-9	---	200.0	149	500	74.0	200.0
PCB120	68194-12-7	---	50.0	147	500	13.0	50.0
PCB121	56558-18-0	---	50.0	209	500	13.0	50.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB122	76842-07-4	---	50.0	117	500	12.0	50.0
PCB123	65510-44-3	---	50.0	150	500	17.0	50.0
PCB124	70424-70-3	---	100.0	200	1000	29.0	100.0
PCB126	57465-28-8	---	50.0	136	500	16.0	50.0
PCB127	39635-33-1	---	50.0	278	1000	14.0	50.0
PCB128/162	38380-07-3/39635-34-2	---	100.0	Not provided in method	Not provided in method	29.0	100.0
PCB129	55215-18-4	---	200.0	211	500	63.0	200.0
PCB130	52663-66-8	---	50.0	136	500	13.0	50.0
PCB131	61798-70-7	---	50.0	121	500	17.0	50.0
PCB132/161	38380-05-1/74472-43-8	---	50.0	Not provided in method	Not provided in method	16.0	50.0
PCB133/142	35694-04-3/41411-61-4	---	50.0	Not provided in method	Not provided in method	12.0	50.0
PCB134/143	52704-70-8/68194-15-0	---	100.0	134	500	33.0	100.0
PCB135	52744-13-5	---	100.0	112	500	46.0	100.0
PCB136	38411-22-2	---	50.0	91	200	16.0	50.0
PCB137	35694-06-5	---	50.0	300	1000	15.0	50.0
PCB138/163/164	35065-28-2/ 74472-44-9/74472-45-0	---	200.0	Not provided in method	Not provided in method	63.0	200.0
PCB139/149	56030-56-9/38380-04-0	---	100.0	Not provided in method	Not provided in method	29.0	100.0
PCB140	59291-64-4	---	100.0	196	500	29.0	100.0
PCB141	52712-04-6	---	50.0	93	200	17.0	50.0
PCB144	68194-14-9	---	50.0	167	500	15.0	50.0
PCB145	74472-40-5	---	50.0	317	1000	16.0	50.0
PCB146/165	51908-16-8/74472-46-1	---	50.0	Not provided in method	Not provided in method	14.0	50.0
PCB147	68194-13-8	---	100.0	179	500	35.0	100.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB148	74472-41-6	---	50.0	324	1000	14.0	50.0
PCB150	68194-08-1	---	50.0	328	1000	15.0	50.0
PCB151	52663-63-5	---	100.0	112	500	46.0	100.0
PCB152	68194-09-2	---	50.0	238	1000	14.0	50.0
PCB153	35065-27-1	---	100.0	130	500	30.0	100.0
PCB154	60145-22-4	---	100.0	112	500	46.0	100.0
PCB155	33979-03-2	---	50.0	339	1000	14.0	50.0
PCB156	38380-08-4	---	100.0	132	500	23.0	100.0
PCB157	69782-90-7	---	100.0	132	500	23.0	100.0
PCB158/160	74472-42-7/41411-62-5	---	50.0	Not provided in method	Not provided in method	16.0	50.0
PCB159	39635-35-3	---	50.0	348	1000	14.0	50.0
PCB166	41411-63-6	---	100.0	124	500	29.0	100.0
PCB167	52663-72-6	---	50.0	115	500	13.0	50.0
PCB168	59291-65-5	---	100.0	130	500	30.0	100.0
PCB169	32774-16-6	---	50.0	161	500	15.0	50.0
PCB170	35065-30-6	---	50.0	162	500	12.0	50.0
PCB171	52663-71-5	---	100.0	374	1000	30.0	100.0
PCB172	52663-74-8	---	50.0	377	1000	13.0	50.0
PCB173	68194-16-1	---	100.0	374	1000	30.0	100.0
PCB174	38411-25-5	---	50.0	186	500	15.0	50.0
PCB175	40186-70-7	---	50.0	383	1000	14.0	50.0
PCB176	52663-65-7	---	50.0	385	1000	12.0	50.0
PCB177	52663-70-4	---	50.0	141	500	11.0	50.0
PCB178	52663-67-9	---	50.0	221	500	14.0	50.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB179	52663-64-6	---	50.0	229	500	14.0	50.0
PCB180	35065-29-3	---	100.0	136	500	30.0	100.0
PCB181	74472-47-2	---	50.0	396	1000	13.0	50.0
PCB182/187	60145-23-5/52663-68-0	---	50.0	Not provided in method	Not provided in method	13.0	50.0
PCB183	52663-69-1	---	100.0	401	1000	28.0	100.0
PCB184	74472-48-3	---	50.0	403	1000	14.0	50.0
PCB185	52712-05-7	---	100.0	401	1000	28.0	100.0
PCB186	74472-49-4	---	50.0	407	1000	15.0	50.0
PCB188	74487-85-7	---	50.0	235	500	15.0	50.0
PCB189	39635-31-9	---	50.0	177	500	13.0	50.0
PCB190	41411-64-7	---	50.0	234	500	14.0	50.0
PCB191	74472-50-7	---	50.0	418	1000	13.0	50.0
PCB192	*74472-51-8*	---	50.0	420	1000	13.0	50.0
PCB193	69782-91-8	---	100.0	136	500	30.0	100.0
PCB194	35694-08-7	---	50.0	170	500	18.0	50.0
PCB195	52663-78-2	---	50.0	427	1000	22.0	50.0
PCB196/203	42740-50-1/52663-76-0	---	50.0	Not provided in method	Not provided in method	20.0	50.0
PCB197	33091-17-7	---	100.0	245	1000	43.0	100.0
PCB198	68194-17-2	---	100.0	203	500	37.0	100.0
PCB199	52663-75-9	---	100.0	203	500	37.0	100.0
PCB200	52663-73-7	---	100.0	245	1000	43.0	100.0
PCB201	40186-71-8	---	50.0	440	1000	20.0	50.0
PCB202	2136-99-4	---	100.0	442	1000	24.0	100.0
PCB204	74472-52-9	---	50.0	447	1000	21.0	50.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
PCB205	74472-53-0	---	50.0	449	1000	15.0	50.0
PCB206	40186-72-9	---	50.0	451	1000	16.0	50.0
PCB207	52663-79-3	---	50.0	453	1000	19.0	50.0
PCB208	52663-77-1	---	50.0	455	1000	16.0	50.0
PCB209	2051-24-3	---	50.0	153	500	16.0	50.0

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: TAL Metals, Mercury, Methylmercury, Titanium
Concentration Level: Low
Analytical Method/SOP Reference: L-3, L-4, L-5, and L-29

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
Aluminum	7429-90-5	---	100	Not provided in method	Not provided in method	8.17	100
Antimony	7440-36-0	---	1	Not provided in method	Not provided in method	0.33	1
Arsenic	7440-38-2	---	2	Not provided in method	Not provided in method	0.82	2
Barium	7440-39-3	---	2	Not provided in method	Not provided in method	0.58	2
Beryllium	7440-41-7	---	0.5	Not provided in method	Not provided in method	0.045	0.5
Cadmium	7440-43-9	---	0.5	Not provided in method	Not provided in method	0.17	0.5
Calcium	7440-70-2	---	200	Not provided in method	Not provided in method	69.7	200
Chromium	7440-47-3	---	2	Not provided in method	Not provided in method	0.5	2
Cobalt	7440-48-4	---	0.5	Not provided in method	Not provided in method	0.1	0.5
Copper	7440-50-8	---	2	Not provided in method	Not provided in method	0.5	2
Iron	7439-89-6	---	100	Not provided in method	Not provided in method	13.1	100
Lead	7439-92-1	---	1	Not provided in method	Not provided in method	0.082	1
Magnesium	7439-95-4	---	100	Not provided in method	Not provided in method	7.0	100
Manganese	7439-96-5	---	2	Not provided in method	Not provided in method	0.55	2
Nickel	7440-02-0	---	2	Not provided in method	Not provided in method	0.79	2
Potassium	7440-09-7	---	200	Not provided in method	Not provided in method	41.2	200
Selenium	7782-49-2	---	2	Not provided in method	Not provided in method	0.5	2
Silver	7440-22-4	---	0.5	Not provided in method	Not provided in method	0.13	0.5
Sodium	7440-23-5	---	200	Not provided in method	Not provided in method	50	200
Titanium	7440-32-6	---	10	Not provided in method	Not provided in method	1.7	10
Thallium	7440-28-0	---	0.5	Not provided in method	Not provided in method	0.15	0.5
Vanadium	7440-62-2	---	0.5	Not provided in method	Not provided in method	0.22	0.5
Zinc	7440-66-6	---	15	Not provided in method	Not provided in method	2.4	15
Mercury	7439-97-6	---	0.5 ng/L	0.2 ng/L	0.5 ng/L	0.08 ng/L	0.5 ng/L
Methylmercury	22967-92-6	---	0.05 ng/L	0.02 ng/L	0.06 ng/L	0.026 ng/L	0.05 ng/L

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Butyltins
Concentration Level: Low
Analytical Method/SOP Reference: L-6

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
Dibutyltin	14488-53-0	---	0.039	Not provided in method	0.039	NA	0.039
Monobutyltin	78763-54-9	---	0.62	Not provided in method	0.62	NA	0.62
Tetrabutyltin	1461-25-2	---	0.050	Not provided in method	0.050	NA	0.050
Tributyltin	36643-28-4	---	0.045	Not provided in method	0.045	NA	0.045

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Semivolatile Organics
Concentration Level: Low
Analytical Method/SOP Reference: L-8

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
Benzaldehyde	100-52-7	---	5	Not provided in method	Not provided in method	1	5
Phenol	108-95-2	---	1	Not provided in method	Not provided in method	0.5	1
bis(2-Chloroethyl) ether	111-44-4	---	1	Not provided in method	Not provided in method	0.5	1
2-Chlorophenol	95-57-8	---	1	Not provided in method	Not provided in method	0.5	1
2-Methylphenol	95-48-7	---	1	Not provided in method	Not provided in method	0.5	1
2,2'-oxybis(1-Chloropropane)	108-60-1	---	1	Not provided in method	Not provided in method	0.5	1
Acetophenone	98-86-2	---	1	Not provided in method	Not provided in method	0.5	1
4-Methylphenol	106-44-5	---	1	Not provided in method	Not provided in method	0.5	1
N-Nitroso-di-n-propylamine	621-64-7	---	1	Not provided in method	Not provided in method	0.5	1
Hexachloroethane	67-72-1	---	5	Not provided in method	Not provided in method	0.1	5
Nitrobenzene	98-95-3	---	1	Not provided in method	Not provided in method	0.5	1
Isophorone	78-59-1	---	1	Not provided in method	Not provided in method	0.5	1
2-Nitrophenol	88-75-5	---	1	Not provided in method	Not provided in method	0.5	1
2,4-Dimethylphenol	105-67-9	---	1	Not provided in method	Not provided in method	0.5	1
bis(2-Chloroethoxy) methane	111-91-1	---	1	Not provided in method	Not provided in method	0.5	1
2,4-Dichlorophenol	120-83-2	---	1	Not provided in method	Not provided in method	0.5	1
4-Chloroaniline	106-47-8	---	1	Not provided in method	Not provided in method	0.5	1
Hexachlorobutadiene	87-68-3	---	1	Not provided in method	Not provided in method	0.5	1
Caprolactam	105-60-2	---	15	Not provided in method	Not provided in method	5	15
4-Chloro-3-methyphenol	59-50-7	---	1	Not provided in method	Not provided in method	0.5	1
Hexachlorocyclopentadiene	77-47-4	---	15	Not provided in method	Not provided in method	5	15
2,4,6-Trichlorophenol	88-06-2	---	1	Not provided in method	Not provided in method	0.5	1
2,4,5-Trichlorophenol	95-95-4	---	1	Not provided in method	Not provided in method	0.5	1
1,1'-Biphenyl	92-52-4	---	1	Not provided in method	Not provided in method	0.5	1

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Semivolatile Organics
Concentration Level: Low
Analytical Method/SOP Reference: L-8

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
2-Chloronaphthalene	91-58-7	---	1	Not provided in method	Not provided in method	0.4	1
2-Nitroaniline	88-74-4	---	1	Not provided in method	Not provided in method	0.5	1
Dimethylphthalate	131-11-3	---	5	Not provided in method	Not provided in method	2	5
2,6-Dinitrotoluene	606-20-2	---	1	Not provided in method	Not provided in method	0.5	1
3-Nitroaniline	99-09-2	---	1	Not provided in method	Not provided in method	0.5	1
2,4-Dinitrophenol	51-28-5	---	30	Not provided in method	Not provided in method	10	30
4-Nitrophenol	100-02-7	---	30	Not provided in method	Not provided in method	10	30
Dibenzofuran	132-64-9	---	1	Not provided in method	Not provided in method	0.5	1
2,4-Dinitrotoluene	121-14-2	---	5	Not provided in method	Not provided in method	1	5
Diethylphthalate	84-66-2	---	5	Not provided in method	Not provided in method	2	5
4-Chlorophenyl-phenylether	7005-72-3	---	1	Not provided in method	Not provided in method	0.5	1
4-Nitroaniline	100-01-6	---	1	Not provided in method	Not provided in method	0.5	1
4,6-Dinitro-2-methylphenol	534-52-1	---	15	Not provided in method	Not provided in method	5	15
N-Nitrosodiphenylamine	86-30-6	---	1	Not provided in method	Not provided in method	0.5	1
1,2,4,5-Tetrachlorobenzene	95-94-3	---	1	Not provided in method	Not provided in method	0.5	1
4-Bromophenyl-phenylether	101-55-3	---	1	Not provided in method	Not provided in method	0.5	1
Atrazine	1912-24-9	---	5	Not provided in method	Not provided in method	2	5
Carbazole	86-74-8	---	1	Not provided in method	Not provided in method	0.5	1
Di-n-butylphthalate	84-74-2	---	5	Not provided in method	Not provided in method	2	5
Butylbenzylphthalate	85-68-7	---	5	Not provided in method	Not provided in method	2	5
3,3'-Dichlorobenzidene	91-94-1	---	5	Not provided in method	Not provided in method	2	5
bis-(2-Ethylhexyl)phthalate	117-81-7	---	5	Not provided in method	Not provided in method	2	5
Di-n-octylphthalate	117-84-0	---	5	Not provided in method	Not provided in method	2	5
2,3,4,6-Tetrachlorophenol	58-90-2	---	1	Not provided in method	Not provided in method	0.5	1

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Semivolatile Organics
Concentration Level: Low
Analytical Method/SOP Reference: L-8

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
Azobenzene	103-33-3	---	1	Not provided in method	Not provided in method	0.5	1
Benzidine	92-87-5	---	60	Not provided in method	Not provided in method	20	60
Benzoic Acid	65-85-0	---	15	Not provided in method	Not provided in method	6	15
Pentachlorophenol	87-86-5	---	5	Not provided in method	Not provided in method	1	5
Pyridine	110-86-1	---	5	Not provided in method	Not provided in method	2	5

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Semivolatile Organics SIM
Concentration Level: Low
Analytical Method/SOP Reference: L-9

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
2-Methylnaphthalene	91-57-6	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Acenaphthylene	208-96-8	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Acenaphthene	83-32-9	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Anthracene	120-12-7	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Benzo[b]fluoranthene	205-99-2	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Benzo[k]fluoranthene	207-08-9	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Benzo[a]anthracene	56-55-3	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Benzo[a]pyrene	50-32-8	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Benzo[e]pyrene	192-97-2	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Indeno[1,2,3-c,d]-pyrene	193-39-5	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Dibenzo[a,h]anthracene	53-70-3	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Naphthalene	91-20-3	---	0.05	Not provided in method	Not provided in method	0.02	0.05
C1-Naphthalenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C2-Naphthalenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C3-Naphthalenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C4-Naphthalenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
1-Methylnaphthalene	90-12-0	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Fluorene	86-73-7	---	0.05	Not provided in method	Not provided in method	0.02	0.05
C1-Fluorenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C2-Fluorenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C3-Fluorenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
Phenanthrene	85-01-8	---	0.05	Not provided in method	Not provided in method	0.02	0.05
C1-Phenanthrenes/Anthracenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C2-Phenanthrenes/Anthracenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C3-Phenanthrenes/Anthracenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C4-Phenanthrenes/Anthracenes	---	---	NA	Not provided in method	Not provided in method	NA	NA

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Semivolatile Organics SIM
Concentration Level: Low
Analytical Method/SOP Reference: L-9

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
Fluoranthene	206-44-0	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Pyrene	129-00-0	---	0.05	Not provided in method	Not provided in method	0.02	0.05
C1-Fluoranthenes/Pyrene	---	---	NA	Not provided in method	Not provided in method	NA	NA
C2-Fluoranthenes/Pyrene	---	---	NA	Not provided in method	Not provided in method	NA	NA
C3-Fluoranthenes/Pyrene	---	---	NA	Not provided in method	Not provided in method	NA	NA
Chrysene	218-01-9	---	0.05	Not provided in method	Not provided in method	0.02	0.05
C1-Chrysenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C2-Chrysenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C3-Chrysenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
C4-Chrysenes	---	---	NA	Not provided in method	Not provided in method	NA	NA
Perylene	198-55-0	---	0.05	Not provided in method	Not provided in method	0.02	0.05
Benzo[g,h,i]perylene	191-24-2	---	0.05	Not provided in method	Not provided in method	0.02	0.05

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Aroclor PCBs
Concentration Level: Low
Analytical Method/SOP Reference: L-10

Analyte	CAS Number	Study Action Level µg/L	Project Quantitation Limit µg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs µg/L	Method QLs µg/L	MDLs µg/L	QLs µg/L
Aroclor-1016	12674-11-2	---	0.5	Not provided in method	1.0	0.1	0.5
Aroclor-1221	11104-28-2	---	0.5	Not provided in method	1.0	0.1	0.5
Aroclor-1232	11141-16-5	---	0.5	Not provided in method	1.0	0.2	0.5
Aroclor-1242	53469-21-9	---	0.5	Not provided in method	1.0	0.1	0.5
Aroclor-1248	12672-29-6	---	0.5	Not provided in method	1.0	0.1	0.5
Aroclor-1254	11097-69-1	---	0.5	Not provided in method	1.0	0.1	0.5
Aroclor-1260	11096-82-5	---	0.5	Not provided in method	1.0	0.15	0.5
Aroclor-1262	37324-23-5	---	0.5	Not provided in method	1.0	0.2	0.5
Aroclor-1268	11100-14-4	---	0.5	Not provided in method	1.0	0.16	0.5

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Pesticides
Concentration Level: Low
Analytical Method/SOP Reference: L-11

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
2,4'-DDD	53-19-0	---	40	3	30	9.64	40
2,4'-DDE	3424-82-6	---	80	3	30	25.2	80
2,4'-DDT	789-02-6	---	80	2	30	17.2	80
4,4'-DDD	72-54-8	---	40	5	30	13.8	40
4,4'-DDE	72-55-9	---	80	6	30	8.61	80
4,4'-DDT	50-29-3	---	80	1	30	17.2	80
Aldrin	309-00-2	---	40	6	90	8.72	40
alpha-BHC	319-84-6	---	40	7	60	7.05	40
alpha-Chlordane	5103-71-9	---	40	7	30	22.7	40
beta-BHC	319-85-7	---	40	6	60	6.99	40
delta-BHC	319-86-8	---	40	5	60	7.60	40
Dieldrin	60-57-1	---	40	5	30	10.5	40
Endosulfan I	959-98-8	---	400	24	100	77.9	400
Endosulfan II	33213-65-9	---	400	30	100	70.7	400
Endosulfan sulfate	1031-07-8	---	400	13	40	70.9	400
Endrin	72-20-8	---	80	3	30	19.6	80
Endrin aldehyde	7421-93-4	---	400	Not provided in method	Not provided in method	70.9	400
Endrin ketone	53494-70-5	---	400	12	40	476	400
gamma-BHC	58-89-9	---	40	9	60	4.96	40

See the last page of Worksheet #15-1 for a description of footnotes.

QAPP Worksheet #15-1 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Rinse/Field Blank (continued)

Matrix: Rinse/Field Blank
Analytical Group: Pesticides
Concentration Level: Low
Analytical Method/SOP Reference: L-11

Analyte	CAS Number	Study Action Level pg/L	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
				MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
gamma-Chlordane	5103-74-2	---	40	6	50	16.0	40
Heptachlor	76-44-8	---	200	7	30	14.0	200
Heptachlor epoxide	1024-57-3	---	40	12	40	9.60	40
Hexachlorobenzene	118-74-1	---	40	4	40	6.78	40
Methoxychlor	72-43-5	---	400	7	30	67.9	400
Nonachlor(cis)	5103-73-1	---	40	4	30	9.28	40
Nonachlor(trans)	39765-80-5	---	40	11	40	15.0	40
Oxychlordane	27304-13-8	---	40	7	60	15.4	40
Mirex	2385-85-5	---	40	35	100	6.64	40

Notes:

[a] Analytical MDLs and QLs are those documented in validated methods.
[b] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

BHC = benzene hexachloride
CAS = Chemical Abstracts Service
HpCDD = heptachlorodibenzo-*p*-dioxin
HpCDF = heptachlorodibenzofuran
HxCDD = hexachlorodibenzo-*p*-dioxin
HxCDF = hexachlorodibenzofuran
NA = not applicable
MDL = method detection limit
mg/L = milligrams per liter
ng/L = nanogram per liter
OCDD = octachlorodibenzo-*p*-dioxin
OCDF = octachlorodibenzofuran
PCBs= polychlorinated biphenyls
PeCDD = pentachlorodibenzo-*p*-dioxin
PeCDF = pentachlorodibenzofuran
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
pg/L = picograms per liter
QL = quantitation limit
SIM = selective ion monitoring
SOP = Standard Operating Procedure
TAL = Target Analyte List
TCDD = tetrachlorodibenzo-*p*-dioxin
TCDF = tetrachlorodibenzofuran
µg/L = micrograms per liter

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue

Matrix: Tissue
Analytical Group: PCDDs/PCDFs
Concentration Level: Low
Analytical Method/SOP Reference: L-1

Analyte	CAS Number	Study Action Level[a] ng/kg	Project Quantitation Limit ng/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs ng/kg	Method QLs ng/kg	MDLs ng/kg	QLs ng/kg
2,3,7,8-TCDD	1746-01-6	0.0243	1.0	Not provided in method	1	0.2	1.0
1,2,3,7,8-PeCDD	40321-76-4	0.0243	5.0	Not provided in method	5	0.4	5.0
1,2,3,6,7,8-HxCDD	57653-85-7	0.243	5.0	Not provided in method	5	0.4	5.0
1,2,3,4,7,8-HxCDD	39227-28-6	0.243	5.0	Not provided in method	5	0.3	5.0
1,2,3,7,8,9-HxCDD	19408-74-3	0.243	5.0	Not provided in method	5	0.3	5.0
1,2,3,4,6,7,8-HpCDD	35822-46-9	2.43	5.0	Not provided in method	5	0.5	5.0
OCDD	3268-87-9	80.9	10.0	Not provided in method	10	3.0	10.0
2,3,7,8-TCDF	51207-31-9	0.243	1.0	Not provided in method	1	0.2	1.0
1,2,3,7,8-PeCDF	57117-41-6	0.809	5.0	Not provided in method	5	0.4	5.0
2,3,4,7,8-PeCDF	57117-31-4	0.0809	5.0	Not provided in method	5	0.3	5.0
1,2,3,6,7,8-HxCDF	57117-44-9	0.243	5.0	Not provided in method	5	0.2	5.0
1,2,3,7,8,9-HxCDF	72918-21-9	0.243	5.0	Not provided in method	5	0.5	5.0
1,2,3,4,7,8-HxCDF	70648-26-9	0.243	5.0	Not provided in method	5	0.3	5.0
2,3,4,6,7,8-HxCDF	60851-34-5	0.243	5.0	Not provided in method	5	0.3	5.0
1,2,3,4,6,7,8-HpCDF	67562-39-4	2.43	5.0	Not provided in method	5	0.3	5.0
1,2,3,4,7,8,9-HpCDF	55673-89-7	2.43	5.0	Not provided in method	5	0.4	5.0
OCDF	39001-02-0	80.9	10.0	Not provided in method	10	0.5	10.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB1	2051-60-7	1580	2.0	8	20	1.0	2.0
PCB2	2051-61-8	1580	2.0	0.4	1	0.7	2.0
PCB3	2051-62-9	1580	5.0	9	20	1.1	5.0
PCB4/10	13029-08-8/33146-45-1	1580	5.0	Not provided in method	Not provided in method	1.3	5.0
PCB6	25569-80-6	1580	2.0	1	5	0.7	2.0
PCB5/8	16605-91-7/34883-43-7	1580	5.0	Not provided in method	Not provided in method	0.8	5.0
PCB7/9	33284-50-3/34883-39-1	1580	2.0	2	5	0.8	2.0
PCB11	2050-67-1	1580	10.0	10	20	3.4	10.0
PCB12/13	2974-92-7/2974-90-5	1580	5.0	3	10	1.9	5.0
PCB14	34883-41-5	1580	2.0	3	10	0.8	2.0
PCB15	2050-68-2	1580	5.0	18	50	1.6	5.0
PCB16/32	38444-78-9/38444-77-8	1580	2.0	Not provided in method	Not provided in method	0.9	2.0
PCB17	37680-66-3	1580	2.0	9	20	0.9	2.0
PCB18	37680-65-2	1580	5.0	17	50	1.6	5.0
PCB19	38444-73-4	1580	2.0	4	10	0.8	2.0
PCB20/21/33	38444-84-7/ 55702-46-0/38444-86-9	1580	5.0	Not provided in method	Not provided in method	2.2	5.0
PCB22	38444-85-8	1580	2.0	9	20	0.9	2.0
PCB23	55720-44-0	1580	2.0	5	20	0.7	2.0
PCB24/27	55702-45-9/38444-76-7	1580	2.0	Not provided in method	Not provided in method	1.0	2.0
PCB25	55712-37-3	1580	2.0	5	20	0.8	2.0
PCB26	38444-81-4	1580	5.0	8	20	1.2	5.0
PCB28	7012-37-5	1580	5.0	19	50	2.2	5.0
PCB29	15862-07-4	1580	5.0	8	20	1.2	5.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB30	35693-92-6	1580	5.0	17	50	1.6	5.0
PCB31	16606-02-3	1580	5.0	15	50	1.8	5.0
PCB34	37680-68-5	1580	2.0	7	20	0.7	2.0
PCB35	37680-69-6	1580	2.0	8	20	0.9	2.0
PCB36	38444-87-0	1580	2.0	8	20	0.8	2.0
PCB37	38444-90-5	1580	2.0	13	50	1.0	2.0
PCB38	53555-66-1	1580	2.0	8	20	0.7	2.0
PCB39	38444-88-1	1580	2.0	9	20	0.8	2.0
PCB40	38444-93-8	1580	10.0	12	50	4.2	10.0
PCB41/64/71/ 72	52663-59-9/52663-58-8/ 41464-46-4/41464-42-0	1580	10	Not provided in method	Not provided in method	4.2	10
PCB42/59	36559-22-5/74472-33-6	1580	5.0	6	20	1.6	5.0
PCB43/49	70362-46-8/41464-40-8	1580	5.0	Not provided in method	Not provided in method	1.4	5.0
PCB44	41464-39-5	1580	10.0	19	50	4.0	10.0
PCB45	70362-45-7	1580	5.0	5	20	2.2	5.0
PCB46	41464-47-5	1580	2.0	10	20	1.0	2.0
PCB47	2437-79-8	1580	10.0	19	50	4.0	10.0
PCB48/75	70362-47-9/32598-12-2	1580	5.0	Not provided in method	Not provided in method	1.4	5.0
PCB50	62796-65-0	1580	10.0	6	20	2.5	10.0
PCB51	68194-04-7	1580	5.0	5	20	2.2	5.0
PCB52/69	35693-99-3/60233-24-1	1580	5.0	Not provided in method	Not provided in method	1.5	5.0
PCB53	41464-41-9	1580	10.0	6	20	2.5	10.0
PCB54	15968-05-5	1580	5.0	12	50	1.4	5.0
PCB55	74338-24-2	1580	5.0	12	50	1.2	5.0

See the last page of Worksheet #15-3 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB56/60	41464-43-1/33025-41-1	1580	5.0	Not provided in method	Not provided in method	1.5	5.0
PCB57	70424-67-8	1580	5.0	12	50	1.1	5.0
PCB58	41464-49-7	1580	5.0	13	50	1.4	5.0
PCB61/70	33284-53-6/32598-11-1	1580	20	17	50	5.9	20
PCB62	54230-22-7	1580	10	6	20	3.7	10
PCB63	74472-34-7	1580	5.0	14	50	1.2	5.0
PCB65	33284-54-7	1580	10	19	50	4	10
PCB67	73575-53-8	1580	5.0	15	50	1.2	5.0
PCB68	73575-52-7	1580	5.0	15	50	1.4	5.0
PCB73	74338-23-1	1580	5.0	16	50	1.4	5.0
PCB74	32690-93-0	1580	20.0	17	50	5.9	20.0
PCB76/66	70362-48-0/32598-10-0	1580	20.0	Not provided in method	Not provided in method	5.9	20.0
PCB77	32598-13-3	240[f]	5.0	17	50	1.4	5.0
PCB78	70362-49-1	1580	5.0	17	50	1.6	5.0
PCB79	41464-48-6	1580	5.0	17	50	1.1	5.0
PCB80	33284-52-5	1580	5.0	18	50	1.1	5.0
PCB81	70362-50-4	80.9	5.0	18	50	1.8	5.0
PCB82	52663-62-4	1580	5.0	13	50	1.5	5.0
PCB83	60145-20-2	1580	10.0	22	50	2.9	10.0
PCB84/92	52663-60-2/52663-61-3	1580	2.0	12	50	1.1	2.0
PCB85/116	65510-45-4/18259-05-7	1580	10.0	10	20	3.8	10.0
PCB86	55312-69-1	1580	20.0	15	50	7.4	20.0
PCB87/117/125	38380-02-8/ 68194-11-6/74472-39-2	1580	20.0	Not provided in method	Not provided in method	7.4	20.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB88/91	55215-17-3/68194-05-8	1580	5.0	12	50	2.2	5.0
PCB89	73575-57-2	1580	5.0	19	50	1.3	5.0
PCB90/101	68194-07-0/37680-73-2	1580	20.0	24	100	4.7	20.0
PCB93	73575-56-1	1580	20.0	22	50	7.7	20.0
PCB94	73575-55-0	1580	5.0	12	50	1.3	5.0
PCB95/98/102	38379-99-6/ 60233-25-2/68194-06-9	1580	20.0	22	50	7.7	20.0
PCB96	73575-54-9	1580	5.0	21	50	1.5	5.0
PCB97	41464-51-1	1580	20.0	15	50	7.4	20.0
PCB99	38380-01-7	1580	10.0	22	50	2.9	10.0
PCB100	39485-83-1	1580	20.0	22	50	7.7	20.0
PCB103	60145-21-3	1580	5.0	23	50	1.1	5.0
PCB104	56558-16-8	1580	5.0	23	50	1.4	5.0
PCB105	32598-14-4	809	5.0	11	20	1.7	5.0
PCB106/118	70424-69-0/31508-00-6	809	5.0	Not provided in method	Not provided in method	1.7	5.0
PCB107/109	70424-68-9/74472-35-8	1580	5.0	Not provided in method	Not provided in method	1.7	5.0
PCB108/112	70362-41-3/74472-36-9	1580	10.0	Not provided in method	Not provided in method	2.9	10.0
PCB110	38380-03-9	1580	10.0	24	100	3.9	10.0
PCB111/115	39635-32-0/74472-38-1	1580	5.0	24	100	1.4	5.0
PCB113	68194-10-5	1580	20.0	24	100	4.7	20.0
PCB114	74472-37-0	809	5.0	12	50	1.5	5.0
PCB119	56558-17-9	1580	20.0	15	50	7.4	20.0
PCB120	68194-12-7	1580	5.0	15	50	1.3	5.0
PCB121	56558-18-0	1580	5.0	21	50	1.2	5.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB122	76842-07-4	1580	5.0	12	50	1.2	5.0
PCB123	65510-44-3	809	5.0	15	50	1.7	5.0
PCB124	70424-70-3	1580	10.0	27	100	2.9	10.0
PCB126	57465-28-8	0.243	5.0	14	50	1.6	5.0
PCB127	39635-33-1	1580	5.0	28	100	1.4	5.0
PCB128/162	38380-07-3/39635-34-2	1580	10.0	Not provided in method	Not provided in method	2.9	10.0
PCB129	55215-18-4	1580	20.0	21	50	6.3	20.0
PCB130	52663-66-8	1580	5.0	14	50	1.3	5.0
PCB131	61798-70-7	1580	5.0	12	50	1.7	5.0
PCB132/161	38380-05-1/74472-43-8	1580	5.0	Not provided in method	Not provided in method	1.6	5.0
PCB133/142	35694-04-3/41411-61-4	1580	5.0	Not provided in method	Not provided in method	1.2	5.0
PCB134/143	52704-70-8/68194-15-0	1580	10.0	13	50	3.3	10.0
PCB135	52744-13-5	1580	10.0	11	50	4.6	10.0
PCB136	38411-22-2	1580	5.0	9	20	1.6	5.0
PCB137	35694-06-5	1580	5.0	30	100	1.5	5.0
PCB138/163/164	35065-28-2/ 74472-44-9/74472-45-0	1580	20.0	Not provided in method	Not provided in method	6.3	20.0
PCB139/149	56030-56-9/38380-04-0	1580	10.0	Not provided in method	Not provided in method	2.9	10.0
PCB140	59291-64-4	1580	10.0	20	50	2.9	10.0
PCB141	52712-04-6	1580	5.0	9	20	1.7	5.0
PCB144	68194-14-9	1580	5.0	17	50	1.5	5.0
PCB145	74472-40-5	1580	5.0	32	100	1.6	5.0
PCB146/165	51908-16-8/74472-46-1	1580	5.0	Not provided in method	Not provided in method	1.4	5.0
PCB147	68194-13-8	1580	10.0	18	50	3.5	10.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB148	74472-41-6	1580	5.0	32	100	1.4	5.0
PCB150	68194-08-1	1580	10.0	33	100	3.5	10.0
PCB151	52663-63-5	1580	10.0	11	50	4.6	10.0
PCB152	68194-09-2	1580	5.0	24	100	1.4	5.0
PCB153	35065-27-1	1580	10.0	13	50	3.0	10.0
PCB154	60145-22-4	1580	10.0	11	50	4.6	10.0
PCB155	33979-03-2	1580	5.0	34	100	1.4	5.0
PCB156	38380-08-4	809	10.0	13	50	2.3	10.0
PCB157	69782-90-7	809	10.0	13	50	2.3	10.0
PCB158/160	74472-42-7/41411-62-5	1580	5.0	Not provided in method	Not provided in method	1.6	5.0
PCB159	39635-35-3	1580	5.0	35	100	1.4	5.0
PCB166	41411-63-6	1580	10.0	12	50	2.9	10.0
PCB167	52663-72-6	809	5.0	11	50	1.3	5.0
PCB168	59291-65-5	1580	10.0	13	50	3.0	10.0
PCB169	32774-16-6	0.809	5.0	16	50	1.5	5.0
PCB170	35065-30-6	1580	5.0	16	50	1.2	5.0
PCB171	52663-71-5	1580	10.0	37	100	3.0	10.0
PCB172	52663-74-8	1580	5.0	38	100	1.3	5.0
PCB173	68194-16-1	1580	10.0	37	100	3.0	10.0
PCB174	38411-25-5	1580	5.0	19	50	1.5	5.0
PCB175	40186-70-7	1580	5.0	38	100	1.4	5.0
PCB176	52663-65-7	1580	5.0	39	100	1.2	5.0
PCB177	52663-70-4	1580	5.0	14	50	1.1	5.0
PCB178	52663-67-9	1580	5.0	22	50	1.4	5.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB179	52663-64-6	1580	5.0	23	50	1.4	5.0
PCB180	35065-29-3	1580	10.0	Not provided in method	Not provided in method	3.0	10.0
PCB181	74472-47-2	1580	5.0	40	100	1.3	5.0
PCB182/187	60145-23-5/52663-68-0	1580	5.0	40	100	1.3	5.0
PCB183	52663-69-1	1580	10.0	40	100	2.8	10.0
PCB184	74472-48-3	1580	5.0	40	100	1.4	5.0
PCB185	52712-05-7	1580	10.0	40	100	2.8	10.0
PCB186	74472-49-4	1580	5.0	41	100	1.5	5.0
PCB188	74487-85-7	1580	5.0	23	50	1.5	5.0
PCB189	39635-31-9	809	5.0	18	50	1.3	5.0
PCB190	41411-64-7	1580	5.0	23	50	1.4	5.0
PCB191	74472-50-7	1580	5.0	42	100	1.3	5.0
PCB192	74472-51-8	1580	5.0	42	100	1.3	5.0
PCB193	69782-91-8	1580	10.0	14	50	3.0	10.0
PCB194	35694-08-7	1580	5.0	17	50	1.8	5.0
PCB195	52663-78-2	1580	5.0	43	100	2.2	5.0
PCB196/203	42740-50-1/52663-76-0	1580	5.0	Not provided in method	Not provided in method	2.0	5.0
PCB197	33091-17-7	1580	10.0	25	100	4.3	10.0
PCB198	68194-17-2	1580	10.0	20	50	3.7	10.0
PCB199	52663-75-9	1580	10.0	20	50	3.7	10.0
PCB200	52663-73-7	1580	10.0	25	100	4.3	10.0
PCB201	40186-71-8	1580	5.0	44	100	2.0	5.0
PCB202	2136-99-4	1580	10.0	44	100	2.4	10.0
PCB204	74472-52-9	1580	5.0	45	100	2.1	5.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: PCB Congeners
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Study Action Level[a] pg/g	Project Quantitation Limit pg/g	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
PCB205	74472-53-0	1580	5.0	45	100	1.5	5.0
PCB206	40186-72-9	1580	5.0	45	100	1.6	5.0
PCB207	52663-79-3	1580	5.0	45	100	1.9	5.0
PCB208	52663-77-1	1580	5.0	46	100	1.6	5.0
PCB209	2051-24-3	1580	5.0	15	50	1.6	5.0

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: TAL Metals, Mercury, Methylmercury, Titanium
Concentration Level: Low
Analytical Method/SOP Reference: L-3, L-4, L-5 and L-29

Analyte	CAS Number	Study Action Level[a] mg/kg	Project Quantitation Limit mg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs mg/kg	Method QLs mg/kg	MDLs mg/kg	QLs mg/kg
Aluminum	7429-90-5	135	20	Not provided in method	Not provided in method	2.92	20
Antimony	7440-36-0	0.0541	0.2	Not provided in method	Not provided in method	0.084	0.2
Arsenic	7440-38-2	0.0021	0.4	Not provided in method	Not provided in method	0.086	0.4
Barium	7440-39-3	27	0.4	Not provided in method	Not provided in method	0.06	0.4
Beryllium	7440-41-7	0.27	0.1	Not provided in method	Not provided in method	0.009	0.1
Cadmium	7440-43-9	0.135	0.1	Not provided in method	Not provided in method	0.0148	0.1
Calcium	7440-70-2	Essential Nutrient	40	Not provided in method	Not provided in method	15.68	40
Chromium	7440-47-3	0.86[f]	0.4	Not provided in method	Not provided in method	0.108	0.4
Cobalt	7440-48-4	0.0406	0.1	Not provided in method	Not provided in method	0.02	0.1
Copper	7440-50-8	5.41	0.4	Not provided in method	Not provided in method	0.154	0.4
Iron	7439-89-6	94.6	20	Not provided in method	Not provided in method	4.82	20
Lead	7439-92-1	1.72[f]	0.4	Not provided in method	Not provided in method	0.0128	0.4
Magnesium	7439-95-4	Essential Nutrient	20	Not provided in method	Not provided in method	2.4	20
Manganese	7439-96-5	18.9	0.4	Not provided in method	Not provided in method	0.076	0.4
Nickel	7440-02-0	2.7	0.4	Not provided in method	Not provided in method	0.084	0.4
Potassium	7440-09-7	Essential Nutrient	40	Not provided in method	Not provided in method	7.76	40
Selenium	7782-49-2	0.34[e]	0.4	Not provided in method	Not provided in method	0.1	0.4
Silver	7440-22-4	0.676	0.1	Not provided in method	Not provided in method	0.02	0.1
Sodium	7440-23-5	Essential Nutrient	40	Not provided in method	Not provided in method	10	40
Titanium	7440-32-6	---	1	Not provided in method	Not provided in method	0.17	1
Thallium	7440-28-0	0.00135	0.1	Not provided in method	Not provided in method	0.03	0.1
Vanadium	7440-62-2	0.681	0.1	Not provided in method	Not provided in method	0.03	0.1
Zinc	7440-66-6	12.7[g]	0.3	Not provided in method	Not provided in method	0.46	0.3
Mercury	7439-97-6	0.0086[f]	0.0008	Not provided in method	Not provided in method	0.00009	0.0008
Methylmercury	22967-92-6	0.0135	0.002	Not provided in method	Not provided in method	0.0005	0.002

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Butyltins
Concentration Level: Low
Analytical Method/SOP Reference: L-6

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
Dibutyltin	14488-53-0	41	1.3	Not provided in method	1.3	NA	1.3
Monobutyltin	78763-54-9	40.6	21	Not provided in method	20.7	NA	21
Tetrabutyltin	1461-25-2	40.6	1.7	Not provided in method	1.7	NA	1.7
Tributyltin	36643-28-4	40.6	1.5	Not provided in method	1.5	NA	1.5

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Semivolatile Organics
Concentration Level: Low
Analytical Method/SOP Reference: L-8, L-30, L-32

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
Benzaldehyde	100-52-7	--	680	Not provided in method	Not provided in method	268	680
Phenol	108-95-2	40,600	132	Not provided in method	Not provided in method	68	132
bis(2-Chloroethyl) ether	111-44-4	2.87	132	Not provided in method	Not provided in method	68	132
2-Chlorophenol	95-57-8	676	132	Not provided in method	Not provided in method	68	132
2-Methylphenol	95-48-7	--	132	Not provided in method	Not provided in method	68	132
2,2'-oxybis(1-Chloropropane)	108-60-1	--	132	Not provided in method	Not provided in method	68	132
Acetophenone	98-86-2	--	132	Not provided in method	Not provided in method	68	132
4-Methylphenol	106-44-5	13,500	132	Not provided in method	Not provided in method	68	132
N-Nitroso-di-n-propylamine	621-64-7	0.451	132	Not provided in method	Not provided in method	68	132
Hexachloroethane	67-72-1	78.9	680	Not provided in method	Not provided in method	132	680
Nitrobenzene	98-95-3	270	132	Not provided in method	Not provided in method	68	132
Isophorone	78-59-1	3,320	132	Not provided in method	Not provided in method	68	132
2-Nitrophenol	88-75-5	--	132	Not provided in method	Not provided in method	68	132
2,4-Dimethylphenol	105-67-9	2700	132	Not provided in method	Not provided in method	68	132
bis(2-Chloroethoxy) methane	111-91-1	406	132	Not provided in method	Not provided in method	68	132
2,4-Dichlorophenol	120-83-2	406	132	Not provided in method	Not provided in method	68	132
4-Chloroaniline	106-47-8	15.8	132	Not provided in method	Not provided in method	68	132
Hexachlorobutadiene	87-68-3	40.4	132	Not provided in method	Not provided in method	68	132
Caprolactam	105-60-2	--	680	Not provided in method	Not provided in method	132	680
4-Chloro-3-methyphenol	59-50-7	13,500	132	Not provided in method	Not provided in method	68	132
Hexachlorocyclopentadiene	77-47-4	811	2000	Not provided in method	Not provided in method	680	2000
2,4,6-Trichlorophenol	88-06-2	135	132	Not provided in method	Not provided in method	68	132
2,4,5-Trichlorophenol	95-95-4	13,500	132	Not provided in method	Not provided in method	68	132
1,1'-Biphenyl	92-52-4	394	132	Not provided in method	Not provided in method	68	132

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Semivolatile Organics
Concentration Level: Low
Analytical Method/SOP Reference: L-8, L-30, L-32

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
2-Chloronaphthalene	91-58-7	10,800	132	Not provided in method	Not provided in method	28	132
2-Nitroaniline	88-74-4	1,350	132	Not provided in method	Not provided in method	68	132
Dimethylphthalate	131-11-3	1,240[f]	680	Not provided in method	Not provided in method	268	680
2,6-Dinitrotoluene	606-20-2	2.1	132	Not provided in method	Not provided in method	68	132
3-Nitroaniline	99-09-2	158	680	Not provided in method	Not provided in method	268	680
2,4-Dinitrophenol	51-28-5	270	4000	Not provided in method	Not provided in method	1200	4000
4-Nitrophenol	100-02-7	--	2000	Not provided in method	Not provided in method	680	2000
Dibenzofuran	132-64-9	135	132	Not provided in method	Not provided in method	68	132
2,4-Dinitrotoluene	121-14-2	10.2	680	Not provided in method	Not provided in method	268	680
Diethylphthalate	84-66-2	1,240[f]	680	Not provided in method	Not provided in method	268	680
4-Chlorophenyl-phenylether	7005-72-3	--	132	Not provided in method	Not provided in method	68	132
4-Nitroaniline	100-01-6	158	680	Not provided in method	Not provided in method	268	680
4,6-Dinitro-2-methylphenol	534-52-1	10.8	2000	Not provided in method	Not provided in method	680	2000
N-Nitrosodiphenylamine	86-30-6	644	132	Not provided in method	Not provided in method	68	132
1,2,4,5-Tetrachlorobenzene	95-94-3	40.6	132	Not provided in method	Not provided in method	68	132
4-Bromophenyl-phenylether	101-55-3	--	132	Not provided in method	Not provided in method	68	132
Atrazine	1912-24-9	--	680	Not provided in method	Not provided in method	132	680
Carbazole	86-74-8	--	132	Not provided in method	Not provided in method	68	132
Di-n-butylphthalate	84-74-2	500[g]	680	Not provided in method	Not provided in method	268	680
Butylbenzylphthalate	85-68-7	1,660	680	Not provided in method	Not provided in method	268	680
3,3'-Dichlorobenzidine	91-94-1	7.01	1320	Not provided in method	Not provided in method	400	1320
bis-(2-Ethylhexyl)phthalate	117-81-7	225	680	Not provided in method	Not provided in method	268	680
Di-n-octylphthalate	117-84-0	1,240[f]	680	Not provided in method	Not provided in method	268	680
2,3,4,6-Tetrachlorophenol	58-90-2	--	680	Not provided in method	Not provided in method	268	680

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Semivolatile Organics
Concentration Level: Low
Analytical Method/SOP Reference: L-8, L-30, L-32

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
Azobenzene	103-33-3	28.7	132	Not provided in method	Not provided in method	68	132
Benzidine	92-87-5	0.0137	13200	Not provided in method	Not provided in method	2800	13200
Benzoic Acid	65-85-0	541,000	2000	Not provided in method	Not provided in method	680	2000
Pentachlorophenol	87-86-5	7.89	680	Not provided in method	Not provided in method	132	680
Pyridine	110-86-1	135	680	Not provided in method	Not provided in method	268	680

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Semivolatile Organics SIM
Concentration Level: Low
Analytical Method/SOP Reference: L-9, L-30, L-31, L-32

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
2-Methylnaphthalene	91-57-6	541	6.68	Not provided in method	Not provided in method	2.68	6.68
Acenaphthylene	208-96-8	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
Acenaphthene	83-32-9	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
Anthracene	120-12-7	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
Benzo[a]anthracene	56-55-3	4.32	6.68	Not provided in method	Not provided in method	2.68	6.68
Benzo[b]fluoranthene	205-99-2	4.32	6.68	Not provided in method	Not provided in method	2.68	6.68
Benzo[k]fluoranthene	207-08-9	43.2	6.68	Not provided in method	Not provided in method	2.68	6.68
Benzo[a]pyrene	50-32-8	0.432	6.68	Not provided in method	Not provided in method	2.68	6.68
Benzo[e]pyrene	192-97-2	4,060	6.68	Not provided in method	Not provided in method	2.68	6.68
Indeno[1,2,3-c,d]-pyrene	193-39-5	4.32	6.68	Not provided in method	Not provided in method	2.68	6.68
Dibenzo[a,h]anthracene	53-70-3	0.432	6.68	Not provided in method	Not provided in method	2.68	6.68
Naphthalene	91-20-3	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
C1-Naphthalenes	---	4,060	NA	Not provided in method	Not provided in method	NA	NA
C2-Naphthalenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C3-Naphthalenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C4-Naphthalenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
1-Methylnaphthalene	90-12-0	109	6.68	Not provided in method	Not provided in method	2.68	6.68
Fluorene	86-73-7	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
C1-Fluorenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C2-Fluorenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C3-Fluorenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
Phenanthrene	85-01-8	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
C1-Phenanthrenes/Anthracenes	---	4,060	NA	Not provided in method	Not provided in method	NA	NA
C2-Phenanthrenes/Anthracenes	---	4,060	NA	Not provided in method	Not provided in method	NA	NA
C3-Phenanthrenes/Anthracenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C4-Phenanthrenes/Anthracenes	---	--	NA	Not provided in method	Not provided in method	NA	NA

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Semivolatile Organics SIM
Concentration Level: Low
Analytical Method/SOP Reference: L-9, L-30, L-31, L-32

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
Fluoranthene	206-44-0	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
Pyrene	129-00-0	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
C1-Fluoranthenes/pyrene	---	--	NA	Not provided in method	Not provided in method	NA	NA
C2-Fluoranthenes/Pyrene	---	--	NA	Not provided in method	Not provided in method	NA	NA
C3-Fluoranthenes/Pyrene	---	--	NA	Not provided in method	Not provided in method	NA	NA
Chrysene	218-01-9	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68
C1-Chrysenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C2-Chrysenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C3-Chrysenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
C4-Chrysenes	---	--	NA	Not provided in method	Not provided in method	NA	NA
Perylene	198-55-0	4,060	6.68	Not provided in method	Not provided in method	2.68	6.68
Benzo[g,h,i]perylene	191-24-2	240[f]	6.68	Not provided in method	Not provided in method	2.68	6.68

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Aroclor PCBs
Concentration Level: Low
Analytical Method/SOP Reference: L-10

Analyte	CAS Number	Study Action Level[a] µg/kg	Project Quantitation Limit µg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs µg/kg	Method QLs µg/kg	MDLs µg/kg	QLs µg/kg
Aroclor-1016	12674-11-2	9.46	34	Not provided in method	Not provided in method	13	34
Aroclor-1221	11104-28-2	1.58	34	Not provided in method	Not provided in method	6.6	34
Aroclor-1232	11141-16-5	1.58	34	Not provided in method	Not provided in method	6.6	34
Aroclor-1242	53469-21-9	1.58	34	Not provided in method	Not provided in method	6.6	34
Aroclor-1248	12672-29-6	1.58	34	Not provided in method	Not provided in method	6.6	34
Aroclor-1254	11097-69-1	1.58	34	Not provided in method	Not provided in method	6.6	34
Aroclor-1260	11096-82-5	1.58	34	Not provided in method	Not provided in method	8.9	34
Aroclor-1262	37324-23-5	--	34	Not provided in method	Not provided in method	6.6	34
Aroclor-1268	11100-14-4	--	34	Not provided in method	Not provided in method	6.6	34

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Pesticides
Concentration Level: Low
Analytical Method/SOP Reference: L-11

Analyte	CAS Number	Study Action Level[a] ng/kg	Project Quantitation Limit ng/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs ng/kg	Method QLs ng/kg	MDLs ng/kg	QLs ng/kg
2,4'-DDD	53-19-0	13,000	40	0.8	5	4.98	40
2,4'-DDE	3424-82-6	9,300	80	0.5	5	9.95	80
2,4'-DDT	789-02-6	9,300	80	0.3	5	10.8	80
4,4'-DDD	72-54-8	13,000	40	1.5	5	7.35	40
4,4'-DDE	72-55-9	9,300	80	0.7	5	7.60	80
4,4'-DDT	50-29-3	9,300	80	0.3	5	52.3	80
Aldrin	309-00-2	190	40	0.6	10	31.5	40
alpha-BHC	319-84-6	500	40	1.3	10	6.40	40
alpha-Chlordane	5103-71-9	9,000	40	0.6	5	8.83	40
beta-BHC	319-85-7	1,800	40	0.6	10	11.1	40
delta-BHC	319-86-8	1,800	40	2.0	10	5.08	40
Dieldrin	60-57-1	200	40	0.5	5	15.4	40
Endosulfan I	959-98-8	31,000	400	Not provided in method	Not provided in method	57.4	400
Endosulfan II	33213-65-9	31,000	400	Not provided in method	Not provided in method	58.3	400
Endosulfan sulfate	1031-07-8	31,000	400	11	50	63.3	400
Endrin	72-20-8	10,000	80	0.4	5	13.9	80
Endrin aldehyde	7421-93-4	10,000	400	Not provided in method	Not provided in method	131	400
Endrin ketone	53494-70-5	10,000	400	1.6	5	76.0	400

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Pesticides
Concentration Level: Low
Analytical Method/SOP Reference: L-11

Analyte	CAS Number	Study Action Level[a] ng/kg	Project Quantitation Limit ng/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs ng/kg	Method QLs ng/kg	MDLs ng/kg	QLs ng/kg
gamma-BHC	58-89-9	2,900	40	0.7	10	7.69	40
gamma-Chlordane	5103-74-2	9,000	40	0.8	5	13.7	40
Heptachlor	76-44-8	700	200	Not provided in method	Not provided in method	110	200
Heptachlor epoxide B (Cis)	1024-57-3	350	40	0.3	5	7.00	40
Hexachlorobenzene	118-74-1	2,000	40	1.9	5	4.06	40
Methoxychlor	72-43-5	50,000	400	0.3	5	238.9	400
Nonachlor(cis)	5103-73-1	---	40	0.5	5	12.6	40
Nonachlor(trans)	39765-80-5	---	40	0.8	5	10.4	40
Oxychlordane	27304-13-8	9,000	40	0.5	10	10.0	40
Mirex	2385-85-5	180	40	Not provided in method	Not provided in method	9.33	40

See the last page of Worksheet #15-2 for a description of footnotes.

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Matrix: Tissue
Analytical Group: Miscellaneous
Concentration Level: Low
Analytical Method/SOP Reference: L-1, L-21

Analyte	CAS Number	Study Action Level[a] mg/kg	Project Quantitation Limit mg/kg	Analytical Method[b]		Achievable Laboratory Limits[c]	
				MDLs mg/kg	Method QLs mg/kg	MDLs mg/kg	QLs mg/kg
% Lipids	% Lipids	--	NA	NA	NA	NA	NA
% Moisture	% Moist	--	NA	NA	NA	NA	NA

Notes:

[a] Study action levels are consistent with those presented for tissue in the Crab/Clam QAPP (Tierra 2014) and are based on the lowest of either human health criteria or ecological screening values. Units represent wet-weight tissue mass. Human health criteria are based on fish tissue consumption (USEPA RSLs for fish ingestion, November 2013). A hazard quotient of 0.1 was utilized. Tierra will adjust the study action levels to utilize the most recent USEPA RSLs for fish ingestion when actual comparisons are made between study results and study action levels.
[b] Analytical MDLs and QLs are those documented in validated methods.
[c] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
[d] Fish tissue threshold is based on the lowest NOAEL or LOAEL TRVs from the literature. Threshold value was obtained from Table 2 of the Lower Passaic River Restoration Project QAPP.
[e] Back-calculated NOAEL mammal threshold is derived by back-calculating tissue thresholds from literature based on dietary NOAEL TRVs using species-specific exposure parameters (i.e., body weight and sediment ingestion rate). The value is the lowest of back-calculated threshold for mink or river otter. NOAEL TRVs derived from toxicity studies were expressed as daily dietary doses normalized for body weight and converted to a concentration in ingested prey tissue using the equation presented in Footnote f. Threshold value was obtained from Table 2 of the Lower Passaic River Restoration Project QAPP.
[f] Back-calculated NOAEL bird threshold is derived by back-calculating tissue thresholds from literature based on NOAEL TRVs using species-specific parameters. The value is the lowest of back-calculated thresholds for shorebirds, eagle, merganser, or osprey. NOAEL TRVs derived from toxicity studies were expressed as daily dietary doses normalized for body weight. To convert these NOAEL TRVs to a concentration in ingested prey tissue, the following equation was used:

C_{Tis} = (Dose x BW)/DFC

Where: C_{Tis} = concentration in prey tissue (mg/kg ww)
Dose = NOAEL TRV (mg/kg BW/day)
BW = body weight (kg)
DFC = daily food consumption rate (kg ww/day)

Threshold value was obtained from Table 2 of the Lower Passaic River Restoration Project QAPP.
[g] Decapod tissue threshold is based on the lowest NOAEL or LOAEL TRVs from the literature. Threshold value was obtained from Table 2 of the Lower Passaic River Restoration Project QAPP.

BHC = benzene hexachloride
CAS = Chemical Abstracts Service
DDD = dichlorodiphenyldichloroethane
DDE = dichlorodiphenyldichloroethylene
DDT = Dichlorodiphenyltrichloroethane
HpCDD = heptachlorodibenzo-*p*-dioxin
HpCDF = heptachlorodibenzofuran
HxCDD = hexachlorodibenzo-*p*-dioxin
HxCDF = hexachlorodibenzofuran
LOAEL = lowest-observed-adverse-effect level
MDL = method detection limit
mg/kg = milligrams per kilogram
NA = not applicable

QAPP Worksheet #15-2 (UFP-QAPP Manual Section 2.8.1): Reference Limits and Evaluation – Tissue (continued)

Notes (continued):

ng/kg = nanograms per kilogram
NOAEL = no-observed-adverse-effect level
OCDD = octachlorodibenzo-p-dioxin
OCDF = octachlorodibenzofuran
PCBs= polychlorinated biphenyls
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
PeCDD = pentachlorodibenzo-*p*-dioxin
PeCDF = pentachlorodibenzofuran
pg/g = picograms per gram
QL = quantitation limit
SIM = selective ion monitoring
SOP = Standard Operating Procedure
TAL = Target Analyte List
TCDD = tetrachlorodibenzo-*p*-dioxin
TCDF = tetrachlorodibenzofuran
TRV = toxicity reference value
µg/kg = micrograms per kilogram
% = percent
-- = not available

QAPP Worksheet #16 (UFP-QAPP Manual Section 2.8.2): Project Schedule/Timeline Table

Activities	Organization	Dates		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Preparation of Fish Sampling and Analysis QAPP	ARCADIS U.S., Inc.	March 2014	August 2014	Fish QAPP	August 13, 2014
Field Readiness Review	Normandeau Associates	prior to field work	prior to field work	Participant sign-off sheet	September 29, 2014[a,b]
Laboratory Readiness Review	Field & Technical Services	prior to field work	prior to field work	Participant sign-off sheet	September 29, 2014[a,b]
Fish Sampling	Normandeau Associates	September 2014	10 days	Samples submitted to laboratories	October 13, 2014[a]
Laboratory Analysis	Vista, eurofins/Lancaster Laboratories, eurofins/Frontier Global Sciences,TestAmerica	During start of sampling	4 weeks after completion of field work	Data Packages	November 10, 2014[a]
Data Validation	Field & Technical Services	Upon receipt of laboratory data	4 weeks after receipt of laboratory data	Data Verification/Validation Reports	December 8, 2014[a]
Data Usability Assessment	Field & Technical Services	Upon completion of data validation	4 weeks after completion of data validation	Data Quality and Usability Assessment Report	January 12, 2014[a]
Preparation of Data Reports	Normandeau Associates	Upon completion and receipt of all Phase III validated data	4 months after receipt of validated data	Phase III Data Report	May 2015[a]

Note:
[a] Deliverable due date is based on an estimated field start date of September 29, 2014. Tierra will stay in close communication with USEPA Region 2 regarding the actual start date.
[b] Deliverable for Readiness Review is anticipated on September 29, 2014 or earlier.

QAPP = Quality Assurance Project Plan

QAPP Worksheet #17 (UFP-QAPP Manual Section 3.1.1): Sampling Design and Rationale

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

The overall sampling design is a simple, stratified random approach within known or likely habitat areas of the NBSA. For simplicity and consistency with the screening level ecological risk assessment and other planning documents and to ensure that the large spatial area of the NBSA is adequately sampled, it has been divided into three zones for planning purposes: Newark Bay North, Newark Bay Central, and Newark Bay South. Dividing the NBSA into three geographical zones was used as a general approach to help guide the planning process so that sufficient data are collected throughout the NBSA. These three zones (or geographic areas) have also been described and used in other aspects of the Remedial Investigation (e.g., DEAR [Tierra 2013]).While geomorphic areas are important for collection of samples tied to geomorphic features, such as sediment samples and benthic organisms, larger geographical zones are important to consider for mobile species such as fish.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups and at what concentration levels, the sampling locations, the number of samples to be collected, and the sampling frequency [Refer to Figure 1 and Worksheet #18 for details]:

Fish samples will be collected using appropriate sample techniques including gill nets, seines, trawls, and traps as described in SOP No. 4. Fish samples will be targeted from areas of similar habitats in the three zones of the NBSA shown on Figure 1. The analytical mass requirement for fish tissue samples is 169 grams post-homogenization (194 grams pre-homogenization). The number of fish in each sample will vary by species and sample type, as both individual and composite fillet and whole-body samples will be collected. In total, 196 fish tissue samples will be targeted as presented in Worksheet # 14. Fish tissue samples will be homogenized and analyzed for the constituents described in Worksheet #10. Details regarding the collection and processing of fish tissue samples can be found in SOP Nos. 4 and 5. Fish will not be depurated prior to processing.

Crabs captured during the fish sampling program will be retained, processed, and analyzed following the Crab/Clam QAPP (Tierra 2014). Crabs collected during the fish sampling program may be combined with existing crabs captured during the crab and clam sampling event to fulfill crab mass requirements (as necessary). If tissue mass is limited, samples will be analyzed following the analytical hierarchy presented in the Crab/Clam QAPP (Tierra 2014). Compositing of by-catch crabs with existing crabs will be discussed with USEPA prior to compositing.

During fish tissue sampling, non-forage fish will be externally examined, and any gross physical abnormalities, lesions, or anomalies will be documented. For the forage fish, a subset of individual fish will be externally examined. In addition, a representative sample of individual non-forage fish – up to at least 20 individuals for each of two different species – will be submitted for internal pathological examination. Both target and non-target species will be sampled, but preference will be on resident and benthic species with sufficient abundance (e.g., white perch, flounder, hake). Fish pathology evaluations will be conducted on the first five fish of each species collected during the fish sampling effort. The internal examination will be conducted by a fish pathologist within hours of capture and will include overall morphology, gonad condition, presence of lesions, gonadosomatic index, and internal physical conditions/abnormalities. These data will be used to provide general qualitative information about the health of fish found within the NBSA. Fish will be examined following pathology-specific laboratory protocol, USGS (2002), or similar guidance. Retaining target species for tissue chemistry analysis is prioritized over sacrificing the fish for pathology evaluation.

Notes:
NBSA = Newark Bay Study Area
SOP = standard operating procedure

QAPP Worksheet #18 (UFP-QAPP Manual Section 3.1.1): Sampling Locations and Methods/SOP Requirements Table

Sampling Location/ Identification Number	Matrix	Method	Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
Newark Bay North	Fish Tissue	Gill nets, trawls, seines, and traps	Up to 27 whole-body, 18 fillet samples, 3 liver samples	4	Spatial coverage; home range for fish
Newark Bay Central	Fish Tissue	Gill nets, trawls, seines, and traps	Up to 27 whole-body, 18 fillet samples, 3 liver samples	4	Spatial coverage; home range for fish
Newark Bay South	Fish Tissue	Gill nets, trawls, seines, and traps	Up to 27 whole-body, 18 fillet samples, 3 liver samples	4	Spatial coverage; home range for fish
Intertidal Areas	Mummichog Tissue	Seines and traps	16 to19 whole-body samples	4	Adequate habitat; spatial coverage; correspond to clam sampling locations; some supplemental intertidal areas requested by USEPA
NBSA	Sportfish Tissue (e.g., bluefish, striped bass)	Gill nets and trawls	Up to 18 fillet samples each of striped bass and bluefish or weakfish	4	Spatial coverage; home range for fish

Notes:
Sample locations are shown on Figure 1.
NBSA = Newark Bay Study Area

QAPP Worksheet #19-1 (UFP-QAPP Manual Section 3.1.2): Analytical SOP Requirements – Rinse/Trip Blank

Matrix[a]	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[b]	Sample Volume (mL)[c]	Containers (number and type)[d]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/analysis)[e,f]
Water	PCDDs/PCDFs	Low	L-1	1 L	1 L, G	4°C	30 days to extraction, 45 days until analysis
Water	PCB Congeners	Low	L-2	1 L	1 L, G	4°C	30 days to extraction, 40 days until analysis
Water	TAL Metals, Titanium	Low	L-3, L-29	500	500 mL, P	4°C, HNO_3 to pH <2	6 months
Water	Mercury	Low	L-4	500	500 mL, fluoropolymer	4°C, HCl to pH <2	48 hours to preservation, 28 days until analysis
Water	Methylmercury[g]	Low	L-5	250	250 mL, fluoropolymer no headspace	4°C, HCl to pH <2	48 hours to preservation, 28 days until analysis
Water	Butyltins	Low	L-6	1 L	1 L, G	4°C	7 days to extraction, 40 days until analysis
Water	Semivolatile Organics	Low	L-8	1 L	1 L, G	4°C	7 days to extraction, 40 days until analysis
Water	Semivolatile Organics SIM	Low	L-9	1 L	1 L, G	4°C	7 days to extraction, 40 days until analysis
Water	Aroclor PCBs	Low	L-10	1 L	1 L, G	4°C	7 days to extraction, 40 days until analysis
Water	Pesticides	Low	L-11	1 L	1 L, G	4°C	7 days to extraction, 40 days until analysis

Notes:
[a] Surface water samples are not planned for collection during this sampling program but this worksheet has been provided to describe rinse and trip blank sample collection requirements only.
[b] Analytical methods are as specified in Worksheet #23-1.
[c] These are minimum sample volume requirements for a single sample analysis. Extra volume will be needed in order to fulfill quality control sample requirements, such as matrix spike/matrix spike duplicate and/or to provide contingency volume for analysis or breakage.
[d] Samples for analyses having identical container and preservation requirements may be combined in the same container. Similarly, smaller- or larger-sized sample containers than those recommended here may be used as long as the quality, container material, and preservative specifications are met, and the containers or container used will hold sufficient mass/volume to meet the minimum requirements specified.
[e] Holding time is calculated from the date and time of sample collection, to the date and time of sample analysis (or extraction as noted).
[f] Maximum holding times listed are based upon those stipulated in corresponding data validation guidance located in Appendix C of this Fish Sampling and Analysis QAPP.
[g] Samples will be shipped at 4°C to the laboratory via overnight carrier on the same day they are collected. Preservation will occur at the laboratory within the specified holding time (immediately upon receipt) in order to minimize the sources of potential field contamination. Samples will be stored for a minimum of 48 hours at 4°C after preservation and prior to analysis to allow the acid to completely dissolve the metals adsorbed on the container walls.

°C = degrees Celsius
G = amber glass
H_2SO_4 = sulfuric acid
HCl = hydrochloric acid
HNO_3 = nitric acid
L = liter
mL = milliliters
P = plastic
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SIM = selective ion monitoring
SOP = standard operating procedure
TAL = Target Analyte List

QAPP Worksheet #19-2 (UFP-QAPP Manual Section 3.1.2): Analytical SOP Requirements – Fish Sample Collection

Matrix[a]	Sample Processing	Sample Homogenization	Analytical Group	Processing SOP[b]	Sample Homogenization SOP[b]	Required Weight (g)[c]	Containers[d]	Preservation Requirements	Maximum Holding Time (preparation /analysis)[e]
Whole body fish	Normandeau	eurofins/ Lancaster	PCDDs/PCDFs, % Lipids, PCB Congeners, TAL Metals, Titanium, Mercury, Methylmercury, Butyltins, Semivolatile Organics, Semivolatile Organics SIM, Aroclor PCBs, Pesticides, % Moisture	SOP-5	SOP-10	194	8.8 oz, G	stored frozen (-15°C)	1 Year
Fish fillets			PCDDs/PCDFs, % Lipids, PCB Congeners, TAL Metals, Titanium, Mercury, Methylmercury, Butyltins, Semivolatile Organics, Semivolatile Organics SIM, Aroclor PCBs, Pesticides, % Moisture	SOP-5	SOP-10	194	8.8 oz, G	stored frozen (-15°C)	1 Year
Fish livers			PCDDs/PCDFs, % Lipids, PCB Congeners, TAL Metals, Titanium, Mercury, Methylmercury, Butyltins, Semivolatile Organics, Semivolatile Organics SIM, Aroclor PCBs, Pesticides, % Moisture	SOP-5	SOP-10	194	8.8 oz, G	stored frozen (-15°C)	1 Year

Notes:

[a] All specimens collected will be rinsed with de-ionized water prior to being placed in a Ziploc® bag.
[b] Referenced from the SOP references on Worksheet #21.
[c] See Worksheet #10 outlining details for prioritization of chemical analysis if post homogenization weight isn't obtained. Extra fish will be needed to fulfill quality control sample requirements, such as matrix spike/matrix spike duplicate and/or to provide contingency mass/volume for re-analysis or breakage.
[d] Containers for fish sample collection. Smaller or larger sized amber glass containers may be used as long as the quality, container material will hold sufficient mass to meet the minimum requirements specified. Containers for chemical analyses are in Worksheets #19-3.
[e] Holding time is calculated from the date and time of the organism collection and processing, to the date and time of homogenization and compositing.

°C = degrees Celsius
G = amber glass
g = gram
oz = ounce
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans
SIM = selective ion monitoring
SOP = standard operating procedure
TAL = Target Analyte List
% = percent

QAPP Worksheet #19-3 (UFP-QAPP Manual Section 3.1.2): Analytical SOP Requirements – Tissue Samples

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[a]	Sample Mass (g)[b]	Containers (number and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/analysis)[c,d]
Tissue	PCDDs/PCDFs	Low	L-1	30	8.8 oz, G	-15°C	1 year to extraction, 45 days to analysis
Tissue	% Lipids	Low	L-1	NA	8.8 oz, G	-15°C	NA
Tissue	PCB Congeners	Low	L-2	20	8.8 oz, G	-15°C	30 days to extraction, 40 days to analysis
Tissue	TAL Metals, Titanium	Low	L-3, L-29	1	8.8 oz, G	-15°C	6 months
Tissue	Mercury	Low	L-4	1	8.8 oz, G	-15°C	28 days
Tissue	Methylmercury	Low	L-5	1	8.8 oz, G	-15°C	28 days
Tissue	Butyltins	Low	L-6	50	8.8 oz, G	-15°C	7 days to extraction, 40 days to analysis
Tissue	Semivolatile Organics	Low	L-8	15	8.8 oz, G	-15°C	14 days to extraction, 40 days to analysis
Tissue	Semivolatile Organics SIM	Low	L-9	15	8.8 oz, G	-15°C	14 days to extraction, 40 days to analysis
Tissue	Aroclor PCBs	Low	L-10	15	8.8 oz, G	-15°C	14 days to extraction, 40 days to analysis
Tissue	Pesticides	Low	L-11	20	8.8 oz, G	-15°C	7 days to extraction, 40 days to analysis
Tissue	% Moisture	Low	L-21	1	8.8 oz, G	-15°C	28 days

Notes:

[a] Analytical methods are as specified in Worksheet #23.
[b] These are minimum sample mass requirements for a single sample analysis post homogenization. Extra mass will be needed in order to fulfill quality control sample requirements, such as matrix spike/matrix spike duplicate and/or to provide contingency mass for re-analysis or breakage.
[c] Holding time is calculated from the date and time of sample homogenization, to the date and time of sample analysis (or extraction as noted).
[d] Maximum holding times listed are based upon those stipulated in corresponding data validation guidance located in Appendix C of this Fish Sampling and Analysis QAPP.

°C = degrees Celsius
G = amber glass
g = gram
NA = not applicable
oz = ounce
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SIM = selective ion monitoring
SOP = standard operating procedure
TAL = Target Analyte List
% = percent

QAPP Worksheet #20 (UFP-QAPP Manual Section 3.1.2): Fish Tissue – Quality Control Sample Summary[a]

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[b]	Number of Samples Collected	Number of Field Duplicate Pairs[c]	Number of MS[d]	Number of MSD or Duplicates	Number of Trip Blanks	Number of Field Blanks[e]	Number of Rinse[f] Blanks	Total Number of Samples to Lab[g]
Tissue	PCDDs/PCDFs	Low	L-1	196	10	10	10	NA	10	10	226
Tissue	% Lipids	Low	L-1	NA[h]	NA	NA	NA	NA	NA	NA	NA
Tissue	PCB Congeners	Low	L-2	196	10	10	10	NA	10	10	226
Tissue	TAL Metals, Titanium	Low	L-3	196	10	10	10	NA	10	10	226
Tissue	Mercury	Low	L-4	196	10	10	10	15[i]	10	10	241
Tissue	Methylmercury	Low	L-5	196	10	10	10	15[i]	10	10	241
Tissue	Butyltins	Low	L-6	196	10	10	10	NA	10	10	226
Tissue	Semivolatile Organics	Low	L-8	196	10	10	10	NA	10	10	226
Tissue	Semivolatile Organics SIM	Low	L-9	196	10	10	10	NA	10	10	226
Tissue	Aroclor PCBs	Low	L-10	196	10	10	10	NA	10	10	226
Tissue	Pesticides	Low	L-11	196	10	10	10	NA	10	10	226
Tissue	% Moisture	Low	L-21	196	NA	NA	NA	NA	NA	NA	196

Notes:

[a] Laboratory performance evaluation samples are part of the planned project quality control program. However, these samples are not listed here, as the quality control samples will be administered separately from sample collection control tasks. Ongoing PE samples will be submitted to the appropriate laboratory according to the following protocol. SDGs containing split samples (shared with USEPA) will have a PE sample submitted at a frequency of 1 for each SDG. USEPA will reserve the right to choose the split samples from the available samples collected. SDGs that do not contain USEPA split samples will have 1 PE sample submitted for laboratory analysis for every 40 field samples collected. Ongoing PE sample analyses are independent of the pre-program performance evaluation study.

[b] Referenced from the Analytical SOP References Table (Worksheet #23-1).

[c] Field duplicates will be created after tissue homogenization. They will be collected at a rate of 1 per 20 samples.

[d] Assumes MS/MSD will be collected at a rate of one MS and one MSD per up to 20 samples or per sample delivery group (whichever is more frequent) for all constituents, except for % moisture.

[e] Field blanks will be created in the field and will serve as blanks controls collected in conjunction with processing equipment. Field blanks will be collected at a rate of 1 per 20 samples, not to exceed 1 per day.

[f] Rinse blanks will be created in the laboratory and will serve as blank controls collected in conjunction with homogenization equipment.

[g] This value excludes MS/MSD and rinse blanks.

[h] The % lipids analysis is part of the analytical procedure for Method 1613B (dioxin analysis) and, therefore, requires no extra sample or quality control samples.

[i] The number of trip blanks may vary depending upon the duration of sampling. One trip blank is required to be transported with each shipment of mercury and methylmercury samples.

MS = matrix spike
MSD = matrix spike duplicate
NA = not applicable
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans
SDG = sample delivery group
SIM = selective ion monitoring
SOP = standard operating procedure
TAL = Target Analyte List
% = percent

QAPP Worksheet #21 (UFP-QAPP Manual Section 3.1.2): Project Sampling SOP References Table

SOP Reference Number	Title, Revision Date, and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
1	Locating Sample Points Using a Hand-Held Global Positioning System (August 2014)	ARCADIS U.S., Inc.	Hand-held GPS unit	N	Appendix A
2	Positioning (September 2014)	ARCADIS U.S., Inc.	Boat-mounted GPS unit	Y	Appendix A
3	Decontamination (August 2014)	ARCADIS U.S., Inc.	NA	N	Appendix A
4	Fish Sample Collection (October 2014)	ARCADIS U.S., Inc.	Nets, traps	Y	Appendix A
5	Fish Tissue Sample Processing (July 2014)	ARCADIS U.S., Inc.	Electronic balance, fillet knives	Y	Appendix A
6	Management and Disposal of Residuals (August 2014)	ARCADIS U.S., Inc.	NA	N	Appendix A
7	Containers, Preservation, Handling, and Tracking of Samples for Analysis (July 2014)	ARCADIS U.S., Inc.	NA	Y	Appendix A
8	Documenting Field Activities (October 2013)	ARCADIS U.S., Inc.	NA	N	Appendix A
9	Data Management (August 2014)	ARCADIS U.S., Inc.	NA	N	Appendix A
10	Laboratory Tissue Homogenization (August 2014)	Environmental Data Services/ARCADIS U.S., Inc.	Cutting board, meat grinder, glass jars, homogenizer, food processor, stainless steel knives	N	Appendix A
11	Measuring Surface Water Quality (June 2014)	ARCADIS U.S., Inc.	Multi-parameter water quality meter (YSI 6000 or equivalent)	N	Appendix A

Notes:
GPS = global positioning system
NA = Not applicable. No equipment requiring calibration needed.

QAPP Worksheet #22 (UFP-QAPP Manual Section 3.1.2.4): Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Field Equipment[a]	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[a]
GPS receiver	The GPS receiver is calibrated automatically using satellite signals each time it is powered on.	Keep one set of fresh batteries available at all times. Keep dirt and dust away from GPS receiver.	Station vessel at the check point to verify GPS position with known land- survey coordinates.	Confirm there are no cracks in the unit and that the antenna has not been damaged.	Each time unit is powered on.	GPS receiver is suitable for use if it is reporting coordinates, indicating it is receiving signals from three independent GPS satellites.	If unit will not obtain a coordinate lock, move to an unobstructed location. If no unobstructed location is available, consider recording position at nearby unobstructed location and measuring horizontal offset that can be used to correct the measured position later.	Field Supervisor or designee	1
Electronic scale	Calibrate scale using calibration weights; calibration weights will bracket the expected tissue weight.	Decontamination; keep one set of fresh batteries available at all times.	NA	Inspect for physical damage that may compromise accuracy.	Daily, prior to use.	Measure to 1 g accuracy.	If scale cannot be calibrated, install new batteries and recalibrate. If scale can still not be calibrated, continue with planned activity and obtain a new scale at the earliest opportunity.	Field Supervisor or designee	5

Notes:

[a] Refer to Project Sampling SOP References table (Worksheet #21).

g = gram
GPS = global positioning system
NA = not applicable
SOP = standard operating procedure

QAPP Worksheet #23-1 (UFP-QAPP Manual Section 3.2.1): Analytical Method/SOP References

Reference Number	Analytical Method/SOP	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-1	USEPA Method 1613B	Definitive	PCDDs/PCDFs	HRGC/HRMS	eurofins/Lancaster Laboratories	N
L-1	USEPA Method 1613B	Definitive	% Lipids	Gravimetric	eurofins/Lancaster Laboratories	N
L-2	USEPA Method 1668A	Definitive	PCB Congeners	HRGC/HRMS	eurofins/Lancaster Laboratories	N
L-3	SW-846 Method 6020/1-P-QM-WI-9015160	Definitive	TAL Metals	ICP/MS	eurofins/Lancaster Laboratories	N
L-4	USEPA 1631	Definitive	Mercury	CVAFS	eurofins/Frontier Global Sciences	N
L-5	USEPA Method 1630	Definitive	Methylmercury	CVAFS	eurofins/Frontier Global Sciences	N
L-6	SOP No. BR-GC-008, Rev. 11, 05/13/14	Definitive	Butyltins	GC/FPD	TestAmerica	N
L-8	SW-846 Method 8270D	Definitive	Semivolatile Organics	GC/MS	eurofins/Lancaster Laboratories	N
L-9	SW-846 Method 8270D	Definitive	Semivolatile Organics SIM	GC/MS SIM	eurofins/Lancaster Laboratories	Y
L-10	SW-846 Method 8082	Definitive	Aroclor PCBs	GC/ECD	eurofins/Lancaster Laboratories	N
L-11	USEPA 1699	Definitive	Pesticides	HRGC/HRMS	Vista Analytical	N
L-21	1-P-QM-WI-9015065	Definitive	% Moisture	Gravimetric	eurofins/Lancaster Laboratories	N
L-29	USEPA Method 6010C/1-P-QM-WI-9015160	Definitive	Titanium	ICP/AES	eurofins/Lancaster Laboratories	N
L-30	SW-846 Method 3640	Definitive	Semivolatile Organics and Semivolatile Organics SIM	Gel-Permeation Column	eurofins/Lancaster Laboratories	N
L-31	SW-846 Method 3611	Definitive	Semivolatile Organics SIM	Alumina Clean-up Columns	eurofins/Lancaster Laboratories	N
L-32	SW-846 Method 3630	Definitive	Semivolatile Organics and Semivolatile Organics SIM	Silica Gel Clean-up Columns	eurofins/Lancaster Laboratories	N

Notes:
CVAFS = cold vapor atomic fluorescence spectrometry
GC = gas chromatography
GC/ECD = gas chromatography/electron capture detector
GC/FPD = gas chromatography/flame photometric detector
GC/MS = gas chromatography/mass spectrometry
HRGC/HRMS = high resolution gas chromatography/high resolution mass spectrometry

ICP/AES = inductively coupled plasma/atomic emission spectrometry
ICP/MS = inductively coupled plasma/mass spectrometry
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SIM = selective ion monitoring
SOP = standard operating procedure
TAL = Target Analyte List
USEPA = U.S. Environmental Protection Agency
% = percent

QAPP Worksheet #23-2 (UFP-QAPP Manual Section 3.2.1): Analytical Method/SOP References Additional Text to Supplement

Modifications to SW-846 8270 for Semivolatile Organics (Select Ion Monitoring Analyses [L-9])

Method U.S. Environmental Protection Agency SW-846 8270 is modified to provide for operation of the gas chromatograph/mass spectrometer in selective ion monitoring mode, thereby achieving lower levels of detection for specific semivolatile organic compounds.

QAPP Worksheet #24 (UFP-QAPP Manual Section 3.2.2): Analytical Instrument Calibration

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[a]
GC/MS	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Wendy Kozma eurofins/Lancaster Laboratories	L-8, L-9
ICP/MS	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Wendy Kozma eurofins/Lancaster Laboratories	L-3
CVAFS	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Amy Goodall eurofins/Frontier Global Sciences	L-4, L-5
HRGC/HRMS	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Martha Maier Vista Analytical Wendy Kozma eurofins/Lancaster Laboratories	L-1, L-2, L-11
GC/ECD	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Wendy Kozma eurofins/Lancaster Laboratories	L-10

See the last page of Worksheet #24 for a description of footnotes.

QAPP Worksheet #24 (UFP-QAPP Manual Section 3.2.2): Analytical Instrument Calibration

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[a]
GC/FPD	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Kirk Young TestAmerica	L-6
Analytical Balance	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Wendy Kozma eurofins/ Lancaster Laboratories Martha Maier Vista Analytical Amy Goodall eurofins/Frontier Global Sciences Kirk Young TestAmerica	All
ICP/AES	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Wendy Kozma eurofins/ Lancaster Laboratories	L-29

Notes:
[a] From the Analytical SOP References Worksheet #23-1.
CVAFS = cold vapor atomic fluorescence spectrometry
GC/ECD = gas chromatograph/electron capture detector
GC/FPD = gas chromatograph/flame photometric detector
GC/MS = gas chromatograph/mass spectrometer
HRGC/HRMS = high resolution gas chromatography/high resolution mass spectrometer
ICP/AES = inductively coupled plasma/atomic emissions spectrometry
ICP/MS = inductively coupled plasma/mass spectrometer
SOP = standard operating procedure

QAPP Worksheet #25 (UFP-QAPP Manual Section 3.2.3): Analytical Instrument and Equipment Maintenance, Testing, and Inspection

All analytical instrumentation/equipment must be inspected, maintained, and tested. Procedures for inspection, maintenance, and testing of laboratory instruments and equipment are provided in the laboratory's quality assurance (QA) manuals and associated laboratory standard operating procedures (SOPs). Appropriate QA manuals and SOPs will be obtained and submitted to the U.S. Environmental Protection Agency for review prior to mobilization.

Documentation of inspections, maintenance, and testing of laboratory instruments and equipment will include details of observed problems, corrective measures, routine maintenance, and instrument repair, including information regarding the repair and the individual who performed the repair.

At a minimum, major instruments will be backed up by comparable (if not equivalent) instrument systems to avoid unscheduled downtime. An inventory of spare parts will also be available to minimize equipment/instrument downtime.

QAPP Worksheet #26 (UFP-QAPP Manual Section 3.3): Sample Handling System

Sample Collection, Packaging, and Shipment	Fish Tissue Samples
Sample collection (personnel/organization):	Normandeau
Sample packaging (personnel/organization):	Normandeau
Coordination of shipment (personnel/organization):	Normandeau
Type of shipment/carrier:	Overnight carrier (FedEx, UPS, or equivalent) from field
Sample Receipt and Analysis	
Sample receipt (personnel/organization):	Contact at appropriate laboratory
Sample custody and storage (personnel/organization):	Contact at appropriate laboratory
Sample preparation (personnel/organization):	Contact at appropriate laboratory
Sample determinative analysis (personnel/organization):	Contact at appropriate laboratory
Sample Archiving	
Field sample storage (number of days from sample collection):	1 year until Tierra, in consultation with USEPA, authorizes disposal
Sample extract/digestate storage (number of days from extraction/digestion):	1 year until Tierra, in consultation with USEPA, authorizes disposal
Sample Disposal	
Personnel/organization:	Tierra in accordance with the USEPA-approved Waste Characterization QAPP (Tierra 2011)
Number of days from analysis:	1 year until Tierra, in consultation with USEPA, authorizes disposal

QAPP Worksheet #27 (UFP-QAPP Manual Section 3.3.3): Sample Custody Requirements

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

Fish tissue samples for chemistry analysis will be collected in the field, processed, and packaged for transport to the laboratory in coolers with ice. The SOPs for collecting and processing fish tissue samples are discussed in Appendix A. The samples will be shipped to the analytical laboratories for chemistry analysis. The original signed COC forms will be placed in a sealable plastic bag, sealed, and taped to the inside lid of the cooler. Fiber tape will be wrapped completely around the cooler. On each side of the cooler, a "This Side Up" arrow label will be attached, a "Handle with Care" label will be attached to the top of the cooler, and the cooler will be sealed with a custody seal in two locations. An example COC form and custody seal are provided in Appendix A.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

The contracted laboratory will have a laboratory-specific SOP that details the procedures used to document sample receipt and custody within the laboratory. The following procedures must be addressed in the laboratory custody SOP:

- Each laboratory must have a designated sample custodian who accepts custody of the samples at the time of delivery to the laboratory and verifies that the information on the sample labels matches the information on the COC. The sample custodian must sign and date all appropriate receiving documents and note any discrepancies in the sample documentation, as well as the condition of the samples at the time of receipt.
- Once the samples have been accepted by the laboratory, checked, and logged in, they must be maintained in accordance with laboratory custody and security requirements, as outlined in the laboratory Quality Management Plan.
- To confirm traceability of samples during the analytical process, the laboratory will assign a sample identification (ID) number based on procedures outlined in the laboratory Quality Management Plan or laboratory SOP.
- The following procedures, at a minimum, must be documented by the laboratory:
  - Sample extraction/preparation
  - Sample analysis
  - Data reduction
  - Data reporting

Laboratory personnel are responsible for sample custody until the samples are returned to the sample custodian.

When sample analysis and quality control procedures are completed, any remaining sample must be stored in accordance with contractual terms. Data sheets, custody documents, and other laboratory records must be retained in accordance with contractual agreements.

Final Evidence Files

Laboratory records, including all field- and laboratory-initiated COCs and other sample receiving records, sample preparation and analysis records, and the final data package, become part of the laboratory final evidence file and must be retained in accordance with the contractual agreement. An original copy of the data package and associated electronic deliverable must be provided to the investigative organization in accordance with the contractual agreement and will be retained by the investigative organization, including associated field records and other related correspondence.

See the last page of Worksheet #27 for a description of footnotes.

QAPP Worksheet #27 (UFP-QAPP Manual Section 3.3.3): Sample Custody Requirements (continued)

Sample Identification Procedures:

Fish tissue samples will be identified with the site name, time, date, sampling location, and field crew initials. Unique alphanumeric ID numbers will be assigned to each sample depending on the analysis. The sample identification schematic is as follows and as discussed in Appendix A:

The first two characters will be "NB" to identify the project area (Newark Bay).

The second two characters will be "03" to identify that this sample was collected as part of Phase III.

The next character will identify if it is a fillet, whole-body, or liver sample, F for fillet, W for whole body, L for liver.

The next two characters will identify the species. The two characters will be the first two letters of the common name of the species, or the first letter of each word for species with two word common names. The following abbreviations will be used: MU= mummichog, SK = striped killifish, BA = bay anchovy, AS = Atlantic silverside, ME = menhaden, WP = white perch, AE = American eel, SB = striped bass, BL = bluefish, SF = summer flounder, WF = winter flounder, WE = weakfish, HA = hake. Additional abbreviations may be developed as necessary if alternate species are used.

The next character will identify the geographic zone the sample was collected from, "N" for Newark Bay North, "C" for Newark Bay Central or "S for Newark Bay South. The final three characters are the sample ID number beginning with 001.
For example, an American eel fillet sample from Newark Bay North would be labeled NB03FAEN001.

For laboratory duplicate samples, the same sample ID will be used but will be noted as –DUP.

Chain-of-Custody Procedures:

COC procedures are documented in detail in Appendix A and summarized briefly below. Samples are considered to be in custody if they are: 1) in the custodian's possession or view, 2) in a secured place (under lock) with restricted access, or 3) in a container and secured with an official seal(s), such that the sample cannot be reached without breaking the seal(s). Custody procedures, as defined in Appendix A, will be used for all samples throughout the collection and transport process. Custody procedures will be initiated during sample collection. An electronic COC form will accompany samples to the analytical laboratory. Each person who has custody of the samples will sign the COC form and confirm that the samples are not left unattended unless properly secured.

The FS will be responsible for all sample tracking and custody procedures for samples in the field. The FS will be responsible for final sample inventory and will maintain sample custody documentation. The FS will also complete COC forms prior to removing samples from the sampling area. After field processing and prior to transfer, COC entries will be made for all samples. Information on the labels will be checked against sample log entries, and samples will be recounted. COC forms will accompany all samples. The COC forms will be signed at each point of transfer. Copies of all COC forms will be retained and included as appendices to QA/QC reports and data reports. Samples will be shipped in sealed coolers.

Normandeau will confirm that COC forms are properly signed upon receipt of the samples and will note questions or observations concerning sample integrity on the COC forms. Normandeau will contact the Facility Coordinator and Project QA/QC Manager immediately if discrepancies are discovered between the COC forms and the sample shipment upon receipt.

Notes:
COC = chain of custody
FS = Field Supervisor
QA/QC = quality assurance/quality control
SOP = standard operating procedure

QAPP Worksheet #28-1 (UFP-QAPP Manual Section 3.4): Tissue Field Quality Control Samples

Matrix	Tissue
Analytical Group	PCDDs/PCDFs, PCB Congeners, TAL Metals, Mercury, Methylmercury, Titanium, Butyltins, Semivolatile Organics, Semivolatile Organics (SIM), Aroclor PCBs, Pesticides, % Lipids, % Moisture
Concentration Level	Low
Sampling SOP	SOP-4, SOP-5
Analytical Method/SOP Reference	L-1, L-2, L-3, L-4, L-5, L-6, L-8, L-9, L-10, L-11, L-21, L-29
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical, eurofins/Lancaster, eurofins/Frontier Global Sciences,TestAmerica
Number of Samples Collected	See Worksheet #20

QC Sample	Frequency Number	Action	Data Quality Indicator	Measurement Performance Criteria
Rinse Blank	1 per 20 samples, not to exceed 1 per day. Note rinse blanks will not be collected for % lipids or % moisture analytical groups.	Associated data will be critically assessed to determine the impact to data quality	Accuracy/Bias Contamination	No target compounds ≥PQL
Field Duplicate	1 field duplicate will be collected at a frequency of 1 per 20 samples per matrix and per method	Associated data will be critically assessed to determine the impact to data quality	Precision	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples
Trip Blank	1 trip blank will be included with each shipment of samples which contains mercury and methylmercury samples.	Associated data will be critically assessed to determine the impact to data quality	Accuracy/Bias Contamination	No target compounds ≥PQL
Field Blank	1 per 20 samples, not to exceed 1 per day. Note field blanks will not be collected for % lipids or % moisture analytical groups.	Associated data will be critically assessed to determine the impact to data quality	Accuracy/Bias Contamination	No target compounds ≥PQL

Notes:
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans
PQL= project quantitation limit
QC = quality control
SIM = selective ion monitoring
SOP = Standard Operating Procedure
TAL = Target Analyte List
% = percent

Description of Terms:

Rinse Blank

Rinse blanks check for sample contamination that may be caused by reuse of decontaminated homogenization equipment. Rinse blanks are collected by pouring de-ionized water or solvent, whichever is appropriate to the contaminants of interest, over the homogenization sampling equipment after it has been cleaned in the laboratory. Rinse blanks are submitted at a rate of 1 per 20 samples and are not to exceed more than one per day.

Field Duplicate

Field duplicates are to be collected as separate and discrete samples after homogenization. Field duplicates are submitted at a rate of 1 per 20 samples.

Trip Blank

A trip blank is a sample matrix that is as free of volatile analytes as possible and that is transported with the samples to the laboratory without being opened. This serves as a check on sample contamination during transport, shipping, and storage before analysis.

Field Blank

Field blanks check for sample contamination that may be caused by reuse of decontaminated filleting equipment, as well as transportation. Field blanks are collected by pouring de-ionized water or solvent, whichever is appropriate to the contaminants of interest, over the filleting equipment after it has been decontaminated. Field blanks serve as a check on contamination prior to sample processing. Field blanks are submitted at a rate of 1 per 20 samples and are not to exceed more than one per day.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples

Matrix	Rinse/Field Blank
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-1
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound concentrations must fall within range provided in Table 6 of L-1	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound concentrations must fall within range provided in Table 6 of L-1
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-1
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-1	Per L-1	Investigate and recalibrate, if necessary, per L-1.	Accuracy/Bias	Per L-1
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-1	Per L-1	Investigate and recalibrate, if necessary, per L-1.	Accuracy/Bias	Per L-1
Labeled Compound Spike	14 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits refer to L-1.	Accuracy/Bias	Per L-1
Labeled Internal Standard	2 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits refer to L-1.	Accuracy/Bias	Per L-1

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-2
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound analytes contained in the OPR must have observed concentration values that fall within the acceptance ranges provided in Table 6 of L-2	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound analytes contained in the OPR must have observed concentration values that fall within the acceptance ranges provided in Table 6 of L-2
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-2
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-2	Per L-2	The laboratory must follow all corrective actions required by L-2.	Accuracy/Bias	Per L-2
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-2	Per L-2	The laboratory must follow all corrective actions required by L-2.	Accuracy/Bias	Per L-2
Labeled Compound Spike	27 per sample	Per L-2	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to L-2.	Accuracy/Bias	Per L-2
Labeled Internal Standards	5 per sample	Per L-2	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to L-2.	Accuracy/Bias	Per L-2

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	TAL Metals, Titanium
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-3, L-29
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
		Compounds	**% Recovery**			**Compounds**	**% Recovery**
Laboratory Control Sample	1 per digestion batch[a]	All target analytes	80-120	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target analytes	80-120
Method Blanks	1 per digestion batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	
Instrument Blanks	Per analytical method	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Re-analyze affected sample digestates. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Trip/Field Blank
Analytical Group	Mercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-4
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per preparation batch[a]	**% Recovery** 77-123	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 77-123
Initial Precision and Recovery	At initial setup per L-4	Per L-4	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits.	Accuracy/Bias	Per L-4
Method Blanks	1 per preparation batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Instrument Blanks	Per L-4	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Re-analyze affected sample digestates. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Trip/Field Blank
Analytical Group	Mercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-4
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-4	Per L-4	The laboratory must follow all corrective actions required per L-4.	Accuracy/Bias	Per L-4
Calibration Verification	Per L-4	Per L-4	Investigate and recalibrate, if necessary, per L-4.	Accuracy/Bias	Per L-4
Quality Control Sample	1 per preparation batch[a]	**% Recovery** 50-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 50-150

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Trip/Field Blank
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-5
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Frontier Global Science
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per preparation batch[a]	**% Recovery** 67-133	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 67-133
Initial Precision and Recovery	At initial setup or when corrective action is taken, which may change calibration per L-5	Per L-5	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits.	Accuracy/Bias	Per L-5
Method Blanks	1 per preparation batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Quality Control Sample	1 per preparation batch[a]	**% Recovery** 50-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 50-150

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Trip/Field Blank
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-5
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Instrument Blanks	Per analytical method	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Re-analyze affected sample digestates. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-5	Per L-5	The laboratory must follow all corrective actions required per L-5.	Accuracy/Bias	Per L-5
Calibration Verification	Per L-5	Per L-5	Investigate and recalibrate, if necessary, per L-5.	Accuracy/Bias	Per L-5

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Butyltins
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-6
Field Sampling Organization	Normandeau
Analytical Organization	TestAmerica
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Surrogate Spikes	1 per sample	**Surrogate Compound** Tripentyltin	**% Recovery** 15-150	The laboratories should evaluate potential corrective actions and implement, as appropriate. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compound** Tripentyltin	**% Recovery** 15-150
Laboratory Control Sample	1 per extraction batch[a]	**Compounds** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-150 30-150 30-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compounds** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-150 30-150 30-150
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Semivolatile Organics
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-8
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Surrogate Spikes	6 per sample	**Surrogate Compounds** Phenol-d_5 2-Fluorobiphenyl 2-Fluorophenol 2,4,6-Tribromophenol Nitrobenzene-d_5 p-Terphenyl-d_{14}	**% Recovery**[a] Per L-8	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compounds** Phenol-d_5 2-Fluorobiphenyl 2-Fluorophenol 2,4,6-Tribromophenol Nitrobenzene-d_5 p-Terphenyl-d_{14}	**% Recovery** Per L-8
Laboratory Control Sample	1 per extraction batch[b]	**Compounds** All target analytes	**% Recovery** 20-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	**Compounds** All target analytes	**% Recovery** 20-150

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Semivolatile Organics
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-8
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blank	1 per extraction batch[b]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Semivolatile Organics (SIM)
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-9
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Surrogate Spikes	3 per sample	**Surrogate Compounds** Fluoranthene-d_{10} Benzo(a)pyrene-d_{12} 1-Methylnaphthalene-d_{10}	**% Recovery** 64-120 62-141 58-134	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compounds** Fluoranthene-d_{10} Benzo(a)pyrene-d_{12} 1-Methylnaphthalene-d_{10}	**% Recovery** 64-120 62-141 58-134
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Aroclor PCBs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/ SOP Reference	L-10
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Surrogate Spikes	2 per sample	**Surrogate Compounds** Tetrachloro-m-xylene Decachlorobiphenyl	**% Recovery** 43-144 43-144	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compounds** Tetrachloro-m-xylene Decachlorobiphenyl	**% Recovery** 43-144 43-144
Laboratory Control Sample	1 per extraction batch[a]	**Compounds** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compounds** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Aroclor PCBs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-10
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Instrument Blanks	1 per 12 hour sequence	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Re-analyze affected sample extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Pesticides
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-11
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Second Source Standard	Prior to every 12-hour period following the daily calibration verification	**Compounds** All target analytes	**% Recovery** 70-130	Poor performance may necessitate the preparation of new standard solutions and recalibration of equipment until performance criteria are met.	Accuracy/Bias	**Compounds** All target analytes	**% Recovery** 70-130
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11	

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Pesticides
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-11
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-11	Per L-11	The laboratory must follow all corrective actions required by L-11.	Accuracy/Bias	Per L-11
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-11	Per L-11	The laboratory must follow all corrective actions required by L-11.	Accuracy/Bias	Per L-11
Labeled Compound Spike	26 per sample	Per L-11	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to L-11.	Accuracy/Bias	Per L-11
Labeled Internal Standards	5 per sample	Per L-11	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to L-11.	Accuracy/Bias	Per L-11

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a (UFP-QAPP Manual Section 3.4): Rinse/Trip/Field Blank Laboratory Quality Control Samples (continued)

Matrix	Rinse/Field Blank
Analytical Group	Pesticides
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-11
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Instrument Blanks	1 per 12 hour sequence	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Re-analyze affected sample extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

Notes:
[a] A batch is defined as a group of up to 20 samples of the same matrix, prepared at the same time, using the same procedure.

OPR = ongoing precision and recovery
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans
PQL = project quantitation limit
QC = quality control
SIM = selective ion monitoring
SOP = Standard Operating Procedure
TAL = Target Analyte List
% = percent

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples

Matrix	Tissue
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-1
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compound** All target analytes	**RPD** <50	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision-Lab	**Compound** All target analytes	**RPD** <50
Matrix Spike	1 per extraction batch[a]	**Compound** All target analytes	**% Recovery** 60-140	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 60-140
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split[c] SDGs A minimum of 1 per SDG	All certified target compound concentrations must fall within ± 25% of certified value when concentrations fall within the range of the initial calibration.		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All certified target compound concentrations must fall within ± 25% of certified value when concentrations fall within the range of the initial calibration.	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-1
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound concentrations must fall within the acceptance ranges provided in Table 6 of L-1	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound concentrations must fall within the acceptance ranges provided in Table 6 of L-1
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-1	Per L-1	Investigate and recalibrate, if necessary, per L-1	Accuracy/Bias	Per L-1

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-1
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See all of Worksheets #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-1	Per L-1	Investigate and recalibrate, if necessary, per L-1.	Accuracy/Bias	Per L-1
Labeled Compound Spike	14 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits, refer to L-1.	Accuracy/Bias	Per L-1
Labeled Internal Standard	2 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits, refer to L-1.	Accuracy/Bias	Per L-1

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-2
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compound** 86 target analytes	**RPD** <50	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision - Lab	**Compound** 86 target analytes	**RPD** <50
Matrix Spike	1 per extraction batch[a]	**Compound** 86 target analytes	**% Recovery** 60-140	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** 86 target analytes	**% Recovery** 60-140
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split[c] SDGs A minimum of 1 per SDG	All certified target compound concentrations must fall within ± 25% of certified value when concentrations fall within the range of the initial calibration.		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All certified target compound concentrations must fall within ± 25% of certified value when concentrations fall within the range of the initial calibration.	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-2
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound concentrations must fall within the acceptance ranges provided in Table 6 per L-2	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound concentrations must fall within the acceptance ranges provided in Table 6 per L-2
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-2
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-2	Per L-2	Investigate and recalibrate, if necessary, per L-2.	Accuracy/Bias	Per L-2
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12 hour period per L-2	Per L-2	Investigate and recalibrate, if necessary, per L-2.	Accuracy/Bias	Per L-2
Labeled Compound Spike	27 per sample	Per L-2	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to protocol in L-2.	Accuracy/Bias	Per L-2
Labeled Internal Standards	5 per sample	Per L-2	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to protocol in L-2.	Accuracy/Bias	Per L-2

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	TAL Metals, Titanium
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-3, L-29
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike	1 per digestion batch[a]	**Compound** All target analytes	**% Recovery** 75-125	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 75-125
Laboratory Control Sample	1 per digestion batch[a]	**Compound** All target analytes	**% Recovery** 80-120	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 80-120
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split[c] SDGs A minimum of 1 per SDG	**Compound** All target analytes	**% Recovery** 70-130	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 70-130

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	TAL Metals, Titanium
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-3, L-29
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per digestion batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Instrument Blanks	1 per digestion batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Laboratory Duplicate	1 per digestion batch[a]	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by <2X the PQL when detects are <5X PQL for both field duplicate samples	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision-Lab	Per L-3

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Mercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-4
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/ Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Matrix Spike	1 per preparation batch[a]	**% Recovery** 71-125	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 71-125
Ongoing Precision and Recovery	1 per preparation batch[a]	**% Recovery** 77-123	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 77-123

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Mercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-4
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/ Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Precision and Recovery	At initial setup per L-4	Per L-4	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits.	Accuracy/Bias	Per L-4
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-4	Per L-4	The laboratory must follow all corrective actions required per L-4.	Accuracy/Bias	Per L-4
Calibration Verification	Per L-4	Per L-4	Investigate and recalibrate, if necessary, per L-4.	Accuracy/Bias	Per L-4
Quality Control Sample	1 per preparation batch[a]	**% Recovery** 50-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 50-150
Performance Evaluaiton Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split [c]SDGs A minimum of 1 per SDG	**% Recovery** 75-125	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 75-125

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Mercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-4
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/ Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per preparation batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Instrument Blanks	1 per preparation batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Matrix Spike Duplicate	1 per preparation batch[a]	**RPD** ≤35%	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision-Lab	**RPD** ≤35%

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-5
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/ Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Matrix Spike Duplicate	1 per preparation batch[a]	**RPD** ≤35%	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision-Lab	**RPD** ≤35%
Matrix Spike	1 per preparation batch[a]	**% Recovery** 65-135	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 65-135
Ongoing Precision and Recovery	1 per preparation batch[a]	**% Recovery** 67-133	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 67-133

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-5
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/ Frontier Global Sciences
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per preparation batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Instrument Blanks	1 per preparation batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Quality Control Sample	1 per preparation batch[a]	**% Recovery** 50-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**% Recovery** 50-150

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-5
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/ Frontier Global Sciences
No. of Samples Collected	See all of Worksheets #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-5	Per L-5	Investigate and recalibrate, if necessary, per L-5.	Accuracy/Bias	Per L-5
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-5	Per L-5	Investigate and recalibrate, if necessary, per L-5.	Accuracy/Bias	Per L-5
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split[c] SDGs A minimum of 1 per SDG	Target compound concentration must be within ± 35% of certified value.	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	Target compound concentration must be within ± 35% of certified value.

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Butyltins
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-6
Field Sampling Organization	Normandeau
Analytical Organization	TestAmerica
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compound** All target analytes	**RPD** <30	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision - Lab	**Compound** All target analytes	**RPD** <30
Matrix Spike	1 per extraction batch[a]	**Compounds** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-160 30-160 30-160	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/ Bias	**Compounds** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-160 30-160 30-160
Surrogate Spikes	1 per sample	**Surrogate Compound** Tripentyltin	**% Recovery** 30-120	The laboratories should evaluate potential corrective actions and implement, as appropriate. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/ Bias	**Surrogate Compound** Tripentyltin	**% Recovery** 30-120

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Butyltins
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-6
Field Sampling Organization	Normandeau
Analytical Organization	TestAmerica
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Laboratory Control Sample	1 per extraction batch[a]	**Compound** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-160 30-160 30-160	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	**% Recovery** 10-48 30-160 30-160 30-160
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Semivolatile Organics
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-8, L-30, L-32
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compounds** All target analytes	**RPD** <30	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision - Lab	**Compounds** All target analytes	**RPD** <30
Matrix Spike	1 per extraction batch[a]	**Compounds** All target analytes	**% Recovery** 20-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compounds** All target analytes	**% Recovery** 20-150

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Semivolatile Organics
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-8, L-30, L-32
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Surrogate Spikes	6 per sample	**Surrogate Compounds** Phenol-d_5 2-Fluorobiphenyl 2-Fluorophenol 2,4,6-Tribromphenol Nitrobenzene-d_5 p-Terphenyl-d_{14}	**% Recovery** Per L-8	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compounds** Phenol-d_5 2-Fluorobiphenyl 2-Fluorophenol 2,4,6-Tribromphenol Nitrobenzene-d_5 p-Terphenyl-d_{14}	**% Recovery** Per L-8
Laboratory Control Sample	1 per extraction batch[a]	**Compounds** All target analytes	**% Recovery** 20-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compounds** All target analytes	**% Recovery** 20-150

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Semivolatile Organics
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-8, L-30, L-32
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Semivolatile Organics (SIM)
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-9, L-30, L-31, L-32
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compounds** All target analytes	**RPD** <40	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision - Lab	**Compounds** All target analytes	**RPD** <40
Matrix Spike	1 per extraction batch[a]	**Compounds** All target analytes	**% Recovery** 60-140	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compounds** All target analytes	**% Recovery** 60-140
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split[c] SDGs A minimum of 1 per SDG	**Compounds** All target analytes	**% Recovery** Recovery within limits set by performance evaluation sample vendor.	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compounds** All target analytes	**% Recovery** Recovery within limits set by performance evaluation sample vendor.

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Semivolatile Organics (SIM)
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-9, L-30, L-31, L-32
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Surrogate Spikes	3 per sample	**Surrogate Compounds** Fluoranthene-d_{10} Benzo(a)pyrene-d_{12} 1-Methylnaphthalene-d_{10}	**% Recovery** 50-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compounds** Fluoranthene-d_{10} Benzo(a)pyrene-d_{12} 1-Methylnaphthalene-d_{10}	**% Recovery** 50-150
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Aroclor PCBs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-10
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compound** Aroclor-1016 Aroclor-1260	**RPD** <15 <20	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision-Lab	**Compound** Aroclor-1016 Aroclor-1260	**RPD** <15 <20
Matrix Spike	1 per extraction batch[a]	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130
Surrogate Spikes	2 per sample	**Surrogate Compound** Tetrachloro-m-xylene Decachlorobiphenyl	**% Recovery** 30-150 30-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Surrogate Compound** Tetrachloro-m-xylene Decachlorobiphenyl	**% Recovery** 30-150 30-150

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Aroclor PCBs
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-10
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Laboratory Control Sample	1 per extraction batch[a]	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** Aroclor-1016 Aroclor-1260	**% Recovery** 70-130 70-130
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	
Instrument Blanks	1 per 12 hour sequence	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Re-analyze affected sample extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Pesticides
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-11
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Matrix Spike Duplicate	1 per extraction batch[a]	**Compound** All target analytes	**RPD** <25	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision - Lab	**Compound** All target analytes	**RPD** <25
Matrix Spike	1 per extraction batch[a]	**Compound** All target analytes	**% Recovery** 50-150	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 50-150
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed. All target compound percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11.		Accuracy/Bias	All target compound percent recoveries must fall within the acceptance criteria provided in Table 5 of L-11	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Pesticides
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-11
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-11	Per L-11	The laboratory must follow all corrective actions required by L-11.	Accuracy/Bias	Per L-11
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-11	Per L-11	The laboratory must follow all corrective actions required by L-11.	Accuracy/Bias	Per L-11
Labeled Compound Spike	26 per sample	Per L-11	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to L-11.	Accuracy/Bias	Per L-11
Labeled Internal Standards	5 per sample	Per L-11	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. Refer to L-11.	Accuracy/Bias	Per L-11

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	Pesticides
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-11
Field Sampling Organization	Normandeau
Analytical Organization	Vista Analytical
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Second Source Standard	Prior to every 12-hour period, following the daily calibration verification	**Compound** All target analytes	**% Recovery** 70-130	Poor performance may necessitate the preparation of new standard solutions and recalibration of equipment until performance criteria are met.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 70-130
Method Blanks	1 per extraction batch[a]	No target compounds ≥PQL		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split[c] SDGs A minimum of 1 per SDG	All target compound percent recoveries must fall within the acceptance criteria provided by the vendor.		The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound percent recoveries must fall within the acceptance criteria provided by the vendor.	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	% Lipids
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-1
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per analytical batch[a]	No target compounds ≥PQL	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL
Laboratory Duplicate	1 per analytical batch[a]	**RPD** ≤50%	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision- Lab	**RPD** ≤50%
Performance Evaluation Sample[b]	Non-Split[c] SDGs 1 per 40 samples Split [c]SDGs A minimum of 1 per SDG	All target compound percent recoveries must fall within the acceptance criteria provided by the vendor.	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy	All target compound percent recoveries must fall within the acceptance criteria provided by the vendor.

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b (UFP-QAPP Manual Section 3.4): Tissue Laboratory Quality Control Samples (continued)

Matrix	Tissue
Analytical Group	% Moisture
Concentration Level	Low
Sampling SOP	SOP-4
Analytical Method/SOP Reference	L-21
Field Sampling Organization	Normandeau
Analytical Organization	eurofins/Lancaster Laboratories
No. of Samples Collected	See Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Laboratory Duplicate	1 per analytical batch[a]	**RPD** ≤20%	The laboratories should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision- Lab	**RPD** ≤20%

Notes:
[a] A batch is defined as a group of up to 20 samples of the same matrix, prepared at the same time, using the same procedure.
[b] Ongoing PE samples will be submitted to the appropriate laboratory according to the following protocol. SDGs containing split samples (shared with USEPA) will have a PE sample submitted at a frequency of 1 for each SDG. USEPA will reserve the right to choose the split samples from the available samples collected. SDGs that do not contain USEPA split samples will have one PE sample submitted for laboratory analysis for every 40 field samples collected. Ongoing PE sample analyses are independent of the pre-program performance evaluation study.
[c] Non-split SDGs – are SDGs that do not contain samples split for analysis between Tierra and USEPA laboratories.
Split SDGs – are SDGs that contain samples which have been split for analysis between Tierra and USEPA laboratories.

PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
PE = performance evaluation
PQL = project quantitation limit
QC = quality control
RPD = relative percent difference
SIM = selective ion monitoring
SOP = Standard Operating Procedure
TAL = Target Analyte List
% = percent

QAPP Worksheet #29-1 (UFP-QAPP Manual Section 3.5): Project Documents and Records

Sample Collection Documents and Records	On-Site Analysis Documents and Records	Off-Site Analysis Documents and Records	Data Assessment Documents and Records
Airbills	Calibration and Sampling Reading Documentation	Hard copy data package as specified in Worksheet #29-2.	Laboratory Quality Assurance Plans
Chain-of-Custody Records	Notebook	Electronic data deliverable as specified in Worksheet #29-4.	Laboratory Certifications
Daily Log			Method Detection Limit Study Information
Employee and Visitor Log			Data Validation Reports
Equipment Calibration and Maintenance Log			Corrective Action Reports - Field and Laboratory
Photograph Logs			Analytical Technical Systems Audit Reports
Refrigeration Unit Sign-in Sheet			Field Technical Systems Audit Reports
Sample Field Data Sheet			Telephone logs
Sample Processing Form			
Pre-Printed Sample Label			
Custody Seal			
Sample Delivery Group Tracking Log			
Notebook			
Fish Sampling and Analysis QAPP			
Bills of Lading			

QAPP Worksheet #29-2 (UFP-QAPP Manual Section 3.5): Required Analytical Chemistry Data Deliverable Elements

Data Deliverable Elements	PCDDs/PCDFs	PCB Congeners	TAL Metals Titanium	Mercury	Methylmercury	% Lipids	Butyltins	Semivolatile Organics	Semivolatile Organics (SIM)	Aroclor PCBs	Pesticides	% Moisture
I**NVENTORY SHEET** (Org. and Inorg. DC-2 Form)	X	X	X	X	X	X	X	X	X	X	X	X
NARRATIVE (Org. Narrative, Inorg. Cover Page)	X	X	X	X	X	X	X	X	X	X	X	X
SHIPPING/RECEIVING DOCUMENTS AND INTERNAL LABORATORY CHAIN-OF-CUSTODY RECORDS:												
Airbills	X	X	X	X	X	X	X	X	X	X	X	X
Chain-of-Custody Records/Forms (Traffic Report)	X	X	X	X	X	X	X	X	X	X	X	X
Miscellaneous Shipping/Receiving Records	X	X	X	X	X	X	X	X	X	X	X	X
Internal Laboratory Sample Transfer Records and Tracking Sheets	X	X	X	X	X	X	X	X	X	X	X	X
SAMPLE DATA:												
Tabulated Summary Form for Field Sample Results (Org. and Inorg. Form I)	X	X	X	X	X	X	X	X	X	X	X	X
RIC for each sample								X	X			
Raw spectra of target compound and background-subtracted spectrum of target compound for each sample								X	X			
Chromatograms from both columns for each sample							X			X		
GC integration report or data system printouts and calibration plots for each sample							X			X		
Pest/PCB/Butyltin Identification Tabulated Summary Form to include % difference of positive results from each analytical column (Org. Form X)							X			X		
For pest/PCBs confirmed by GC/MS, copies of raw spectra and background-subtracted spectrum of target compounds										X	X	
Gel permeation chromatography sample chromatograms								X	X	X		
Sample preparation/extraction/digestion log (Inorg. Form XIII) and notebook pages	X	X	X	X	X	X	X	X	X	X	X	X
Sample analysis run log (Inorg. Form XIV) and notebook pages	X	X	X	X	X	X	X	X	X	X	X	X
ICP/ICPMS/Methyl Mercury/Mercury/Titanium raw data			X	X	X							

See the last page of Worksheet #29-2 for a description of footnotes.

QAPP Worksheet #29-2 (UFP-QAPP Manual Section 3.5): Required Analytical Chemistry Data Deliverable Elements (Continued)

Data Deliverable Elements	PCDDs/PCDFs	PCB Congeners	TAL Metals Titanium	Mercury	Methylmercury	% Lipids	Butyltins	Semivolatile Organics	Semivolatile Organics (SIM)	Aroclor PCBs	Pesticides	% Moisture
STANDARDS DATA:												
Method Detection Limit Study Tabulated Summary Form	X	X	X	X	X		X	X	X	X	X	
Initial Calibration Tabulated Summary Form (Org. Form VI, Inorg. Form IIA)			X	X	X		X	X	X	X		
Continuing Calibration Tabulated Summary Form (Org. Form VII, Inorg. Form IIA)			X	X	X		X	X	X	X		
RICs and quantitation reports for all GC/MS standards								X	X			
Pest/Aroclor/Butyltin Calibration Verification Tabulated Summary Form (Org. Form VII, Pest-1 and Pest-2)							X			X		
Pest/Aroclor/Butyltin Analytical Sequence Tabulated Summary Form (Org. Form VIII-Pest)							X			X		
GC chromatograms and data system printouts for all GC standards					X		X			X		
For PCB Aroclors confirmed by GC/MS, copies of spectra for standards used										X		
Gel Permeation Chromatrography Calibration Tabulated Summary Form (Org. Form IX, Pest-2)								X	X	X		
Florisil Cartridge Check Tabulated Summary Form (Org. Form IX, Pes-1)										X		
ICP Interelement Correction Factors Summary Form (Inorg. Form XIA and XIB)			X									
ICP Linear Ranges Tabulated Summary Form (Inorg. Form XII)			X									
Contract-Required Detection Limit Standards for atomic absorption and ICP Tabulated Summary Form (Inorg. Form IIB)			X									
Standards preparation notebook pages	X	X	X	X	X	X	X	X	X	X	X	X

See the last page of Worksheet #29-2 for a description of footnotes.

QAPP Worksheet #29-2 (UFP-QAPP Manual Section 3.5): Required Analytical Chemistry Data Deliverable Elements (Continued)

Data Deliverable Elements	PCDDs/PCDFs	PCB Congeners	TAL Metals Titamium	Mercury	Methylmercury	% Lipids	Butyltins	Semivolatile Organics	Semivolatile Organics (SIM)	Aroclor PCBs	Pesticides	% Moisture
QC DATA:												
Tuning and Mass Calibration Tabulated Summary Form (Org. Form V)			X					X	X			
Surrogate Percent Recovery Tabulated Summary Form (Org. Form II)							X	X	X	X		
MS/MSD Recovery Tabulated Summary Form (Org. Form III and Inorganic Form V)				X	X		X	X	X	X	X	
Method Blank Tabulated Summary Form (Org. Form IV and Inorg. Form III)			X	X	X		X	X	X	X	X	
Internal Standard Area ICPMS and GC/MSand Retention Time GC/MS only Tabulated Summary Form (Org. Form VIII)			X					X	X			
QC Raw Data - RICs, chromatograms, quantitation reports, integration reports, mass spectra, etc.							X	X	X	X		
ICP Interference Check Sample Tabulated Summary Form (Inorg. Form IV)			X									
Spike Sample Recovery Tabulated Summary Form (Inorg. Form VA)			X	X	X							
Post-Digest Spike Sample Recovery Tabulated Summary Form (Inorg. Form VB)			X	X	X							
Duplicates Tabulated Summary Form (Inorg. Form VI)			X	X	X							
Internal Laboratory Control Sample Tabulated Summary Form (Inorg. Form VII)			X	X	X							
Standard Addition Results Tabulated Summary Form (Inorg. Form VIII)			X	X	X							
ICP Serial Dilutions Tabulated Summary Form (Inorg. Form IX)			X	X	X							
QC raw data	X	X	X	X	X		X	X	X	X	X	
QC Sample preparation notebook pages	X	X	X	X	X		X	X	X	X	X	
Data of Sample preparation and analysis	X	X	X	X	X	X	X	X	X	X	X	X
Sample Holding Temperature Documentation	X	X	X	X	X	X	X	X	X	X	X	X
Sample Preservation Verification Documents	X	X	X	X	X	X	X	X	X	X	X	X

See the last page of Worksheet #29-2 for a description of footnotes.

QAPP Worksheet #29-2 (UFP-QAPP Manual Section 3.5): Required Analytical Chemistry Data Deliverable Elements (Continued)

Data Deliverable Elements	PCDDs/PCDFs	PCB Congeners	TAL Metals Titanium	Mercury	Methylmercury	% Lipids	Butyltins	Semivolatile Organics	Semivolatile Organics (SIM)	Aroclor PCBs	Pesticides	% Moisture
MISCELLANEOUS DATA:												
Airbills	X	X	X	X	X	X	X	X	X	X	X	X
Chain-of-Custody Records/Forms (Traffic Report)	X	X	X	X	X	X	X	X	X	X	X	X
Miscellaneous Shipping/Receiving Records	X	X	X	X	X	X	X	X	X	X	X	X
Internal Laboratory Sample Transfer Records and Tracking Sheets	X	X	X	X	X	X	X	X	X	X	X	X
HIGH RESOLUTION MASS SPECTROMETRY:												
Analysis Data Sheet	X	X									X	
Confirmation analysis datasheet	X											
Cleanup standard recoveries	X	X									X	
Tabulated relative retention times for samples	X	X									X	
SICPs for each sample	X	X									X	
Method blank summarized results	X	X									X	
SICPs for each method blank	X	X									X	
Mass Spectrometer resolutions demonstration SICPs for each analysis shift	X	X									X	
SICPs for 12-hour continuing calibration standard	X	X									X	
GC resolution demonstration SICPs for each 12-hour sequence	X	X									X	
Initial Calibration Relative Retention Times	X	X									X	
Initial Calibration Response Factors	X	X									X	
Initial Calibration Ion Abundance Ratios	X	X									X	
SICPs for the Initial Calibration	X	X									X	
Initial Precision and Recovery	X	X		X	X						X	
Ongoing Precision and Recovery	X	X		X	X						X	
MS/MSD Results and Spiked Level Summary	X	X									X	

See the last page of Worksheet #29-2 for a description of footnotes.

Notes:
( ) = form number; refer to CLP Statement of Work forms if CLP is used
CLP = Contract Laboratory Program
GC = gas chromatography
GC/MS = gas chromatography/mass spectrometry
ICP = inductively coupled plasma
Inorg. = inorganic
MS/MSD = matrix spike/matrix spike duplicate
Org. = organic
PCBs = polychlorinated biphenyls
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
Pest = pesticides
RIC = reconstructed total ion chromatogram
QC = quality control
SIM = selective ion monitoring
SIPCs = selected ion current profiles
TAL = Target Analyte List
% = percent

QAPP Worksheet #29-3 (UFP-QAPP Manual Section 3.5): Standard Laboratory Data Qualifiers

The laboratory qualifiers and their stated definitions provided below will be used by the laboratories exclusively when reporting sample results for this Fish Sampling and Analysis Quality Assurance Project Plan[a].

Qualifier	Description
B	Inorganics – The reported value was obtained from an instrument reading that was less than the project quantitation limit. Organics – The associated analyte was also detected in the method blank.
D	The organic analyte was quantitated from a diluted analysis.
E	Inorganics – The reported value is estimated because of the presence of interference. Organics – The associated compound concentration exceeded the calibration range of the instrument.
J	Organic data indicated the presence of a compound that meets the identification criteria; the result is below the PQL but above the method detection limit or estimated detection limit, where appropriate.
N	The inorganic analysis is associated with a spike sample not within control limits.
P	The percent difference between the primary and confirmation column for pesticide/Aroclor analyses is greater than 25%.
U *	The analyte was analyzed for, but was not detected above the reported sample quantitation limit. The inorganic duplicate analysis was not within the established quality control limit.
S +	Inorganics - The reported value was determined by Method of Standard Additions. Inorganics - Correlation coefficient for MSA is less than 0.995.
W	Inorganics - The post-digestion spike for furnace atomic absorption analysis is out of control.
I	The laboratory indicated the presence of interference during the sample analysis.

Other Data Reporting Requirements:

Only analytical data that are verified/validated (see Worksheets #34, #35, and #36) will be reported.

- Organic analytes detected below the PQL, but above the MDL/EDL, will be reported with a "J" flag, and organic analytes detected below the PQL and MDL/EDL as non-detects at the PQL.
- Inorganic analytes detected below the PQL, but above the MDL, will be reported with a "B" flag, and inorganic analytes detected below the PQL and MDL as non-detects at the MDL.

Notes:
[a] A final deliverable will be provided with standard laboratory qualifiers consistent with U.S. Environmental Protection Agency Electronic Deliverable Region 2 MEDD Format Reference Manual (www.epa.gov/region02/superfund/medd.html)
EDL = estimated detection limit
MDL = method detection limit
MSA = Method of Standard Additions
PQL = project quantitation limit
% = percent
.

QAPP Worksheet #29-4 (UFP-QAPP Manual Section 3.5): Example Format for Electronic Loading of Laboratory Files

A final deliverable will be provided with standard laboratory qualifiers consistent with U.S. Environmental Protection Agency Electronic Deliverable Region 2 Multimedia Electronic Data Deliverable Format Reference Manual (www.epa.gov/region02/superfund/medd.html).

QAPP Worksheet #30 (UFP-QAPP Manual Section 3.5): Analytical Services

Matrix: All
Concentration: Low

Analytical Group	Sample Locations/ID Numbers	Analytical SOP	Data Package[a] Turnaround Time	Laboratory/Organization
PCDDs/PCDFs	As specified in Worksheet #18	L-1	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257
% Lipids	As specified in Worksheet #18	L-1	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257
PCB Congeners	As specified in Worksheet #18	L-2	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257
Target Analyte List Metals, Titanium	As specified in Worksheet #18	L-3, L-29	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257
Mercury	As specified in Worksheet #18	L-4	30 days	Amy Goodall eurofins/Frontier Global Sciences 11720 North Creek Parkway N., Suite 400 Bothell, WA 98011 425-686-3557

See the last page of Worksheet #30 for a description of footnotes.

QAPP Worksheet #30 (UFP-QAPP Manual Section 3.5): Analytical Services

Matrix: All
Concentration: Low

Analytical Group	Sample Locations/ID Numbers	Analytical SOP	Data Package[a] Turnaround Time	Laboratory/Organization
Methylmercury	As specified in Worksheet #18	L-5	30 days	Amy Goodall eurofins/Frontier Global Sciences 11720 North Creek Parkway N., Suite 400 Bothell, WA 98011 425-686-3557
Butyltins	As specified in Worksheet #18	L-6	30 days	Kirk Young TestAmerica Laboratory 30 Community Drive, Suite 11 South Burlington, VT 05403 802-660-1990
SVOCs	As specified in Worksheet #18	L-8, L-30, L-32	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257
SVOCs SIM	As specified in Worksheet #18	L-9, L-30, L-31, L-32	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257

See the last page of Worksheet #30 for a description of footnotes.

QAPP Worksheet #30 (UFP-QAPP Manual Section 3.5): Analytical Services (continued)

Matrix: All
Concentration: Low

Analytical Group	Sample Locations/ID Numbers	Analytical SOP	Data Package[a] Turnaround Time	Laboratory/Organization
Aroclor PCBs	As specified in Worksheet #18	L-10	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257
Pesticides	As specified in Worksheet #18	L-11	30 days	Martha Maier Vista Analytical 1104 Windfield Way El Dorado Hills, CA 95762 916-673-1520
% Moisture	As specified in Worksheet #18	L-21	30 days	Wendy Kozma eurofins/Lancaster Laboratories 2425 New Holland Pike Lancaster, PA 17601 717-556-7257

Notes:
[a] Turnaround time based on day the last sample in the sample delivery group is received by laboratory.
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SIM = selective ion monitoring
SOP = standard operating procedure
SVOC = semivolatile organic compound
% = percent

QAPP Worksheet #31 (UFP-QAPP Manual Section 4.1): Planned Project Assessments

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organization Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Field Sampling Technical Systems Audit	1 audit of each program task	External	Field & Technical Services	Angela Gatchie Quality Assurance Coordinator Field & Technical Services	Bryan Lees Field Supervisor Normandeau Associates, Inc.	Bryan Lees Field Supervisor Normandeau Associates, Inc.	William Ettinger Project Manager Normandeau Associates, Inc.
Laboratory Technical Systems Audit	1 audit of each participating laboratory prior to use or again after a period of inactivity associated with Tierra exceeding 2 years	External	Environmental Standards, Inc. (ESI)	Rock J. Vitale CEAC CPC ESI	Laboratory Project Manager	Laboratory Project Manager	Rock J. Vitale CEAC CPC ESI
Field Readiness Review	1 at sampling startup	Internal	Normandeau Associates, Inc.	William Ettinger Project Manager Normandeau Associates, Inc.	Bryan Lees Field Supervisor Normandeau Associates, Inc.	Bryan Lees Field Supervisor Normandeau Associates, Inc.	William Ettinger Project Manager Normandeau Associates, Inc.
Laboratory Readiness Review	1 at sampling startup	Internal	eurofins/Lancaster Laboratories Lancaster, PA	Wendy Kozma Laboratory Project Manager eurofins/Lancaster Laboratories Lancaster, PA	Various Laboratory Personnel	Various Laboratory Personnel	Wendy Kozma Laboratory Project Manager eurofins/Lancaster Laboratories Lancaster, PA
Laboratory Readiness Review	1 at sampling startup	Internal	Vista Analytical El Dorado Hills, CA	Martha Maier Laboratory Project Manager Vista Analytical El Dorado Hills, CA	Various Laboratory Personnel	Various Laboratory Personnel	Martha Maier Laboratory Project Manager Vista Analytical El Dorado Hills, CA
Laboratory Readiness Review	1 at sampling startup	Internal	eurofins/Frontier Global Sciences Bothell, WA	Amy Goodall Laboratory Project Manager eurofins/Frontier Global Sciences Bothell, WA	Various Personnel Vista Analytical	Various Personnel Vista Analytical	Amy Goodall Laboratory Project Manager eurofins/Frontier Global Sciences Bothell, WA

See the last page of Worksheet #31 for a description of footnotes.

QAPP Worksheet #31 (UFP-QAPP Manual Section 4.1): Planned Project Assessments

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organization Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Laboratory Readiness Review	1 at sampling startup	Internal	TestAmerica Burlington, VT	Kirk Young Laboratory Project Manager TestAmerica Burlington, VT	Various Laboratory Personnel	Various Laboratory Personnel	Kirk Young Laboratory Project Manager TestAmerica Burlington, VT
Internal Field Audits	1 during field operations	Internal	Normandeau Associates, Inc.	Richard Kling Health and Safety Manager Normandeau Associates, Inc.	Bryan Lees Field Supervisor Normandeau Associates, Inc.	Bryan Lees Field Supervisor Normandeau Associates, Inc.	Richard Kling Health and Safety Manager Normandeau Associates, Inc.
Data Validation	All analytical data collected are validated[a]	External	Field & Technical Services	Angela Gatchie Quality Assurance Coordinator Field & Technical Services.	Field and Laboratory Contractors	Field and Laboratory Contractors	Angela Gatchie Quality Assurance Coordinator Field & Technical Services

Notes:
[a] All data collected will undergo full data validation (with the exception of % moisture and % lipids) as outlined in Worksheet #36. % moisture and % lipids data collected will be verified per standard operating procedure.
% = percent

QAPP Worksheet #32 (UFP-QAPP Manual Section 4.1.2): Assessment Findings and Corrective Action Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, and Organization)	Timeframe for Response
Field Readiness Review	Meeting and memo	Bryan Lees Field Supervisor Normandau Associates, Inc.	24 hours after review complete	Memo	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate
Laboratory Readiness Review	Meeting and memo	Martha Maier Laboratory Project Manager Vista Analytical	24 hours after review complete	Memo	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate
Laboratory Readiness Review	Meeting and memo	Wendy Kozma Laboratory Project Manager eurofins/Lancaster Laboratories	24 hours after review complete	Memo	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate
Laboratory Readiness Review	Meeting and memo	Amy Goodall Laboratory Project Manager eurofins/Frontier Global Sciences	24 hours after review complete	Memo	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate
Laboratory Readiness Review	Meeting and memo	Kirk Young Laboratory Project Manager Test America Laboratory	24 hours after review complete	Memo	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate
Internal Field Audit	Audit Report	Bryan Lees Field Supervisor Normandeau Associates, Inc.	1 week after audit is complete	Memo	William Ettinger Project Manager Normandeau Associates, Inc.	1 week

See the last page of Worksheet #32 for a description of footnotes.

QAPP Worksheet #32 (UFP-QAPP Manual Section 4.1.2): Assessment Findings and Corrective Action Responses (continued)

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Time frame of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, and Organization)	Time frame for Response
Data Validation[a]	Validation Reports	All of those listed above as impacted	40 days after receipt of laboratory and field deliverables	Resubmission of missing or corrected documents	Carlie Thompson Facility Coordinator Tierra Solutions, Inc., Eugenia Naranjo Remedial Project Manager USEPA Region 2	1 week after request for completion/correction
Field Sampling Technical Systems Audit	Audit Report/ Corrective Action Form	Bryan Lees Field Supervisor Normandeau Associates, Inc.,	1 day after audit is complete	Audit Report/ Corrective Action Form	Carlie Thompson Facility Coordinator Tierra Solutions, Inc., Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate
Laboratory Technical Systems Audit	Audit Report/ Corrective Action Form	Impacted Laboratory Project Manager	1 week after audit is complete	Audit Report/ Corrective Action Form	Carlie Thompson Facility Coordinator Tierra Solutions, Inc., Eugenia Naranjo Remedial Project Manager USEPA Region 2	Immediate

Notes:
[a] All data collected will undergo full data validation (with the exception of % moisture and % lipids) as outlined in Worksheet #36. Percent moisture and % lipids data collected will be verified per Standard Operating Procedure.
USEPA = U.S. Environmental Protection Agency
% = percent

QAPP Worksheet #33 (UFP-QAPP Manual Section 4.2): Quality Assurance Management Reports

Type of Report	Frequency (e.g., daily, weekly, monthly, quarterly, annually)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Field Sampling Technical Systems Audit Reports	1 per audit conducted	Within 30 days of audit completion	Angela Gatchie Quality Assurance Coordinator Field & Technical Services	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2
Laboratory Technical Systems Audit	1 per audit conducted	Within 30 days of audit completion	Rock J. Vitale CEAC CPC Environmental Standards, Inc.	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2
Internal Field Audit Report	1 per audit conducted	Within 30 days of audit completion	William Ettinger Project Manager Normandeau Associates, Inc.	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2
Data Validation Reports	1 per sample delivery group, per analytical group	Within 40 days of receipt of final deliverables in the sample delivery group, per analytical group	Angela Gatchie Quality Assurance Coordinator Field & Technical Services	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2
Data Usability Assessment Report	1 after completion of validation task	Within 40 days of validation completion	Angela Gatchie Quality Assurance Coordinator Field & Technical Services	Carlie Thompson Facility Coordinator Tierra Solutions, Inc. Eugenia Naranjo Remedial Project Manager USEPA Region 2

Notes:
All data collected will undergo full data validation (with the exception of % moisture and % lipids data) as outlined in Worksheet #36. % moisture and % lipids data collected will be verified per standard operating procedure.

USEPA = U.S. Environmental Protection Agency
% = percent

QAPP Worksheet #34 (UFP-QAPP Manual Section 5.2.1): Verification (Step I) Process

Verification Input	Action	Internal/ External	Organization Responsible for Verification
Chain-of-custody and shipping forms	Chain-of-custody/requests for analysis forms and shipping documentation will be reviewed internally upon their completion and verified against the packed sample coolers they represent. The shipper's signature on the chain of custody should be initialed by the reviewer, a copy of the chain of custody retained in the site file, and the original and remaining copies taped inside the cooler for shipment.	I/E	Normandeau Associates, Inc. Field & Technical Services
Field notes	Field notes will be reviewed internally and placed in the project file.	I	Normandeau Associates, Inc.
Corrective action reports	Corrective action reports (when necessary) will be verified for completeness and signed by the Facility Coordinator and Quality Assurance Coordinator. Corrective actions must also be communicated to appropriate field staff, as well as project review personnel.	I	Tierra Solutions, Inc. Field & Technical Services
Documentation of deviation from sample collection methods	Verify completeness and accuracy prior to distribution and placement in the project file. Communicate deviations to pertinent field staff, as well as project review personnel.	I	Normandeau Associates, Inc.
Field-generated electronic data deliverables[a]	Verify completeness and accuracy prior to distribution and placement in the project file.	I	Normandeau Associates, Inc.
Identification of QC samples	Verify completeness and accuracy prior to distribution and placement in the project file.	I	Normandeau Associates, Inc.
Observed climatological condition recordings	Verify completeness and accuracy prior to distribution and placement in the project file.	I	Normandeau Associates, Inc.
Equipment decontamination records	Verify completeness and accuracy prior to distribution and placement in the project file.	I	Normandeau Associates, Inc.
Sampling equipment calibration logs	Verify completeness and accuracy prior to distribution and placement in the project file.	I	Normandeau Associates, Inc.
Field measurements documentation	Verify completeness and accuracy prior to distribution and placement in the project file.	I	Normandeau Associates, Inc.

See the last page of Worksheet #34 for a description of footnotes.

QAPP Worksheet #34 (UFP-QAPP Manual Section 5.2.1): Verification (Step I) Process (continued)

Verification Input	Action	Internal/ External	Organization Responsible for Verification
Sample condition upon receipt and storage records	Chain of custody/requests for analysis forms and shipping documentation will be reviewed upon cooler receipt. The contents of each cooler will be checked against information provided on the chain of custody/request for analysis forms. Cooler temperatures and specified sample preservation will also be verified and recorded.	I/E	eurofins/Lancaster Laboratories Vista Analytical eurofins/Frontier Global Sciences TestAmerica
Internal laboratory chain of custody records	A complete set of chain of custody records must be produced and submitted with the data package for each sample delivery group.	I	eurofins/Lancaster Laboratories Vista Analytical eurofins/Frontier Global Sciences TestAmerica
Case Narrative to include the following: • Identification of QC samples • Communication logs • Corrective action reports • Documentation of corrective action results • Documentation of laboratory method deviations • Signatures for laboratory sign-off	Verify completeness and accuracy prior to shipping the laboratory report.	I	eurofins/Lancaster Laboratories Vista Analytical eurofins/Frontier Global Sciences TestAmerica
Laboratory data package deliverables as specified in Worksheet #29-2	All laboratory data packages will be verified by the laboratory performing the work for completeness and technical accuracy prior to shipping the laboratory report.	I	eurofins/Lancaster Laboratories Vista Analytical eurofins/Frontier Global Sciences TestAmerica
Laboratory electronic data deliverables as specified in Worksheet #29-4	All laboratory electronic data deliverables will be verified by the laboratory performing the work for completeness and accuracy prior to shipping the laboratory report.	I	eurofins/Lancaster Laboratories Vista Analytical eurofins/Frontier Global Sciences TestAmerica
Laboratory and field data packages and electronic data deliverables as specified in Worksheets #29-2, #29-3, and #29-4	All received data packages will be verified externally for completeness according to the data verification/validation procedures specified in Worksheet #36.	E	Field & Technical Services

See the last page of Worksheet #34 for a description of footnotes.

QAPP Worksheet #34 (UFP-QAPP Manual Section 5.2.1): Verification (Step I) Process (continued)

Notes:
[a] Field-generated electronic data deliverables will be formatted and submitted in USEPA Region 2 MEDD format with the correct reference codes provided as per the USEPA Electronic Data Deliverable Valid Values Reference Manual (available at http://www.epa.gov/region02/superfund/medd.htm)
E = external in relation to data generator
I = internal in relation to data generator
QC = quality control
USEPA = U.S. Environmental Protection Agency

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QAPP Worksheet #35 (UFP-QAPP Manual Section 5.2.2): Validation (Steps IIa and IIb) Process

Step IIa/IIb	Validation Input	Description of Validation Procedure	Organization Responsible for Validation
IIa	Data Deliverables and QAPP	Confirm that all required information on sampling and analysis from data verification was provided.	Field & Technical Services
IIa	Analytes	Confirm that required lists of analytes were reported as specified in this Fish QAPP.	Field & Technical Services
IIa	Chain of Custody	Examine the traceability of the data from time of sample collection until reporting of data. Examine chain-of-custody records against contract, method, or procedural requirements.	Field & Technical Services
IIa	Holding Times	Identify holding time criteria and either confirm that they were met or document deviations. Confirm that samples were analyzed within holding times specified in this Fish QAPP. If holding times were not met, confirm that deviations were documented, that appropriate notifications were made (consistent with procedural requirements), and that approval to proceed was received prior to analysis.	Field & Technical Services
IIa	Sample Handling	Confirm that required sample handling, receipt, and storage procedures were followed, and that any deviations were documented. Sample preservation and temperature will specifically be evaluated and documented.	Field & Technical Services
IIa	Sampling Methods and Procedures	Establish that required sampling methods were used and that any deviations were noted. Confirm that the sampling procedures and field measurements met performance criteria and that any deviations were documented.	Field & Technical Services
IIa	Analytical Methods and Procedures	Establish that required analytical methods were used and that any deviations were noted.	Field & Technical Services
IIa	Data Qualifiers	Determine that the laboratory data qualifiers were defined and applied as specified in this Fish QAPP.	Field & Technical Services
IIa	Laboratory Transcription	Authenticate accuracy of the transcription of analytical data (i.e., laboratory notebook to reporting form or instrument to laboratory information management system).	Field & Technical Services
IIa	Standards	Determine that standards are traceable and meet contract, method, or procedural requirements.	Field & Technical Services
IIa	Communication	Establish that required communication procedures were followed by field or laboratory personnel.	Field & Technical Services
IIb	Project Quantitation Limits	Determine that quantitation limits were achieved, as outlined in this Fish QAPP.	Field & Technical Services

See the last page of Worksheet #35 for a description of footnotes.

QAPP Worksheet #35 (UFP-QAPP Manual Section 5.2.2): Validation (Steps IIa and IIb) Process (continued)

Step IIa/IIb	Validation Input	Description of Validation Procedure	Organization Responsible for Validation
IIb	Confirmatory Analyses	Evaluate agreement between results of confirmatory analyses.	Field & Technical Services
IIb	Performance Criteria	Evaluate QC data against project-specific performance criteria in this Fish QAPP (i.e., evaluate quality parameters beyond those outlined in the methods).	Field & Technical Services
IIb	Analytical Methods and Procedures	Evaluate results of required QC samples and compare with acceptance criteria established in this Fish QAPP.	Field & Technical Services
IIb	Data Validation or Verification Reports	Full data validation will be performed on all analytical parameters. Summarize deviations from methods, procedures, or contracts. Summarize outcome of comparison of data to measurement performance criteria in this Fish QAPP. Include qualified data and explanation of all data qualifiers.	Field & Technical Services

Notes:
Fish QAPP = Fish Sampling and Analysis Quality Assurance Project Plan
QC = quality control

QAPP Worksheet #36 (UFP-QAPP Manual Section 5.2.2.1): Validation Guidance Summary Table[a]

Concentration Level: Low

Analytical Group	Validation Criteria	Data Validator
PCDDs/PCDFs	USEPA Region 2 SOP HW-25, Revision 3, 12/10	Field & Technical Services
PCB Congeners	EDS SOP: Congener PCB, Rev.3, 7/10	Field & Technical Services
TAL Metals & Titanium	USEPA Region 2 SOP HW-2a and HW-2b, Rev.15, 12/12	Field & Technical Services
Mercury	EDS SOP: Mercury by CVAFS USEPA 1631, Rev.1, 5/14	Field & Technical Services
Methylmercury	EDS SOP: Methyl Mercury by CVAFS, USEPA 1630, Rev.1, 5/14	Field & Technical Services
Butyltins	EDS SOP: Organotins Prep. 8/05	Field & Technical Services
Semivolatile Organics	USEPA Region 2 SOP HW-22 Rev.3, 10/06	Field & Technical Services.
Semivolatile Organics (SIM)	USEPA Region 2 HW-35, Revision 2, 3/13	Field & Technical Services
Aroclor PCBs	USEPA Region 2 SOP HW-37, Revision 1, 8/07	Field & Technical Services
Pesticides	EDS SOP: Organochlorine Pesticides by HRGC/HRMS USEPA 1699, Rev.0, 7/10	Field & Technical Services
% Moisture	EDS SOP V-14, Rev.2, 2/10 – Verification/Validation Geotechnical Data	Field & Technical Services
% Lipids	Completeness Check EDS SOP: % Lipids, Rev. 0, 7/14	Field & Technical Services.

Notes:
[a] All validation and verification reference documents have been provided as appendices to this Fish Sampling and Analysis Quality Assurance Project Plan.
CVAFS = cold vapor atomic fluorescence spectrometry
PCB = polychlorinated biphenyl
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SOP = Standard Operating Procedure
SIM = selective ion monitoring
TAL = Target Analyte List
USEPA = U.S. Environmental Protection Agency
% = percent

QAPP Worksheet #37 (UFP-QAPP Manual Section 5.2.3): Usability Assessment

The Data Usability Assessment will be performed by Angela Gatchie, Data Manager, Field & Technical Services. Note that the Data Usability Assessment will be conducted on validated data. The results of the Data Usability Assessment will be presented in the final project report, which will be provided to U.S. Environmental Protection Agency for review and approval. The following items will be assessed and conclusions drawn based on their results.

Precision

Results of all laboratory duplicates will be evaluated based on the measurement performance criteria presented in Worksheets #12-1 and 12-2 discussion will follow summarizing the results of the laboratory precision. Any conclusions about the precision of the analyses or sample collection techniques will be drawn and any limitations on the use of the data will be described.

Accuracy/Bias Contamination

Results for all laboratory method blanks and instrument blanks, as well as field rinsate equipment and trip blanks will be evaluated. The results for each analyte will be checked against the measurement performance criteria presented in Worksheets #12-1 and 12-2 discussion will follow summarizing the results of the laboratory and field accuracy/bias. Any conclusions about the accuracy/bias of the analyses based on contamination will be drawn and any limitations on the use of the data will be described.

Overall Accuracy/Bias

The results for all matrix spike and surrogate standard spike analyses will be evaluated based on the requirements listed in Worksheets #12-1 and 12-2 discussion will follow summarizing overall accuracy/bias. Any conclusions about the overall accuracy/bias of the analyses will be drawn and any limitations on the use of the data will be described.

Sensitivity

All analytical results reported will be evaluated to determine if adequate sensitivity was achieved. The results for each analyte will be cross-checked against the quantitation limits presented in Worksheets #15-1 and 15-2. Results for analytes that do not meet project quantitation limit criteria will be summarized. A discussion will follow detailing the results of the laboratory-sensitivity evaluation. Any conclusions about the sensitivity of the analyses will be drawn and any limitations on the use of the data will be described.

Representativeness

Representativeness is achieved through adherence to sampling and analytical procedures described in this Fish Sampling and Analysis QAPP and compliance with stipulated sample holding times. After evaluation of relative compliance with specified procedures and holding times, conclusions about data representativeness will be drawn and any limitations on the use of data will be described.

QAPP Worksheet #37 (UFP-QAPP Manual Section 5.2.3): Usability Assessment (continued)

Comparability

Data comparability will be assessed through evaluation of achieved sample-specific reporting limits, units of measure, and adherence to specified analytical methodologies and field/sample collection standard operating procedures specified in this Fish Sampling and Analysis QAPP. Evaluation of field procedures used will include assessment of the affects of any deviation from the established filed procedures to data usability. After the evaluations are completed, conclusions about data comparability will be drawn and any limitations on the use of data will be described.

Completeness

A completeness check will be done on all of the data generated. Field and analytical completeness criteria are presented in Worksheets #12-1 and 12-2. Field and analytical completeness will be calculated for each analytical group as follows:

The field completeness will be calculated by the ratio of the number of samples received in acceptable condition by the laboratories to the number of samples planned to be collected as specified in this document. The equation for field completeness is:

$$\%\ Field\ Completeness = \frac{Number\ of\ Samples\ Received\ by\ Laboratories}{Total\ Number\ of\ Samples\ Planned\ to\ be\ Collected}\ x\ 100$$

The analytical completeness will be calculated by the ratio of total valid analytical data results (including estimated values) to the total number of analytical results requested on samples submitted for analysis. Valid analytical data results are defined as those that were not rejected during data validation, due to a significant quality assurance/quality control problem. The equation for analytical completeness is:

$$\%\ Analytical\ Completeness = \frac{Total\ Valid\ Analytical\ Data}{Analytical\ Data\ Obtained}\ x\ 100$$

Figure

LEGEND:

- PROPOSED MUMMICHOG STATION
- PROPOSED OTTER TRAWL LOCATION
- INTERTIDAL AREAS FOR PROPOSED SAMPLING
- PROPOSED GILL NET STATION
- RIVER/BAY MILE
- GEOGRAPHIC AREAS (ZONES)
- SHORELINE
- UNDERGROUND TRIBUTARY

GEOMORPHIC AREAS

- INTERTIDAL AREAS
- NAVIGATION CHANNELS
- PORT CHANNELS
- SUBTIDAL FLATS
- TRANSITIONAL SLOPES
- INDUSTRIAL WATERFRONT

0 3,000 6,000 Feet

GRAPHIC SCALE

PASSAIC RIVER
HACKENSACK RIVER
CONRAIL BRIDGE REMNANTS
PIERSONS CREEK
PORT NEWARK CHANNEL
ELIZABETH CHANNEL
NEWARK LIBERTY INTERNATIONAL AIRPORT
NEWARK BAY CDF (CELL 1S)
PERIPHERAL DITCH
NEWARK BAY NORTH
NEWARK BAY CENTRAL
NEWARK BAY SOUTH
LEHIGH VALLEY RAILROAD BRIDGE
NEW JERSEY TURNPIKE
SOUTH ELIZABETH CHANNEL
ELIZABETH RIVER
ARTHUR KILL
SHOOTERS ISLAND
BAYONNE BRIDGE
KILL VAN KULL
GOETHALS BRIDGE
122
123
124
125
126
127
128
129
130
131
132
133

NOTES:

1. HORIZONTAL DATUM: NEW JERSEY STATE PLANE COORDINATE SYSTEM, NAD83.
2. SHORELINE IS DIGITIZED FROM AERIAL PHOTO DATED JULY 2002 (INTRASEARCH, ENGLEWOOD, CO).
3. THE GEOMORPHIC AREAS SHOWN ARE CONSISTENT WITH THOSE PRESENTED IN THE CSM (TIERRA 2013b).
4. RIVER/BAY MILES CREATED BY DIVIDING RIVER CENTERLINE PROVIDED BY USEPA INTO 0.01-MILE SEGMENTS. HALF-MILE INCREMENTS ARE DISPLAYED ON THIS FIGURE.
5. PROPOSED GILL NET AND OTTER TRAWL LOCATIONS ARE APPROXIMATE AND LIKELY TO CHANGE BASED ON FIELD CONDITIONS AND LEVEL OF FISHING EFFORT REQUIRED. GPS COORDINATES OF FISHING ATTEMPTS WILL BE RECORDED.
6. PROPOSED MUMMICHOG SAMPLING LOCATIONS BASED UPON CLAM LOCATIONS AND MAY CHANGE BASED ON FISH ABUNDANCE AND FIELD CONDITIONS. FINAL SAMPLING LOCATIONS WILL BE CONFIRMED IN THE FIELD WITH USEPA.
7. ABBREVIATIONS ARE AS FOLLOWS:
   AK = ARTHUR KILL
   EC = ELIZABETH CHANNEL
   HR = HACKENSACK RIVER
   KVK = KILL VAN KULL
   NB = NEWARK BAY
   PNC = PORT NEWARK CHANNEL
   PR = PASSAIC RIVER
   SEC = SOUTH ELIZABETH CHANNEL
   SI = SHOOTERS ISLAND

NEWARK BAY STUDY AREA REMEDIAL INVESTIGATION
FISH SAMPLING AND ANALYSIS QUALITY ASSURANCE PROJECT PLAN

PROPOSED FISH TISSUE SAMPLING LOCATIONS

OCTOBER 2014

FIGURE 1

Appendix A

Field SOPs

Standard Operating Procedure No. 1

Locating Sample Points Using Hand-Held Global Positioning System

August 2014

Revision 1

1. Purpose and Scope

The purpose of this procedure is to provide reference information regarding the collection and documentation of sample coordinates for the Newark Bay Study Area (NBSA) Remedial Investigation/Feasibility Study (RI/FS) using a global positioning system (GPS).

This standard operating procedure (SOP) may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s (Tierra's) Facility Coordinator and the United States Environmental Protection Agency Remedial Project Manager. The ultimate procedure employed will be documented in the field notebook.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Definition

GPS provides navigation and positioning information from a constellation of GPS satellites, operated by the United States Department of Defense. The system includes a control station and five monitoring locations that track each satellite. Information received by the monitoring stations is used to calculate satellite orbits and update the information sent to receivers. Satellite signals can be received by any GPS receiver on land or water or in the air. The system incorporates a minimum of 24 satellites, which are positioned around the world, such that six satellites are available at a given location, 24 hours a day. The NBSA RI/FS will use a handheld GPS unit to collect and record sampling location coordinates. The signals received by the hand-held GPS will produce locations with sub-foot accuracy.

3. Equipment and Supplies

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- a hand-held differential global positioning system (DGPS) unit or equivalent model such as the Trimble® ProXH™, with sub-foot accuracy

- an additional DGPS unit with equivalent accuracy as the primary unit (described above) to be carried as a backup to the Trimble® unit in the case of malfunction or loss (if necessary, the backup GPS unit will only be used temporarily until the primary unit can be replaced or repaired)

- AA or AAA batteries depending on the device

- USB port cable to download information

4. Field Procedure

Power on the GPS unit and wait several minutes for the GPS to locate the initial position via satellite. Confirm that the date and time are correct.

Locate the coordinate system information in the main menu and verify the following settings:

1. units = feet

2. coordinate system = New Jersey State Plane (easting and northing)

3. map datum = North American Datum of 1983 (NAD83)

4. north reference = magnetic north (Magnetic north will be used for navigational purposes; however, either magnetic or true north can be used to collect fixed coordinates. The north reference setting will be recorded in the field notebook.)

Confirm that the background map is set to North America. Record the date, time, and all relevant coordinate system information in the field notebook.

Once the unit has acquired the initial position and has indicated that it is ready, follow directions on the GPS to begin collecting sample coordinates.

At each sampling location, allow the GPS to receive satellite data for at least 1 minute before recording the sampling location. A minimum of three satellites is required for a three-dimensional reading, but four satellites are preferred. Save the location information at each sampling location. Record the date, time, and easting/northing (NAD83 New Jersey State Plane) in feet for each location in the field notebook. Readings will be stored in the GPS unit for easy downloading and also to reduce error.

The manufacturer's user's manual will be reviewed and referenced to address technical difficulties and/or malfunctions with the unit.

5. Quality Control

The GPS has quality control features within the system that maintain reliable readings. The GPS will indicate the number of satellites available, the strength of each satellite signal, and will not display coordinates for a given location if there is not a sufficient number of satellites available to take an accurate measurement. The GPS will also make sure that the satellite geometry is able to account for the three-dimensional position. The GPS averages data from satellites over time; therefore, waiting at least 1 minute before recording coordinates at each sampling location will provide a more accurate reading. To confirm the accuracy of the navigation system, a checkpoint will be located at a known point, such as a pier face, dock, piling, or similar structure that is accessible by the sampling vessel. At the beginning and end of each day, the vessel will be stationed at the

check point, a GPS position reading will be taken, and the reading will be compared with the known land-survey coordinates. The two position readings should agree, within the limits of survey vessel operational mobility, to within 1 foot.

Standard Operating Procedure
No. 2

Positioning

September 2014

Revision 1

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for positioning vessels for the Newark Bay Study Area Fish Sampling and Analysis Quality Assurance Project Plan (QAPP). Positioning will be conducted to locate the vessel(s) and sample locations with sufficient accuracy and precision to meet project objectives during sampling activities.

This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to position vessels and locate sampling locations. Specific information regarding proposed sampling locations is provided in the QAPP.

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s (Tierra's) Facility Coordinator and the United States Environmental Protection Agency Remedial Project Manager. The ultimate procedure employed will be documented in the field notebook.

Other SOPs will be utilized with this procedure, including:

- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

Sampling activities will be conducted from a vessel or on land, depending on tidal stage and water depth. In accordance with the procedures outlined below, the vessels must be properly positioned and their position recorded before each activity can begin.

2.1 Equipment List

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- personal protective equipment and other safety equipment, as required by the Health and Safety/Contingency Plan, Rev. 1 (Tierra 2007)

- vessel(s) adequate for Newark Bay conditions

- 25-watt marine VHF radio
- navigation charts and sample location figure
- differential global positioning system (DGPS) receivers (x2) with an accuracy of ±1 foot
- DGPS external antennas (x2)
- equipment user manuals
- table of target sampling location coordinates
- assorted nautical equipment (e.g., anchors, lines, personal flotation devices)
- field notebook
- Sample collection forms
- permanent marker or grease pencil.

2.2 Positioning Vessel

This section gives the step-by-step procedures for vessel positioning. Observations made during vessel positioning should be recorded in the logbook, as appropriate.

A DGPS will be used to establish locations during implementation of activities specified in the QAPP. One handheld DGPS unit will be on board the vessel. Its receiving antenna will be aligned with the sample to be collected.

While this SOP provides general guidance and procedural steps, personnel performing positioning activities also should follow the appropriate sections of the equipment user's manuals and have the manuals available for reference at all times.

The following procedures describe the steps to establish position at a location, as well as the steps to adjust the positioning for collection of additional samples.

2.2.1 Establishing Position at a Location

Preliminary Activities

1. Obtain the appropriate sample collection form(s). Complete the Daily Activity Log provided in SOP No. 8 – Documenting Field Activities.

2. Obtain the target sampling locations. For Phase III activities, these locations will have been selected prior to commencement of field activities, as described in the QAPP. The location of each target sampling location will be established in the New Jersey State Plane Coordinate System with respect to the North American Datum of 1983.

3. Enter coordinates for the locations into the DGPS unit that will be on board the vessel as a waypoint.

Field Activities

1. The operation and horizontal accuracy of the handheld DGPS will be verified at a shore-based marker by recording observed horizontal (XY) data and comparing these data to the published XY data for that point. A temporary benchmark may be established at a location convenient to the vessel to facilitate daily DGPS system performance verification. DGPS system performance verification will be conducted twice per day and documented in the field notebook and data logger. The horizontal accuracy will be compared to shore-based markers to verify performance.

2. Verify receiving antenna is properly aligned with the sampling device.

3. Identify and approach actual sampling locations by using data from the DGPS unit in the navigation mode. The navigation mode provides information on heading, distance remaining, and time remaining. This information is based on the selected waypoint location and the present location of the vessel.

4. Anchor the vessel adjacent to the planned location, if desired.

5. Once the vessel is on location and secured, note the coordinates from the DGPS unit and check the coordinates to verify that the vessel is within the pre-determined range of the target location. For the initial attempt, confirm that the coordinates are within 5 feet of the target. (For subsequent attempts, see Section 2.2.2 below.) If not acceptable, adjust the vessel's location and recheck the position. Repeat this process until the vessel's position is within acceptable range of the target. Record the final coordinates on the appropriate form.

6. Once the coordinates are acceptable, perform sampling activity at the location. Record final location coordinates on the appropriate form. Plot locations onto a master chart or use computer-based, real-time software to verify location.

7. At the end of the sampling day, check the data loaded onto the DGPS units to verify the existence of locations where data were collected.

2.2.2 Adjusting Position

The following steps will be used to adjust position for sampling activities:

1. Move vessel 10 feet from the initial sampling location and within a 50-foot radius of the target coordinates.

2. Check the coordinates to verify that the vessel is within 50 feet of the target coordinate and note coordinates on the Collection Form.

3. Once the coordinates are acceptable and recorded, collect samples. Record the final location.

4. Repeat Steps 1 through 3 until the appropriate number of samples is collected.

2.3 Calibration, Maintenance, and Use of Field Instruments

Prior to use, the DGPS units will be inspected in accordance with the QAPP. DGPS units will be calibrated in accordance with the QAPP, appropriate sections of the equipment user's manual, and as described in Section 2.2 of this SOP. Maintenance and use of DGPS units should follow the appropriate sections of the equipment user's manual. Field personnel will have the manual available for reference. Equipment inspection and maintenance will be recorded in the equipment maintenance log presented in Worksheet# 22 of the QAPP.

Despite virtually worldwide, 24-hour coverage, technical difficulties with GPS satellites can still occur. In the event of system-wide or other long-term problems with GPS (e.g., satellite failures), vessel positioning will be achieved using land-based methods. If a land-based method is selected, an SOP will be developed for its use.

3. Quality Assurance

For the Phase III Program, quality assurance (QA) activities for positioning procedures include verification of the sampling location by comparing the target coordinates specified in the QAPP with coordinates entered into the DGPS, by plotting the

coordinates on a master chart, and by performing the daily check with shore-based markers.

4. Documentation

Detailed positioning data will be recorded on the Sample Collection Forms provided in SOP No. 8 – Documenting Field Activities. In addition, the following information will be recorded in a field notebook (at a minimum):

- notes on breaking position during sampling
- equipment calibration information
- summary of vessel activities.

5. References

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

Standard Operating Procedure
No. 3

Decontamination

August 2014

Revision 1

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for decontamination of equipment, instruments, and other materials used during implementation of the Newark Bay Study Area Fish Sampling and Analysis Quality Assurance Project Plan (Fish QAPP). Decontamination is the process of neutralizing, washing, and rinsing exposed surfaces of equipment to minimize the potential for contaminant migration and/or cross-contamination. This procedure does not apply to personnel decontamination, which is described in the Health and Safety/Contingency Plan (HASCP), Rev. 1 (Tierra Solutions, Inc. [Tierra] 2007).

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra's Facility Coordinator and the United States Environmental Protection Agency (USEPA) Remedial Project Manager. The ultimate procedure employed will be documented in the field notebook.

Other SOPs will be utilized with this procedure, including:

- SOP No. 4 – Fish Sample Collection
- SOP No. 6 – Management and Disposal of Residuals
- SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for Analysis
- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

2.1 Equipment List

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- personal protective equipment (PPE) and other safety equipment, as required by the HASCP, Rev. 1 (Tierra 2007)

- bristle brushes
- wash/rinse tubs
- low phosphate detergent
- 10% nitric acid, ultrapure
- acetone, methanol, and hexane (pesticide grade or better in separate Teflon® bottles), as necessary
- deionized "analyte-free" water
- stainless steel bowls
- aluminum foil
- tap water (from any treated municipal water supply)
- high-pressure/steam cleaner
- sample container(s) for rinsate blank, if collected
- field notebook.

2.2 Sample Equipment and Decontamination

Sampling equipment (including newly purchased equipment) that comes into contact with the media to be sampled will be decontaminated prior to use in the field to eliminate or minimize cross-contamination. The frequency of decontamination is provided in SOP No. 4 – Fish Sample Collection. Sufficient decontaminated equipment must be available to be dedicated to the sampling locations planned for each day. Equipment will be decontaminated in the area designated for decontamination.

The decontamination procedure followed by USEPA Region 2 (USEPA 1989) – with the exception of the second tap water rinse being replaced with a deionized “analyte-free” water rinse – will be used prior to each sampling event for equipment that will come into contact with the media to be sampled. The USEPA Region 2 procedures are summarized below:

1. Wash and scrub with low phosphate detergent.

2. Rinse with tap water.

3. Rinse with 10% nitric acid (HNO_3), ultrapure.

4. Rinse with deionized “analyte-free” water.

5. Spray or rinse with acetone only or a methanol followed by hexane spray or rinse (solvents must be pesticide grade or better).

6. Rinse thoroughly with deionized ("analyte-free") water.

7. Air dry.

8. Wrap in aluminum foil, shiny side out, for temporary storage and transport.

Sampling equipment will be decontaminated as described in Section 2.2.1 below. Decontamination of the sampling equipment will be sufficient for collecting samples for the analysis of dioxin/furan congeners and homologues (PCDDs/PCDFs), including all other analytes, and will consist of a methanol rinse followed by a hexane rinse as described in Section 2.2.1.

Solvents used during decontamination activities will be collected and handled in accordance with residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals.

Not all sampling equipment will require the full decontamination procedures listed in the USEPA Region 2 Comprehensive Environmental Response, Compensation, and Liability Act Quality Assurance Manual. Three levels of decontamination (i.e., solvent, soap and water, or ambient [Newark Bay] water decontamination) will be performed based on the usage of the sampling equipment as defined below.

2.2.1 Decontamination with Solvents

The following steps will be used to decontaminate small sampling equipment that will come into contact with sediment designated for chemical analysis (e.g., stainless steel trowels, spoons and bowls, Lexan® tube, and plastic caps for the core tubes):

- Personnel will dress in suitable PPE to reduce exposure to chemicals and contaminants Phase II RIWP HASCP Rev. 1 (Tierra, 2007).

- Residual sample media at the coring location (i.e., on the vessel) will be scraped off and the equipment rinsed with Newark Bay water.

- Residual sample media on equipment at the sample processing site will be scraped off and collected according to residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals.

- Equipment will be placed in a wash tub or bucket containing Alconox (or other low-phosphate detergent) along with tap water, and scrubbed with a bristle brush or similar utensil. Equipment will be rinsed with tap water in a second wash tub or bucket, followed by a nitric acid rinse (for metals analyses), a deionized "analyte-free" water rinse, a methanol rinse followed by a hexane rinse (for organic analyses), and lastly with a deionized water rinse. Rinses shall utilize sufficient amounts of solvent/water to flush rather than just wet the surface. The volume of deionized water used during the rinse must be at least five times the volume of solvent used.

- Following decontamination, equipment will be placed in a clean area and allowed to air dry. Following air drying, the equipment will be wrapped in aluminum foil, shiny side out, until used for sample collection.

- Used decontamination water will be collected and handled in accordance with residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals.

2.2.2 Decontamination with Soap and Water

The following steps will be used to decontaminate equipment that is not intended to collect samples for chemical analysis:

- Personnel will dress in suitable PPE to reduce exposure to contaminants as discussed in the HASCP, Rev. 1 (Tierra 2007).

- Residual sample media at the sampling location (i.e., on the vessel) will be scraped off and the equipment rinsed with Newark Bay water.

- Residual sample media on equipment at the sample processing site will be scraped off and collected according to residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals.

- Equipment will be placed in a wash tub or bucket containing Alconox (or other low phosphate detergent) and tap water, and scrubbed with a bristle brush or similar

utensil. Equipment will be rinsed with tap water in a second wash tub or bucket, and then rinsed again.

- Following decontamination, equipment will be placed in a dedicated clean area.

- Rinse water and detergent water will be replaced frequently. Used decontamination water will be collected and handled in accordance with residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals.

2.2.3 Decontamination with Ambient (Newark Bay) Water

The following steps will be used to decontaminate sampling and support vessels, vessel anchors, lines, ropes, submersible pump and hose (not intended for sample collection), and buoy marker weights:

- Personnel will dress in suitable PPE to reduce exposure to contaminants (HASCP, Rev. 1 [Tierra 2007]).

- Equipment will be rinsed with Newark Bay water onboard the sampling vessel.

- Rinse water will not be contained.

Daily decontamination of the decks of the vessels will consist of a Newark Bay water washing as soon as possible after concluding work. Further wash-down with tap water at the marina is at the discretion of the boat's captain.

2.3 Field Instruments and Equipment

Instrumentation should be cleaned according to the manufacturer's instructions. Care will be taken to prevent damage to equipment. When possible, instruments that are difficult to decontaminate, such as cameras and data logging instruments, may be protectively wrapped to reduce or eliminate the need for decontamination.

2.4 Other Equipment Decontamination

Other sampling equipment that might be used that has had direct contact with sediments or wastes will be decontaminated at a designated area prior to leaving the site. The decontamination procedure will be as follows:

- Equipment will be wrapped or draped in plastic or placed in the plastic-lined cargo area of a truck for transport to the area designated for decontamination.

- Equipment will first be washed with a hot water, high-pressure spray or steam-cleaned.

- Equipment will then be rinsed, by hose or high pressure spray, with tap water.

- Wash and rinse water will be collected and handled in accordance with residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals.

2.5 Equipment Leaving Newark Bay

Equipment leaving the site upon the completion of on-site investigation activities will be decontaminated according to Sections 2.2, 2.3, or 2.4 above.

2.6 Collection of Rinsate Blank

Rinsate blanks will be collected to assess the adequacy of equipment decontamination procedures. Rinsate blanks are submitted for testing each day a decontamination event is carried out (not to exceed one per day). Following sample collection and processing, all pieces of equipment (both used and unused) belonging to the equipment set will be decontaminated during the decontamination event. One set of equipment will be used throughout the sample collection and processing activities to confirm the rinsate blank corresponds to one set of samples (e.g., a given stainless steel bowl and spoon will be considered a set and will be used together throughout the sample processing activities).

The rinsate blank collection procedures for all analytes, except dioxin/furan analysis, are as follows:

- Pour analyte-free water over a representative set of sampling equipment (e.g., stainless steel bowl, stainless steel pan) after it has been decontaminated.

- Collect rinsate in a previously decontaminated stainless steel bowl and transfer rinsate to sample bottles for analysis.

- Preserve rinsate sample, as necessary, in accordance with SOP No. 7 – Containers, Preservatives, Handling, and Tracking of Samples for Analysis.

For the purposes of the Phase III Program, rinsate blank samples for dioxin/furan analysis will be collected using hexane, rather than spectrophotometric-grade trichloroethene (TCE) as specified by USEPA Region 2 (USEPA1989). As TCE is a potential target analyte for this RI Program, hexane was substituted to eliminate the

potential for obtaining erroneous positive TCE results in collected field samples. Rinsate blank collection procedures for dioxin/furan analysis will be as follows:

- Following collection of the rinsate blank samples for all other analytes, pour hexane over a representative set of sampling equipment (e.g., stainless steel bowl, stainless steel pan) after it has been decontaminated.

- Collect rinsate in a previously decontaminated stainless steel bowl and transfer rinsate to sample bottles for analysis with other sediment samples.

- Preserve rinsate sample, as necessary, in accordance with SOP No. 7 – Containers, Preservatives, Handling, and Tracking of Samples for Analysis.

3. Quality Assurance

Decontamination quality assurance/quality control procedures described in Section 2.6 will be performed to assess the adequacy of equipment decontamination procedures. Rinsate blanks will be collected at the frequency specified in Worksheet No. 28 of the Fish QAPP.

4. Documentation

Field personnel are responsible for documenting decontamination activities related to their on-site activities in accordance with SOP No. 8 – Documenting Field Activities. In addition to this, the following information should also be included in the field notebook (at a minimum):

- Information concerning items decontaminated and the procedure utilized.

- Information related to the collection of rinsate blank samples.

5. References

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

USEPA. 1989. Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA] Quality Assurance Manual, Revision 1. October.

Standard Operating Procedure No. 4

Fish Sample Collection

October 2014

Revision 2

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for collecting fish samples in the Newark Bay Study Area (NBSA). The methodologies described in this SOP are for collection of fish samples for chemical analysis and fish population and health metrics. Fish tissue samples will be analyzed for the constituents outlined in the associated Quality Assurance Project Plan (QAPP).

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s Facility Coordinator and the United States Environmental Protection Agency (USEPA) Remedial Project Manager, in consultation with the Partner Agencies (United States Fish and Wildlife Service, National Oceanic and Atmospheric Administration, United States Army Corps of Engineers, and New Jersey Department of Environmental Protection).

Other SOPs will be utilized with this procedure, including:

- SOP No. 5 – Fish Sample Processing
- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

Several types of fish will be collected to meet the objectives of the sampling program including forage fish, benthic or demersal fish, pelagic predatory fish, and sport fish. Details of the sampling including target species, sample sizes, and sample mass requirements are described in the associated QAPP. To collect the different target species, fish sampling will include the use of various collection techniques, including traps, gill nets, trawl nets, and seine nets. Collection efforts will follow the general procedures described in Section 2.2.

2.1 Equipment List

The following list includes equipment and materials needed to perform the procedures outlined in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment not listed here may be required depending on field conditions at the time activities are being conducted.

- PPE or other safety equipment, as required by the Health and Safety/Contingency Plan, Rev. 1 (Tierra 2007)
- sampling vessel adequate for site conditions and with appropriate equipment for the task (e.g., winches, cables for trawling)
- station location map
- scientific collector's permit or equivalent
- fish and crab traps (i.e., minnow traps and/or eel pots)
- buoys (fluorescent and labeled with study information or scientific collector's permit [or equivalent] information)
- weights for minnow traps and/or eel pots (5 to 10 pounds)
- bait (e.g., cut fish, clams, crabs)
- gill nets sized for the target species or multi-panel gillnets with weights, floats, anchors and buoys labeled with study information or scientific collector's permit (or equivalent) information
- bottom trawl sized for the target species with cables, otter boards, winches, and rigging
- chest or hip waders
- seine net sized for target species and mesh with floats, weights, and brails
- 5-gallon buckets or plastic totes
- field data sheets
- fluorescent or reflective paint or tape
- field notebook
- indelible ink pens
- measuring tape, fish measuring board and ruler

- electronic scale
- sealable plastic zip-top bags of various sizes (e.g., quart, 1 gallon, 2 gallon)
- laboratory-supplied sample coolers
- wet ice
- sample labels
- camera
- fish identification keys
- global positioning system (GPS).

2.2 Collection Procedures

Fish will be collected primarily using traps, gill nets, seine nets, and trawl nets. If necessary, additional methods such as angling may be used to fill sample size. State personnel (conservation officers) will be notified of the sampling activities prior to mobilization. Collection of alternate species may occur if target species are absent, and as approved by Tierra Solutions Inc.'s Facility Coordinator and the USEPA Remedial Project Manager, in consultation with the Partner Agencies. Non-target species will be released back to the NBSA. Fish will be collected using trained personnel and approved sampling techniques. Fish sample collection procedures are described in the sections below.

2.2.1 Fish Collection Using Traps

The following procedures will be used to collect fish using minnow traps or eel pots (collectively referred to as fish traps):

- Select the area to be sampled based on habitat conditions and water depth.
- Use buoys to visibly mark fish traps. The buoy will have a permanent identification tag bearing the license/collection permit number or equivalent. The buoy will be marked with fluorescent/reflective paint or tape.
- Place a minimum of three fish traps at each sampling station.

- Upon arrival at sample locations, check fish traps to confirm they are working properly and, if necessary, attach weights prior to baiting.

- Bait the traps and lower them over the side of the boat.

- Confirm the trap is resting on the bottom and that the buoy is clearly visible on the water surface with enough slack to account for tide so that the trap can be easily retrieved.

- Use a hand-held or boat mounted GPS unit to take coordinates of the trap locations and record any pertinent sampling location and condition descriptions in the field notebook.

- Check fish traps at least once per day (i.e., every 24 hours).

- To check the trap, pick up the buoy and pull up the line and trap to check for catch. If target species have been collected, remove them from the trap and measure. If they meet the minimum target size, place them in a labeled, sealable plastic bag and place on ice. For non-target species, count, weigh, measure and release these individuals at the location where they were collected.

- Place retained fish in an individually labeled, sealable plastic bag following the procedures listed in SOP No. 5 – Fish Sample Processing. The bags will be kept on ice in a laboratory-supplied cooler or secure refrigerator until processing.

2.2.2 Fish Collection Using a Gill Net

The following procedures will be used to collect fish using gill nets:

- Select the area to be sampled based on habitat conditions and water depth. Do not set gill nets in or close to navigation channels, marinas, or other areas of high boat traffic.

- Record coordinates using a hand-held or boat mounted GPS unit.

- Mark gill nets with a flagged buoy at each end of the net and place regularly spaced floats along the net. The buoys will have a permanent identification tag bearing the license/collection permit number or equivalent. Buoys will be marked with fluorescent/reflective paint or tape.

- Remove any obstructions from the deck of the boat so as to not entangle the net. Prior to paying out the net, remove or secure buttons, straps/buckles, and other

loose articles of clothing that may catch in the net so these items do not to become entangled.

- Use net with appropriately sized mesh and appropriate depth for the target species. Attach the end of the gill net to a buoy, anchor it, and deploy it overboard. Back the boat in reverse while allowing the net to pay out.

- Set the net perpendicular to the likely direction of fish travel and once it is stretched taught; anchor the other end and attach a buoy.

- Observe the net to make sure it is holding and that the buoys are visible prior to departing.

- After the prescribed set time (nets will be checked at least once every 24 hours) return to the net and check for fish. Clear the boat deck of obstructions and secure any loose or entangling articles of clothing.

- Upon arrival at the net, approach the net from the downwind or down current side, pick up the buoy from one end, and walk the boat along the net, lifting it up to check for fish.

- Remove any captured fish from the net and placed them in a clean holding container (e.g., cooler, buckets, plastic tote) with site water.

- After the entire net has been checked for fish, remove the captured fish from the holding container for observation. Retain any target species that meet the minimum target size. For non-target species, count, weigh, measure and release these individuals at the location where they were collected.

- Pull the net into the boat and coil it carefully in a plastic tub or container so that it can easily be re-set.

- Place retained fish in a labeled, sealable plastic bag following sample management procedures listed in SOP No. 5 Fish Sample Processing. The bags will be kept on ice in a laboratory-supplied cooler or secure refrigerator until processing.

2.2.3 Fish Collection Using a Trawl Net

The following procedures will be used to collect fish using a trawl net:

- Select area to be sampled based on habitat conditions and consulting navigational charts for the presence of potential obstructions. Areas with potential underwater obstructions should be avoided.

- Record the start and stop points of each trawl using a hand-held or boat mounted GPS unit.

- Upon arrival at target sampling locations, set up the trawl net with appropriate sized mesh for the target species.

- Attach the trawl net to the rope or cables, deploy the net from the back of the boat and allow it to settle to the bottom.

- Motor the boat forward at an appropriate speed to keep the net in contact with the bottom (if benthic fish are being targeted).

- While the boat is in motion, do not stand between the trawl, ropes, or winches or within the swing radius of the winch arm in case there is a snag.

- After the prescribed trawl time (approximately 10 minutes), winch or pull the net into the boat, and release the cod end to empty the catch onboard.

- Remove organisms from the net and place them in a clean holding container with site water. Retain target species that meet the minimum target size. For non-target species, count, weigh, measure, and release these individuals at the location where they were collected.

- Pull the net into the boat and store it securely.

- Place retained fish in a labeled, sealable plastic bag following sample management procedures listed in SOP No. 5 Fish Sample Processing. The bags will be kept on ice in a laboratory-supplied cooler or secure refrigerator until processing.

2.2.3 Fish Collection Using a Seine Net

Fish collection procedures using a seine net will be as follows:

- Select the area to be sampled based on habitat conditions and water depth. Seine nets will not be deployed in or close to navigation channels, marinas, or other areas of high boat traffic or in areas with swift water, in-water obstructions, or other hazards.

- Record the coordinates using a hand-held GPS unit.

- Select a net with appropriate length, depth, and mesh size for the target species and habitat at the sample location.

- One person will take an end of the net attached to a brail and walk out in a semi-circle to set the net.

- Once the net is stretched out, another crew member takes the other end of the net and both crew members drag the net behind them.

- Haul the seine over the sampling area, keeping the lead line in front of the floating line.

- Once an adequate distance has been covered (e.g., approximately 20 yards for forage fish, approximately 100 yards for larger fish), the person on the outside will return to shore and “close” the net so that any organisms within the semi-circle of the net will be pinned between the net and shore.

- Crew members at both ends of the net will pull in the net, keeping the lead line in front of the floating line and shaking back any fish towards the middle of the net.

- When there is only a small section of the net remaining in the water, lift the lead lines and float lines simultaneously from both directions to entrap any organisms in the net. The net may then be moved to shore or a boat to sort the catch.

- Remove organisms from the net and store them in clean holding containers with site water. Retain target species that meet the minimum target size. For non-target species, count, weigh, measure and release these individuals at the location where they were collected.

- Pull the net into the boat and store it securely.

- Place retained fish in a labeled, sealable plastic bag following sample management procedures listed in SOP No. 5 Fish Sample Processing. The bags will be kept on ice in a laboratory-supplied cooler or secure refrigerator until processing.

3. Quality Assurance/Quality Control

The following quality assurance/quality control procedures will be performed during the collection events:

- A trained scientist or technician will make observations regarding habitat type, tide, water depth, and any other pertinent information including collection method and time of gear deployment and retrieval and GPS coordinates. The field team manger will confirm that pertinent information is being accurately recorded in the field notebook and/or on field data sheets.

- Station locations in the NBSA will be marked on maps in the field and registered in a GPS unit.

4. Documentation

Documentation of fish collection activities will be conducted in accordance with SOP No. 8 – Documentation of Field Activities. Field personnel are responsible for documenting field activities related to the fish collection events. Observations and data will be recorded with a waterproof pen or marker in a field notebook with consecutively numbered pages. Information to be recorded in the field notebook will include, at a minimum:

- Responsible person's name

- Dates and times of activities and collection method

- Station locations

- Any changes to procedures will be documented in a Field Change Memorandum, and recorded in the field notebook

5. References

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

Standard Operating Procedure No. 5

Fish Tissue Sample Processing

July 2014

Revision 0

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for the processing of fish samples collected from the site for chemical analysis. This SOP describes the initial processing done after sample collection and prior to shipment to the analytical laboratory. Fish tissue samples will be analyzed for constituents as outlined in the associated Quality Assurance Project Plan (QAPP).

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s Facility Coordinator, the United States Environmental Protection Agency (USEPA) Remedial Project Manager in consultation with the Partner Agencies (United States Fish and Wildlife Service, National Oceanic and Atmospheric Administration, United States Army Corps of Engineers, and New Jersey Department of Environmental Protection).

The following SOPs will be utilized with this procedure:

- SOP No. 4 – Fish Sample Collection
- SOP No. 6 – Management and Disposal of Residuals
- SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for Analysis
- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

This section of the SOP covers processing activities following fish collection and prior to shipment of fish samples to the analytical laboratory. For collection procedures, refer to SOP No. 4 – Fish Sample Collection. For shipping procedures, refer to SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for Analysis.

2.1 Equipment List

The following list includes equipment and materials that may be needed to perform the procedures outlined in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment not listed here may be required depending on field conditions at the time activities are being conducted.

- PPE or other safety equipment, as required by the Health and Safety/Contingency Plan, Rev. 1 (Tierra 2007)
- field notebook
- indelible ink pens
- sample labels
- ruler and fish measuring board
- fillet knives (6-inch and 9-inch)
- cutting boards
- camera
- skinning pliers
- sample containers
- freezer paper
- laboratory wipes or paper towels
- weigh pans
- distilled or deionized water
- electronic balance with 1.0 gram accuracy and with calibration weights
- sealable zip-top bags of various sizes (e.g., quart, gallon, 2-gallon)
- talc free nitrile gloves
- wet or dry ice
- freezer.

2.2 Equipment Decontamination and Calibration Procedures

Equipment decontamination will be completed (as needed) prior to processing. Either certified clean (defined as cleaned to the quality control standard described in USEPA

Office of Solid Waste and Emergency Response Directive #9240.0-05A) equipment or decontaminated dedicated equipment (e.g. fillet knife, cutting board) will be used for each sample to reduce the potential for cross-contamination and the need for repetitive decontamination between samples.

Prior to the start of processing, the designated electronic balance will be calibrated using certified sample weights. The mass of the target calibration weight will be recorded in the field notebook. The electronic balance will be tared to zero, and the calibrated weight will be measured using the electronic balance. The mass will be recorded in the field notebook. No adjustments will be made if the mass is within the specified tolerances set forth in the QAPP or by the manufacturer. If the measured weight falls outside of the tolerances, a calibration adjustment will then be made to the electronic balance following the manufacturer's specifications and/or procedures.

2.3 Sample Processing (Whole-body Composite)

Use the flow chart (Figure 1 of this SOP) to determine which type of sample it will be (i.e., whole body composite or individual, individual skin-off or skin-on fillet). Whole-body composite fish samples will be processed as follows:

- Remove fish from the cooler or refrigerator and the sealed plastic bag.
- Rinse fish with potable water.
- Observe fish for any gross external anomalies (e.g., deformities, fin erosion, tumors, lesions). If anomalies are observed, record in the field notebook or data sheet and photograph the anomaly.
- The target number of fish per composite sample will be the number of individuals required to achieve the sample weight described in the associated QAPP. At a minimum, each whole-body composite sample will consist of two individual fish.
- Each whole-body composite sample will be made up of individual fish of the same species and similar sizes collected from the same location. The lengths of all specimens in a composite should be within 25% of the mean length for that composite.
- If sufficient quantities of similar sized fish collected from a location on the same day are unavailable to meet the required sample weight, the collected fish from that day will be processed and held in frozen storage to potentially combine with additional fish from subsequent sampling days to form a single composite sample in the lab following discussion with Tierra and USEPA.
- Take a photograph of the sample with the sample ID clearly visible. Record the

species and number of fish, collection date, and processing date in the field notebook or data sheet.

- Lay the fish on the measuring board, push its snout to the end of the board, pinch the caudal lobes together and record, in the field notebook or data sheet, the total length of each of the fish in the sample. Record length in the field notebook or on the data sheet.

- Use the calibrated electronic balance to measure, in grams, the mass of each of the fish in the sample. Record mass in the field notebook or on the data sheet.

- Upon completion of processing, each sample will be placed in appropriate, pre-labeled sample containers and kept in frozen storage until shipment to the analytical laboratory. Refer to SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for shipping procedures.

- Dedicated equipment such as freezer paper, gloves, etc. will be changed between samples and disposed of in accordance with the procedures outlined in SOP No. 6 – Management and Disposal of Residuals

2.4 Sample Processing (Whole-body Individual)

Use the flow chart (Figure 1 of this SOP) to determine which type of sample it will be (i.e. whole body composite or individual, individual skin-off or skin-on fillet). Whole-body individual fish samples will be processed as follows:

- Remove fish from the cooler or refrigerator and the sealed plastic bag.

- Rinse fish with potable water.

- Observe fish for any gross external anomalies (e.g., deformities, fin erosion, tumors, lesions). If anomalies are observed, record in the field notebook or data sheet and photograph the anomaly.

- Take a photograph of the fish with the sample ID clearly visible. Record the species of fish, collection date, and processing date in the field notebook or data sheet.

- Lay the fish on the measuring board, push its snout to the end of the board, pinch the caudal lobes together and record the total length in the field notebook or data sheet.

- Use the calibrated electronic balance to measure, in grams, the total mass of the

sample. Record mass in the field notebook or data sheet.

- Upon completion of processing, each sample will be placed in appropriate, pre-labeled sample containers and kept in frozen storage until shipment to the analytical laboratory. Refer to SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for shipping procedures.

- Dedicated equipment such as freezer paper, gloves, etc. will be changed between samples and disposed of in accordance with the procedures outlined in SOP No. 6 – Management and Disposal of Residuals

2.5 Sample Processing (Fillet)

Use the flow chart (Figure 1 of this SOP) to determine which type of sample it will be (i.e. whole body composite or individual, individual skin-off or skin-on fillet). Fish fillet samples will be processed as follows:

- Remove fish from the cooler or refrigerator and the sealed plastic bag.

- Rinse fish with potable water.

- Take a photograph of the sample with the sample ID clearly visible. Record the species of fish, collection date, and processing date in the field notebook or data sheet.

- Lay the fish on the measuring board, push its snout to the end of the board, pinch the caudal lobes together and record the total length, in centimeters, in the field notebook or data sheet.

- Use the calibrated electronic balance to measure, in grams, the total mass of the sample. Record mass in the field notebook or data sheet.

- If the fish is not one of the samples selected for a fish health examination, proceed to the next step. If the fish is selected for internal examination, provide the fish to the fish pathologist for examination. Following examination, the fish can be filleted following the steps below.

- Observe fish for any gross external anomalies (e.g., deformities, fin erosion, tumors, lesions). If anomalies are observed, record in the field notebook or data sheet and photograph the anomaly.

- Fillet samples will be processed as skin-on or skin-off fillet samples depending on species. American eel samples will be processed as skin-off fillets, all other fillet samples will be processed as skin-on, scales off samples.

- For skin-on samples, scale the fish by running the knife blade or other instrument from the tail towards the head and pressing down to remove scales.

- For skin-off samples (American eel), use skinning pliers to separate the skin from the fish prior to filleting these samples. To skin the fish, begin by loosening the skin behind the operculum, and using skinning pliers, pull skin off toward the tail, cutting lightly along the inside of the skin. Slowly separate the skin from the muscle tissue of the body.

- Begin filleting by making a cut behind the operculum, making sure to cut through the skin and flesh, as close to the bone as possible. Make a cut across the caudal peduncle, keeping as close as possible to the caudal fin. Starting at the operculum, slice down the entire length of the fish following along the backbone until reaching the cut made at the caudal peduncle. Remove the fillet from the fish, making sure to include the belly flap, and dark muscle tissue in the vicinity of the lateral line, in each fillet. Remove any remaining bones.

- Use the calibrated electronic balance to measure, in grams, the total mass of the fillet. Record mass in the field notebook or data sheet. Repeat the process above on other side of fish if minimum sample mass requirements have not been met. Fillets from multiple fish of the same species and similar sizes may be used if minimum sample mass requirements are still not met after taking both fillets from a single fish.

- If sufficient quantities of similarly sized fish collected from a location on the same day are unavailable to meet the required sample weight, the collected fish from that day will be processed and held in frozen storage to potentially combine with additional fish from subsequent sampling days to form a single composite sample in the lab following discussions with Tierra and USEPA.

- Upon completion of processing, each sample will be placed in appropriate, pre-labeled sample containers and kept in frozen storage until shipment to the analytical laboratory. Refer to SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for shipping procedures.

- Dedicated equipment such as freezer paper, gloves, etc. will be changed between samples and disposed of, along with fish carcasses, in accordance with the procedures outlined in SOP No. 6 – Management and Disposal of Residuals

2.6 Sample Processing (Liver)

Three composite liver samples will be collected from resident fish from each zone for a total of nine composite liver samples. Fish liver samples will be processed as follows:

- Lay the fish on the cutting board and carefully slice open the gut cavity working the knife blade forward from the fish's vent. Take care to not cut too deeply and puncture internal organs.

- After the body cavity is open, find the liver and carefully slice it away from the body using a fillet knife or scalpel. Take care to not rupture the gall bladder and remove the gall bladder and any connective tissue from the liver.

- Use the calibrated electronic balance to measure, in grams, the total mass of the liver. Record mass in the field notebook or data sheet.

- Repeat the process above on the next selected fish if minimum sample mass requirements have not been met.

- If sufficient quantities of similarly sized fish collected from a location on the same day are unavailable to meet the required sample weight, the collected livers from that day will be processed and held in frozen storage to potentially combine with additional livers from subsequent sampling days to form a single composite sample in the lab following discussions with Tierra and USEPA.

- Upon completion of processing, each liver sample will be placed in appropriate, pre-labeled sample containers and kept in frozen storage until shipment to the analytical laboratory. Refer to SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for shipping procedures.

- Dedicated equipment such as freezer paper, gloves, etc. will be changed between samples and disposed of, along with fish carcasses, in accordance with the procedures outlined in SOP No. 6 – Management and Disposal of Residuals

3. Quality Assurance/Quality Control

The following quality assurance/quality control procedures will be performed during fish sample processing:

- Daily calibration of electronic balances will be recorded on the data sheets or in the field notebook prior to processing.

- A trained technician will confirm all pertinent sample information is recorded in the data sheets or field notebook and verify sample identification labels between the notes and the sample containers are correct.

- All pertinent field information and chains of custody will be provided to the sample processing team. The designated technician will review the sample information and confirm that the number of samples, collection date(s), collection time(s), and required analyses match the chains of custody. If any questions arise, the biologist/ecologist will contact the Project Manager for resolution.

4. Documentation

Documentation of fish sample processing activities will be carried out in accordance with SOP No. 8 – Documenting Field Activities. Field personnel are responsible for accurately documenting procedures conducted during fish sample processing. Observations and data will be recorded with a waterproof pen or marker in field notebooks or data sheets. Information to be recorded includes the following, at minimum:

- Responsible person's name

- Dates and times of activities (including collection and processing)

- Measurements and observations described herein

- Sample IDs

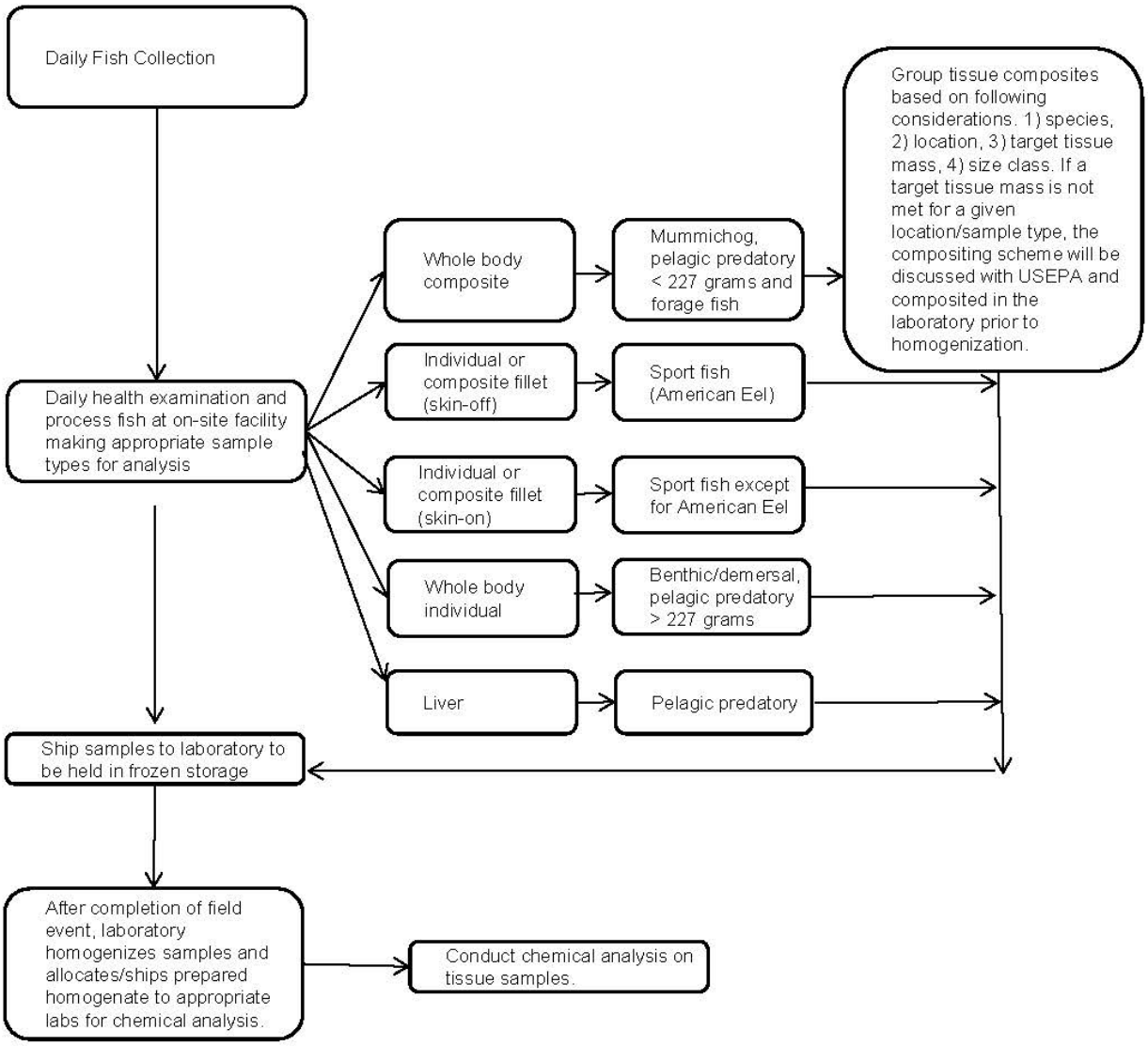
- Total lengths, weights, species, and numbers of fish in each sample

- Any changes to procedures will be documented in a Field Change Memorandum and recorded in the field notebook.

5. References

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

Fish Sample Processing Flow Chart



Standard Operating Procedure No. 6

Management and Disposal of Residuals

August 2014

Revision 2

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for disposal of sediment, water, personal protective equipment (PPE), and other potentially contaminated materials generated during Newark Bay Study Area Fish Sampling and Analysis Quality Assurance Project Plan (Fish QAPP) operations.

This SOP provides procedures for handling potentially contaminated sediment, water, PPE, and other materials during coring and sampling activities through their ultimate disposal. Specific information regarding handling and disposal of residuals is provided in the Fish QAPP.

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modifications to this SOP will be approved in advance by Tierra Solutions Inc.'s (Tierra's) Facility Coordinator and the United States Environmental Protection Agency (USEPA) Remedial Project Manager. The ultimate procedure employed will be documented in the field notebook.

Other SOPs will be utilized in conjunction with this SOP, including:

- SOP No. 3 – Decontamination
- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

Potentially contaminated sediment, water, PPE, and other materials will be classified into three categories: 1) solid materials consisting of sediments, sediment samples returned from the laboratory, used core tubes, used PPE, and other materials used in the handling, processing, and storage of sediment (addressed in Section 2.2); 2) liquid wastes, such as wastewater, decontamination water, and aqueous samples returned from the laboratory (addressed in Section 2.3); and 3) spent and residual chemicals (liquids) from decontamination (addressed in Section 2.3). Sediment from samples that is not processed for chemical analysis may be either archived or disposed, and will be segregated and handled separately according to its classification. To the extent practical, liquids generated during sampling/decontamination operations should be separated from the solid material. Each type of material should be handled in the manner described in this SOP.

2.1 Equipment List

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- PPE or other safety equipment, as required by the Health and Safety/Contingency Plan, Rev. 1 (Tierra 2007)
- 55-gallon open-top drums (Department of Transportation- [DOT-] approved) with lid
- 30-gallon (minimum) garbage bags
- permanent marking pens and/or paint pens
- labels
- duct tape
- storage racks
- small (cooler-size) storage containers
- walk-in cooler or refrigerated trailer
- chemical storage cabinet (meeting Occupational Safety and Health Administration and National Fire Protection Association Code 30 specifications/Factory Manual approved)
- field notebook
- indelible ink pens.

2.2 Solid Materials

2.2.1 Solid Residuals for Disposal

Solid residuals generated during field activities will be characterized for appropriate off-site disposal. Characterization procedures will be completed in accordance with the Waste Characterization QAPP (Tierra 2011). Solid residuals consist of two types of materials: non-sediment solid materials generated during the collection and processing of sediment, crab, and clam samples (e.g., used core tubes, aluminum foil, and PPE [e.g., gloves, Tyvek® suits, boot covers]) and sediment solid materials (i.e., left-over sediment not used for analyses including waste sediment and residual sediment). Non-sediment and sediment wastes will be segregated and temporarily stored in separate containers pending disposal. Loose sediment will be removed from non-sediment waste items prior to disposal and stored with sediment waste.

If recovered sediment is determined to be unusable, the sediment will be stored in an appropriate container for disposal as sediment waste. Sediment solid material will be placed in 55-gallon drums, labeled, and stored temporarily until disposal.

Non-sediment solid materials will be placed in 55-gallon drums, bulk bags, and/or a roll-off container and stored temporarily pending characterization and off-site disposal in accordance with the February 2006 IDW Management Plan (including any subsequent USEPA-approved modifications). All drums and bags containing solids residuals will be labeled and handled as described in Section 2.4 of this SOP.

2.3 Liquid Wastes

2.3.1 Waste Water

Waste water will be generated during sample collection and decontamination activities. Water mixed with detergent or chemicals will be treated and handled at the Lister Avenue groundwater treatment plant. Water from gross decontamination (e.g., to wash sediment from sampling equipment) will be allowed to flow overboard on the vessel when decontamination activities occur over water. If decontamination activities occur in an upland area, the water will be captured and treated at the Lister Avenue groundwater treatment plant. Sediment recovered during this process will be handled according to Section 2.2.1 of this SOP.

In the event that waste water is not treated through the Lister Avenue groundwater treatment plant, it will be stored at the Lister Avenue Site in appropriate containers pending characterization for off-site disposal. Modifications to the February 2006 IDW Management Plan will be submitted to the USEPA for review and approval for characterization and off-site disposal.

2.3.2 Chemical Liquid Wastes

Spent solvents, acids, and other residual chemicals generated during the decontamination process (SOP No. 3 – Decontamination) will be collected and treated through the Lister Avenue groundwater treatment plant in accordance with procedures outlined in the February 2006 IDW Management Plan.

In the event that these liquids are not treated through the Lister Avenue groundwater treatment plant, they will be stored at the Lister Avenue site in appropriate containers pending characterization for off-site disposal. Modifications to the February 2006 IDW Management Plan will be submitted to the USEPA for review and approval for characterization and off-site disposal.

2.4 Handling and Tracking of Solid Materials and Containers

As they are generated during field activities, waste sediment and other solid waste materials will be placed in DOT-approved 55-gallon drums or 30-gallon bags. Solid waste materials that are initially placed in bags may be bulked into 55-gallon drums for storage. The following procedures will be followed for storing sediment and other solid waste in these drums:

- A drum number will be assigned to each drum by the Field Supervisor or designee. The drum number will be clearly marked on multiple places on the drum.

- A log will be kept for each drum, listing the materials placed in that drum. All solid materials will be segregated based on the type of material (e.g., sediment, coring tubes, PPE, waste plastic, paper, foil) and, to the extent practicable, by where they were generated (e.g., location within Newark Bay).

- Drums will be closed or covered at the end of the day's work.

- Collection drums may be reused at the processing facility after emptying.

- Drums containing solid materials will be stored in a secured temporary facility until proper off-site disposal can be coordinated.

2.5 Handling and Tracking of Waste Water and Chemical Liquid Wastes and Containers

As they are generated during field activities, waste water and chemical liquid wastes will be treated directly through the on-site Lister Avenue groundwater treatment plant and/or will be placed in separate DOT-approved 55-gallon drums. The following procedures will be followed for treating the liquids through the on-site groundwater treatment plant:

- A sump will be isolated in the processing area to collect and handle liquids.
- Liquids collected in the sump will be combined and treated with the liquids treated at the on-site groundwater treatment plant.
- Treated liquids will be monitored, characterized, and disposed in accordance with the requirements for the on-site groundwater treatment plant.

The following procedures will be followed for storing waste water and chemical liquid wastes in drums:

- A separate drum will be used for each non-commingled chemical. Another, separate drum will be used for chemicals and/or water that have been mixed.
- A drum number will be assigned to each drum by the Field Supervisor or designee. The drum number will be clearly marked on multiple places on the drum.
- A log will be kept for each drum, listing the materials placed in that drum.
- All drums will be closed or covered at the end of the day's work.
- Collection drums may be reused at the Sample Processing Area after emptying.
- Drums containing wastewater and chemical liquid wastes will be stored in a secured temporary facility until proper off-site disposal can be coordinated upon the completion of the sampling event.

2.6 Samples Returned from Off-Site Laboratories

Upon completion of the required chemical analyses, remaining sample material and sample containers from the laboratory will be returned to the Sample Processing Area. Returned sample material/containers will be transported under chain of custody procedures, and remain in custody until disposal. Upon receipt, the chain of custody

form will be signed and the samples will be logged in by a project staff member. The approximate volume of sample material and the condition of the containers in which the samples are returned will be checked and recorded in a field notebook.

Samples will be separated into sediment and aqueous sample groups; empty sample containers will be grouped accordingly by sample matrix. Sediment samples will be placed in a DOT-approved 55-gallon drum and will be characterized and disposed off site in accordance with the procedures outlined in the February 2006 IDW Management Plan (including any subsequent USEPA-approved modifications).

Aqueous samples returned from the analytical laboratories will be treated through the Lister Avenue groundwater treatment plan in accordance with procedures outlined in the February 2006 IDW Management Plan (including any subsequent USEPA-approved modifications). In the event that these liquids are not treated through the Lister Avenue groundwater treatment plant, they will be stored at the Lister Avenue site in appropriate containers pending characterization for off-site disposal. Modifications to the February 2006 IDW Management Plan will be submitted to the USEPA for review and approval for characterization and off-site disposal.

3. Quality Assurance

Disposal procedures will be documented in a field notebook to confirm that disposal activities are conducted in accordance with the procedures outlined in the SOPs. Waste manifests will be obtained for solid and aqueous waste disposal to verify that proper transportation and disposal of these materials has occurred in accordance with the February 2006 IDW Management Plan (including any subsequent USEPA-approved modifications).

4. Documentation

Documentation of sample handling activities will be conducted in accordance with SOP No. 8 – Documenting Field Activities. In addition, the following information should be included in the field notebook (at a minimum):

- name of person performing residual management or disposal activities
- date and time of activity
- information coordinating container numbers for drums or bags containing solid materials with sample numbers, core boring numbers, or origin
- information coordinating origin of waste liquid (water or chemical[s]) with specific waste drum or tank

5. References

Tierra, 2006. Newark Bay Study Area Remedial Investigation Work Plan Sediment Investigation Program Investigation Derived Waste Management Plan [Rev. 0]. February.

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

Tierra. 2011. Final Waste Characterization Quality Assurance Project Plan, Diamond Alkali Superfund Site, Operable Unit 1/CERCLA Non-Time-Critical Removal Action – Lower Passaic River Study Area and Newark Bay Study Area, Revision 1, December 2011.

Standard Operating Procedure No. 7

Containers, Preservation, Handling, and Tracking of Samples for Analysis

July 2014

Revision 1

Attachments

Pre-Printed Sample Label

Chain-of-Custody Form

Custody Seal

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for containerizing, preserving, handling, tracking, and shipping biological samples collected as part of the Newark Bay Study Area (NBSA) Phase III sampling activities. This SOP is intended to be complete enough so that: 1) the steps that could affect tracking, documentation, or integrity of samples are explained in sufficient detail and 2) different sampling personnel following these procedures will deliver samples to the laboratory that are equally reliable and consistent, and in compliance with regulatory agency requirements. Specific information regarding sample collection and analysis is found in the associated QAPP.

This SOP may change depending on field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions, Inc. (Tierra) Facility Coordinator and the United States Environmental Protection Agency (USEPA) Remedial Project Manager and On-Scene Coordinator. The ultimate procedure employed will be documented in the field notebook.

Other SOPs will be utilized with this procedure, including:

- SOP No. 6 – Management and Disposal of Residuals
- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

2.1 Equipment List

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, depending field conditions.

- personal protective equipment and other safety equipment, as required by the Health and Safety/Contingency Plan, Rev. 1 (Tierra 2007)
- inert packing material (e.g., foam peanuts, vermiculite, cardboard, bubble wrap)

- sample containers as specified in the associated QAPP
- sample labels
- shipping supplies (e.g., “Environmental Sample” stickers, “This Side Up” labels, FedEx shipping documents, and hangtags)
- chain of custody forms
- ice chest(s)
- custody seals
- indelible ink pens
- shipping tape
- sealable plastic bags
- temperature blanks (if not provided by the laboratory)
- field notebook
- ice or similar chilling source
- plastic lining material
- clear tape.

2.2 Sample Identification and Labeling

The standard sample identification number will consist of a unique 11-character sting used to identify each sample collected and submitted to the laboratories for analysis, as follows:

Characters 1 and 2:	Two characters to describe the water body where the sample was collected (i.e., for Phase III this will be NB for Newark Bay).
Characters 3 and 4:	Two digits to describe the phase during which the sample was collected. For example, the Phase III SI Program will be described as “03.”

Character 5:	One character to identify if it is a fillet or whole-body sample, F for fillet, W for whole body.
Characters 6 and 7:	Two characters to identify the species. The two characters will be the first two letters of the common name of the species, or the first letter of each word for species with two word common names. For example, MU= mummichog, WP = white perch etc.
Character 8:	One character to identify the geographic zone the sample was collected from, “N” for Newark Bay North, “C” for Newark Bay Central or “S for Newark Bay South.
Characters 9, 10 and 11:	The final three characters are the sample ID number beginning with 001 and increasing sequentially.

Example of Sample Identification Code

Following is an example of a fish tissue identification code:

NB03FAEN001

Explanation:

Sample collected from Newark Bay, Phase III Program, fillet sample, American eel from the North zone, sample number 1.

2.2.1 Sample Labeling

A label will be attached to each container used for sampling. An example of a preprinted sample label is attached to this SOP. When practical, the project number, sample matrix, laboratory designation, and sample identification code will be typed or printed onto the label before sampling. Once affixed to the sample container, the label will be protected from water and solvents with clear packing tape.

2.3 Sample Containers

To confirm that the appropriate sample quantities are collected in certified, pre-cleaned containers, sample containers for this project will be supplied from commercial suppliers or laboratories. Sample containers will be cleaned to the quality control standard defined in USEPA Office of Solid Waste and Emergency Response (OSWER) Directive #9240.0-05A.

Certification of sample container quality per the OSWER directive will be kept in the Newark Bay project file. The associated QAPP summarizes container types that will be provided for samples collected.

Prior to use, the sample containers will be visually inspected for cracks, chips, or other damage. Damaged sample containers will not be used and will be disposed in the proper waste receptacle.

2.4 Sample Handling and Shipping

Sample packaging and shipping will be done in accordance with applicable regulations, as described below.

1. After filling a sample container, affix cap and securely seal with clear tape and complete the sample label. Apply the label to the sample container and cover with clear tape.

2. Seal each sample container inside a sealable plastic bag. Place samples in secure freezer immediately after processing.

3. To ship samples transfer the samples from the freezer to a plastic-lined ice chest that will be used as a shipping container. Use inert packaging material (e.g., cardboard, vermiculite) to cushion the samples and minimize the potential for breakage. Seal the drains on the ice chest (if present) with shipping tape or plug the drains with silicone sealant or a similar inert substance.

4. Ice chests will contain ice or similar chilling sources sufficient to maintain a temperature of 4° Celsius or less inside the cooler during transport. Use sufficient ice to accommodate reasonable delays in shipment. A temperature blank provided by the analytical laboratory with each cooler will be included in the shipment.

5. Complete sample tracking documentation as described in Section 2.5 of this SOP, and place the documents in a sealable plastic bag inside the ice chest, taped to the inside of the lid. Prior to sealing for shipment, check the list of samples against the container contents to verify the presence of each sample listed on the chain of custody.

6. Secure chest lid with shipping tape by covering the entire seal with tape. Complete information on the custody seal and affix the custody seal over the taped seal. An example of a custody seal is attached to this SOP.

7. Transport the shipping container directly to the laboratory, the laboratory courier, or to the overnight carrier for overnight delivery.

2.5 Sample Tracking

From the time of collection through transportation, the handling of samples will follow chain of custody procedures.

A sample is considered under the sampler's custody if one or more of the criteria are met:

- sample is in the sampler's possession
- sample is in the sampler's view after being in sampler's possession
- sample was in the sampler's possession and then locked up to prevent tampering
- sample is in a designated secure area.

Samples collected for analysis will be continuously tracked in the Sample Processing Area and while in transit to the laboratory by use of the following procedures below. The Sample Processing Area will be secured (locked) with limited access.

- Individual sample containers will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory.
- Pertinent information will be entered on the chain of custody form in the field (see attached chain of custody form and form key). Assignment of the SDG number, matrix spike/matrix spike duplicate (MS/MSD) assignments, and the analyses requested for each sample will be made on the chain of custody form.
- The chain of custody form must include the following, as required by guidance in SW-846, Test Methods for Evaluating Solid Waste (USEPA 1993): 1) project name; 2) signatures of samplers; 3) sample number, date and time of collection, and grab or composite sample designation; 4) signatures of individuals involved in sample transfer; and 5) if applicable, the air bill or other shipping number.
- The completed chain of custody form will be signed, dated, enclosed in a sealable plastic bag and placed in the container prior to shipment. A copy will be retained by field personnel and stored in a dedicated binder. Additional copies will be distributed as follows:

  - A copy will be faxed or emailed to the Facility Coordinator or the Facility Coordinator's designee.

  - A copy will be faxed or emailed to the data validator.

  - A copy will be faxed or emailed to the laboratory manager/client service representative at each laboratory being used.

- Samples will be considered in the sampler's custody while in his/her possession or within sight, or locked in a secure area prior to shipment. If the person packing the container and verifying the sample list is different than the sampler, both the sampler and the packer will sign the chain of custody form.

- Upon receipt at the laboratory, the designated laboratory sample custodian will sign the chain of custody form indicating receipt of the incoming field samples. The samples will be checked against the chain of custody form upon arrival at the laboratory. The receiving personnel will enter all arriving samples into a laboratory logbook. Any discrepancies between the samples and the chain of custody form(s), or any evidence of tampering with the shipping container or the custody seal will be immediately reported to the Facility Coordinator. The sample custodian will immediately check the temperature of the cooler upon arrival at the laboratory and record the measured temperature on the chain of custody form and in a laboratory logbook.

- A completed copy of the chain of custody form will be distributed to the following individuals on the day of sample receipt at the laboratory:

  - A copy will be faxed or emailed to the Facility Coordinator or the Facility Coordinator's designee.

  - A copy will be faxed or emailed to the data validator.

  - A copy will be faxed or emailed to the field office.

The original will be retained by the laboratory's sample custodian.

3. Documentation

3.1 Field Notes

Documentation of sample handling activities will be conducted in accordance with SOP No. 8 – Documenting Field Activities. The following information should also be included in the logbook (at a minimum):

- sampling activities conducted that day
- brief synopsis of types of equipment and methods used in collecting the samples

3.2 Chain of Custody Documentation

Samples will be tracked through chain of custody documentation as described in Section 2.5 of this SOP.

4. References

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

USEPA. 1993. SW-846, Test Methods for Evaluating Solid Waste, Third Ed., including Promulgated Update I, Chapter One.

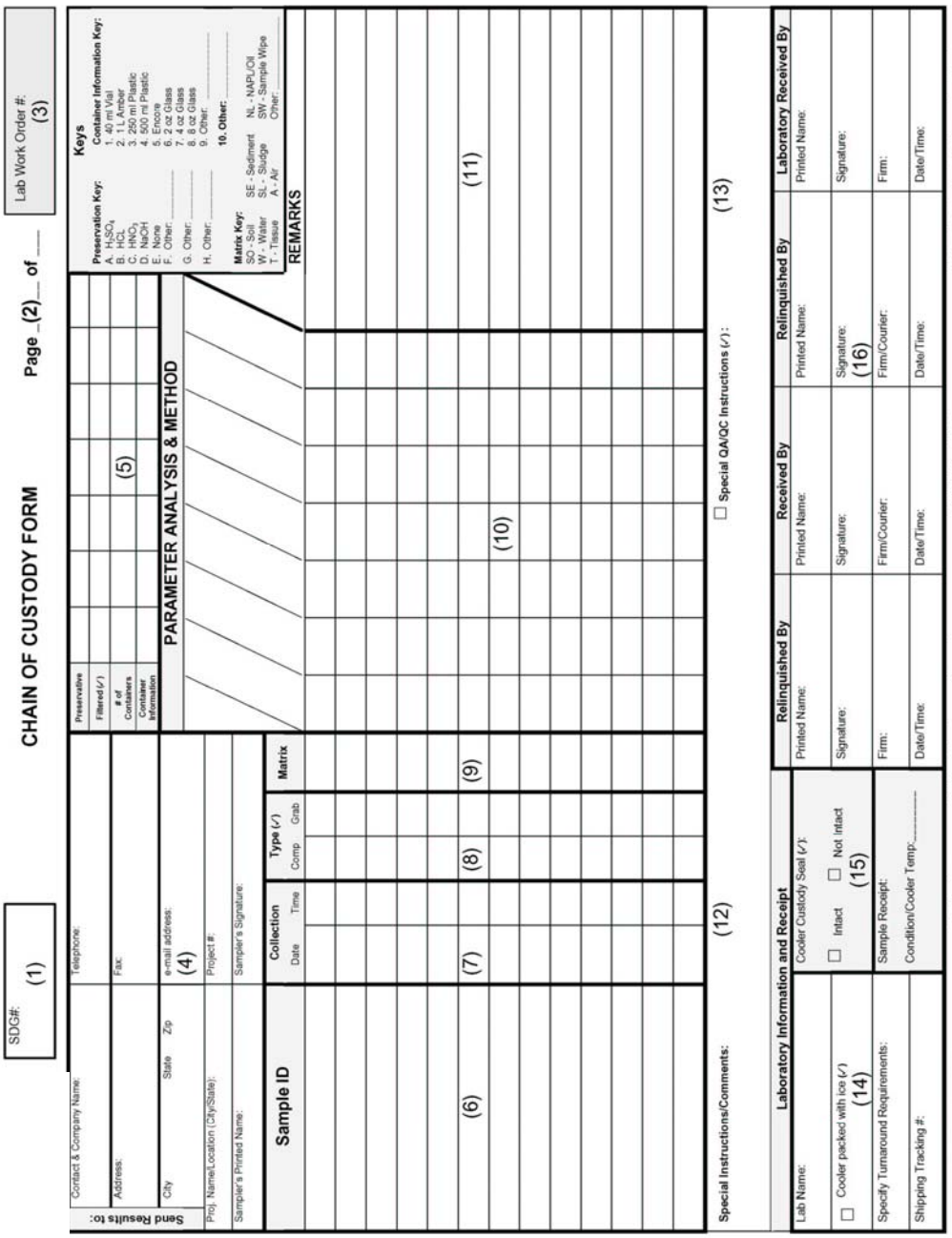
PRE-PRINTED SAMPLE LABEL

PROJECT NAME: Newark Bay Phase III Program	PROJECT #: (1)
SAMPLE #: (2)	SAMPLER: (3)
DATE SAMPLE COLLECTED: (4)	TIME SAMPLE COLLECTED: (5)
SAMPLE MATRIX: (6)	
REMARKS: (7)	

Key:

(1) Company-specific project number, if appropriate
(2) Sample ID (e.g., NB03SED122)
(3) Sampler name
(4) Date sample was collected (e.g., 1/1/2013)
(5) Time sample was collected (24-hour format)
(6) Sample matrix type (e.g., fish, whole body or fillet)
(7) Remarks pertinent to proposed analyses

CHAIN OF CUSTODY FORM



CHAIN OF CUSTODY FORM KEY

(1) SDG number (to be filled out by the laboratory)

(2) Page number and total number of pages for the set of chain of custody form submitted with the samples for analysis.

(3) Analytical laboratory's internal work order number (to be completed by analytical laboratory).

(4) Address where the analytical results are to be sent, project identifiers (location and internal project numbers), and sampler's signature.

(5) Preservation methods and bottles.

(6) Sample ID; refer to Section 2.2.1 of this SOP for sample IDs.

(7) Date and time (24-hour format) of sample collection.

(8) Check if sample was a composite sample.

(9) Sample matrix (e.g., fish, whole body or fillet).

(10) Provide analysis and method for which sample is being submitted. Check the appropriate box for which analyses the sample is being submitted.

(11) Provide any pertinent comments regarding the sample submitted for analyses (e.g., not enough sample volume for full analyses).

(12) Provide any special instructions to the analytical laboratory.

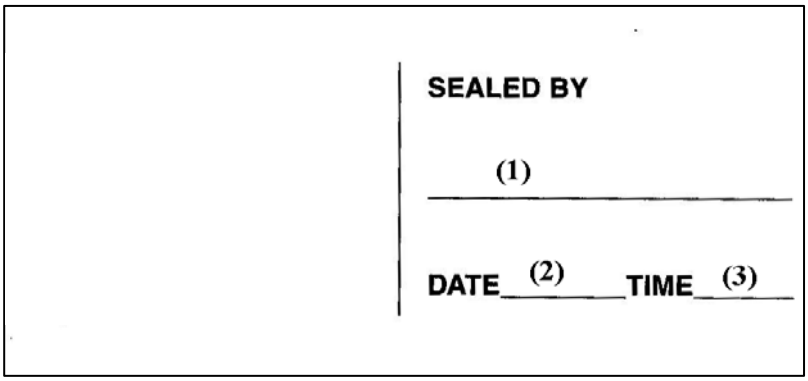
(13) Provide any special QA/QC instructions to the analytical laboratory.

(14) Provide details regarding the cooler shipment (analytical laboratory name, whether the cooler was packed with ice, turnaround requirements, and shipping tracking number).

(15) Provide details as to receipt of cooler (to be completed by analytical laboratory on receipt). Indicate if the chain of custody seal was intact and the cooler temperature upon receipt.

(16) Signatures for custody to be completed by sampler and analytical laboratory.

Custody Seal



Key:

(1) Name of individual sealing ice chest.

(2) Date ice chest is sealed.

(3) Time ice chest is sealed (24-hour format).

Standard Operating Procedure
No. 8

Documenting Field Activities

October 2013

Revision 0

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for the documentation of field activities associated with the Newark Bay Study Area (NBSA), including sample collection events, field measurements, and site visits. Appropriate documentation of field activities provides an accurate and comprehensive record of the work performed, sufficient for a technical peer to reconstruct the day's activities and determine that necessary requirements were met. Field records also provide evidence and support technical interpretations and judgments. The procedures and systems defined in this SOP help confirm that the records are identifiable (reference the project task/activity), retrievable, and protected from loss or damage.

NBSA field data will be recorded in field notebook entries, standardized forms, annotated maps, or photos. This SOP provides general guidance on field recordkeeping; additional details for specific procedures (e.g., chain of custody) are provided in the SOPs for the individual task.

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s (Tierra's) Facility Coordinator and the United States Environmental Protection Agency Remedial Project Manager and On-Scene Coordinator. The ultimate procedure employed will be documented in the field notebook.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Guidelines

The documentation of field activities at uncontrolled hazardous waste sites is governed by a variety of legal guidelines that must be understood prior to the commencement of field activities. It is imperative that the personnel who will be conducting the field activities understand how the overall constitutional, statutory, and evidentiary legal requirements apply to the site inspection documentation and to the rights of potentially responsible parties.

The description of and observations made during field activities often provide the basis for technical site evaluations and other related written reports. All records and notes generated in the field will be considered controlled evidentiary documents and may be subject to scrutiny in litigation. Consequently, it is essential that the Field Supervisor or designee pay attention to detail and document to the greatest extent practicable every aspect of the inspection.

Personnel designated as responsible for the documentation of field activities must be aware that all notes taken may provide the basis for the preparation of responses to legal interrogatories.

Field documentation must provide sufficient information and data to enable the reconstruction of field activities. A wireless field application using standardized electronic data forms may provide the basic means for documenting field activities.

Control and maintenance of wireless field applications used in the documentation of field activities is the responsibility of the Field Supervisor, and the transfer of responsibility (e.g., alternate Field Supervisor) must be documented.

3. Equipment and Materials

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- standardized field data forms (electronic and printed copies)
- site maps (electronic and printed copies)
- clipboard
- three-ring binder or equivalent
- camera
- time piece
- hand-held electronic recording device (e.g., laptop)
- bound field notebook
- black, ballpoint pen or Sharpie® (or equivalent).

4. Procedures

4.1 General Requirements

The field records will contain sufficient detail so that the collection effort can be reconstructed without reliance on the collector's memory.

Pertinent field information will be recorded legibly in field notebook entries and/or in an appropriate standardized form (as described herein).

Field notebook entries will be signed and dated. No erasures or obliterations will be made. A single line (i.e., strikeout) will be drawn through incorrect entries and the corrected entry typed next to the original strikeout. Strikeouts are to be initialed and dated by the originator.

The field notebook will be a bound waterproof notebook with entries made in black ballpoint pen (or pencil, as necessary). All logbook entries will be electronically scanned at the end of each day or as frequently as possible and saved in the project files.

Entries will be factual and observational (i.e., no speculation or opinion), and will not contain any personal information or non-project-related entries. Abbreviations and acronyms will be defined.

Field information will be recorded without delay – information recorded significantly after the fact will be dated as such.

Field activities and other events pertinent to the field activities will be documented in chronological order. Times will be recorded using Eastern Standard Time (EST) or Eastern Daylight Savings Time (EDT) notation for each entry.

4.2 Field Notebook

The field notebook will be a bound waterproof notebook with entries made in black ballpoint pen (or pencil as necessary).

The title page of each logbook entry will contain the following:

- Tierra contact, Tierra office location, and phone number
- logbook entry number (corresponding to the number of days in the field event)
- project name and number
- start and end date and time of work covered by that field notebook entry.

A page header will appear on the first page of each field notebook entry (i.e., the beginning of notes for each day's events), and activities for each day will be recorded as a new logbook entry. The page header will include:

- name of author and other personnel on site (and affiliated organization if applicable)
- date
- time of arrival (military time)
- proposed activity (task)
- current weather and tidal conditions, and weather forecast for the day.

An abbreviated header, containing at least the date, will appear at the top of each additional page for the active date. Field forms require similar header information.

The field notebook will provide a chronology of events. At a minimum, documentation in a field notebook will include the following (unless documented on a standard form):

- names of visitor(s), including time of arrival and departure, the visitor's affiliation, and reason for visit
- summary of project-related communications, including names of people involved and time
- time daily work commences and ceases
- start and stop times of new tasks
- start and stop times of significant standby time (work interruptions)
- safety or other monitoring data, including units with each measurement
- deviations from approved scope of work, including the necessary approvals
- progress updates
- problems/delays encountered
- unusual events
- initials of author on every page

The field notebook will cross-reference the standardized field forms if necessary; however, whenever possible, details recorded on the standardized forms will not be replicated in the field notebook.

In the case of equipment malfunction or other unforeseen events, additional bound waterproof field notebooks will be carried by field personnel to serve as backup documentation methods. NBSA field notebooks will be dedicated to the project and will not be used for any other project or purpose. Separate and dedicated field notebooks will be kept for different operations running concurrently (e.g., sampling on board the vessel, processing at the field facility); individual tasks making up each operation will be maintained in the same field notebook, if possible. The cover and binding of each field notebook will be labeled to identify the operation and dates included with the notebook; each page in the field notebook will be consecutively numbered. Pages will not be removed or torn out of the notebook. If there are additional lines on the page at the end of the day's activities, a line will be drawn through the empty space, and initialed and dated, leaving no room for additional entries. Logbook entries will be electronically scanned at the end of each day, or as frequently as possible, and electronically saved as described in Section 4.6.

4.3 Standardized Forms

The information collected on any field forms will be collected and/or scanned and stored (if a printed form) electronically (described in Section 4.6).

The following rules apply to the standardized forms:

- Each form will be printed (if electronic), signed, and dated by the person completing the form and stored as described in Section 5.
- There will be no blank spaces on the form – unused spaces will have "not applicable" or "not available" explanations.
- Field forms require similar header information as field notebook entries (see Section B of this SOP).
- At the end of each day, or as frequently as possible, all forms completed will be saved as described in Section 4.6.

4.4 Maps and Drawings

Pre-existing maps and drawings that include notations made in the field (i.e., relocating of sample locations) will be referenced in the field notebook and, like all field records,

include the project/task name and number, site identification, and be signed or initialed and dated by the person who prepared them.

Maps and drawings will include compass orientation and scale. Sketches will include points of reference and distances to the reference points.

If notations are made on electronic map or drawing files, these will be referenced in the logbook as described above and initialed and dated by the person who prepared them. Notations made by hand on maps and drawings will be electronically scanned at the end of each day, or as frequently as possible, and electronically saved as described in Section 4.6.

4.5 Photographs and Other Photo Documentation

Photographs or videos may be taken by the field team to help document site conditions, sampling locations, or sample characteristics. Photographs and videos will be identified in the field notebook or on the electronic standard form by a unique numbering system. If photographs are collected using a digital camera, the file number, as well as the photograph number, will accompany the description of the photograph in the notebook. At a minimum, the date/time the photograph was taken, the general location, a brief description, and the photographer's name will be recorded. Additional information may include differential global positioning system coordinates, direction the photographer was facing, and/or weather conditions. If necessary, an object will be included to indicate the scale of the object in the photograph.

4.6 Electronic Files

Electronic recording devices may include data logging systems, personal digital assistants (PDAs), laptops, or tablet personal computers.

Sufficient backup systems will be in place to protect against electronic data loss. Information will be saved to a disk or backed up immediately upon completion. The backup disk or other media (CD, flash drive) will then be stored in a secure location separate from the laptop, tablet, or PDA.

Files will be uniquely identified and stored in the project files. File names should include the date, a description of the file contents or a unique title, and a version number (i.e., "YYYYMMDD_Name of documentV#). An unedited version of the file will be maintained, and all subsequent manipulations tracked.

5. Quality Assurance/Quality Control

Entries in the field forms will be double-checked by the samplers to verify that the information is correct.

Completed field forms will be reviewed periodically by the Facility Coordinator and/or Project Quality Assurance Manager or their designees to verify that the requirements are being met. At a minimum, this should occur at the end of each day. When the review is complete, the reviewer will append his/her initials and date to the pages reviewed for documentation purposes.

If information recorded in the field is transcribed to another format, the original record will be retained for comparison purposes.

6. Data and Records Management

Deviations to the procedures detailed in the SOP will be recorded in the field notebook.

Notebooks, field forms, chain of custody forms, and all other records associated with the activities described in this SOP will be ultimately maintained by the investigative organization.

Field notebook entries, field data forms, and chain of custody forms will be electronically stored once they have been completed and distributed (if necessary) at the end of each field day or as frequently as possible. Printed copies of these documents will be maintained in labeled three-ring binders or contained in some other organized manner that prevents loss in the field facility. Bound waterproof field notebooks will be electronically scanned and saved in project files at the end of each day, or as frequently as possible, to mitigate against the loss of historical entries should the notebook be lost in the field.

Distribution of daily forms will be performed according to the needs of the project team and at the direction of the Field Supervisor or designee.

The Field Supervisor is responsible for reviewing and approving the field records for accuracy, completeness, and conformance to the procedures in this SOP. The Field Supervisor is also responsible for confirming that the field records are distributed to the appropriate personnel during field activities, confirming that records are maintained properly on site, and for archiving the records upon completion of field activities.

Standard Operating Procedure
No. 9

Data Management

August 2014

Revision 1

Attachment

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for data management. This SOP describes the procedures necessary to manage the field sampling and laboratory data. In addition to the sample collection efforts, all requirements set forth in this SOP are to apply to data collected as part of the sampling activities.

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s (Tierra's) Facility Coordinator and the United States Environmental Protection Agency Remedial Project Manager. The ultimate procedure employed will be documented in the field notebook.

Other SOPs will be utilized with this procedure, including:

- SOP No. 8 – Documenting Field Activities.

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

2.1 Data Handling and Management

The following sections trace the paths of data from generation to final use and storage, as well as the associated quality reviews for error detection that are performed to promote data integrity.

2.1.1 Field Data Management

2.1.1.1 Data Recording

Field data and information collected during sample collection may be recorded by hand using the associated forms or directly into an electronic field database (MS Access or equivalent), and will be recorded in accordance with requirements described in SOP No. 8 – Documenting Field Activities. Once sample collection data are transcribed into the electronic field database, the sample processing team may enter data into the associated forms by hand or within the electronic field database during sample processing activities. The electronic field database will be maintained for field parameter entries only (e.g., date, time, flow rates) and will not be joined with the

analytical database. In addition, a daily field notebook will be maintained per SOP No. 8 – Documenting Field Activities.

2.1.1.2 Data Review

Each day after the completion of field activities, an on-site review of the bulk sample collection data will be performed by a designated team member, who will be different from the originator of the field data. This review will include verifying:

- bulk samples were collected at pre-identified sampling locations following sampling procedures
- data and information, as well as associated forms, were completed in their entirety for each sample
- data and information entered into the database or forms are accurate and consistent with that recorded in the logbooks (i.e., sample ID, location, and time of collection).

Once these have been verified, the selected reviewer will sign and date hard copy forms and the field notebook. Hard copies from the electronic field database will be printed for placement in the project file. Additionally, electronic versions (in Portable Document Format [PDF] format, or equivalent) of all forms will be placed on a secure network drive accessible only to project personnel. The data will be sent to the ARCADIS office for review each day.

Upon receipt of daily documentation (including the electronic field database and scanned hard copy forms and notebook), the office data manager will perform a secondary review of the daily field data for consistency and accuracy.

Once the electronic field database has been reviewed and deemed accurate, a Daily Report will be generated by the office database team member and provided to the Facility Coordinator for review and comment. Upon approval by the Facility Coordinator, the Daily Report may be provided to USEPA.

If an electronic field database is maintained, the data sent from the site will be imported by the office data manager. If generated, the electronic field database will contain data collected during sample collection and sample processing activities for the entire project. The electronic field database will be placed on a secure network drive, accessible only to project personnel, for storage/filing purposes.

2.1.2 Analytical Data Management

2.1.2.1 Data Recording

The laboratory(ies) will prepare and retain full analytical and quality control (QC) documentation. Laboratory records (both handwritten and electronic) will be documented per the procedures contained in the laboratory-specific quality assurance (QA) manual. Once the hard copy data packages and Electronic Data Deliverables (EDDs) are ready, they will be verified by the laboratory for completeness and compliance prior to submittal to the Quality Assurance Coordinator (QAC).

2.1.2.2 Data Transformation and Data Reductions

Calculations involved in reducing raw data to reportable data are defined in the specified analytical methods. Automated data processing steps not provided in the procedures listed can be found in the laboratory-specific QA manuals. Verification of records and calculations generated by the laboratories will be performed as required tasks and documented by signature of reviewer/data validation contractor.

Significant digits for hard copy and electronic results will be reported as specified in the analytical method reference.

2.1.2.3 Data Transfer

Unverified/unvalidated data will be transferred electronically from the identified analytical laboratories to the QAC using the EDD format, specified in Worksheet No. 29 of the Quality Assurance Project Plan (QAPP). The data will be transferred in Microsoft Excel spreadsheet format (or equivalent) via email or similar information transfer mechanism.

2.1.3 Quality Assurance Coordinator

2.1.3.1 Data Recording

The QAC will document the data verification/validation tasks as described in Worksheet Nos. 34, 35, and 36 of the QAPP.

2.1.3.2 Data Transfer

Once the analytical data have been reviewed and verified/validated, the Data Verification Reports will be generated. The QAC will transfer the EDDs containing

verified/validated sample results and completed Data Verification Reports to Tierra's Facility Coordinator. The EDD files will be transferred in Microsoft Excel (or equivalent) spreadsheets via email or similar information transfer mechanism, and Data Verification Reports will be transferred in hard copy or electronic PDF file format via FedEx or similar delivery service.

2.1.3.3 Review of Verified/Validated Laboratory Data and Agency Submittal

EDDs received by Tierra's Facility Coordinator will be saved to a secure network drive for storage/archive purposes. The EDD files will then be imported into a Microsoft Access (or equivalent) database, which will also be maintained on a secure network drive. Completed Data Verification Reports will be scanned or uploaded, as appropriate, and stored on a secure network drive as PDF files.

Importation of the verified/validated EDD files will be an automated process using macros and queries developed in an EQuIS database. Once EDDs have been entered into the analytical database, data output tables will be prepared so that the data can be checked for errors. This check will consist of a 10 percent comparison of the data output tables to marked-up Form 1s that have been initialed and dated by the reviewer upon completion of the data verification/validation task. This data review will be documented using the Data Review Form attached to this SOP.

Once EDDs have been entered into the analytical database and the data have been checked for errors, new EDDs will be created in the format required by USEPA Region 2. The EDDs will be created using various update and append queries in an EQuIS database. Once the EDDs have been reviewed for accuracy, they will be transmitted to USEPA via email or similar information transfer mechanism. Copies of the EDDs will be stored in the project file on compact disc and on the secure network drive in EQuIS format.

2.2 Data Tracking and Control

The following sections provide a discussion of the procedures for data tracking, storage, archiving, retrieval, and security for both hard copy and electronic data and information.

2.2.1 Data Storage, Archiving, and Retrieval

2.2.1.1 Hard Copy Files

Hard copies of project documentation and data will be placed in the project file, parts of which will exist in several locations, including:

- ARCADIS, Syracuse, New York and Cranbury, New Jersey
- Tierra Solutions, Inc., East Brunswick, New Jersey.

Such files will be maintained in secure locations within each facility. Hard copies of project documentation and data will be provided to USEPA upon request.

Duplicate copies of pertinent field-related correspondence/documentation will be maintained at the field office during field operations. Once such field operations have been completed, this documentation will be transferred to the project file.

Upon completion of the data verification/validation process, project documents and records will be stored in the project file. At such time that it is deemed appropriate to archive the project file, either in parts or in its entirety, files may be boxed and shipped off site to a secure document storage facility. The assigned barcode identifier for each box being archived will be logged into a tracking spreadsheet, as well as with a brief description of the contents of the box. Archived boxes will be retrieved from the document storage facility, if/when necessary, using the logged barcode identifier.

2.2.1.2 Electronic Files

Electronic data and information will be maintained and managed by the entities listed above using password-protected computers and on secure network drives with access limited to project personnel. Files will generally consist of the same components as the hard copy files.

Reports (including QA reports), analytical laboratory documentation, data verification reports, and field data will be in PDF (or equivalent). Additionally, electronic copies of EDDs containing verified/validated sample results will be filed in Microsoft Excel format (or equivalent), and daily and cumulative electronic field databases will be filed in Microsoft Access format (or equivalent).

2.2.2 Data Security

Hard copy information/data will be stored in secure areas within the three project file locations. Electronic data and information will be maintained and managed using password-protected computers and on secure network drives with access limited to project personnel.

2.3 Final Data Evaluation

Data evaluation activities may be performed by Tierra's Facility Coordinator. The computer programs that will be utilized during data evaluation include EQuIS, Microsoft Access, Microsoft Excel, MatLab, and ArcGIS or similar software (including ArcMap application [distributed by Environmental Systems Research Institute, Inc.]).

3. Quality Assurance

Appropriate QA/QC procedures will be followed during data management in accordance with SOP No. 8 – Documenting Field Activities and this SOP.

4. Documentation

Field and laboratory documentation will be maintained in accordance with SOP No. 8 – Documenting Field Activities and this SOP.

5. References

USEPA. 1996. Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Criterion Levels, U.S. Environmental Protection Agency, Office of Water Engineering and Analysis Division (4303), July 1996.

DATA REVIEW FORM

(Sheet 1 of 1)

Date: (1)

SDG: (2)

Analytical Group: (3)

Samples Reviewed: (4)

Identified Errors:

(5)

Corrective Actions Taken:

(6)

Person Responsible: (7)

Attach original data table from analytical database, and final data table showing changes (if applicable) to this form for data tracking/filing purposes. Also, attach any communications (e.g., emails, conversation records) related to the data changes discussed above.

DATA REVIEW FORM KEY
(Sheet 1 of 1)

DESCRIPTION OF ITEMS:

(1) Date of data review (e.g., 1/1/2013).

(2) Sample delivery group number assigned to data package under review.

(3) Analytical group requested for analysis under review (e.g., chlorinated herbicides).

(4) Sample ID(s) of samples chosen for review.

(5) Errors identified during comparison of data table from database to initialed and dated Form 1s in Data Verification Reports.

(6) Actions taken to correct errors identified during comparison of data table from database to marked-up Form 1s in Data Verification Reports.

(7) Name of person entering information into this form.

Standard Operating Procedure No. 10

Laboratory Tissue Homogenization

August 2014

Revision 0

1. Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for homogenizing tissue samples from the Newark Bay Study Area for analysis at the analytical laboratory. Tissue samples will be analyzed for constituents as outlined in the Fish Sampling and Analysis Quality Assurance Project Plan (Fish QAPP). This SOP is based on and is in general accordance with the methods used on the Lower Passaic River Restoration Project Cooperating Parties Group Quality Assurance Project Plan, Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey (Windward 2009).

This SOP may change depending upon equipment limitations or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by Tierra Solutions Inc.'s Facility Coordinator and the United States Environmental Protection Agency Remedial Project Manager. The ultimate procedure employed will be documented in the laboratory notebook.

Other SOPs will be utilized with this procedure, including:

- SOP No. 4 – Fish Sample Collection
- SOP No. 5 – Fish Tissue Sample Processing
- SOP No. 6 – Management and Disposal of Residuals
- SOP No. 7 – Containers, Preservation, Handling, and Tracking of Samples for Analysis

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2. Procedures

Following shipment to the analytical laboratory, the previously processed tissue samples will be placed in a food processor and blended to achieve acceptable homogenization prior to analysis. Tissue samples will be homogenized in a timely manner to meet the specified holding times documented in the Fish QAPP.

The following procedures will be used to homogenize processed tissue samples.

2.1 Equipment List

The following equipment list contains materials that may be needed to perform the procedures outlined in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment not listed here may be required dependent on field conditions.

- food processor with titanium blade and glass bowl
- Teflon®-coated spatula
- talc-free polyvinyl chloride (PVC) gloves
- glass or Teflon® cutting board
- electronic balance with calibration weights (checked for accuracy at least daily, and documented in accordance with laboratory protocols)
- labeled sample jars
- laboratory logbook or individual bench sheet forms
- bristle brushes
- wash/rinse tubs
- low-phosphate detergent
- 10% nitric acid, ultra pure
- acetone, methanol, and hexane (pesticide grade or better in separate Teflon® bottles), as necessary
- deionized “analyte free” water
- tap water (from any treated municipal water supply).

2.2 Equipment Decontamination and Calibration Procedures

The following steps will be used to decontaminate sample homogenization equipment that will come into contact with tissue designated for chemical analysis (e.g., food processor bowl, food processor blade, glass or Teflon® cutting board and Teflon®-coated spatula). Decontamination of laboratory homogenization equipment will occur

prior to initial use and again between homogenization of each tissue sample or tissue sample composite.

1. Personnel will dress in suitable protective equipment to reduce exposure to chemicals and contaminants per laboratory health and safety SOPs.

2. Prior to start of tissue processing for each individual tissue or tissue composite sample, all laboratory glassware and instruments will be cleaned per the steps outlined below. Decontamination of equipment will occur again between each tissue or tissue composite homogenized using the equipment, to minimize the likelihood of cross contamination from one tissue sample to another. Decontamination taking place between tissue samples being homogenized will begin with residual sample media being scraped off and the equipment rinsed with tap water.

3. Equipment will be placed in a wash tub or bucket containing Alconox (or other low-phosphate detergent), as well as with tap water, and scrubbed with a bristle brush or similar utensil. Equipment will be rinsed with tap water in a second wash tub or bucket, followed by a nitric acid rinse, a deionized “analyte free” water rinse, a methanol rinse followed by a hexane rinse, and lastly with a deionized water rinse. Rinses shall utilize sufficient amounts of solvent/water to flush rather than just wet the surface. The volume of deionized water used during the rinse must be at least five times the volume of solvent used.

4. Following decontamination, equipment will be placed in a clean area and allowed to air dry.

5. Used decontamination water will be collected and handled in accordance with residuals management procedures outlined in SOP No. 6 – Management and Disposal of Residuals or alternatively in accordance with the laboratory’s established protocols.

6. A calibrated laboratory electronic balance capable of reading to 0.1 grams will be used to measure the homogenized crab and clam tissue.

7. At the start of each sample homogenizing day, the designated laboratory’s electronic balance will be calibrated using certified sample weights supplied by the manufacturer. The target calibration weight mass will be recorded in the laboratory logbook. The electronic balance will be tared to zero and the calibrated weight will be measured using the electronic balance. The mass will be recorded in the laboratory logbook and if within the specified tolerances set forth in the Fish QAPP or by the manufacturer, then no adjustments will be made. If the measured weight

falls outside of the tolerances, then a calibration adjustment will be made to the electronic balance following the manufacturer's specifications and/or procedures.

2.3 Tissue Homogenizing Procedure

Tissue homogenizing will follow the following procedures:

1. Personal protective equipment will be donned and procedures will be reviewed prior to performing tissue or tissue composite homogenization. Talc-free PVC gloves must be worn throughout the homogenization procedure.

2. Tissue or tissue composite samples will be retrieved from laboratory frozen (-15 degrees Celsius [°C]) storage prior to homogenization with sufficient time allowed for tissue to partially thaw before homogenizing.

3. After the tissue sample has partially thawed, use the Teflon®-coated spatula to place the tissue in a clean processor with the titanium blade to be homogenized. Remove as much of the processed tissue in the sample jar as possible to maximize the tissue mass available for analysis post-homogenization. Using the processor, grind the sample until it appears to be fully and consistently homogenized and there are no large chunks.

4. Place the homogenized sample into the appropriate pre-weighed, pre-cleaned glass jars using the Teflon®-coated spatula. Again, every effort shall be made to remove as much of the homogenized tissue in the food processor as possible to maximize the tissue mass available for analysis post-homogenization. If necessary, the laboratory will segregate homogenized samples for distribution to other analytical laboratories. Record weights of homogenized samples and glass jars. If the samples will not be extracted/digested immediately, the samples must be placed back into the freezer (-15°C) until analytical work commences. Record placement of the samples in the freezer storage logbook. Note return of the samples to the Internal Tracking chain of custody.

5. All utensils and equipment must be washed in between samples according to the procedures described previously in Section 2.2.

6. Repeat steps 3 though 5 until all of the samples are homogenized.

3. Quality Assurance

The following quality assurance/quality control procedures will be performed during sample homogenization:

1. All pertinent field information and chains of custody (COCs) will be provided to the sample processing team. The designated laboratory personnel will review the sample information and confirm that the number of individuals, collection date(s), collection time(s), species, and required tissue analyses match the COCs. If any questions arise, the laboratory personnel will contact the project manager and laboratory project manager to resolve.

2. Laboratory logbook will be checked between individual and composite tissue processing and homogenizing steps to make sure required information is completed per the next section.

3. Rinse blanks will be collected once per 20 samples (not to exceed 1 per day), to measure the effectiveness of the equipment cleaning procedures. A rinse blank will be collected for all determinative analyses, with the exception of % lipids and % moisture. The rinse blanks will be collected by pouring contaminate-free reagent water over the homogenization equipment after completion of the cleaning procedure detailed in Section 2.2. The water will be collected in an appropriate container with the appropriate preservative, as specified in the Fish QAPP.

4. Documentation

Sample measurements and observations will be noted in the laboratory logbook or on individual bench sheets. Information to be recorded in the laboratory lobook will include, at a minimum:

- responsible person's name
- dates and times of activities
- sample IDs
- tissue weights (both individual and total sample).

5. References

Windward. 2009. Lower Passaic River Restoration Project. Quality Assurance Project Plan. Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey. Final. August 6.

Standard Operating Procedure No. 11

Measuring Surface Water Quality

June 2014

Revision 0

1. Purpose and Scope

The purpose of this document is to define the standard operation procedure (SOP) for measurement of surface water quality parameters. Surface water quality parameters (pH, temperature, conductivity, salinity, and dissolved oxygen) will be measured, *in-situ*, using a multi-parameter water quality meter (YSI 6000 or equivalent). This SOP describes equipment, field procedures, and quality assurance for measuring surface water quality. This SOP is based on and is in general accordance with the methods used on the Treatability Studies – Phase I Removal Action Quality Assurance Project Plan, CERCLA Non-Time Critical Removal Action, Lower Passaic River Study Area, Revision 1 (Tierra Solutions, Inc. [Tierra] 2009).

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. The ultimate procedure employed will be documented in the field notebook.

Other SOPs will be utilized with this procedure, including:

- SOP No. 1 – Locating Sample Points Using Hand-Held Global Positioning System
- SOP No. 2 – Positioning
- SOP No. 3 – Decontamination
- SOP No. 8 – Documenting Field Activities.

2. Procedures

In instances where this SOP will be utilized, a hard copy or electronic version will be available at the point of use.

2.1 Equipment List

The following equipment list contains materials that may be needed in carrying out the procedures for this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions:

- personal protective equipment (PPE) and other safety equipment, as required in the Health and Safety/Contingency Plan, Rev. 1 (HASCP; Tierra 2007)
- decontamination supplies (see SOP No. 3 – Decontamination)

- vessel(s) adequate for site conditions
- navigation chart(s) for on-water activities
- fathometer
- surveyor's rod
- multi-parameter water quality meter (YSI 6000 or equivalent) (description of the water quality meter is in Attachment 1)
- duct tape
- servicing supplies, such as, but not limited to, o-rings, spare screws, parts, clamps, and miscellaneous hardware
- replacement parts for water quality meter and pump
- disposable plastic beakers
- distilled water
- thermometer
- calibration solutions
- calibration logbook
- decontamination equipment (refer to SOP No. 3 – Decontamination)
- deployment equipment (e.g., winches, generator)
- field notebook.

2.2 Calibration Procedures

The water quality meters will be calibrated at the beginning and end of each day of use following the manufacturer's instructions. Calibration information will be recorded in the field notebook and a calibration log will be completed.

2.3 Maintenance Procedure

The water quality meters will be maintained according to the manufacturer's instructions. Maintenance information will be recorded in the field notebook. A replacement water quality meter will be available on site or ready for overnight shipment, as necessary.

2.4 Sampling Procedures

This section gives the step-by-step procedures for measuring water quality parameters. Observations made during surface-water quality parameter measurements should be recorded in the field notebook. Field water quality parameters (including salinity) will be measured using a water quality meter.

2.4.1 Decontamination of Equipment

Decontamination of the sampling equipment will be performed prior to vessel departure in accordance with procedures outlined in SOP No. 3 – Decontamination. Additional decontamination equipment and expendable supplies will be carried on board the vessel in case additional decontamination activities are needed. A sufficient amount of decontamination equipment and supplies will be brought on the vessel to accommodate the need for the ambient water decontamination activities described in SOP No. 3 – Decontamination.

2.4.2 Positioning

1. The sampling schedule will be established prior to vessel departure, and sufficient equipment to complete the work will be on board the sampling vessel. The sampling crew will be informed prior to departure of the sampling locations and provided with tidal charts to monitor for tide cycles.

2. The vessel will move to a sampling location in accordance with SOP No. 1 – Locating Sample Points Using Hand-Held Global Positioning System or SOP No. 2 – Positioning.

Water quality measurements will be collected from a boat with the multi-parameter water quality meter. The procedures for measurement of water quality parameters are provided below:

1. Don PPE (as required by the HASCP [Tierra 2007]).

2. Move sample vessel to location per SOP No. 1 – Locating Sample Points Using Hand-Held Global Positioning System or SOP No. 2 – Positioning, and secure.

3. Note water depth using the fathometer or a surveyor's rod. Note the time of the water depth measurement.

4. Water quality parameters will be measured throughout the water column from the water surface to 2 feet above the sediment surface. Lower the water quality meter at a rate of 0.5 feet per second while observing and recording the data in real time. Stop lowering the water quality meter at a height of 2 feet off the bottom, taking care not to impact or disturb bottom sediments.

5. Retrieve the water quality meter onto the deck of the vessel.

6. Retrieve the anchor and move the vessel to the next location in accordance with SOP No. 1 – Locating Sample Points Using Hand-Held Global Positioning System or SOP No. 2 – Positioning, or return to marina.

7. Prior to proceeding to the next location or returning to the marina, decontaminate the water quality meter as described in SOP No. 3 – Decontamination.

3. Quality Assurance

Entering data into the field notebook will document that the process is being followed and pertinent information is being collected and recorded in accordance with the procedures outlined in this SOP. Entries in the field notebook will be double-checked by the samplers to verify that the information is correct.

Calibration standards must be stored properly according to manufacturer's instructions. Check and replace all calibration standards per manufacturer's suggestions to confirm accurate water quality meter readings.

4. Documentation

Field notes will be kept during calibration, operation, and maintenance activities, in accordance with SOP No. 10 – Documenting Field Activities. All readings taken and adjustments made during calibrations and calibration checks will be recorded in the calibration logbook, as well as with the date and time at which the procedure was completed. The serial number of the meter and calibration solutions will be recorded if applicable.

Field notes will be kept during surface-water sampling activities in accordance with SOP No. 10 – Documenting Field Activities.

Information will be recorded in the field notebook during water quality measurements, including:

- date and time of measurements
- location of water quality meter measurements in New Jersey State Plane Coordinates (feet)
- weather condition information
- unusual conditions or problems with sampling equipment or water quality meter.

5. References

Tierra. 2007. Newark Bay Study Area Remedial Investigation Work Plan [Rev. 1]. Volume 2 Health and Safety/Contingency Plan. September.

Tierra. 2009. Treatability Studies – Phase I Removal Action Quality Assurance Project Plan. CERCLA Non-Time-Critical Removal Action, Lower Passaic River Study Area, Revision 1. August.

Appendix B

Laboratory SOPs

No. L-1

PCDDs/PCDFs and % Lipids (tissue)

USEPA Method 1613B

Method 1613

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

October 1994

U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460

Acknowledgments

This method was prepared under the direction of William A. Telliard of the Engineering and Analysis Division within the EPA Office of Water. This document was prepared under EPA Contract No. 68-C3-0337 by DynCorp Environmental Services Division with assistance from its subcontractor Interface, Inc.

Disclaimer

This method has been reviewed by the Engineering and Analysis Division, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Introduction

Method 1613 was developed by the United States Environmental Protection Agency's Office of Science and Technology for isomer-specific determination of the 2,3,7,8-substituted, tetra- through octa-chlorinated, dibenzo-*p*-dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS).

Questions concerning this method or its application should be addressed to:

W.A. Telliard
US EPA Office of Water
Analytical Methods Staff
Mail Code 4303
401 M Street, SW
Washington, D.C. 20460
202/260-7120

Requests for additional copies should be directed to:

Water Resource Center
Mail Code RC-4100
401 M Street, SW
Washington, D.C. 20460
202/260-7786 or 202/260-2814

Method 1613, Revision B
Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

1.0 Scope and Application

1.1 This method is for determination of tetra- through octa-chlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs) in water, soil, sediment, sludge, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a compilation of EPA, industry, commercial laboratory, and academic methods (References 1-6).

1.2 The seventeen 2,3,7,8-substituted CDDs/CDFs listed in Table 1 may be determined by this method. Specifications are also provided for separate determination of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachloro-dibenzofuran (2,3,7,8-TCDF).

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the CDDs/CDFs can be determined with no interferences present. The Method Detection Limit (MDL) for 2,3,7,8-TCDD has been determined as 4.4 pg/L (parts-per-quadrillion) using this method.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.5 This method is "performance-based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in Section 9.1.2.

1.6 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

2.0 Summary of Method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

2.1 Extraction

2.1.1 Aqueous samples (samples containing less than 1% solids)—Stable isotopically labeled analogs of 15 of the 2,3,7,8-substituted CDDs/CDFs are spiked into a 1 L sample, and the sample is extracted by one of three procedures:

2.1.1.1 Samples containing no visible particles are extracted with methylene chloride in a separatory funnel or by the solid-phase extraction technique summarized in Section 2.1.1.3. The extract is concentrated for cleanup.

2.1.1.2 Samples containing visible particles are vacuum filtered through a glass-fiber filter. The filter is extracted in a Soxhlet/Dean-Stark (SDS) extractor (Reference 7), and the filtrate is extracted with methylene chloride in a separatory funnel. The methylene chloride extract is concentrated and combined with the SDS extract prior to cleanup.

2.1.1.3 The sample is vacuum filtered through a glass-fiber filter on top of a solid-phase extraction (SPE) disk. The filter and disk are extracted in an SDS extractor, and the extract is concentrated for cleanup.

2.1.2 Solid, semi-solid, and multi-phase samples (but not tissue)—The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in an SDS extractor. The extract is concentrated for cleanup.

2.1.3 Fish and other tissue—The sample is extracted by one of two procedures:

2.1.3.1 Soxhlet or SDS extraction—A 20 g aliquot of sample is homogenized, and a 10 g aliquot is spiked with the labeled compounds. The sample is mixed with sodium sulfate, allowed to dry for 12-24 hours, and extracted for 18-24 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.1.3.2 HCl digestion—A 20 g aliquot is homogenized, and a 10 g aliquot is placed in a bottle and spiked with the labeled compounds. After equilibration, 200 mL of hydrochloric acid and 200 mL of methylene chloride:hexane (1:1) are added, and the bottle is agitated for 12-24 hours. The extract is evaporated to dryness, and the lipid content is determined.

2.2 After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanups may include back-extraction with acid and/or base, and gel permeation, alumina, silica gel, Florisil and activated carbon chromatography. High-performance liquid chromatography (HPLC) can be used for further isolation of the 2,3,7,8-isomers or other specific isomers or congeners. Prior to the cleanup procedures cited above, tissue extracts are cleaned up using an anthropogenic isolation column, a batch silica gel adsorption, or sulfuric acid and base back-extraction, depending on the tissue extraction procedure used.

2.3 After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, internal standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.4 An individual CDD/CDF is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. The non-2,3,7,8 substituted isomers and congeners are identified when retention times and ion-abundance ratios agree within predefined limits. Isomer specificity for 2,3,7,8-TCDD and 2,3,7,8-TCDF is achieved using GC columns that resolve these isomers from the other tetra-isomers.

2.5 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of three ways:

2.5.1 For the 15 2,3,7,8-substituted CDDs/CDFs with labeled analogs (see Table 1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.

2.5.2 For 1,2,3,7,8,9-HxCDD, OCDF, and the labeled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique.

2.5.3 For non-2,3,7,8-substituted isomers and for all isomers at a given level of chlorination (i.e., total TCDD), concentrations are determined using response factors from calibration of the CDDs/CDFs at the same level of chlorination.

2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3.0 Definitions

Definitions are given in the glossary at the end of this method.

4.0 Contamination and Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms (References 8-9). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with

removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.

4.2.3 Do not bake reusable glassware in an oven as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered but should be minimized, as repeated baking of glassware may cause active sites on the glass surface that will irreversibly adsorb CDDs/CDFs.

4.2.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with toluene for approximately three hours (see Sections 12.3.1 through 12.3.3). Separatory funnels should be shaken with methylene chloride/toluene (80/20 mixture) for two minutes, drained, and then shaken with pure methylene chloride for two minutes.

4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the CDDs/CDFs in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed. For example, a reference sample of human adipose tissue containing pentachloronaphthalene can be used to exercise the cleanup systems when samples containing pentachloronaphthalene are expected.

4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.

4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the CDDs/CDFs. The most frequently encountered interferences are chlorinated biphenyls, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of CDDs/CDFs are measured by this method, the elimination of interferences is essential. The cleanup steps given in Section 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the CDDs/CDFs at the levels shown in Table 2.

4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with

highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Cleanup of tissue—The natural lipid content of tissue can interfere in the analysis of tissue samples for the CDDs/CDFs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the lipid removal procedures in Section 13.7, followed by alumina (Section 13.4) or Florisil (Section 13.8), and carbon (Section 13.5) as minimum additional cleanup steps. If chlorodiphenyl ethers are detected, as indicated by the presence of peaks at the exact m/z's monitored for these interferents, alumina and/or Florisil cleanup must be employed to eliminate these interferences.

5.0 Safety

5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. It is soluble in water to approximately 200 ppt and in organic solvents to 0.14%. On the basis of the available toxicological and physical properties of 2,3,7,8-TCDD, all of the CDDs/CDFs should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this method. However, if primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator shall be worn when high concentrations are handled.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 10-13. The references and bibliography at the end of Reference 13 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 The CDDs/CDFs and samples suspected to contain these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. The CDDs/CDFs are extremely toxic to laboratory animals. Each laboratory must develop a strict safety program for handling these compounds. The practices in References 2 and 14 are highly recommended.

5.3.1 Facility—When finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the CDDs/CDFs, an additional set of gloves can also be worn beneath the latex gloves.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluents of sample splitters from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols to condense CDD/CDF vapors.

5.3.7 Waste Handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Chlorothene NU Solvent is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. If glassware is first rinsed with solvent, then the dish water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the

hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by GC with an electron capture detector (ECD) can achieve a limit of detection of 0.1 µg per wipe; analysis using this method can achieve an even lower detection limit. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

5.3.11 Table or wrist-action shaker—The use of a table or wrist-action shaker for extraction of tissues presents the possibility of breakage of the extraction bottle and spillage of acid and flammable organic solvent. A secondary containment system around the shaker is suggested to prevent the spread of acid and solvents in the event of such a breakage. The speed and intensity of shaking action should also be adjusted to minimize the possibility of breakage.

6.0 Apparatus and Materials

NOTE: *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the laboratory.*

6.1 Sampling Equipment for Discrete or Composite Sampling

6.1.1 Sample bottles and caps

6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5% solids or less)—Sample bottle, amber glass, 1.1 L minimum, with screw cap.

6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5% solids)—Sample bottle, wide mouth, amber glass, 500 mL minimum.

6.1.1.3 If amber bottles are not available, samples shall be protected from light.

6.1.1.4 Bottle caps—Threaded to fit sample bottles. Caps shall be lined with fluoropolymer.

6.1.1.5 Cleaning

6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.

6.1.1.5.2 Liners are detergent water washed, rinsed with reagent water (Section 7.6.1) followed by solvent, and baked at approximately 200°C for a minimum of 1 hour prior to use.

6.1.2 Compositing equipment—Automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

6.2 Equipment for Glassware Cleaning—Laboratory sink with overhead fume hood.

6.3 Equipment for Sample Preparation

6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.3.2 Glove box (optional).

6.3.3 Tissue homogenizer—VirTis Model 45 Macro homogenizer (American Scientific Products H-3515, or equivalent) with stainless steel Macro-shaft and Turbo-shear blade.

6.3.4 Meat grinder—Hobart, or equivalent, with 3-5 mm holes in inner plate.

6.3.5 Equipment for determining percent moisture

6.3.5.1 Oven—Capable of maintaining a temperature of 110 ±5°C.

6.3.5.2 Dessicator.

6.3.6 Balances

6.3.6.1 Analytical—Capable of weighing 0.1 mg.

6.3.6.2 Top loading—Capable of weighing 10 mg.

6.4 Extraction Apparatus

6.4.1 Water samples

6.4.1.1 pH meter, with combination glass electrode.

6.4.1.2 pH paper, wide range (Hydrion Papers, or equivalent).

6.4.1.3 Graduated cylinder, 1 L capacity.

6.4.1.4 Liquid/liquid extraction—Separatory funnels, 250 mL, 500 mL, and 2000 mL, with fluoropolymer stopcocks.

6.4.1.5 Solid-phase extraction

6.4.1.5.1 One liter filtration apparatus, including glass funnel, glass frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.

6.4.1.5.2 Vacuum source capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge.

6.4.1.5.3 Glass-fiber filter—Whatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1.

6.4.1.5.4 Solid-phase extraction disk containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1.

6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5)—For filters and solid/sludge samples.

6.4.2.1 Soxhlet—50 mm ID, 200 mL capacity with 500 mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500 mL round-bottom flask for 300 mL flat-bottom flask).

6.4.2.2 Thimble—43 x 123 to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent).

6.4.2.3 Moisture trap—Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet.

6.4.2.4 Heating mantle—Hemispherical, to fit 500 mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent).

6.4.2.5 Variable transformer—Powerstat (or equivalent), 110 volt, 10 amp.

6.4.3 Apparatus for extraction of tissue.

6.4.3.1 Bottle for extraction (if digestion/extraction using HCl is used)—500-600 mL wide-mouth clear glass, with fluoropolymer-lined cap.

6.4.3.2 Bottle for back-extraction—100-200 mL narrow-mouth clear glass with fluoropolymer-lined cap.

6.4.3.3 Mechanical shaker—Wrist-action or platform-type rotary shaker that produces vigorous agitation (Sybron Thermolyne Model LE "Big Bill" rotator/shaker, or equivalent).

6.4.3.4 Rack attached to shaker table to permit agitation of four to nine samples simultaneously.

6.4.4 Beakers—400-500 mL.

6.4.5 Spatulas—Stainless steel.

6.5 Filtration Apparatus

6.5.1 Pyrex glass wool—Solvent-extracted by SDS for three hours minimum.

NOTE: *Baking glass wool may cause active sites that will irreversibly adsorb CDDs/CDFs.*

6.5.2 Glass funnel—125-250 mL.

6.5.3 Glass-fiber filter paper—Whatman GF/D (or equivalent), to fit glass funnel in Section 6.5.2.

6.5.4 Drying column—15-20 mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.

6.5.5 Buchner funnel—15 cm.

6.5.6 Glass-fiber filter paper—to fit Buchner funnel in Section 6.5.5.

6.5.7 Filtration flasks—1.5-2.0 L, with side arm.

6.5.8 Pressure filtration apparatus—Millipore YT30 142 HW, or equivalent.

6.6 Centrifuge Apparatus

6.6.1 Centrifuge—Capable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5,000 rpm minimum.

6.6.2 Centrifuge bottles—500 mL, with screw-caps, to fit centrifuge.

6.6.3 Centrifuge tubes—12-15 mL, with screw-caps, to fit centrifuge.

6.7 Cleanup Apparatus

6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent).

6.7.1.1 Column—600-700 mm long x 25 mm ID, packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent).

6.7.1.2 Syringe—10 mL, with Luer fitting.

6.7.1.3 Syringe filter holder—stainless steel, and glass-fiber or fluoropolymer filters (Gelman 4310, or equivalent).

6.7.1.4 UV detectors—254 nm, preparative or semi-preparative flow cell (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman-Altex 152W, 8 µL micro-prep flow cell, 2 mm path; Pharmacia UV-1, 3 mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent).

6.7.2 Reverse-phase high-performance liquid chromatograph.

6.7.2.1 Column oven and detector—Perkin-Elmer Model LC-65T (or equivalent) operated at 0.02 AUFS at 235 nm.

6.7.2.2 Injector—Rheodyne 7120 (or equivalent) with 50 µL sample loop.

6.7.2.3 Column—Two 6.2 mm x 250 mm Zorbax-ODS columns in series (DuPont Instruments Division, Wilmington, DE, or equivalent), operated at 50°C with 2.0 mL/min methanol isocratic effluent.

6.7.2.4 Pump—Altex 110A (or equivalent).

6.7.3 Pipets

6.7.3.1 Disposable, pasteur—150 mm long x 5-mm ID (Fisher Scientific 13-678-6A, or equivalent).

6.7.3.2 Disposable, serological—10 mL (6 mm ID).

6.7.4 Glass chromatographic columns

6.7.4.1 150 mm long x 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250 mL reservoir.

6.7.4.2 200 mm long x 15 mm ID, with coarse-glass frit or glass-wool plug and 250 mL reservoir.

6.7.4.3 300 mm long x 25 mm ID, with 300 mL reservoir and glass or fluoropolymer stopcock.

6.7.5 Stirring apparatus for batch silica cleanup of tissue extracts.

6.7.5.1 Mechanical stirrer—Corning Model 320, or equivalent.

6.7.5.2 Bottle—500-600 mL wide-mouth clear glass.

6.7.6 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.8 Concentration Apparatus

6.8.1 Rotary evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.

6.8.1.1 Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge.

6.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.8.1.3 Round-bottom flask—100 mL and 500 mL or larger, with ground-glass fitting compatible with the rotary evaporator.

6.8.2 Kuderna-Danish (K-D) Concentrator

6.8.2.1 Concentrator tube—10 mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.8.2.2 Evaporation flask—500 mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

6.8.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232, or equivalent).

6.8.2.4 Boiling chips

6.8.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for one hour minimum.

6.8.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride.

6.8.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within ±2°C, installed in a fume hood.

6.8.3 Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30-60°C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood.

6.8.4 Sample vials

6.8.4.1 Amber glass—2-5 mL with fluoropolymer-lined screw-cap.

6.8.4.2 Glass—0.3 mL, conical, with fluoropolymer-lined screw or crimp cap.

6.9 Gas Chromatograph—Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.9.1 GC column for CDDs/CDFs and for isomer specificity for 2,3,7,8-TCDD—60 ±5 m long x 0.32 ±0.02 mm ID; 0.25 µm 5% phenyl, 94% methyl, 1% vinyl silicone bonded-phase fused-silica capillary column (J&W DB-5, or equivalent).

6.9.2 GC column for isomer specificity for 2,3,7,8-TCDF—30 ±5 m long x 0.32 ±0.02 mm ID; 0.25 µm bonded-phase fused-silica capillary column (J&W DB-225, or equivalent).

6.10 Mass Spectrometer—28-40 eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately one second, and shall meet all of the performance specifications in Section 10.

6.11 GC/MS Interface—The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.12 Data System—Capable of collecting, recording, and storing MS data.

7.0 Reagents and Standards

7.1 pH Adjustment and Back-Extraction

7.1.1 Potassium hydroxide—Dissolve 20 g reagent grade KOH in 100 mL reagent water.

7.1.2 Sulfuric acid—Reagent grade (specific gravity 1.84).

7.1.3 Hydrochloric acid—Reagent grade, 6N.

7.1.4 Sodium chloride—Reagent grade, prepare at 5% (w/v) solution in reagent water.

7.2 Solution Drying and Evaporation

7.2.1 Solution drying—Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Tissue drying—Sodium sulfate, reagent grade, powdered, treated and stored as above.

7.2.3 Prepurified nitrogen.

7.3 Extraction

7.3.1 Solvents—Acetone, toluene, cyclohexane, hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

7.3.2 White quartz sand, 60/70 mesh—For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450°C for four hours minimum.

7.4 GPC Calibration Solution—Prepare a solution containing 300 mg/mL corn oil, 15 mg/mL bis(2-ethylhexyl) phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur.

7.5 Adsorbents for Sample Cleanup

7.5.1 Silica gel

7.5.1.1 Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methylene chloride, baked at 180°C for a minimum of one hour, cooled in a dessicator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.5.1.2 Acid silica gel (30% w/w)—Thoroughly mix 44.0 g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

7.5.1.3 Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

7.5.1.4 Potassium silicate

7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750-1000 mL flat-bottom flask.

7.5.1.4.2 Add 100 g of silica gel and a stirring bar, and stir on a hot plate at 60-70°C for one to two hours.

7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100 mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.

7.5.1.4.4 Spread the potassium silicate on solvent-rinsed aluminum foil and dry for two to four hours in a hood.

7.5.1.4.5 Activate overnight at 200-250°C.

7.5.2 Alumina—Either one of two types of alumina, acid or basic, may be used in the cleanup of sample extracts, provided that the laboratory can meet the performance specifications for the recovery of labeled compounds described in Section 9.3. The same type of alumina must be used for all samples, including those used to demonstrate initial precision and recovery (Section 9.2) and ongoing precision and recovery (Section 15.5).

7.5.2.1 Acid alumina—Supelco 19996-6C (or equivalent). Activate by heating to 130°C for a minimum of 12 hours.

7.5.2.2 Basic alumina—Supelco 19944-6C (or equivalent). Activate by heating to 600°C for a minimum of 24 hours. Alternatively, activate by heating in a tube furnace at 650-700°C under an air flow rate of approximately 400 cc/minute. Do not heat over 700°C, as this can lead to reduced capacity for retaining the analytes. Store at 130°C in a covered flask. Use within five days of baking.

7.5.3 Carbon

7.5.3.1 Carbopak C—(Supelco 1-0258, or equivalent).

7.5.3.2 Celite 545—(Supelco 2-0199, or equivalent).

7.5.3.3 Thoroughly mix 9.0 g Carbopak C and 41.0 g Celite 545 to produce an 18% w/w mixture. Activate the mixture at 130°C for a minimum of six hours. Store in a dessicator.

7.5.4 Anthropogenic isolation column—Pack the column in Section 6.7.4.3 from bottom to top with the following:

7.5.4.1 2 g silica gel (Section 7.5.1.1).

7.5.4.2 2 g potassium silicate (Section 7.5.1.4).

7.5.4.3 2 g granular anhydrous sodium sulfate (Section 7.2.1).

7.5.4.4 10 g acid silica gel (Section 7.5.1.2).

7.5.4.5 2 g granular anhydrous sodium sulfate.

7.5.5 Florisil column

7.5.5.1 Florisil—60-100 mesh, Floridin Corp (or equivalent). Soxhlet extract in 500 g portions for 24 hours.

7.5.5.2 Insert a glass wool plug into the tapered end of a graduated serological pipet (Section 6.7.3.2). Pack with 1.5 g (approx 2 mL) of Florisil topped with approx 1 mL of sodium sulfate (Section 7.2.1) and a glass wool plug.

7.5.5.3 Activate in an oven at 130-150°C for a minimum of 24 hours and cool for 30 minutes. Use within 90 minutes of cooling.

7.6 Reference Matrices—Matrices in which the CDDs/CDFs and interfering compounds are not detected by this method.

7.6.1 Reagent water—Bottled water purchased locally, or prepared by passage through activated carbon.

7.6.2 High-solids reference matrix—Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450°C for a minimum of four hours.

7.6.3 Paper reference matrix—Glass-fiber filter, Gelman Type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.

7.6.4 Tissue reference matrix—Corn or other vegetable oil. May be prepared by extraction with methylene chloride.

7.6.5 Other matrices—This method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the CDDs/CDFs, but in no case shall the background level of the CDDs/CDFs in the reference matrix exceed three times the minimum levels in Table 2. If low background levels of the CDDs/CDFs are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio in the range of 1:1 to 5:1 (Reference 15).

7.7 Standard Solutions—Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.

7.8 Stock Solutions

7.8.1 Preparation—Prepare in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories (CIL), Woburn, MA, or equivalent). Observe the safety precautions in Section 5, and the recommendation in Section 5.1.2.

7.8.2 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1-2 mg of 2,3,7,8-TCDD to three significant figures in a 10 mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the TCDD is completely dissolved, transfer the solution to a clean 15 mL vial with fluoropolymer-lined cap.

7.8.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from CIL and may be available from other vendors.

7.9 PAR Stock Solution

7.9.1 All CDDs/CDFs—Using the solutions in Section 7.8, prepare the PAR stock solution to contain the CDDs/CDFs at the concentrations shown in Table 3. When diluted, the solution will become the PAR (Section 7.14).

7.9.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the PAR stock solution to contain these compounds only.

7.10 Labeled-Compound Spiking Solution

7.10.1 All CDDs/CDFs—From stock solutions, or from purchased mixtures, prepare this solution to contain the labeled compounds in nonane at the concentrations shown in Table 3. This solution is diluted with acetone prior to use (Section 7.10.3).

7.10.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the labeled-compound solution to contain these compounds only. This solution is diluted with acetone prior to use (Section 7.10.3).

7.10.3 Dilute a sufficient volume of the labeled compound solution (Section 7.10.1 or 7.10.2) by a factor of 50 with acetone to prepare a diluted spiking solution. Each sample requires 1.0 mL of the diluted solution, but no more solution should be prepared than can be used in one day.

7.11 Cleanup Standard—Prepare $^{37}Cl_4$-2,3,7,8-TCDD in nonane at the concentration shown in Table 3. The cleanup standard is added to all extracts prior to cleanup to measure the efficiency of the cleanup process.

7.12 Internal Standard(s)

7.12.1 All CDDs/CDFs—Prepare the internal standard solution to contain $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD in nonane at the concentration shown in Table 3.

7.12.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the internal standard solution to contain $^{13}C_{12}$-1,2,3,4-TCDD only.

7.13 Calibration Standards (CS1 through CS5)—Combine the solutions in Sections 7.9 through 7.12 to produce the five calibration solutions shown in Table 4 in nonane. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER). If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, combine the solutions appropriate to these compounds.

7.14 Precision and Recovery (PAR) Standard—Used for determination of initial (Section 9.2) and ongoing (Section 15.5) precision and recovery. Dilute 10 µL of the precision and recovery standard (Section 7.9.1 or 7.9.2) to 2.0 mL with acetone for each sample matrix for each sample batch. One mL each are required for the blank and OPR with each matrix in each batch.

7.15 GC Retention Time Window Defining Solution and Isomer Specificity Test Standard—Used to define the beginning and ending retention times for the dioxin and furan isomers and to demonstrate isomer specificity of the GC columns employed for determination of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The standard must contain the compounds listed in Table 5 (CIL EDF-4006, or equivalent), at a minimum. It is not necessary to monitor the window-defining compounds if only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be

determined. In this case, an isomer-specificity test standard containing the most closely eluted isomers listed in Table 5 (CIL EDF-4033, or equivalent) may be used.

7.16 QC Check Sample—A QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified reference material containing the CDDs/CDFs in known concentrations in a sample matrix similar to the matrix under test.

7.17 Stability of Solutions—Standard solutions used for quantitative purposes (Sections 7.9 through 7.15) should be analyzed periodically, and should be assayed against reference standards (Section 7.8.3) before further use.

8.0 Sample Collection, Preservation, Storage, and Holding Times

8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 16). Aqueous samples that flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide-mouth jars.

8.2 Maintain aqueous samples in the dark at 0-4°C from the time of collection until receipt at the laboratory. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 17). If sample pH is greater than 9, adjust to pH 7-9 with sulfuric acid.

Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <4°C from the time of collection until receipt at the laboratory.

Store aqueous samples in the dark at 0-4°C. Store solid, semi-solid, oily, mixed-phase, and tissue samples in the dark at <-10°C.

8.3 Fish and Tissue Samples

8.3.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.3.2 Fish collected in the field should be wrapped in aluminum foil, and must be maintained at a temperature less than 4°C from the time of collection until receipt at the laboratory.

8.3.3 Samples must be frozen upon receipt at the laboratory and maintained in the dark at <-10°C until prepared. Maintain unused sample in the dark at <-10°C.

8.4 Holding Times

8.4.1 There are no demonstrated maximum holding times associated with CDDs/CDFs in aqueous, solid, semi-solid, tissues, or other sample matrices. If stored in the dark at 0-4°C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10°C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.4.2 Store sample extracts in the dark at <-10°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 18). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied to sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate matrix (Sections 7.6.2 through 7.6.5) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to allow the analyst to overcome sample matrix interferences, the analyst is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, cleanup procedures, and changes in columns and detectors. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-third the regulatory compliance level or one-third the ML in this method, whichever is higher. If calibration will be affected by the change, the analyst must recalibrate the instrument per Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

a) Calibration (Section 10.5 through 10.7).
b) Calibration verification (Section 15.3).
c) Initial precision and recovery (Section 9.2).
d) Labeled compound recovery (Section 9.3).
e) Analysis of blanks (Section 9.5).
f) Accuracy assessment (Section 9.4).

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers.
b) Extraction dates.
c) Analysis dates and times.
d) Analysis sequence/run chronology.
e) Sample weight or volume (Section 11).
f) Extract volume prior to each cleanup step (Section 13).
g) Extract volume after each cleanup step (Section 13).
h) Final extract volume prior to injection (Section 14).
I) Injection volume (Section 14.3).
j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5).
k) Instrument and operating conditions.
l) Column (dimensions, liquid phase, solid support, film thickness, etc).
m) Operating conditions (temperatures, temperature program, flow rates).
n) Detector (type, operating conditions, etc).
o) Chromatograms, printer tapes, and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are described in Sections 9.5 and 15.6.

9.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 9.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits. Procedures for dilution are given in Section 17.5.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery aliquot that

the analytical system is in control. These procedures are described in Sections 15.1 through 15.5.

9.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Section 9.4.

9.2 Initial Precision and Recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1 L aliquots of reagent water spiked with the diluted labeled compound spiking solution (Section 7.10.3) and the precision and recovery standard (Section 7.14) according to the procedures in Sections 11 through 18. For an alternative sample matrix, four aliquots of the alternative reference matrix (Section 7.6) are used. All sample processing steps that are to be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), shall be included in this test.

9.2.2 Using results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration (s) in ng/mL for each compound, by isotope dilution for CDDs/CDFs with a labeled analog, and by internal standard for 1,2,3,7,8,9-HxCDD, OCDF, and the labeled compounds.

9.2.3 For each CDD/CDF and labeled compound, compare s and X with the corresponding limits for initial precision and recovery in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare s and X with the corresponding limits for initial precision and recovery in Table 6a. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).

9.3 The laboratory shall spike all samples with the diluted labeled compound spiking solution (Section 7.10.3) to assess method performance on the sample matrix.

9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.

9.3.2 Compute the percent recovery of the labeled compounds and the cleanup standard using the internal standard method (Section 17.2).

9.3.3 The recovery of each labeled compound must be within the limits in Table 7 when all 2,3,7,8-substituted CDDs/CDFs are determined, and within the limits in Table 7a when only 2,3,7,8-TCDD and 2,3,7,8-TCDF are determined. If the recovery of any compound falls outside of these limits, method performance is unacceptable for that compound in that sample. To overcome such difficulties, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are reanalyzed per Section 18.4.

9.4 Recovery of labeled compounds from samples should be assessed and records should be maintained.

9.4.1 After the analysis of five samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (S_R) for the labeled compounds only. Express the assessment as a percent recovery interval from $R-2S_R$ to $R+2S_R$ for each matrix. For example, if R = 90% and S_R = 10% for five analyses of pulp, the recovery interval is expressed as 70-110%.

9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each 5-10 new measurements).

9.5 Method Blanks—Reference matrix method blanks are analyzed to demonstrate freedom from contamination (Section 4.3).

9.5.1 Prepare, extract, clean up, and concentrate a method blank with each sample batch (samples of the same matrix started through the extraction process on the same 12-hour shift, to a maximum of 20 samples). The matrix for the method blank shall be similar to sample matrix for the batch, e.g., a 1 L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3); tissue blank (Section 7.6.4) or alternative reference matrix blank (Section 7.6.5). Analyze the blank immediately after analysis of the OPR (Section 15.5) to demonstrate freedom from contamination.

9.5.2 If any 2,3,7,8-substituted CDD/CDF (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance level, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each level of chlorination given in Table 2 (assuming a response factor of 1 relative to the $^{13}C_{12}$-1,2,3,4-TCDD internal standard for compounds not listed in Table 1), analysis of samples is halted until the blank associated with the sample batch shows no evidence of contamination at this level. All samples must be associated with an uncontaminated method blank before the results for those samples may be reported for regulatory compliance purposes.

9.6 QC Check Sample—Analyze the QC Check Sample (Section 7.16) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.

9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.5) precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of CDDs/CDFs by this method.

9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

10.0 Calibration

10.1 Establish the operating conditions necessary to meet the minimum retention times for the internal standards in Section 10.2.4 and the relative retention times for the CDDs/CDFs in Table 2.

10.1.1 Suggested GC operating conditions:

Injector temperature:	270°C
Interface temperature:	290°C
Initial temperature:	200°C
Initial time:	Two minutes
Temperature program:	200-220°C, at 5°C/minute
	220°C for 16 minutes
	220-235°C, at 5°C/minute
	235°C for seven minutes
	235-330°C, at 5°C/minute

NOTE: *All portions of the column that connect the GC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.*

Optimize GC conditions for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.

10.1.2 Mass spectrometer (MS) resolution—Obtain a selected ion current profile (SICP) of each analyte in Table 3 at the two exact m/z's specified in Table 8 and at ≥10,000 resolving power by injecting an authentic standard of the CDDs/CDFs either singly or as part of a mixture in which there is no interference between closely eluted components.

10.1.2.1 The analysis time for CDDs/CDFs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory and a lock-mass m/z from PFK is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 8. The level of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: *Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.*

10.1.2.2 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below 10,000 to save reanalysis time.

10.1.2.3 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 304 (from TCDF). For each descriptor (Table 8), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The resolution must be greater than or equal to 10,000, and the deviation between the exact m/z and the theoretical m/z (Table 8) for each exact m/z monitored must be less than 5 ppm.

10.2 Ion Abundance Ratios, Minimum Levels, Signal-to-Noise Ratios, and Absolute Retention Times—Choose an injection volume of either 1 µL or 2 µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 µL or 2 µL aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the operating conditions and specifications below apply to analysis of those compounds only.

10.2.1 Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z's specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.

10.2.1.1 The exact m/z's to be monitored in each descriptor are shown in Table 8. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all CDDs/CDFs are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the five descriptors listed in Table 8, provided that the laboratory is able to monitor the m/z's of all the CDDs/CDFs that may elute from the GC in a given retention-time window. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the descriptors may be modified to include only the exact m/z's for the tetra- and penta-isomers, the diphenyl ethers, and the lock m/z's.

10.2.1.2 The mass spectrometer shall be operated in a mass-drift correction mode, using perfluorokerosene (PFK) to provide lock m/z's. The lock-mass for each group of m/z's is shown in Table 8. Each lock mass shall be monitored and shall not vary by more than ±20% throughout its respective retention time window. Variations of the lock mass by more than 20% indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.

10.2.2 All CDDs/CDFs and labeled compounds in the CS1 standard shall be within the QC limits in Table 9 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.

10.2.3 Verify that the HRGC/HRMS instrument meets the minimum levels in Table 2. The peaks representing the CDDs/CDFs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the minimum levels in Table 2 are met.

10.2.4 The absolute retention time of $^{13}C_{12}$-1,2,3,4-TCDD (Section 7.12) shall exceed 25.0 minutes on the DB-5 column, and the retention time of $^{13}C_{12}$-1,2,3,4-TCDD shall exceed 15.0 minutes on the DB-225 column; otherwise, the GC temperature program shall be adjusted and this test repeated until the above-stated minimum retention time criteria are met.

10.3 Retention-Time Windows—Analyze the window defining mixtures (Section 7.15) using the optimized temperature program in Section 10.1. Table 5 gives the elution order (first/last) of the window-defining compounds. If 2,3,7,8-TCDD and 2,3,7,8-TCDF only are to be analyzed, this test is not required.

10.4 Isomer Specificity

10.4.1 Analyze the isomer specificity test standards (Section 7.15) using the procedure in Section 14 and the optimized conditions for sample analysis (Section 10.1.1).

10.4.2 Compute the percent valley between the GC peaks that elute most closely to the 2,3,7,8-TCDD and TCDF isomers, on their respective columns, per Figures 6 and 7.

10.4.3 Verify that the height of the valley between the most closely eluted isomers and the 2,3,7,8-substituted isomers is less than 25% (computed as 100 x/y in Figures 6 and 7). If the valley exceeds 25%, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate (Sections 10.1.2 through 10.7).

10.5 Calibration by Isotope Dilution—Isotope dilution calibration is used for the 15 2,3,7,8-substituted CDDs/CDFs for which labeled compounds are added to samples prior to extraction. The reference compound for each CDD/CDF compound is shown in Table 2.

10.5.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (RR) (labeled to native) vs. concentration in standard solutions is plotted or computed using a linear regression. Relative response is determined according to the procedures described below. Five calibration points are employed.

10.5.2 The response of each CDD/CDF relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 8, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ C_n}$$

where,

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the CDD/CDF.

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_l = The concentration of the labeled compound in the calibration standard (Table 4).

C_n = The concentration of the native compound in the calibration standard (Table 4).

10.5.3 To calibrate the analytical system by isotope dilution, inject a volume of calibration standards CS1 through CS5 (Section 7.13 and Table 4) identical to the volume chosen in Section 10.2, using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the relative response (RR) at each concentration.

10.5.4 Linearity—If the relative response for any compound is constant (less than 20% coefficient of variation) over the five-point calibration range, an averaged relative response may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point calibration range.

10.6 Calibration by Internal Standard—The internal standard method is applied to determination of 1,2,3,7,8,9-HxCDD (Section 17.1.2), OCDF (Section 17.1.1), the non-2,3,7,8-substituted compounds, and to the determination of labeled compounds for intralaboratory statistics (Sections 9.4 and 15.5.4).

10.6.1 Response factors—Calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ C_s}$$

where,

$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the CDD/CDF.

$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard

C_{is} = The concentration of the internal standard (Table 4).

C_s = The concentration of the compound in the calibration standard (Table 4).

NOTE: *There is only one m/z for $^{37}Cl_4$-2,3,7,8-TCDD. See Table 8.*

10.6.2 To calibrate the analytical system by internal standard, inject 1.0 µL or 2.0 µL of calibration standards CS1 through CS5 (Section 7.13 and Table 4) using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the response factor (RF) at each concentration.

10.6.3 Linearity—If the response factor (RF) for any compound is constant (less than 35% coefficient of variation) over the five-point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point range.

10.7 Combined Calibration—By using calibration solutions (Section 7.13 and Table 4) containing the CDDs/CDFs and labeled compounds and the internal standards, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (Section 15.3) by analyzing the calibration verification standard (VER, Table 4). Recalibration is required if any of the calibration verification criteria (Section 15.3) cannot be met.

10.8 Data Storage—MS data shall be collected, recorded, and stored.

10.8.1 Data acquisition—The signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

10.8.2 Response factors and multipoint calibrations—The data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity. Statistics on initial performance (Section 9.2) and ongoing performance (Section 15.5) should be computed and maintained, either on the instrument data system, or on a separate computer system.

11.0 Sample Preparation

11.1 Sample preparation involves modifying the physical form of the sample so that the CDDs/CDFs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 10 lists the phases and suggested quantities for extraction of various sample matrices.

For samples known or expected to contain high levels of the CDDs/CDFs, the smallest sample size representative of the entire sample should be used (see Section 17.5).

For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.

11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.

11.1.2 Aqueous samples—Because CDDs/CDFs may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.

11.1.2.1 Aqueous samples visibly absent particles are prepared per Section 11.4 and extracted directly using the separatory funnel or SPE techniques in Sections 12.1 or 12.2, respectively.

11.1.2.2 Aqueous samples containing visible particles and containing one percent suspended solids or less are prepared using the procedure in Section 11.4. After preparation, the sample is extracted directly using the SPE technique in 12.2 or filtered per Section 11.4.3. After filtration, the particles and filter are extracted using the SDS procedure in Section 12.3 and the filtrate is extracted using the separatory funnel procedure in Section 12.1.

11.1.2.3 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.

11.1.3 Solid samples are prepared using the procedure described in Section 11.5 followed by extraction via the SDS procedure in Section 12.3.

11.1.4 Multiphase samples—The phase(s) containing the CDDs/CDFs is separated from the non-CDD/CDF phase using pressure filtration and centrifugation, as described in Section 11.6. The CDDs/CDFs will be in the organic phase in a multiphase sample in which an organic phase exists.

11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.

11.1.6 Tissue samples—Preparation procedures for fish and other tissues are given in Section 11.8.

11.2 Determination of Percent Suspended Solids

NOTE: *This aliquot is used for determining the solids content of the sample, not for determination of CDDs/CDFs.*

11.2.1 Aqueous liquids and multi-phase samples consisting of mainly an aqueous phase.

11.2.1.1 Dessicate and weigh a GF/D filter (Section 6.5.3) to three significant figures.

11.2.1.2 Filter 10.0 ±0.02 mL of well-mixed sample through the filter.

11.2.1.3 Dry the filter a minimum of 12 hours at 110 ±5°C and cool in a dessicator.

11.2.1.4 Calculate percent solids as follows:

$$\%solids = \frac{weight\ of\ sample\ aliquot\ after\ drying\ (g) - weight\ of\ filter\ (g)}{10\ g} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous; but not tissues.

11.2.2.1 Weigh 5-10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at 110 ±5°C, and cool in a dessicator.

11.2.2.3 Calculate percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying}{weight\ of\ sample\ aliquot\ before\ drying} \times 100$$

11.3 Determination of Particle Size

11.3.1 Spread the dried sample from Section 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of Aqueous Samples Containing 1% Suspended Solids or Less

11.4.1 Aqueous samples visibly absent particles are prepared per the procedure below and extracted directly using the separatory funnel or SPE techniques in Sections 12.1 or 12.2, respectively. Aqueous samples containing visible particles and one percent suspended solids or less are prepared using the procedure below and extracted using either the SPE technique in Section 12.2 or further prepared using the filtration procedure in Section 11.4.3. The filtration procedure is followed by SDS extraction of the filter and particles (Section 12.3) and separatory funnel extraction of the filtrate (Section 12.1). The SPE procedure is followed by SDS extraction of the filter and disk.

11.4.2 Preparation of sample and QC aliquots

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to ±1 g.

11.4.2.2 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for one to two hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0 L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into both reagent water aliquots. One of these aliquots will serve as the method blank.

11.4.2.5 Spike 1.0 mL of the PAR standard (Section 7.14) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.5).

11.4.2.6 If SPE is to be used, add 5 mL of methanol to the sample, cap and shake the sample to mix thoroughly, and proceed to Section 12.2 for extraction. If SPE is not to be used, and the sample is visibly absent particles, proceed to Section 12.1 for extraction. If SPE is not to be used and the sample contains visible particles, proceed to the following section for filtration of particles.

11.4.3 Filtration of particles

11.4.3.1 Assemble a Buchner funnel (Section 6.5.5) on top of a clean filtration flask. Apply vacuum to the flask, and pour the entire contents of the sample bottle through a glass-fiber filter (Section 6.5.6) in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.4.3.2 Rinse the sample bottle twice with approximately 5 mL portions of reagent water to transfer any remaining particles onto the filter.

11.4.3.3 Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.4.3.4 Weigh the empty sample bottle to ±1 g. Determine the weight of the sample by difference. Save the bottle for further use.

11.4.3.5 Extract the filtrate using the separatory funnel procedure in Section 12.1.

11.4.3.6 Extract the filter containing the particles using the SDS procedure in Section 12.3.

11.5 Preparation of Samples Containing Greater Than 1% Solids

11.5.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar.

11.5.2 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into the sample.

11.5.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, weigh two 10 g aliquots of the appropriate reference matrix (Section 7.6) into clean beakers or glass jars.

11.5.4 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into each reference matrix aliquot. One aliquot will serve as the method blank. Spike 1.0 mL of the PAR standard (Section 7.14) into the other reference matrix aliquot. This aliquot will serve as the OPR (Section 15.5).

11.5.5 Stir or tumble and equilibrate the aliquots for one to two hours.

11.5.6 Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

11.5.7 If particles >1mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).

11.5.8 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.

11.6 Multiphase Samples

11.6.1 Using the percent solids determined in Section 11.2.1 or 11.2.2, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.

11.6.2 Pressure filter the amount of sample determined in Section 11.6.1 through Whatman GF/D glass-fiber filter paper (Section 6.5.3). Pressure filter the blank and OPR aliquots through GF/D papers also. If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration.

11.6.3 Discard any aqueous phase (if present). Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample (Section 11.6.1) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.5).

11.6.4 If particles >1mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced particles using the SDS procedure in Section 12.3. If particles >1mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

11.7 Sample grinding, homogenization, or blending—Samples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.

11.7.1 Each size-reducing preparation procedure on each matrix shall be verified by running the tests in Section 9.2 before the procedure is employed routinely.

11.7.2 The grinding, homogenization, or blending procedures shall be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.7.3 Grinding—Certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Section 11.5.7 or 11.6.4 in a clean grinder. Do not allow the sample temperature

to exceed 50°C. Grind the blank and reference matrix aliquots using a clean grinder.

11.7.4 Homogenization or blending—Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the particles or filter from Section 11.5.7 or 11.6.4 for the sample, blank, and OPR aliquots.

11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.

11.8 Fish and Other Tissues—Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish–skin on, whole fish–skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.

11.8.1 Homogenization

11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.

11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extraction of a second aliquot of the same homogenized sample, if re-analysis is required. When whole fish analysis is necessary, the entire fish is homogenized.

11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.

11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400-500 mL beaker. For the alternate HCl digestion/extraction, transfer the tissue to a clean, tared 500-600 mL wide-mouth bottle. Record the weight to the nearest 10 mg.

11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-lined lid. Seal the jar and store the tissue at <-10°C. Return any tissue that was not homogenized to its original container and store at <-10°C.

11.8.2 QC aliquots

11.8.2.1 Prepare a method blank by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a 400-500 mL beaker. For the alternate HCl digestion/extraction, add the reference matrix to a 500-600 mL wide-mouth bottle. Record the weight to the nearest 10 mg.

11.8.2.2 Prepare a precision and recovery aliquot by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400-500 mL beaker or wide-mouth bottle, depending on the extraction procedure to be used. Record the weight to the nearest 10 mg. If the initial precision and recovery test is to be performed, use four aliquots; if the ongoing precision and recovery test is to be performed, use a single aliquot.

11.8.3 Spiking

11.8.3.1 Spike 1.0 mL of the labeled compound spiking solution (Section 7.10.3) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the PAR standard (Section 7.14) into the OPR aliquot.

11.8.4 Extract the aliquots using the procedures in Section 12.4.

12.0 Extraction and Concentration

Extraction procedures include separatory funnel (Section 12.1) and solid phase (Section 12.2) for aqueous liquids; Soxhlet/Dean-Stark (Section 12.3) for solids, filters, and SPE disks; and Soxhlet extraction (Section 12.4.1) and HCl digestion (Section 12.4.2) for tissues. Acid/base back-extraction (Section 12.5) is used for initial cleanup of extracts.

Macro-concentration procedures include rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish (K-D) evaporation (Section 12.6.3). Micro-concentration uses nitrogen blowdown (Section 12.7).

12.1 Separatory funnel extraction of filtrates and of aqueous samples visibly absent particles.

12.1.1 Pour the spiked sample (Section 11.4.2.2) or filtrate (Section 11.4.3.5) into a 2 L separatory funnel. Rinse the bottle or flask twice with 5 mL of reagent water and add these rinses to the separatory funnel.

12.1.2 Add 60 mL methylene chloride to the empty sample bottle (Section 12.1.1), seal, and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms and is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation (see note below). Drain the methylene chloride extract through a solvent-rinsed glass funnel approximately one-half full of granular

anhydrous sodium sulfate (Section 7.2.1) supported on clean glass-fiber paper into a solvent-rinsed concentration device (Section 12.6).

NOTE: *If an emulsion forms, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase or other extraction techniques may be used to prevent emulsion formation. Any alternative technique is acceptable so long as the requirements in Section 9 are met.*

Experience with aqueous samples high in dissolved organic materials (e.g., paper mill effluents) has shown that acidification of the sample prior to extraction may reduce the formation of emulsions. Paper industry methods suggest that the addition of up to 400 mL of ethanol to a 1 L effluent sample may also reduce emulsion formation. However, studies by EPA suggest that the effect may be a result of sample dilution, and that the addition of reagent water may serve the same function. Mechanical techniques may still be necessary to complete the phase separation. If either acidification or addition of ethanol is utilized, the laboratory must perform the startup tests described in Section 9.2 using the same techniques.

12.1.3 Extract the water sample two more times with 60 mL portions of methylene chloride. Drain each portion through the sodium sulfate into the concentrator. After the third extraction, rinse the separatory funnel with at least 20 mL of methylene chloride, and drain this rinse through the sodium sulfate into the concentrator. Repeat this rinse at least twice. Set aside the funnel with sodium sulfate if the extract is to be combined with the extract from the particles.

12.1.4 Concentrate the extract using one of the macro-concentration procedures in Section 12.6.

12.1.4.1 If the extract is from a sample visibly absent particles (Section 11.1.2.1), adjust the final volume of the concentrated extract to approximately 10 mL with hexane, transfer to a 250 mL separatory funnel, and back-extract using the procedure in Section 12.5.

12.1.4.2 If the extract is from the aqueous filtrate (Section 11.4.3.5), set aside the concentration apparatus for addition of the SDS extract from the particles (Section 12.3.9.1.2).

12.2 SPE of Samples Containing Less Than 1% Solids (References 19-20)

12.2.1 Disk preparation

12.2.1.1 Place an SPE disk on the base of the filter holder (Figure 4) and wet with toluene. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with toluene and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1 L glass reservoir and the vacuum filtration flask.

12.2.1.2 Rinse the sides of the filtration flask with approx 15 mL of toluene using a squeeze bottle or syringe. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the toluene through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

12.2.1.3 Re-wet the filter/disk with approximately 15 mL of methanol, allowing the filter/disk to soak for approximately one minute. Pull the methanol through the filter/disk using the vacuum, but retain a layer of methanol approximately 1 mm thick on the filter. Do not allow the disk to go dry from this point until the end of the extraction.

12.2.1.4 Rinse the filter/disk with two 50-mL portions of reagent water by adding the water to the reservoir and pulling most through, leaving a layer of water on the surface of the filter.

12.2.2 Extraction

12.2.2.1 Pour the spiked sample (Section 11.4.2.2), blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into the reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10 minutes. For samples containing a high concentration of particles (suspended solids), filtration times may be eight hours or longer.

12.2.2.2 Before all of the sample has been pulled through the filter/disk, rinse the sample bottle with approximately 50 mL of reagent water to remove any solids, and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all visible solids are removed.

12.2.2.3 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.

12.2.2.4 Allow the filter/disk to dry, then remove the filter and disk and place in a glass Petri dish. Extract the filter and disk per Section 12.3.

12.3 SDS Extraction of Samples Containing Particles, and of Filters and/or Disks

12.3.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2).

NOTE: *Do not disturb the silica layer throughout the extraction process.*

12.3.2 Place the thimble in a clean extractor. Place 30-40 mL of toluene in the receiver and 200-250 mL of toluene in the flask.

12.3.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, one to two drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of three hours.

12.3.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

12.3.5 Load the wet sample, filter, and/or disk from Section 11.4.3.6, 11.5.8, 11.6.4, 11.7.3, 11.7.4, or 12.2.2.4 and any nonaqueous liquid from Section 11.6.3 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.

12.3.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of toluene to the receiver and reflux flask. Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.3.7 Drain the water from the receiver at one to two hours and eight to nine hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

12.3.8 Remove the distilling flask. Drain the water from the Dean-Stark receiver and add any toluene in the receiver to the extract in the flask.

12.3.9 Concentrate the extract using one of the macro-concentration procedures in Section 12.6 per the following:

12.3.9.1 Extracts from the particles in an aqueous sample containing less than 1% solids (Section 11.4.3.6).

12.3.9.1.1 Concentrate the extract to approximately 5 mL using the rotary evaporator or heating mantle procedures in Section 12.6.1 or 12.6.2.

12.3.9.1.2 Quantitatively transfer the extract through the sodium sulfate (Section 12.1.3) into the apparatus that was set aside (Section 12.1.4.2) and reconcentrate to the level of the toluene.

12.3.9.1.3 Adjust to approximately 10 mL with hexane, transfer to a 250 mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.3.9.2 Extracts from particles (Sections 11.5 through 11.6) or from the SPE filter and disk (Section 12.2.2.4)—Concentrate to approximately 10 mL using the rotary evaporator or heating mantle (Section 12.6.1

or 12.6.2), transfer to a 250 mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.4 Extraction of Tissue—Two procedures are provided for tissue extraction.

12.4.1 Soxhlet extraction (Reference 21)

12.4.1.1 Add 30-40 g of powdered anhydrous sodium sulfate to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with aluminum foil and allow to equilibrate for 12-24 hours. Remix prior to extraction to prevent clumping.

12.4.1.2 Assemble and pre-extract the Soxhlet apparatus per Sections 12.3.1 through 12.3.4, except use the methylene chloride:hexane (1:1) mixture for the pre-extraction and rinsing and omit the quartz sand. The Dean-Stark moisture trap may also be omitted, if desired.

12.4.1.3 Reassemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride:hexane to the reflux flask.

12.4.1.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.

12.4.1.5 Rinse the beaker with several portions of solvent mixture and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18-24 hours.

12.4.1.6 After extraction, cool and disassemble the apparatus.

12.4.1.7 Quantitatively transfer the extract to a macro-concentration device (Section 12.6), and concentrate to near dryness. Set aside the concentration apparatus for re-use.

12.4.1.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.1.9 Percent lipid determination—The lipid content is determined by extraction of tissue with the same solvent system (methylene chloride:hexane) that was used in EPA's National Dioxin Study (Reference 22) so that lipid contents are consistent with that study.

12.4.1.9.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.

12.4.1.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.7.1) or bottle for the acidified silica gel batch cleanup (Section 13.7.2), retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.1.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$\textit{Percent lipid} = \frac{\textit{Weight of residue (g)}}{\textit{Weight of tissue (g)}} \times 100$$

12.4.1.9.4 It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.

12.4.2 HCl digestion/extraction and concentration (References 23-26)

12.4.2.1 Add 200 mL of 6 N HCl and 200 mL of methylene chloride:hexane (1:1) to the sample and QC aliquots (Section 11.8.4).

12.4.2.2 Cap and shake each bottle one to three times. Loosen the cap in a hood to vent excess pressure. Shake each bottle for 10-30 seconds and vent.

12.4.2.3 Tightly cap and place on shaker. Adjust the shaker action and speed so that the acid, solvent, and tissue are in constant motion. However, take care to avoid such violent action that the bottle may be dislodged from the shaker. Shake for 12-24 hours.

12.4.2.4 After digestion, remove the bottles from the shaker. Allow the bottles to stand so that the solvent and acid layers separate.

12.4.2.5 Decant the solvent through a glass funnel with glass-fiber filter (Sections 6.5.2 through 6.5.3) containing approximately 10 g of granular anhydrous sodium sulfate (Section 7.2.1) into a macro-concentration apparatus (Section 12.6). Rinse the contents of the bottle with two 25 mL portions of hexane and pour through the sodium sulfate into the apparatus.

12.4.2.6 Concentrate the solvent to near dryness using a macro-concentration procedure (Section 12.6).

12.4.2.7 Complete the removal of the solvent using the nitrogen blowdown apparatus (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.2.8 Percent lipid determination—The lipid content is determined in the same solvent system [methylene chloride:hexane (1:1)] that was used in EPA's National Dioxin Study (Reference 22) so that lipid contents are consistent with that study.

12.4.2.8.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.

12.4.2.8.2 Transfer the residue/hexane to the narrow-mouth 100-200 mL bottle retaining the boiling chips in the receiver. Use several rinses to assure that all material is transferred, to a maximum hexane volume of approximately 70 mL. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.2.8.3 Calculate the percent lipid per Section 12.4.1.9.3. It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.

12.4.2.9 Clean up the extract per Section 13.7.3.

12.5 Back-Extraction with Base and Acid

12.5.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the separatory funnels containing the sample and QC extracts from Section 12.1.4.1, 12.3.9.1.3, or 12.3.9.2.

12.5.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1). Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the CDDs/CDFs. Stronger potassium hydroxide solutions may be employed for back-extraction, provided that the laboratory meets the specifications for labeled compound recovery and demonstrates acceptable performance using the procedure in Section 9.2.

12.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with base. Discard the aqueous layer.

12.5.4 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.5.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.

12.5.6 Pour each extract through a drying column containing 7-10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30-50 mL of solvent, and pour through the drying column. Collect each extract in a round-bottom flask. Re-concentrate the sample and QC aliquots per Sections 12.6 through 12.7, and clean up the samples and QC aliquots per Section 13.

12.6 Macro-Concentration—Extracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danish apparatus.

12.6.1 Rotary evaporation—Concentrate the extracts in separate round-bottom flasks.

12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2-3 mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.

12.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15-20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

NOTE: *If the rate of concentration is too fast, analyte loss may occur.*

12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

12.6.1.5 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.2 Heating mantle—Concentrate the extracts in separate round-bottom flasks.

12.6.2.1 Add one or two clean boiling chips to the round-bottom flask, and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottom flask in a heating mantle, and apply heat as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottom flask from the heating mantle and allow the solvent to drain and cool for at least 10 minutes.

Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.

12.6.2.3 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.3 Kuderna-Danish (K-D)—Concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-D technique unless a water bath fed by a steam generator is used.

12.6.3.1 Add one to two clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of solvent. A 5 mL syringe is recommended for this operation.

12.6.3.4 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

12.6.3.7 Proceed to 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4 Preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4.1 For back-extraction (Section 12.5), transfer the extract to a 250 mL separatory funnel. Rinse the concentration vessel with small

portions of hexane, adjust the hexane volume in the separatory funnel to 10-20 mL, and proceed to back-extraction (Section 12.5).

12.6.4.2 For determination of the weight of residue in the extract, or for clean-up procedures other than back-extraction, transfer the extract to a blowdown vial using two to three rinses of solvent. Proceed with micro-concentration and solvent exchange (Section 12.7).

12.7 Micro-Concentration and Solvent Exchange

12.7.1 Extracts to be subjected to GPC or HPLC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, alumina, carbon, and/or Florisil are exchanged into hexane.

12.7.2 Transfer the vial containing the sample extract to a nitrogen blowdown device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

NOTE: *A large vortex in the solvent may cause analyte loss.*

12.7.3 Lower the vial into a 45°C water bath and continue concentrating.

12.7.3.1 If the extract is to be concentrated to dryness for weight determination (Sections 12.4.1.8, 12.4.2.7, and 13.7.1.4), blow dry until a constant weight is obtained.

12.7.3.2 If the extract is to be concentrated for injection into the GC/MS or the solvent is to be exchanged for extract cleanup, proceed as follows:

12.7.4 When the volume of the liquid is approximately 100 µL, add 2-3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other cleanups) and continue concentration to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, further concentrate the extract to 30 µL. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.6, respectively).

12.7.6 If the extract is to be cleaned up by column chromatography (alumina, silica gel, Carbopak/Celite, or Florisil), bring the final volume to 1.0 mL with hexane. Proceed with column cleanups (Sections 13.3 through 13.5 and 13.8).

12.7.7 If the extract is to be concentrated for injection into the GC/MS (Section 14), quantitatively transfer the extract to a 0.3 mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100 µL. Add 10 µL of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for

GC/MS analysis. If GC/MS analysis will not be performed on the same day, store the vial at <-10°C.

13.0 Extract Cleanup

13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the analyst must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the cleanup procedures may be optimized for isolation of these two compounds.

13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids).

13.1.2 Acid, neutral, and basic silica gel (Section 13.3), alumina (Section 13.4), and Florisil (Section 13.8) are used to remove nonpolar and polar interferences. Alumina and Florisil are used to remove chlorodiphenyl ethers.

13.1.3 Carbopak/Celite (Section 13.5) is used to remove nonpolar interferences.

13.1.4 HPLC (Section 13.6) is used to provide specificity for the 2,3,7,8-substituted and other CDD and CDF isomers.

13.1.5 The anthropogenic isolation column (Section 13.7.1), acidified silica gel batch adsorption procedure (Section 13.7.2), and sulfuric acid and base back-extraction (Section 13.7.3) are used for removal of lipids from tissue samples.

13.2 Gel Permeation Chromatography (GPC)

13.2.1 Column packing

13.2.1.1 Place 70-75 g of SX-3 Bio-beads (Section 6.7.1.1) in a 400-500 mL beaker.

13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).

13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5-5.5 mL/minute prior to connecting the column to the detector.

13.2.1.4 After purging the column with solvent for one to two hours, adjust the column head pressure to 7-10 psig and purge for four to five hours to remove air. Maintain a head pressure of 7-10 psig. Connect the column to the detector (Section 6.7.1.4).

13.2.2 Column calibration

13.2.2.1 Load 5 mL of the calibration solution (Section 7.4) into the sample loop.

13.2.2.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethyl hexyl)phthalate, pentachlorophenol, perylene, and sulfur.

13.2.2.3 Set the "dump time" to allow >85% removal of the corn oil and >85% collection of the phthalate.

13.2.2.4 Set the "collect time" to the peak minimum between perylene and sulfur.

13.2.2.5 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated GPC system.

13.2.3 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5 mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50 µL aliquot.

13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove the particles. Load the 5.0 mL extract onto the column.

13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400-500 mL beaker.

13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

13.2.3.4 If a particularly dirty extract is encountered, a 5.0 mL methylene chloride blank shall be run through the system to check for carry-over.

13.2.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the GC/MS.

13.3 Silica Gel Cleanup

13.3.1 Place a glass-wool plug in a 15 mm ID chromatography column (Section 6.7.4.2). Pack the column bottom to top with: 1 g silica gel (Section 7.5.1.1), 4 g basic silica gel (Section 7.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.5.1.2), 2 g silica gel,

and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

13.3.2 Pre-elute the column with 50-100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

13.3.4 Rinse the receiver twice with 1 mL portions of hexane, and apply separately to the column. Elute the CDDs/CDFs with 100 mL hexane, and collect the eluate.

13.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.3.6 For extracts of samples known to contain large quantities of other organic compounds (such as paper mill effluents), it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 44% w/w (7.9 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used.

NOTE: *The use of stronger acid silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of CDDs/CDFs. Increasing the strengths of the acid and basic silica gel may also require different volumes of hexane than those specified above to elute the analytes off the column. Therefore, the performance of the method after such modifications must be verified by the procedure in Section 9.2.*

13.4 Alumina Cleanup

13.4.1 Place a glass-wool plug in a 15 mm ID chromatography column (Section 6.7.4.2).

13.4.2 If using acid alumina, pack the column by adding 6 g acid alumina (Section 7.5.2.1). If using basic alumina, substitute 6 g basic alumina (Section 7.5.2.2). Tap the column to settle the adsorbents.

13.4.3 Pre-elute the column with 50-100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the alumina.

13.4.4 Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.4.5 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the alumina.

13.4.6 Rinse the receiver twice with 1 mL portions of hexane and apply separately to the column. Elute the interfering compounds with 100 mL hexane and discard the eluate.

13.4.7 The choice of eluting solvents will depend on the choice of alumina (acid or basic) made in Section 13.4.2.

13.4.7.1 If using acid alumina, elute the CDDs/CDFs from the column with 20 mL methylene chloride:hexane (20:80 v/v). Collect the eluate.

13.4.7.2 If using basic alumina, elute the CDDs/CDFs from the column with 20 mL methylene chloride:hexane (50:50 v/v). Collect the eluate.

13.4.8 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.5 Carbon Column

13.5.1 Cut both ends from a 10 mL disposable serological pipet (Section 6.7.3.2) to produce a 10 cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 0.55 g of Carbopak/Celite (Section 7.5.3.3) to form an adsorbent bed approximately 2 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

13.5.2 Pre-elute the column with 5 mL of toluene followed by 2 mL of methylene chloride: methanol:toluene (15:4:1 v/v), 1 mL of methylene chloride:cyclohexane (1:1 v/v), and 5 mL of hexane. If the flow rate of eluate exceeds 0.5 mL/minute, discard the column.

13.5.3 When the solvent is within 1 mm of the column packing, apply the sample extract to the column. Rinse the sample container twice with 1 mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.

13.5.4 Elute the interfering compounds with two 3 mL portions of hexane, 2 mL of methylene chloride:cyclohexane (1:1 v/v), and 2 mL of methylene chloride:methanol:toluene (15:4:1 v/v). Discard the eluate.

13.5.5 Invert the column, and elute the CDDs/CDFs with 20 mL of toluene. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.5.6 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.6 HPLC (Reference 6)

13.6.1 Column calibration

13.6.1.1 Prepare a calibration standard containing the 2,3,7,8-substituted isomers and/or other isomers of interest at a concentration of approximately 500 pg/µL in methylene chloride.

13.6.1.2 Inject 30 µL of the calibration solution into the HPLC and record the signal from the detector. Collect the eluant for reuse. The elution order will be the tetra- through octa-isomers.

13.6.1.3 Establish the collection time for the tetra-isomers and for the other isomers of interest. Following calibration, flush the injection system with copious quantities of methylene chloride, including a minimum of five 50 µL injections while the detector is monitored, to ensure that residual CDDs/CDFs are removed from the system.

13.6.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the CDDs/CDFs from the calibration standard (Section 13.6.1.1) is 75-125% compared to the calibration (Section 13.6.1.2). If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated system.

13.6.2 Extract cleanup—HPLC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 30 µL of extract. If the extract cannot be concentrated to less than 30 µL, it is split into fractions and the fractions are combined after elution from the column.

13.6.2.1 Rinse the sides of the vial twice with 30 µL of methylene chloride and reduce to 30 µL with the evaporation apparatus (Section 12.7).

13.6.2.2 Inject the 30 µL extract into the HPLC.

13.6.2.3 Elute the extract using the calibration data determined in Section 13.6.1. Collect the fraction(s) in a clean 20 mL concentrator tube containing 5 mL of hexane:acetone (1:1 v/v).

13.6.2.4 If an extract containing greater than 100 ng/mL of total CDD or CDF is encountered, a 30 µL methylene chloride blank shall be run through the system to check for carry-over.

13.6.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/MS.

13.7 Cleanup of Tissue Lipids—Lipids are removed from the Soxhlet extract using either the anthropogenic isolation column (Section 13.7.1) or acidified silica gel (Section 13.7.2), or are removed from the HCl digested extract using sulfuric acid and base back-extraction (Section 13.7.3).

13.7.1 Anthropogenic isolation column (References 22 and 27)—Used for removal of lipids from the Soxhlet/SDS extraction (Section 12.4.1).

13.7.1.1 Prepare the column as given in Section 7.5.4.

13.7.1.2 Pre-elute the column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

13.7.1.3 Load the sample and rinses (Section 12.4.1.9.2) onto the column by draining each portion to the top of the bed. Elute the CDDs/CDFs from the column into the apparatus used for concentration (Section 12.4.1.7) using 200 mL of hexane.

13.7.1.4 Concentrate the cleaned up extract (Sections 12.6 through 12.7) to constant weight per Section 12.7.3.1. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.

13.7.1.5 Redissolve the extract in a solvent suitable for the additional cleanups to be used (Sections 13.2 through 13.6 and 13.8).

13.7.1.6 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.

13.7.1.7 Clean up the extract using the procedures in Sections 13.2 through 13.6 and 13.8. Alumina (Section 13.4) or Florisil (Section 13.8) and carbon (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.1.8 Following cleanup, concentrate the extract to 10 µL as described in Section 12.7 and proceed with the analysis in Section 14.

13.7.2 Acidified silica gel (Reference 28)—Procedure alternate to the anthropogenic isolation column (Section 13.7.1) that is used for removal of lipids from the Soxhlet/SDS extraction (Section 12.4.1).

13.7.2.1 Adjust the volume of hexane in the bottle (Section 12.4.1.9.2) to approximately 200 mL.

13.7.2.2 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.

13.7.2.3 Drop the stirring bar into the bottle, place the bottle on the stirring plate, and begin stirring.

13.7.2.4 Add 30-100 g of acid silica gel (Section 7.5.1.2) to the bottle while stirring, keeping the silica gel in motion. Stir for two to three hours.

NOTE: *30 grams of silica gel should be adequate for most samples and will minimize contamination from this source.*

13.7.2.5 After stirring, pour the extract through approximately 10 g of granular anhydrous sodium sulfate (Section 7.2.1) contained in a funnel with glass-fiber filter into a macro contration device (Section 12.6). Rinse the bottle and sodium sulfate with hexane to complete the transfer.

13.7.2.6 Concentrate the extract per Sections 12.6 through 12.7 and clean up the extract using the procedures in Sections 13.2 through 13.6 and 13.8. Alumina (Section 13.4) or Florisil (Section 13.8) and carbon (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.3 Sulfuric acid and base back-extraction—Used with HCl digested extracts (Section 12.4.2).

13.7.3.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent (Section 12.4.2.8.2).

13.7.3.2 Add 10 mL of concentrated sulfuric acid to the bottle. Immediately cap and shake one to three times. Loosen cap in a hood to vent excess pressure. Cap and shake the bottle so that the residue/solvent is exposed to the acid for a total time of approximately 45 seconds.

13.7.3.3 Decant the hexane into a 250 mL separatory funnel making sure that no acid is transferred. Complete the quantitative transfer with several hexane rinses.

13.7.3.4 Back extract the solvent/residue with 50 mL of potassium hydroxide solution per Section 12.5.2, followed by two reagent water rinses.

13.7.3.5 Drain the extract through a filter funnel containing approximately 10 g of granular anhydrous sodium sulfate in a glass-fiber filter into a macro concentration device (Section 12.6).

13.7.3.6 Concentrate the cleaned up extract to a volume suitable for the additional cleanups given in Sections 13.2 through 13.6 and 13.8. Gel permeation chromatography (Section 13.2), alumina (Section 13.4) or Florisil (Section 13.8), and Carbopak/Celite (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.3.7 Following cleanup, concentrate the extract to 10 µL as described in Section 12.7 and proceed with analysis per Section 14.

13.8 Florisil Cleanup (Reference 29)

13.8.1 Pre-elute the activated Florisil column (Section 7.5.3) with 10 mL of methylene chloride followed by 10 mL of hexane:methylene chloride (98:2 v/v) and discard the solvents.

13.8.2 When the solvent is within 1 mm of the packing, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1 mL portions of hexane and apply to the column.

13.8.3 Elute the interfering compounds with 20 mL of hexane:methylene chloride (98:2) and discard the eluate.

13.8.4 Elute the CDDs/CDFs with 35 mL of methylene chloride and collect the eluate. Concentrate the eluate per Sections 12.6 through 12.7 for further cleanup or for injection into the HPLC or GC/MS.

14.0 HRGC/HRMS Analysis

14.1 Establish the operating conditions given in Section 10.1.

14.2 Add 10 µL of the appropriate internal standard solution (Section 7.12) to the sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more instrument internal standard solution. Rather, bring the extract back to its previous volume (e.g., 19 µL) with pure nonane only (18 µL if 2 µL injections are used).

14.3 Inject 1.0 µL or 2.0 µL of the concentrated extract containing the internal standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10). Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the OCDD and OCDF have eluted. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, stop data collection after elution of these compounds. Return the column to the initial temperature for analysis of the next extract or standard.

15.0 System and Laboratory Performance

15.1 At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all CDDs/CDFs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.13 and Table 4) and the isomer specificity test standards (Section 7.15 and Table 5) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.

15.2 MS Resolution—A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour shift according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

15.3 Calibration Verification

15.3.1 Inject the VER standard using the procedure in Section 14.

15.3.2 The m/z abundance ratios for all CDDs/CDFs shall be within the limits in Table 9; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

15.3.3 The peaks representing each CDD/CDF and labeled compound in the VER standard must be present with S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

15.3.4 Compute the concentration of each CDD/CDF compound by isotope dilution (Section 10.5) for those compounds that have labeled analogs (Table 1). Compute the concentration of the labeled compounds by the internal standard method (Section 10.6). These concentrations are computed based on the calibration data in Section 10.

15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare the concentration to the limit in Table 6a. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10).

15.4 Retention Times and GC Resolution

15.4.1 Retention times

15.4.1.1 Absolute—The absolute retention times of the $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD GCMS internal standards in the verification test (Section 15.3) shall be within ±15 seconds of the retention times obtained during calibration (Sections 10.2.1 and 10.2.4).

15.4.1.2 Relative—The relative retention times of CDDs/CDFs and labeled compounds in the verification test (Section 15.3) shall be within the limits given in Table 2.

15.4.2 GC resolution

15.4.2.1 Inject the isomer specificity standards (Section 7.15) on their respective columns.

15.4.2.2 The valley height between 2,3,7,8-TCDD and the other tetra-dioxin isomers at m/z 319.8965, and between 2,3,7,8-TCDF and the other tetra-furan isomers at m/z 303.9016 shall not exceed 25% on their respective columns (Figures 6 and 7).

15.4.3 If the absolute retention time of any compound is not within the limits specified or if the 2,3,7,8-isomers are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.

15.5 Ongoing Precision and Recovery

15.5.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.4, 11.6.2, 11.7.4, or 11.8.3.2) prior to analysis of samples from the same batch.

15.5.2 Compute the concentration of each CDD/CDF by isotope dilution for those compounds that have labeled analogs (Section 10.5). Compute the concentration of 1,2,3,7,8,9-HxCDD, OCDF, and each labeled compound by the internal standard method (Section 10.6).

15.5.3 For each CDD/CDF and labeled compound, compare the concentration to the OPR limits given in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare the concentration to the limits in Table 6a. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.5).

15.5.4 Add results that pass the specifications in Section 15.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each CDD/CDF in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (S_R). Express the accuracy as a recovery interval from $R-2S_R$ to $R+2S_R$. For example, if R = 95% and S_R = 5%, the accuracy is 85-105%.

15.6 Blank—Analyze the method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

16.0 Qualitative Determination

A CDD, CDF, or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

16.1 The signals for the two exact m/z's in Table 8 must be present and must maximize within the same two seconds.

16.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each CDD or CDF detected in a sample extract, and greater than or equal to 10 for all CDDs/CDFs in the calibration standard (Sections 10.2.3 and 15.3.3).

16.3 The ratio of the integrated areas of the two exact m/z's specified in Table 8 must be within the limit in Table 9, or within ±10% of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

16.4 The relative retention time of the peak for a 2,3,7,8-substituted CDD or CDF must be within the limit in Table 2. The retention time of peaks representing non-2,3,7,8-substituted CDDs/CDFs must be within the retention time windows established in Section 10.3.

16.5 Confirmatory Analysis—Isomer specificity for 2,3,7,8-TCDF cannot be achieved on the DB-5 column. Therefore, any sample in which 2,3,7,8-TCDF is identified by analysis on a DB-5 column must have a confirmatory analysis performed on a DB-225, SP-2330, or equivalent GC column. The operating conditions in Section 10.1.1 may be adjusted to optimize the analysis on the second GC column, but the GC/MS must meet the mass resolution and calibration specifications in Section 10.

16.6 If the criteria for identification in Sections 16.1 through16.5 are not met, the CDD or CDF has not been identified and the results may not be reported for regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

17.0 Quantitative Determination

17.1 Isotope Dilution Quantitation—By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the CDD/CDF can be made because the CDD/CDF and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative response (RR) values are used in conjunction with the initial calibration data described in Section 10.5 to determine concentrations directly, so long as labeled compound spiking levels are constant, using the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

where,

C_{ex} = The concentration of the CDD/CDF in the extract, and the other terms are as defined in Section 10.5.2.

17.1.1 Because of a potential interference, the labeled analog of OCDF is not added to the sample. Therefore, OCDF is quantitated against labeled OCDD. As a result, the concentration of OCDF is corrected for the recovery of the labeled OCDD. In instances where OCDD and OCDF behave differently during sample extraction, concentration, and cleanup procedures, this may decrease the accuracy of the OCDF results. However, given the low toxicity of this compound relative to the other dioxins and furans, the potential decrease in accuracy is not considered significant.

17.1.2 Because $^{13}C_{12}$-1,2,3,7,8,9-HxCDD is used as an instrument internal standard (i.e., not added before extraction of the sample), it cannot be used to quantitate the 1,2,3,7,8,9-HxCDD by strict isotope dilution procedures. Therefore, 1,2,3,7,8,9-HxCDD is quantitated using the averaged response of the labeled analogs of the other two 2,3,7,8-substituted HxCDD's: 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. As a result, the concentration of 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other two HxCDD's.

17.1.3 Any peaks representing non-2,3,7,8-substituted CDDs/CDFs are quantitated using an average of the response factors from all of the labeled 2,3,7,8-isomers at the same level of chlorination.

17.2 Internal Standard Quantitation and Labeled Compound Recovery

17.2.1 Compute the concentrations of 1,2,3,7,8,9-HxCDD, OCDF, the ^{13}C-labeled analogs and the ^{37}C-labeled cleanup standard in the extract using the response factors determined from the initial calibration data (Section 10.6) and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ RF}$$

where,

C_{ex} = The concentration of the CDD/CDF in the extract, and the other terms are as defined in Section 10.6.1.

NOTE: *There is only one m/z for the ^{37}Cl-labeled standard.*

17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the ^{13}C-labeled compounds and the^{37} C-labeled cleanup standard using the following equation:

$$Recovery\ (\%) = \frac{Concentration\ found\ (\mu g/mL)}{Concentration\ spiked\ (\mu g/mL)} \times 100$$

17.3 The concentration of a CDD/CDF in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.5.1), as follows:

$$Concentration\ in\ solid\ (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where,

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
W_s = The sample weight (dry weight) in kg.

17.4 The concentration of a CDD/CDF in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4 or 11.5), as follows:

$$\text{Concentration in aqueous phase (pg/L)} = \frac{(C_{ex} \times V_{ex})}{V_s}$$

where,

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
V_s = The sample volume in liters.

17.5 If the SICP area at either quantitation m/z for any compound exceeds the calibration range of the system, a smaller sample aliquot is extracted.

17.5.1 For aqueous samples containing 1% solids or less, dilute 100 mL, 10 mL, etc., of sample to 1 L with reagent water and re-prepare, extract, clean up, and analyze per Sections 11 through 14.

17.5.2 For samples containing greater than 1% solids, extract an amount of sample equal to 1/10, 1/100, etc., of the amount used in Section 11.5.1. Re-prepare, extract, clean up, and analyze per Sections 11 through 14.

17.5.3 If a smaller sample size will not be representative of the entire sample, dilute the sample extract by a factor of 10, adjust the concentration of the instrument internal standard to 100 pg/µL in the extract, and analyze an aliquot of this diluted extract by the internal standard method.

17.6 Results are reported to three significant figures for the CDDs/CDFs and labeled compounds found in all standards, blanks, and samples.

17.6.1 Reporting units and levels

17.6.1.1 Aqueous samples—Report results in pg/L (parts-per-quadrillion).

17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost)—Report results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be corrected.

17.6.1.3 Tissues—Report results in ng/kg of wet tissue, not on the basis of the lipid content of the sample. Report the percent lipid content, so that the data user can calculate the concentration on a lipid basis if desired.

17.6.1.4 Reporting level

17.6.1.4.1 Standards (VER, IPR, OPR) and samples—Report results at or above the minimum level (Table 2). Report results below the minimum level as not detected or as required by the regulatory authority.

17.6.1.4.2 Blanks—Report results above one-third the ML.

17.6.2 Results for CDDs/CDFs in samples that have been diluted are reported at the least dilute level at which the areas at the quantitation m/z's are within the calibration range (Section 17.5).

17.6.3 For CDDs/CDFs having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the method (Section 9.3 and Tables 6, 6a, 7, and 7a).

17.6.4 Additionally, if requested, the total concentration of all isomers in an individual level of chlorination (i.e., total TCDD, total TCDF, total Paced, etc.) may be reported by summing the concentrations of all isomers identified in that level of chlorination, including both 2,3,7,8-substituted and non-2,3,7,8-substituted isomers.

18.0 Analysis of Complex Samples

18.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts will not concentrate to 10 µL (Section 12.7); others may overload the GC column and/or mass spectrometer.

18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to 10 µL after all cleanup procedures have been exhausted.

18.3 Chlorodiphenyl Ethers—If chromatographic peaks are detected at the retention time of any CDDs/CDFs in any of the m/z channels being monitored for the chlorodiphenyl ethers (Table 8), cleanup procedures must be employed until these interferences are removed. Alumina (Section 13.4) and Florisil (Section 13.8) are recommended for removal of chlorodiphenyl ethers.

18.4 Recovery of Labeled Compounds—In most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).

18.4.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 7), a diluted sample shall be analyzed (Section 17.5).

18.4.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.13) shall be analyzed and calibration verified (Section 15.3).

18.4.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.

18.4.4 If the calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the method does not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this method must be employed to resolve the interference. If all cleanup procedures in this method have been employed and labeled compound recovery remains outside of the normal range, extraction and/or cleanup procedures that are beyond this scope of this method will be required to analyze these samples.

19.0 Pollution Prevention

19.1 The solvents used in this method pose little threat to the environment when managed properly. The solvent evaporation techniques used in this method are amenable to solvent recovery, and it is recommended that the laboratory recover solvents wherever feasible.

19.2 Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standards.

20.0 Waste Management

20.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

20.2 Samples containing HCl to pH <2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.

20.3 The CDDs/CDFs decompose above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

20.4 Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the CDDs/CDFs can no longer be detected.

20.5 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better–Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

21.0 Method Performance

Method performance was validated and performance specifications were developed using data from EPA's international interlaboratory validation study (References 30-31) and the

EPA/paper industry Long-Term Variability Study of discharges from the pulp and paper industry (58 FR 66078).

22.0 References

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23.0 Tables and Figures

TABLE 1. CHLORINATED DIBENZO-*P*-DIOXINS AND FURANS DETERMINED BY ISOTOPE DILUTION AND INTERNAL STANDARD HIGH RESOLUTION GAS CHROMATOGRAPHY (HRGC)/HIGH RESOLUTION MASS SPECTROMETRY (HRMS)

CDDs/CDFs [1]	CAS Registry	Labeled analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
		$^{37}Cl_4$-2,3,7,8-TCDD	85508-50-5
Total TCDD	41903-57-5	—	—
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total-TCDF	55722-27-5	—	—
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total-PeCDD	36088-22-9	—	—
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total-PeCDF	30402-15-4	—	—
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total-HxCDD	34465-46-8	—	—
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
Total-HxCDF	55684-94-1	—	—
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total-HpCDD	37871-00-4	—	—
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total-HpCDF	38998-75-3	—	—
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	not used	—

[1] Chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans

TCDD = Tetrachlorodibenzo-*p*-dioxin
PeCDD = Pentachlorodibenzo-*p*-dioxin
HxCDD = Hexachlorodibenzo-*p*-dioxin
HpCDD = Heptachlorodibenzo-*p*-dioxin
OCDD = Octachlorodibenzo-*p*-dioxin

TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran

TABLE 2. RETENTION TIME REFERENCES, QUANTITATION REFERENCES, RELATIVE RETENTION TIMES, AND MINIMUM LEVELS FOR CDDS AND CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum level[1] Water (pg/L; ppq)	Solid (ng/kg; ppt)	Extract (pg/µL; ppb)
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the injection internal standard					
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999–1.003	10	1	0.5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999–1.002	10	1	0.5
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999–1.002	50	5	2.5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999–1.002	50	5	2.5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999–1.002	50	5	2.5
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923–1.103			
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976–1.043			
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989–1.052			
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.425			
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011–1.526			
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.567			
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the injection internal standard					
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999–1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997–1.005	50	5	2.5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999–1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	0.999–1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999–1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	0.998–1.004	50	5	2.5
1,2,3,7,8,9-HxCDD	—[2]	1.000–1.019	50	5	2.5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999–1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999–1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999–1.001	50	5	2.5
OCDF	$^{13}C_{12}$-OCDD	0.999–1.008	100	10	5.0
OCDD	$^{13}C_{12}$-OCDD	0.999–1.001	100	10	5.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944–0.970			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949–0.975			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.047			
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959–1.021			
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.000			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981–1.003			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043–1.085			

TABLE 2. RETENTION TIME REFERENCES, QUANTITATION REFERENCES, RELATIVE RETENTION TIMES, AND MINIMUM LEVELS FOR CDDS AND CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum level[1] Water (pg/L; ppq)	Solid (ng/kg; ppt)	Extract (pg/µL; ppb)
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057–1.151			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086–1.110			
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032–1.311			

[1]The Minimum Level (ML) for each analyte is defined as the level at which the entire analytical system must give a recognizable signal and acceptable calibration point. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

[2]The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

TABLE 3. CONCENTRATION OF STOCK AND SPIKING SOLUTIONS CONTAINING CDDS/CDFS AND LABELED COMPOUNDS

CDD/CDF	Labeled Compound Stock Solution [1] (ng/mL)	Labeled Compound Spiking Solution [2] (ng/mL)	PAR Stock Solution [3] (ng/mL)	PAR Spiking Solution [4] (ng/mL)
2,3,7,8-TCDD	—	—	40	0.8
2,3,7,8-TCDF	—	—	40	0.8
1,2,3,7,8-PeCDD	—	—	200	4
1,2,3,7,8-PeCDF	—	—	200	4
2,3,4,7,8-PeCDF	—	—	200	4
1,2,3,4,7,8-HxCDD	—	—	200	4
1,2,3,6,7,8-HxCDD	—	—	200	4
1,2,3,7,8,9-HxCDD	—	—	200	4
1,2,3,4,7,8-HxCDF	—	—	200	4
1,2,3,6,7,8-HxCDF	—	—	200	4
1,2,3,7,8,9-HxCDF	—	—	200	4
2,3,4,6,7,8-HxCDF	—	—	200	4
1,2,3,4,6,7,8-HpCDD	—	—	200	4
1,2,3,4,6,7,8-HpCDF	—	—	200	4
1,2,3,4,7,8,9-HpCDF	—	—	200	4
OCDD	—	—	400	8
OCDF	—	—	400	8
$^{13}C_{12}$-2,3,7,8-TCDD	100	2	—	—
$^{13}C_{12}$-2,3,7,8-TCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	2	—	—
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	2	—	—
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	2	—	—
$^{13}C_{12}$-OCDD	200	4	—	—

TABLE 3. CONCENTRATION OF STOCK AND SPIKING SOLUTIONS CONTAINING CDDS/CDFS AND LABELED COMPOUNDS

CDD/CDF	Labeled Compound Stock Solution [1] (ng/mL)	Labeled Compound Spiking Solution [2] (ng/mL)	PAR Stock Solution [3] (ng/mL)	PAR Spiking Solution [4] (ng/mL)
	Concentration (ng/mL)			
Cleanup Standard [5]				
$^{37}Cl_4$-2,3,7,8-TCDD	0.8			
Internal Standards [6]				
$^{13}C_{12}$-1,2,3,4-TCDD	200			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	200			

[1] Section 7.10—prepared in nonane and diluted to prepare spiking solution.
[2] Section 7.10.3—prepared in acetone from stock solution daily.
[3] Section 7.9—prepared in nonane and diluted to prepare spiking solution.
[4] Section 7.14—prepared in acetone from stock solution daily.
[5] Section 7.11—prepared in nonane and added to extract prior to cleanup.
[6] Section 7.12—prepared in nonane and added to the concentrated extract immediately prior to injection into the GC (Section 14.2).

TABLE 4. CONCENTRATION OF CDDS/CDFS IN CALIBRATION AND CALIBRATION VERIFICATION SOLUTIONS [1] (section 15.3)

	CDD/CDF	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 5. GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION 7.15)

DB-5 Column GC Retention-Time Window Defining Solution		
CDD/CDF	**First Eluted**	**Last Eluted**
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 Column TCDD Specificity Test Standard

1,2,3,7+1,2,3,8-TCDD
2,3,7,8-TCDD
1,2,3,9-TCDD

DB-225 Column TCDF Isomer Specificity Test Standard

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	6.7–15.8	7.8–12.9
2,3,7,8-TCDF	10	2.0	8.7–13.7	7.5–15.8	8.4–12.0
1,2,3,7,8-PeCDD	50	7.5	38–66	35–71	39–65
1,2,3,7,8-PeCDF	50	7.5	43–62	40–67	41–60
2,3,4,7,8-PeCDF	50	8.6	36–75	34–80	41–61
1,2,3,4,7,8-HxCDD	50	9.4	39–76	35–82	39–64
1,2,3,6,7,8-HxCDD	50	7.7	42–62	38–67	39–64
1,2,3,7,8,9-HxCDD	50	11.1	37–71	32–81	41–61
1,2,3,4,7,8-HxCDF	50	8.7	41–59	36–67	45–56
1,2,3,6,7,8-HxCDF	50	6.7	46–60	42–65	44–57
1,2,3,7,8,9-HxCDF	50	6.4	42–61	39–65	45–56
2,3,4,6,7,8-HxCDF	50	7.4	37–74	35–78	44–57
1,2,3,4,6,7,8-HpCDD	50	7.7	38–65	35–70	43–58
1,2,3,4,6,7,8-HpCDF	50	6.3	45–56	41–61	45–55
1,2,3,4,7,8,9-HpCDF	50	8.1	43–63	39–69	43–58
OCDD	100	19	89–127	78–144	79–126
OCDF	100	27	74–146	63–170	63–159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	20–175	82–121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31–113	22–152	71–140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27–184	21–227	62–160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27–156	21–192	76–130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16–279	13–328	77–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29–147	21–193	85–117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34–122	25–163	85–118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27–152	19–202	76–131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30–122	21–159	70–143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24–157	17–205	74–135
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	37	29–136	22–176	73–137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34–129	26–166	72–138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32–110	21–158	78–129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28–141	20–186	77–129
$^{13}C_{12}$-OCDD	200	95	41–276	26–397	96–415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9–15.4	3.1–19.1	7.9–12.7

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 6A. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ONLY TETRA COMPOUNDS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3]		OPR (ng/mL)	VER (ng/mL)
		s (ng/mL)	X (ng/mL)		
2,3,7,8-TCDD	10	2.7	8.7–12.4	7.3–14.6	8.2–12.3
2,3,7,8-TCDF	10	2.0	9.1–13.1	8.0–14.7	8.6–11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32–115	25–141	85–117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35–99	26–126	76–131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5–13.4	3.7–15.8	8.3–12.1

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 7. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ALL CDDS/CDFS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery	
		(ng/mL) [1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25–164	25–164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24–169	24–169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25–181	25–181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24–185	24–185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21–178	21–178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32–141	32–141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28–130	28–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26–152	26–152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26–123	26–123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29–147	29–147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28–136	28–136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23–140	23–140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28–143	28–143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26–138	26–138
$^{13}C_{12}$-OCDD	200	34–313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5–19.7	35-197

[1] Specification given as concentration in the final extract, assuming a 20-µL volume.

TABLE 7A. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ONLY TETRA COMPOUNDS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled compound recovery	
		(ng/mL) [1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2–16.4	42–164

[1] Specification given as concentration in the final extract, assuming a 20 µL volume.

TABLE 8. DESCRIPTORS, EXACT M/Z's, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs

Descriptor	Exact M/Z [1]	M/Z Type	Elemental Composition	Substance [2]
1	292.9825	Lock	$C_7 F_{11}$	PFK
	303.9016	M	$C_{12} H_4 {}^{35}Cl_4 O$	TCDF
	305.8987	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF
	315.9419	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O$	TCDF[3]
	317.9389	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF[3]
	319.8965	M	$C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD
	321.8936	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD
	327.8847	M	$C_{12} H_4 {}^{37}Cl_4 O_2$	TCDD[4]
	330.9792	QC	$C_7 F_{13}$	PFK
	331.9368	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD[3]
	333.9339	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD[3]
	375.8364	M+2	$C_{12} H_4 {}^{35}Cl_5 {}^{37}Cl O$	HxCDPE
2	339.8597	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF
	341.8567	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF
	351.9000	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF
	353.8970	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF [3]
	354.9792	Lock	$C_9 F_{13}$	PFK
	355.8546	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD
	357.8516	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD [3]
	369.8919	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD [3]
	409.7974	M+2	$C_{12} H_3 {}^{35}Cl_6 {}^{37}Cl O$	HpCDPE
3	373.8208	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF
	375.8178	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O$	HxCDF
	383.8639	M	$^{13}C_{12} H_2 {}^{35}Cl_6 O$	HxCDF [3]
	385.8610	M+2	$^{13}C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF [3]
	389.8157	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O_2$	HxCDD
	391.8127	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O_2$	HxCDD

TABLE 8. DESCRIPTORS, EXACT M/Z's, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs

Descriptor	Exact M/Z [1]	M/Z Type	Elemental Composition	Substance [2]
	392.9760	Lock	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD [3]
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD [3]
	430.9729	QC	C_9F_{17}	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF [3]
	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF [3]
	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	430.9729	Lock	C_9F_{17}	PFK
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD [3]
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD [3]
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCDPE
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	442.9728	Lock	$C_{10}F_{17}$	PFK
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD [3]
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD [3]
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE

[1] Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

[2]
TCDD = Tetrachlorodibenzo-*p*-dioxin
PeCDD = Pentachlorodibenzo-*p*-dioxin
HxCDD = Hexachlorodibenzo-*p*-dioxin
HpCDD = Heptachlorodibenzo-*p*-dioxin
OCDD = Octachlorodibenzo-*p*-dioxin
HxCDPE = Hexachlorodiphenyl ether
OCDPE = Octachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether
TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran
HpCDPE = Heptachlorodiphenyl ether
NCDPE = Nonachlorodiphenyl ether
PFK = Perfluorokerosene

[3] Labeled compound.

[4] There is only one m/z for $^{37}Cl_4$-2,3,7,8,-TCDD (cleanup standard).

TABLE 9. THEORETICAL ION ABUNDANCE RATIOS AND QC LIMITS

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	QC Limit [1]	
			Lower	Upper
4 [2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6 [3]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7 [4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1] QC limits represent ±15% windows around the theoretical ion abundance ratios.
[2] Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[3] Used for $^{13}C_{12}$-HxCDF only.
[4] Used for $^{13}C_{12}$-HpCDF only.

TABLE 10. SUGGESTED SAMPLE QUANTITIES TO BE EXTRACTED FOR VARIOUS MATRICES [1]

Sample Matrix [2]	Example	Percent Solids	Phase	Quantity Extracted
Single-phase				
Aqueous	Drinking water Groundwater Treated wastewater	<1	—[3]	1000 mL
Solid	Dry soil Compost Ash	>20	Solid	10 g
Organic	Waste solvent Waste oil Organic polymer	<1	Organic	10 g
Tissue	Fish Human adipose	—	Organic	10 g
Multi-phase				
Liquid/Solid				
Aqueous/Solid	Wet soil Untreated effluent Digested municipal sludge Filter cake Paper pulp	1–30	Solid	10 g
Organic/solid	Industrial sludge Oily waste	1–100	Both	10 g
Liquid/Liquid				
Aqueous/organic	In-process effluent Untreated effluent Drum waste	<1	Organic	10 g
Aqueous/organic/solid	Untreated effluent Drum waste	>1	Organic & solid	10 g

[1] The quantitity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing 1% solids will contain 10 g of solids. For aqueous samples containing greater than 1% solids, a lesser volume is used so that 10 g of solids (dry weight) will be extracted.

[2] The sample matrix may be amorphous for some samples. In general, when the CDDs/CDFs are in contact with a multiphase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.

[3] Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

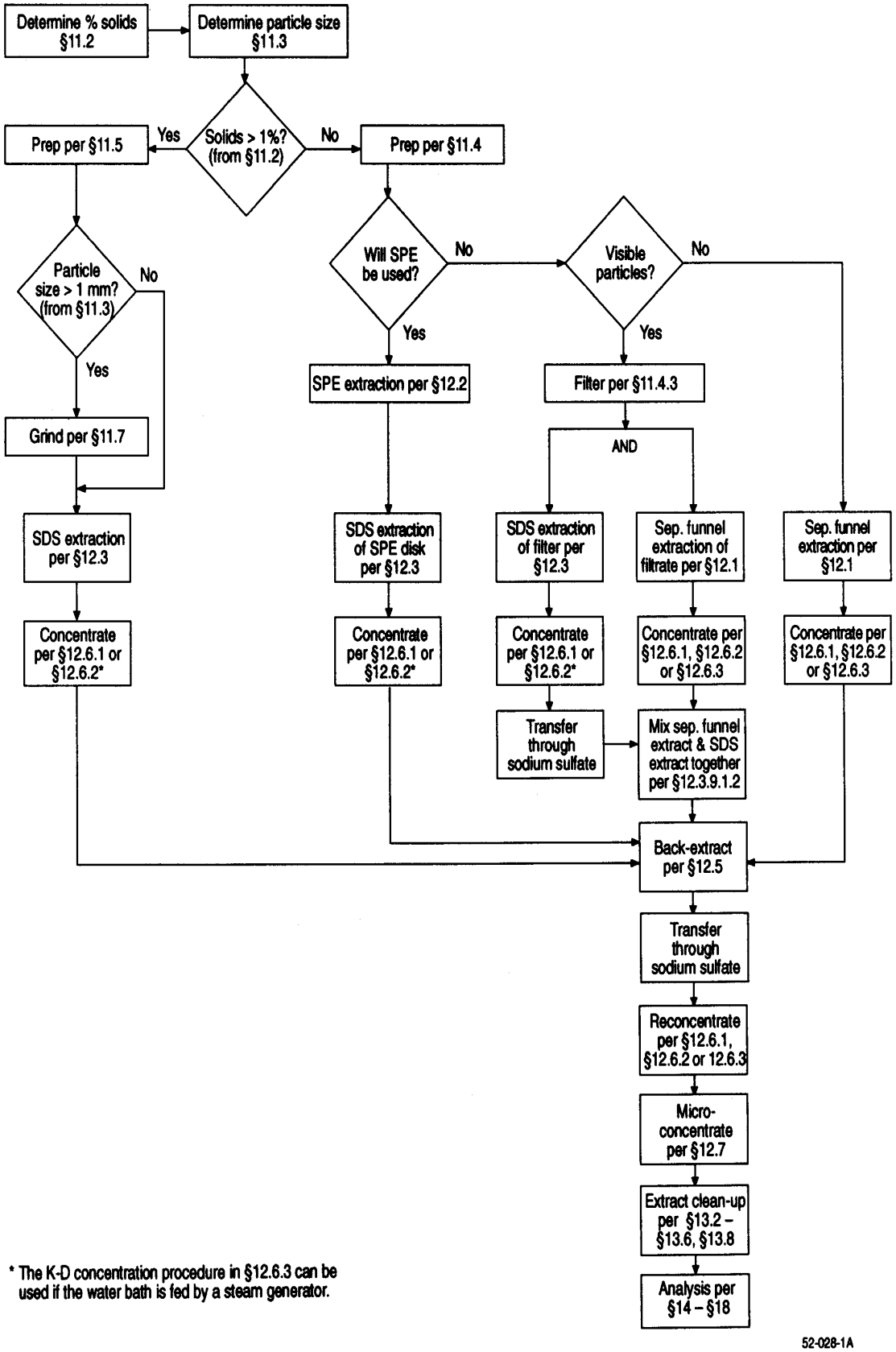

Figure 1. Flow Chart for Analysis of Aqueous and Solid Samples

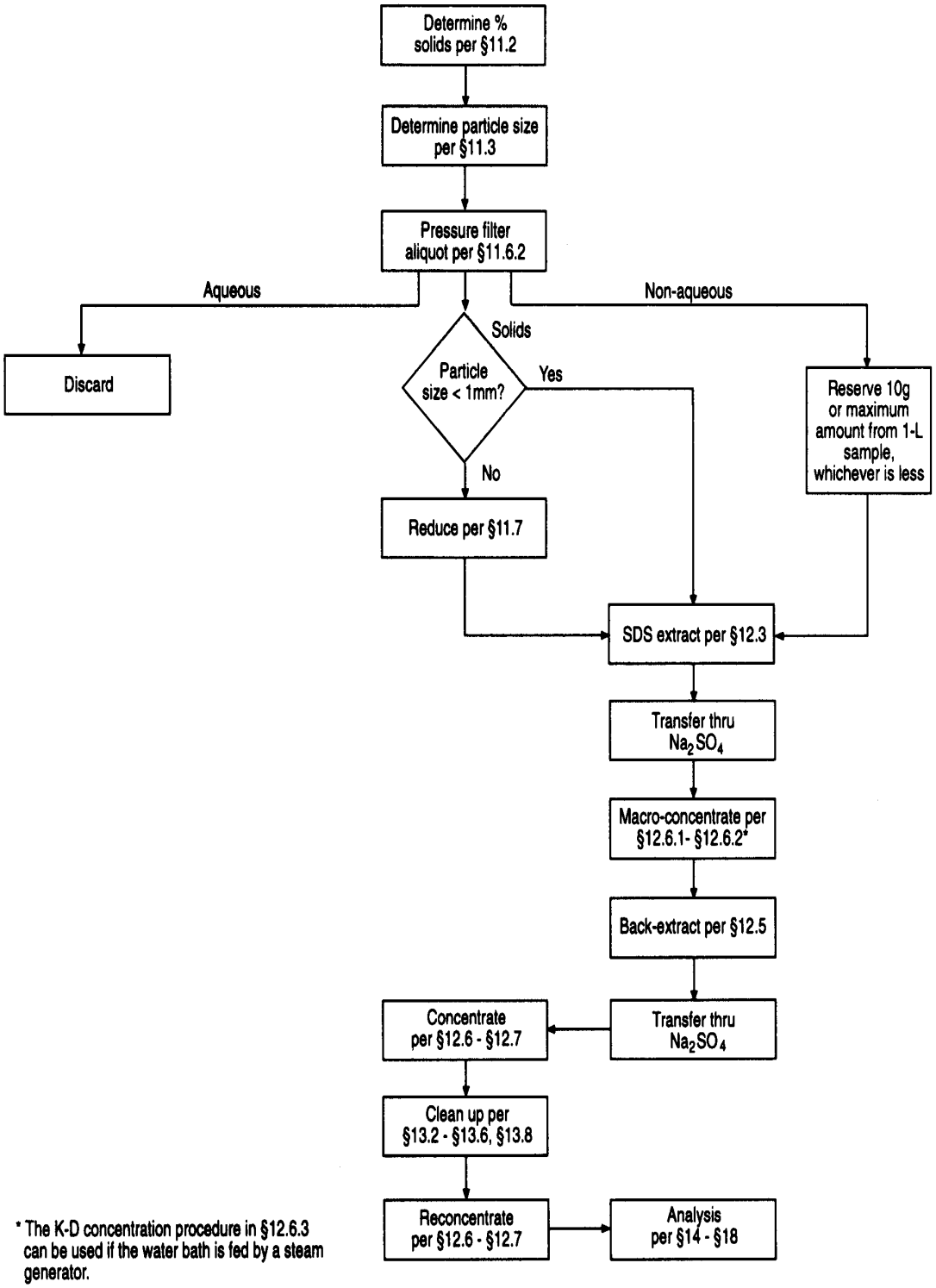

Figure 2. Flow Chart for Analysis of Multi-Phase Samples

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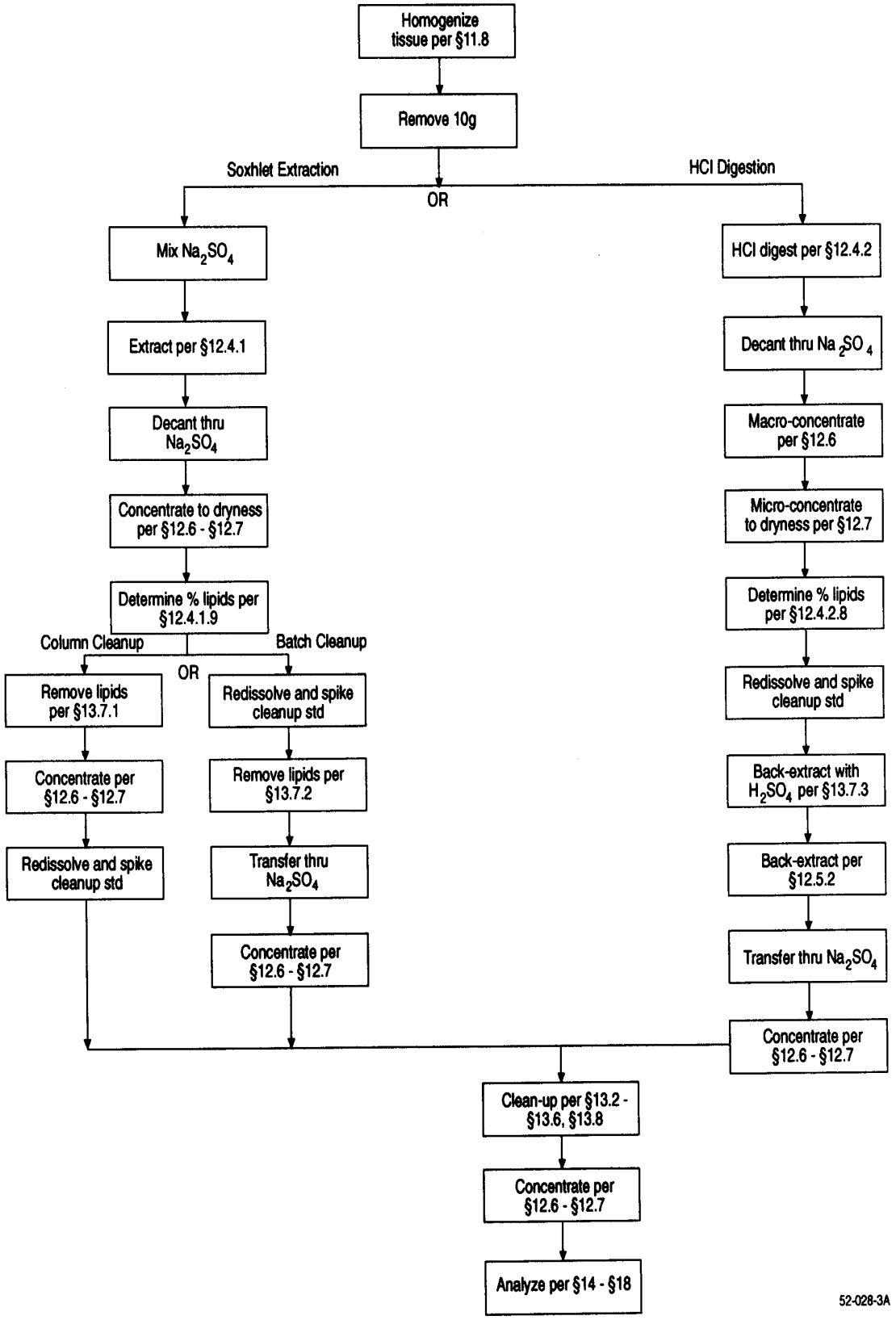

Figure 3. Flow Chart for Analysis of Tissue Samples

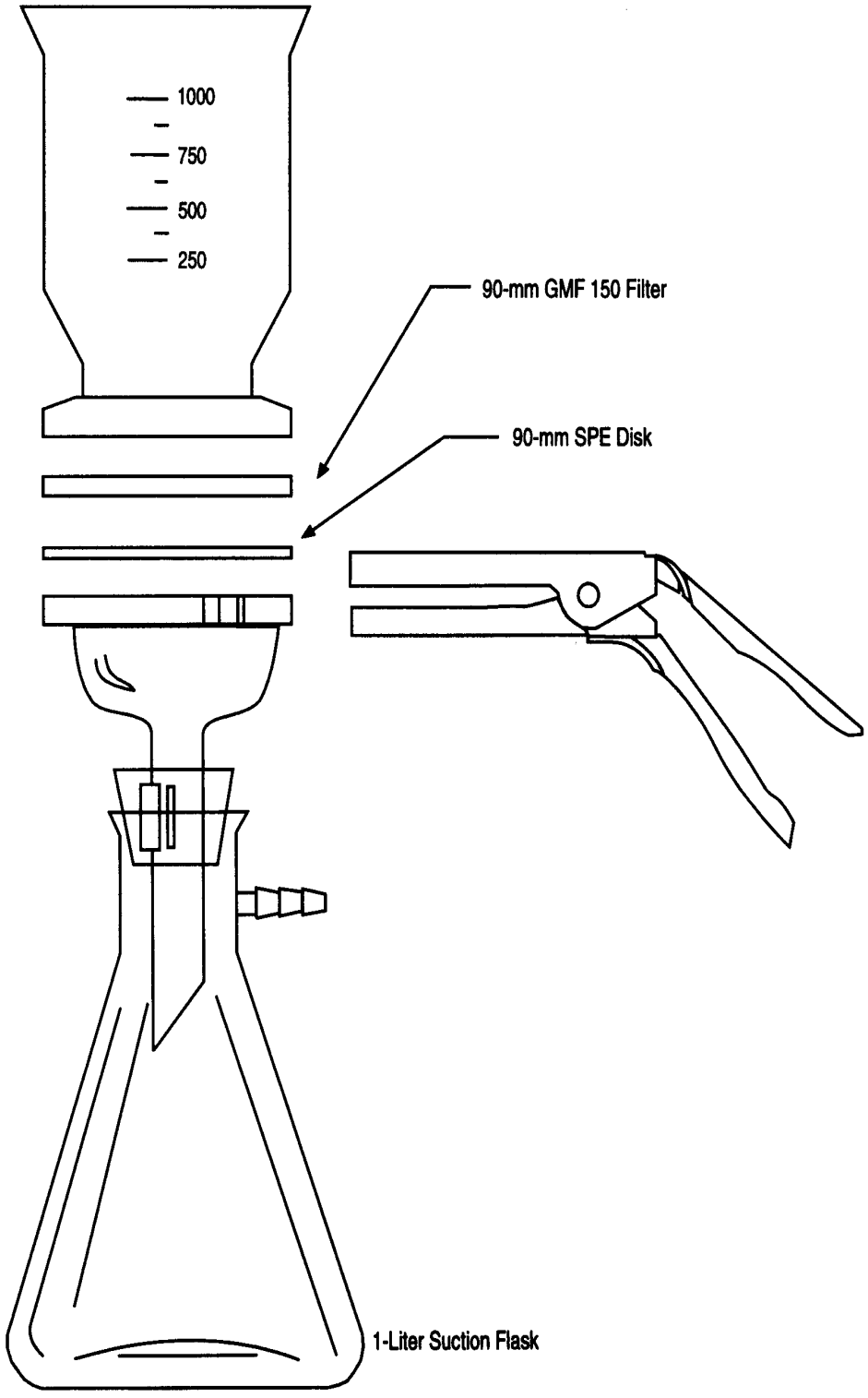

Figure 4. Solid-Phase Extraction Apparatus

52-027-1A

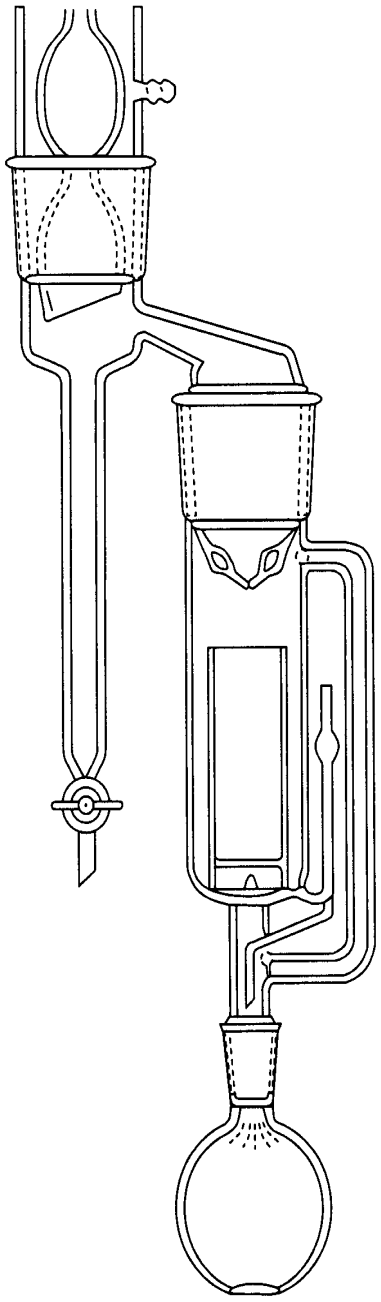

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Figure 5. Soxhlet/Dean-Stark Extractor

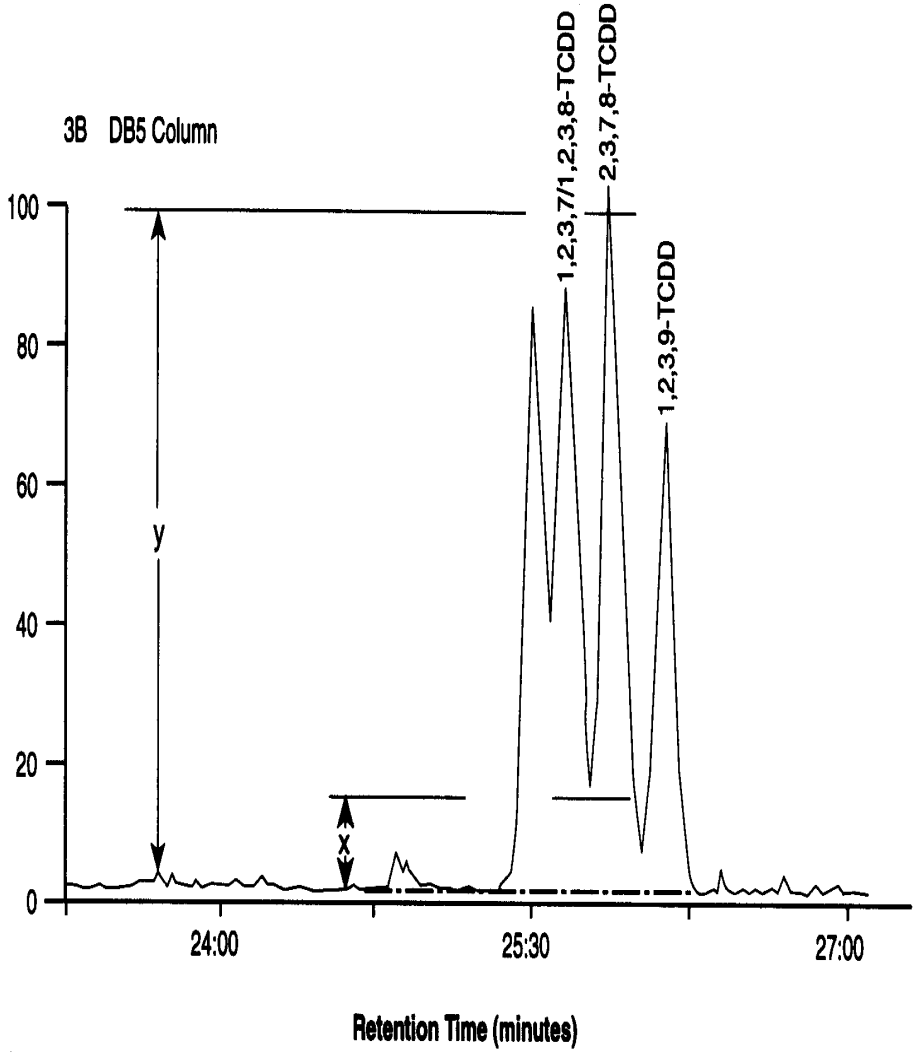

Figure 6. Isomer-Specific Separation of 2,3,7,8-TCDD on DB-5 Column

52-027-03

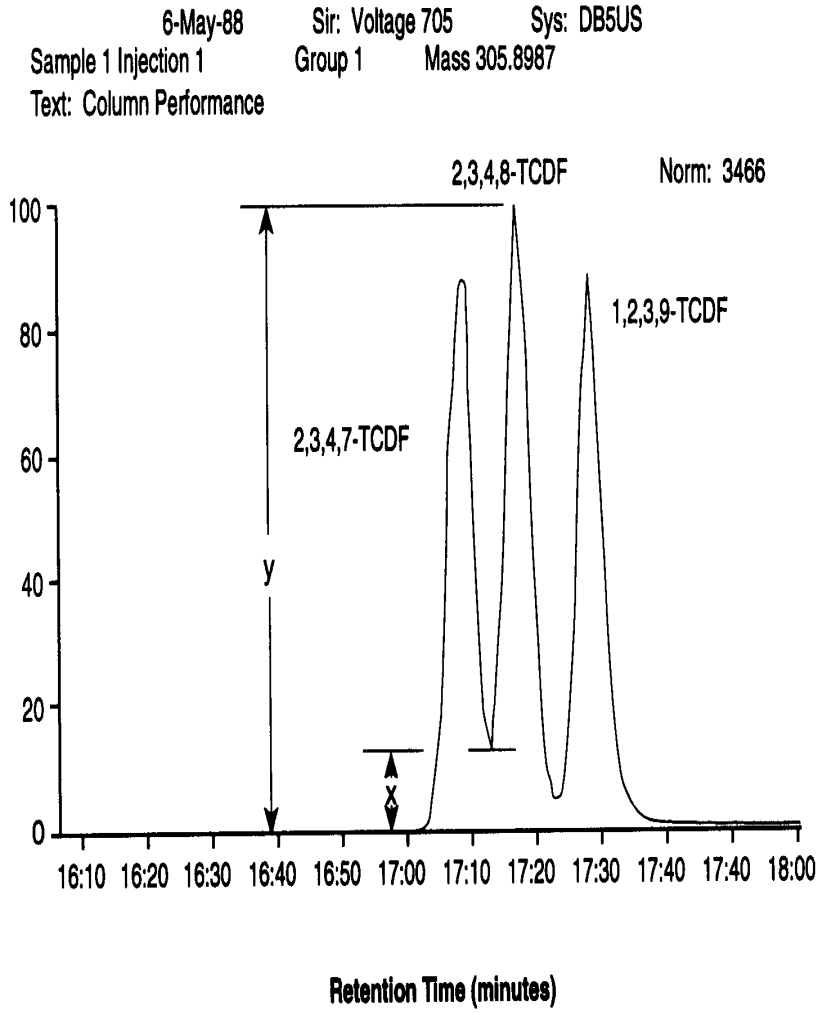

Figure 7. Isomer-Specific Separation of 2,3,7,8-TCDF on DB-5 Column

52-027-4A

24.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

24.1 Units of weight and Measure and Their Abbreviations

24.1.1 Symbols

°C	degrees Celsius
µL	microliter
µm	micrometer
<	less than
>	greater than
%	percent

24.1.2 Alphabetical abbreviations

amp	ampere
cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppq	part-per-quadrillion
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

24.2 Definitions and Acronyms (in Alphabetical Order)

Analyte—A CDD or CDF tested for by this method. The analytes are listed in Table 1.

Calibration Standard (CAL)—A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

Calibration Verification Standard (VER)—The mid-point calibration standard (CS3) that is used in to verify calibration. See Table 4.

CDD—Chlorinated Dibenzo-*p*-ioxin—The isomers and congeners of tetra- through octa-chlorodibenzo-*p*-dioxin.

CDF—Chlorinated Dibenzofuran—The isomers and congeners of tetra- through octa-chlorodibenzofuran.

CS1, CS2, CS3, CS4, CS5—See Calibration standards and Table 4.

Field Blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography.

GPC—Gel permeation chromatograph or gel permeation chromatography.

HPLC—High performance liquid chromatograph or high performance liquid chromatography.

HRGC—High resolution GC.

HRMS—High resolution MS.

IPR—Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

K-D—Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

Laboratory Blank—See method blank.

Laboratory Control sample (LCS)—See ongoing precision and recovery standard (OPR).

Laboratory Reagent Blank—See method blank.

May—This action, activity, or procedural step is neither required nor prohibited.

May Not—This action, activity, or procedural step is prohibited.

Method Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum Level (ML)—The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

MS—Mass spectrometer or mass spectrometry.

Must—This action, activity, or procedural step is required.

OPR—Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

PAR—Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

PFK—Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation Blank—See method blank.

Primary Dilution Standard—A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

Quality Control Check Sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

Reagent Water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative Standard Deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RF—Response factor. See Section 10.6.1.

RR—Relative response. See Section 10.5.2.

RSD—See relative standard deviation.

SDS—Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials (Reference 7).

Should—This action, activity, or procedural step is suggested but not required.

SICP—Selected ion current profile; the line described by the signal at an exact m/z.

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock Solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TCDD—Tetrachlorodibenzo-*p*-dioxin.

TCDF—Tetrachlorodibenzofuran.

VER—See calibration verification standard.

No. L-2

PCB Congeners

USEPA Method 1668A

United States
Environmental Protection
Agency

Method 1668, Revision A
Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS

August 2003

U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division (4303T)
1200 Pennsylvania Avenue, NW
Washington, DC 20460

EPA-821-R-07-004

Method 1668, Revision A
Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS

With corrections and changes through August 20, 2003

Introduction

Method 1668A, with corrections and changes through August 20, 2003, was developed by the Office of Water's Office of Science and Technology (OST) to determine chlorinated biphenyl congeners in environmental samples by isotope dilution and internal standard high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This method is applicable to aqueous, solid, tissue, and multi-phase matrices.

Acknowledgments

This method was prepared under EPA contract by Interface, Inc. and DynCorp Environmental. EPA acknowledges the analysts and laboratories that contributed corrections and suggested improvements. Data for this version were provided by Axys Analytical Services, Ltd., Sidney, BC, Canada.

Disclaimer

This method has been reviewed by the Engineering and Analytical Support Branch of the Engineering and Analysis Division (EAD) in OST. The method is available for general use, but has not been published in 40 CFR Part 136. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Please address your questions or comments to:

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Method 1668, Revision A [with corrections and changes through 8/20/03]

Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids and Tissue by HRGC/HRMS

1.0 Scope and application

1.1 Method 1668, Revision A (Method 1668A; the Method) is for determination of chlorinated biphenyl congeners (CBs) in water, soil, sediment, biosolids, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

1.1.1 The CBs that can be determined by this Method are the 12 polychlorinated biphenyls (PCBs) designated as toxic by the World Health Organization (WHO) plus the remaining 197 CBs, approximately 125 of which are resolved adequately on an SPB-octyl gas chromatographic column to be determined as individual congeners. The remaining approximately 70 congeners are determined as mixtures of isomers (co-elutions).

1.1.2 The 12 PCBs designated as toxic by WHO (Toxics; also known as dioxin-like PCBs; DLPCBs) and the earliest and latest eluted congener at each level of chlorination (LOC CBs) are determined by the isotope dilution quantitation technique; the remaining congeners are determined by the internal standard quantitation technique.

1.1.3 This Method allows determination of the PCB toxicity equivalent (TEQ_{PCB}) for the Toxics in a sample using toxicity equivalency factors (TEFs; Reference 1) and allows unique determination of 19 of 21 CBs of interest to the National Oceanic and Atmospheric Administration (NOAA; Reference 2). A second-column option is provided for resolution of the two toxic PCB congeners (with congener numbers 156 and 157) that are not resolved on the SPB-octyl column and for resolution of other CB congeners.

1.1.4 This Method also allows estimation of homolog totals by level of chlorination (LOC) and estimation of total CBs in a sample by summation of the concentrations of the CB congeners and congener groups.

1.1.5 The list of 209 CBs is given in Table 1 with the Toxics, the CBs of interest to NOAA, and the LOC CBs identified.

1.2 This Method is for use in data gathering and monitoring associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. It is based on a compilation of methods from the technical literature (References 3-5) and on EPA Method 1613.

1.3 The detection limits and quantitation levels in this Method are usually dependent on the level of interferences and laboratory background levels rather than instrumental limitations. The estimated minimum levels of quantitation (EMLs) in Table 2 are the levels at which the CBs can be determined with laboratory contamination present. The estimated method detection

limit (EMDL) for CB 126 in water is 5 pg/L (picograms-per-liter; parts-per-quadrillion) with no interferences present.

1.4 The GC/MS portions of this Method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.5 This Method is "performance-based." The laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurements, provided that all performance criteria are met. The requirements for establishing Method equivalency are given in Section 9.1.2.

1.6 Any modification of this Method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

2.0 Summary of method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

2.1 Extraction

2.1.1 Aqueous samples (samples containing less than one percent solids)—Stable isotopically labeled analogs of the Toxics and labeled LOC CBs are spiked into a 1-L sample. The sample is extracted using solid-phase extraction (SPE), separatory funnel extraction (SFE), or continuous liquid/liquid extraction (CLLE).

2.1.2 Solid, semi-solid, and multi-phase samples (excluding tissue)—The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in a Soxhlet/Dean-Stark (SDS) extractor. The extract is concentrated for cleanup.

2.1.3 Fish and other tissue—A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is mixed with anhydrous sodium sulfate, allowed to dry for 12 - 24 hours, and extracted for 18-24 hours using methylene chloride in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.2 After extraction, a labeled cleanup standard is spiked into the extract which is then cleaned up using back-extraction with sulfuric acid and/or base, and gel permeation, silica gel, or Florisil chromatography. Activated carbon and high-performance liquid chromatography (HPLC) can be used for further isolation of specific congener groups. Prior to the cleanup procedures cited above, tissue extracts are cleaned up using an anthropogenic isolation column.

2.3 After cleanup, the extract is concentrated to 20 µL. Immediately prior to injection, labeled injection internal standards are added to each extract and an aliquot of the extract is injected into the gas chromatograph (GC). The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored at each level of chlorination (LOC) throughout a pre-determined retention time window.

2.4 An individual CB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. Isomer specificity for certain of the CB congeners is achieved using GC columns that resolve these congeners.

2.5 Quantitative analysis is performed in one of two ways using selected ion current profile (SICP) areas:

2.5.1 For the Toxics and the LOC CBs, the GC/MS is multi-point calibrated and the concentration is determined using the isotope dilution technique.

2.5.2 For all congeners other than the Toxics and LOC CBs, the GC/MS is calibrated at a single concentration and the concentrations are determined using the internal standard technique.

2.5.3 For the labeled Toxics, labeled LOC CBs, and the cleanup standards, the GC/MS is calibrated using replicates at a single concentration and the concentrations of these labeled compounds in samples are determined using the internal standard technique.

2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3.0 Definitions

Definitions are given in the glossary at the end of this Method.

4.0 Contamination and interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts, elevated baselines, and/or lock-mass suppression causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse. Environmentally abundant CBs, as well as toxic congeners 105, 114, 118, 123, 156, 157, and 167 have been shown to be very difficult to completely eliminate from the laboratory at levels lower than the EMDLs in this Method (Table 2), and baking of glassware in a kiln or furnace at 450 - 500 °C may be necessary to remove these and other contaminants.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.

4.2.3 Baking of glassware in a kiln or other high temperature furnace (300 - 500 °C) may be warranted after particularly dirty samples are encountered. The kiln or furnace should be vented to prevent laboratory contamination by CB vapors. Baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb CBs.

4.2.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with toluene for approximately 3 hours (see Sections 12.3.1-12.3.3). The extraction apparatus (Section 6.4) should be rinsed with methylene chloride/toluene (80/20 mixture).

4.2.5 A separate set of glassware may to necessary to effectively preclude contamination when low-level samples are analyzed.

4.3 All materials used in the analysis must be demonstrated to be free from interferences by running reference matrix method blanks (Section 9.5) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the CBs in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed.

4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.

4.4 Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the CBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, brominated diphenyl ethers, polynuclear aromatics, polychlorinated naphthalenes, and pesticides. Because very low levels of CBs are measured by this Method, the elimination of interferences is essential. The cleanup steps given in Section 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the CBs at the levels shown in Table 2.

4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Contamination of calibration solutions—The EMDLs and EMLs in Table 2 are the levels that can be achieved with normal laboratory backgrounds present. Many of the EMLs are greater than the equivalent concentrations of the calibration solutions. In order to prevent contamination of the calibration solutions with the backgrounds allowed by the EMLs, the calibration solutions must be prepared in an area free from CB contamination using glassware free from contamination. If these requirements cannot be met or are difficult to meet in the laboratory, the laboratory should prepare the calibration solutions in a contamination-free facility or have a vendor prepare the calibration standards and guarantee freedom from contamination.

4.7 Cleanup of tissue—The natural lipid content of tissue can interfere in the analysis of tissue samples for the CBs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the anthropogenic isolation column procedure in Section 13.6, followed by the gel permeation chromatography procedure in Section 13.2. Florisil (Section 13.7) is recommended as an additional cleanup step.

4.8 If the laboratory air is a potential source of CB contamination, samples, reagents, glassware, and other materials should be dried in a glove box or other area free from contamination.

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. On the basis of the available toxicological and physical properties of the CBs, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this Method. However, if primary solutions are prepared, they must be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator must be worn when high concentrations are handled.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this Method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this Method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 6-9. The

references and bibliography at the end of Reference 8 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 The pure CBs and samples suspected to contain these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a strict safety program for handling these compounds. The practices in Reference 10 for handling chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDDs/CDFs) are also recommended for handling the CBs.

5.3.1 Facility—When finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the CBs, an additional set of gloves can also be worn beneath the latex gloves.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluent of the sample splitter from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols to condense CB vapors.

5.3.7 Waste Handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel should be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Chlorothene NU Solvent is a less toxic solvent that should be effective in removing CBs. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. If glassware is first rinsed with solvent, the wash water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons that convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to perform a wipe test of the surface suspected of being contaminated.

5.3.10.1 Using a piece of filter paper moistened with Chlorothene or other solvent, wipe an area approximately 10 x 10 cm.

5.3.10.2 Extract and analyze the wipe by GC with an electron capture detector (ECD) or by this Method.

5.3.10.2 Using the area wiped (e.g., 10 x 10 cm = 0.01 m^2), calculate the concentration in µg/m^2. A concentration less than 1 µg/m^2 indicates acceptable cleanliness; anything higher warrants further cleaning. More than 100 µg/m^2 constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

6.0 Apparatus and materials

Note: *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this Method is the responsibility of the laboratory.*

6.1 Sampling equipment for discrete or composite sampling

6.1.1 Sample bottles and caps

6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5 percent solids or less)—Sample bottle, amber glass, 1.1-L minimum, with screw cap.

6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5 percent solids)—Sample bottle, wide mouth, amber glass, 500-mL minimum.

6.1.1.3 If amber bottles are not available, samples must be protected from light.

6.1.1.4 Bottle caps—Threaded to fit sample bottles. Caps must be lined with fluoropolymer.

6.1.1.5 Cleaning

6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.

6.1.1.5.2 Liners are detergent water washed and rinsed with reagent water (Section 7.6.1).

6.1.2 Compositing equipment—Automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing must be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing must be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

6.2 Equipment for glassware cleaning

Note: *If blanks from bottles or other glassware or with fewer cleaning steps than required above show no detectable CB contamination, unnecessary cleaning steps and equipment may be eliminated.*

6.2.1 Laboratory sink with overhead fume hood

6.2.2 Kiln—Capable of reaching 450 °C within 2 hours and maintaining 450 - 500 °C within ±10 °C, with temperature controller and safety switch (Cress Manufacturing Co, Santa Fe Springs, CA, B31H, X31TS, or equivalent). See the precautions in Section 4.2.3.

6.3 Equipment for sample preparation

6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.3.2 Glove box (optional)

6.3.3 Tissue homogenizer—VirTis Model 45 Macro homogenizer (American Scientific Products H-3515, or equivalent) with stainless steel Macro-shaft and Turbo-shear blade.

6.3.4 Meat grinder—Hobart, or equivalent, with 3- to 5-mm holes in inner plate.

6.3.5 Equipment for determining percent moisture

6.3.5.1 Oven—Capable of maintaining a temperature of 110 ±5 °C

6.3.5.2 Desiccator

6.3.6 Balances

6.3.6.1 Analytical—Capable of weighing 0.1 mg

6.3.6.2 Top loading—Capable of weighing 10 mg

6.4 Extraction apparatus

6.4.1 Water samples

6.4.1.1 pH meter, with combination glass electrode

6.4.1.2 pH paper, wide range (Hydrion Papers, or equivalent)

6.4.1.3 Graduated cylinder, 1-L capacity

6.4.1.4 Liquid/liquid extraction—Separatory funnels, 250-, 500-, and 2000-mL, with fluoropolymer stopcocks

6.4.1.5 Solid-phase extraction

6.4.1.5.1 1-L filtration apparatus, including glass funnel, frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.

6.4.1.5.2 Vacuum source—Capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge

6.4.1.5.3 Glass-fiber filter—Whatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1

6.4.1.5.4 Solid-phase extraction disk containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1

6.4.1.6 Continuous liquid/liquid extraction (CLLE)—Fluoropolymer or glass connecting joints and stopcocks without lubrication, 1.5-2 L capacity (Hershberg-Wolf Extractor, Cal-Glass, Costa Mesa, California, 1000 mL or 2000 mL, or equivalent).

6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5 and Reference 11) for filters and solid/sludge samples

6.4.2.1 Soxhlet—50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask)

6.4.2.2 Thimble—43 × 123 to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent)

6.4.2.3 Moisture trap—Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet

6.4.2.4 Heating mantle—Hemispherical, to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent)

6.4.2.5 Variable transformer—Powerstat (or equivalent), 110-volt, 10-amp

6.4.3 Beakers—400- to 500-mL

6.4.4 Spatulas—Stainless steel

6.5 Filtration apparatus

6.5.1 Pyrex glass wool—Solvent-extracted using a Soxhlet or SDS extractor for 3 hours minimum

6.5.2 Glass funnel—125- to 250-mL

6.5.3 Glass-fiber filter paper—Whatman GF/D (or equivalent), to fit glass funnel in Section 6.5.2.

6.5.4 Drying column—15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug

6.5.5 Buchner funnel—15-cm

6.5.6 Glass-fiber filter paper for Buchner funnel above

6.5.7 Filtration flasks—1.5- to 2.0-L, with side arm

6.5.8 Pressure filtration apparatus—Millipore YT30 142 HW, or equivalent

6.6 Centrifuge apparatus

6.6.1 Centrifuge—Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum

6.6.2 Centrifuge bottles—500-mL, with screw-caps, to fit centrifuge

6.6.3 Centrifuge tubes—12- to 15-mL, with screw-caps, to fit centrifuge

6.7 Cleanup apparatus

6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent)

6.7.1.1 Column—600-700 mm long × 25 mm ID glass, packed with 70 g of 200-400 mesh SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent)

6.7.1.2 Syringe—10-mL, with Luer fitting

6.7.1.3 Syringe filter holder—stainless steel, and glass-fiber or fluoropolymer filters (Gelman 4310, or equivalent)

6.7.1.4 UV detectors—254-nm, preparative or semi-preparative flow cell (Isco, Inc., Type 6; Schmadzu, 5-mm path length; Beckman-Altex 152W, 8-µL micro-prep flow cell, 2-mm path; Pharmacia UV-1, 3-mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent).

6.7.2 Reverse-phase high-performance liquid chromatograph (Reference 4)

6.7.2.1 Pump—Perkin-Elmer Series 410, or equivalent

6.7.2.2 Injector—Perkin-Elmer ISS-100 Autosampler, or equivalent

6.7.2.3 6-Port switching valve—Valco N60, or equivalent

6.7.2.4 Column—Hypercarb, 100 x 4.6 mm, 5 µm particle size, Keystone Scientific, or equivalent

6.7.2.5 Detector—Altex 110A (or equivalent) operated at 0.02 AUFS at 235 nm

6.7.2.6 Fraction collector—Isco Foxy II, or equivalent

6.7.3 Pipets

6.7.3.1 Disposable, Pasteur, 150-mm long x 5-mm ID (Fisher Scientific 13-678-6A, or equivalent)

6.7.3.2 Disposable, serological, 50-mL (8- to 10- mm ID)

6.7.4 Glass chromatographic columns

6.7.4.1 150-mm long x 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir

6.7.4.2 200-mm long x 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir

6.7.4.3 300-mm long x 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock

6.7.5 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (± 5 °C) in the range of 105-250 °C

6.8 Concentration apparatus

6.8.1 Rotary evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath

6.8.1.1 Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge

6.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.8.1.3 Round-bottom flask—100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator

6.8.2 Kuderna-Danish (K-D) concentrator

6.8.2.1 Concentrator tube—10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.8.2.2 Evaporation flask—500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent)

6.8.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232, or equivalent)

6.8.2.4 Boiling chips

6.8.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hour minimum

6.8.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride

6.8.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within ± 2 °C, installed in a fume hood

6.8.3 Nitrogen evaporation apparatus—Equipped with water bath controlled in the range of 30 - 60 °C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood

6.8.4 Sample vials

6.8.4.1 Amber glass, 2- to 5-mL with fluoropolymer-lined screw-cap

6.8.4.2 Glass, 0.3-mL, conical, with fluoropolymer-lined screw or crimp cap

6.9 Gas chromatograph—Must have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and must meet all of the performance specifications in Section 10.

6.9.1 GC column—Any GC column or column system (2 or more columns) that provides unique resolution and identification of the Toxics for determination of a TEQ_{PCB} using TEFs (Reference 1). Isomers may be unresolved so long as they have the same TEF and response factor and so long as these unresolved isomers are uniquely resolved from all other congeners. For example, the SPB-octyl column (Section 6.9.1.3) achieves unique GC resolution of all Toxics except congeners with congener numbers 156 and 157. This isomeric pair is uniquely resolved from all other congeners and these congeners have the same TEF and response factor.

6.9.1.1 If an SPB-octyl column is used, it must meet the specification in Section 6.9.1 and the following additional specifications:

6.9.1.1.1 The retention time for decachlorobiphenyl (DFB; PCB 209) must be greater than 55 minutes.

6.9.1.1.2 The column must uniquely resolve congeners 34 from 23 and 187 from 182, and congeners 156 and 157 must co-elute within 2 seconds at the peak maximum. Unique resolution means a valley height less than 40 percent of the shorter of the two peaks that result when the Diluted combined 209 congener solution (Section 7.10.2.2) is analyzed (see Figures 6 and 7).

6.9.1.1.3 The column must be replaced when any of the criteria in Sections 6.9.1 - 6.9.1.1.2 are not met.

6.9.1.2 If a column or column system alternate to the SPB-octyl column is used, specifications similar to those for the SPB-octyl column (Sections 6.9.1 - 6.9.1.1.2) must be developed and be functionally equivalent to those specifications.

6.9.1.3 Suggested column—30 ± 5-m long x 0.25 ± 0.02-mm ID; 0.25-µm film SPB-octyl (Supelco 2-4218, or equivalent). This column is capable of meeting the requirements in Sections 6.9.1 - 6.9.1.1.2.

Note: *The SPB-octyl column is subject to rapid degradation when exposed to oxygen. The analyst should exclude oxygen from the carrier gas, should eliminate air leaks, and should cool the injector, column, and transfer line before opening the column to the atmosphere. For further information on precluding oxidation, contact the column manufacturer.*

6.9.1.4 Column for resolution of additional congeners—See Appendix A for details on the DB-1 column. The DB-1 column is optional and is capable of

uniquely resolving the congener pair with congener numbers 156 and 157. When used in combination with the SPB-octyl column (Section 6.9.1.3), the two-column system is capable of resolving a total of approximately 180 CB congeners.

6.10 Mass spectrometer—28- to 40-eV electron impact ionization, must be capable of selectively monitoring a minimum of 22 exact m/z's minimum at high resolution (≥10,000) during a period less than 1.5 seconds, and must meet all of the performance specifications in Section 10.

6.11 GC/MS interface—The mass spectrometer (MS) must be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.12 Data system—Capable of collecting, recording, storing, and processing MS data

6.12.1 Data acquisition—The signal at each exact m/z must be collected repetitively throughout the monitoring period and stored on a mass storage device.

6.12.2 Response factors and multipoint calibrations—The data system must record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibrations. Computations of relative standard deviation (RSD) are be used to test calibration linearity. Statistics on initial (Section 9.4) and ongoing (Section 15.5.4) performance should be computed and maintained, either on the instrument data system, or on a separate computer system.

7.0 Reagents and standards

7.1 pH adjustment and back-extraction

7.1.1 Potassium hydroxide—Dissolve 20 g reagent grade KOH in 100 mL reagent water.

7.1.2 Sulfuric acid—Reagent grade (specific gravity 1.84)

7.1.3 Hydrochloric acid—Reagent grade, 6N

7.1.4 Sodium chloride—Reagent grade, prepare at 5% (w/v) solution in reagent water

7.2 Solution drying and evaporation

7.2.1 Solution drying—Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400 °C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Tissue drying—Sodium sulfate, reagent grade, powdered, treated and stored as in Section 7.2.1

7.2.3 Prepurified nitrogen

7.3 Extraction

7.3.1 Solvents—Acetone, toluene, cyclohexane, hexane, methanol, methylene chloride, isooctane, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences

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Note: *Some solvents; e.g., isooctane and nonane, may need to be re-distilled to eliminate CB backgrounds.*

7.3.2 White quartz sand, 60/70 mesh—For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450 °C for 4 hour minimum.

7.4 GPC calibration solution—Prepare a solution containing 2.5 mg/mL corn oil, 0.05 mg/mL bis(2-ethylhexyl) phthalate (BEHP), 0.01 mg/mL methoxychlor, 0.002 mg/mL perylene, and 0.008 mg/mL sulfur, or at concentrations appropriate to the response of the detector.

7.5 Adsorbents for sample cleanup

7.5.1 Silica gel

7.5.1.1 Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), 100-200 mesh, rinsed with methylene chloride, baked at 180 °C for a minimum of 1 hour, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.5.1.2 Acid silica gel (30% w/w)—Thoroughly mix 44 g of concentrated sulfuric acid with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.5.1.3 Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.5.1.4 Potassium silicate

7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750- to 1000-mL flat-bottom flask.

7.5.1.4.2 Add 100 g of activated silica gel (Section 7.5.1.1) and a stirring bar, and stir on an explosion-proof hot plate at 60-70 °C for 1-2 hours.

7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100-mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.

7.5.1.4.4 Spread the potassium silicate on solvent-rinsed aluminum foil and dry for 2-4 hours in a hood. Observe the precaution in Section 4.8.

7.5.1.4.5 Activate overnight at 200-250 °C prior to use.

7.5.2 Carbon

7.5.2.1 Carbopak C—(Supelco 1-0258, or equivalent)

7.5.2.2 Celite 545—(Supelco 2-0199, or equivalent)

7.5.2.3 Thoroughly mix 18.0 g Carbopak C and 18.0 g Celite 545 to produce a 50% w/w mixture. Activate the mixture at 130 °C for a minimum of 6 hours. Store in a desiccator.

Note: *The carbon column has been included in this Method to allow separation of co-planar congeners 77, 126, and 169 from other congeners and interferences, should such separation be desired.*

7.5.3 Anthropogenic isolation column—Pack the column in Section 6.7.4.3 from bottom to top with the following:

7.5.3.1 2 g silica gel (Section 7.5.1.1)

7.5.3.2 2 g potassium silicate (Section 7.5.1.4)

7.5.3.3 2 g granular anhydrous sodium sulfate (Section 7.2.1)

7.5.3.4 10 g acid silica gel (Section 7.5.1.2)

7.5.3.5 2 g granular anhydrous sodium sulfate

7.5.4 Florisil column

7.5.4.1 Florisil—PR grade, 60-100 mesh (U.S. Silica Corp, Berkeley Springs, WV, or equivalent). Alternatively, prepacked Florisil columns may be used. Use the following procedure for Florisil activation and column packing.

7.5.4.1.1 Fill a clean 1- to 2-L bottle ½ to 2/3 full with Florisil and place in an oven at 130-150 °C for a minimum of three days to activate the Florisil.

7.5.4.1.2 Immediately prior to use, dry pack a 300-mm x 22-mm ID glass column (Section 6.7.4.3) bottom to top with 0.5-1.0 cm of warm

to hot anhydrous sodium sulfate (Section 7.2.1), 10-10.5 cm of warm to hot activated Florisil (Section 7.5.4.1.1), and 1-2 cm of warm to hot anhydrous sodium sulfate. Allow the column to cool and wet immediately with 100 mL of n-hexane to prevent water from entering.

7.5.4.2 Using the procedure in Section 13.7.3, establish the elution pattern for each carton of Florisil or each lot of Florisil columns received.

7.6 Reference matrices—Matrices in which the CBs and interfering compounds are not detected by this Method

7.6.1 Reagent water—Bottled water purchased locally, or prepared by passage through activated carbon

7.6.2 High-solids reference matrix—Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450 °C for a minimum of 4 hours.

7.6.3 Paper reference matrix—Glass-fiber filter, Gelman type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.

7.6.4 Tissue reference matrix—Corn or other vegetable oil.

7.6.5 Other matrices—This Method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the CBs, but in no case must the background level of the CBs in the reference matrix exceed the minimum levels in Table 2. If low background levels of the CBs are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio of approximately 5 (Reference 11).

7.7 Standard solutions—Prepare from materials of known purity and composition or purchase as solutions or mixtures with certification to their purity, concentration, and authenticity. If the chemical purity is 98 % or greater, the weight may be used without correction to calculate the concentration of the standard. Observe the safety precautions in Section 5 and the recommendation in Section 5.1.2.

Note: *Native PCB standards are available from several suppliers. $^{13}C_{12}$-labeled congeners are available from Cambridge Isotope Laboratories and Wellington Laboratories, and may be available from other suppliers. Listing of these suppliers does not constitute a recommendation or endorsement for use. Part numbers are for reference only.*

7.7.1 For preparation of stock solutions from neat materials, dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1 to 2 mg of PCB 126 to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the compound is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.

7.7.2 When not being used, store standard solutions in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps. Place a mark on the vial at the level

of the solution so that solvent loss by evaporation can be detected. Replace the solution if solvent loss has occurred.

7.8 Native (unlabeled) stock solutions

7.8.1 Native Toxics/LOC stock solution—Prepare to contain the native Toxics and LOC CBs at the concentrations shown in Table 3, or purchase Accu-Standard M1668A-C-NT-LOC-WD-GCPC, or equivalent. If additional CBs are to be determined by isotope dilution (e.g., 170 and 180), include the additional native compounds in this stock solution.

7.8.2 Native 209 CB congener stock solutions—Solutions containing CB congeners to calibrate the SPB-octyl column.

Note: *If a column other than the SPB-octyl column is used, solutions that will allow separation of all 209 congeners on that column must be prepared.*

7.8.2.1 Native congener mix stock solutions for separation of individual congeners on the SPB-octyl column—Prepare the five solutions with the congeners listed in Table 4 at the concentrations shown in Table 3 or purchase Accu-Standard M-1668A-1, M-1668A-2, M-1668A-3, M-1668-4, and M-1668-5, or equivalent.

7.8.2.2 Combined 209 congener stock solution—Combine equal volumes of the standards in Section 7.8.2.1 to form a stock solution containing all CB congeners. This solution will be at 1/5 the concentration of the 5 individual solutions.

7.8.3 Stock solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of standard solutions are available from several vendors.

7.9 Labeled compound stock solutions (Table 3)

7.9.1 Labeled Toxics/LOC/window-defining stock solution—Prepare in isooctane or nonane at the concentrations in Table 3 or purchase Cambridge Isotope Laboratories (CIL) EC-4977, or equivalent. If additional CBs are to be determined by isotope dilution (e.g., 170 and 180), include the additional labeled compounds in this stock solution.

7.9.2 Labeled cleanup standard stock solution—Prepare labeled CBs 28, 111, and 178 in iso-octane or nonane at the concentration shown in Table 3 or purchase CIL EC-4978, or equivalent.

7.9.3 Labeled injection internal standard stock solution—Prepare labeled CBs 9, 52, 101, 138, and 194 in nonane or isooctane at the concentrations shown in Table 3, or purchase CIL EC-4979, or equivalent.

7.10 Calibration standards

7.10.1 Calibration standards—Combine and dilute the solutions in Sections 7.8.1 and 7.9 to produce the calibration solutions in Table 5 or purchase CIL EC-4976, or equivalent, for the CS-1 to CS-5 set of calibration solutions. If a 6-point calibration is used, prepare the CS-0.2 solution or purchase CIL EC-4976-0.2, or equivalent. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS-3 standard (CIL EC-4976-3, or equivalent) is used for calibration verification (VER).

7.10.2 Solutions of congener mixes

7.10.2.1 Diluted individual solutions

7.10.2.1.1 The 5 individual solutions, when analyzed individually, allow resolution of all 209 congeners on the SPB-octyl column, and are used for establishing retention time and other data for each congener. The elution order of the congeners present in each of the 5 solutions (Section 7.8.2.1) is given in Table 4.

7.10.2.1.2 Individually combine an aliquot of each individual mix stock solution (Section 7.8.2.1) with an aliquot of the Labeled Toxics/ LOC/window-defining stock solution (Section 7.9.1), the Labeled cleanup standard stock solution (Section 7.9.2), and the Labeled injection internal standard stock solution (7.9.3) to produce concentrations of 100 ng/mL for the labeled compounds and 25, 50, and 75 ng/mL for the MoCB-TrCB, TeCB-HpCB, and OcCB-DeCB congeners, respectively, as shown in Table 3.

7.10.2.2 Diluted combined 209 congener solution

7.10.2.2.1 This solution combines the 5 individual mixes with the labeled compounds to allow single-point calibration of the congeners not included in the multi-point calibration, and establishes an average response factor for the co-eluting isomeric congeners.

7.10.2.2.2 Combine an aliquot of the combined 209 congener solution (Section 7.8.2.2) with an aliquot of the Labeled Toxics/LOC/ window-defining stock solution (Section 7.9.1), the Labeled cleanup standard stock solution (Section 7.9.2), and the Labeled injection internal standard stock solution (7.9.3) to produce the same concentrations as in the diluted individual mix solutions (Section 7.10.2.1.2 and Table 3).

7.11 Native Toxics/LOC standard spiking solution—Used for determining initial precision and recovery (IPR; Section 9.2) and ongoing precision and recovery (OPR; Section 15.5). Dilute the Native Toxics/LOC stock solution (Section 7.8.1) with acetone to produce a concentration of the Toxics at 1 ng/mL, as shown in Table 3. When 1 mL of this solution spiked into the IPR (Section 9.2.1) or OPR (Section 15.5) and concentrated to a final volume of 20 µL, the

concentration in the final volume will be 50 ng/mL (50 pg/µL). Prepare only the amount necessary for each reference matrix with each sample batch.

7.12 Labeled Toxics/LOC/window-defining standard spiking solution—This solution is spiked into each sample (Section 9.3) and into the IPR (Section 9.2.1), OPR (Section 15.5), and blank (Section 9.5) to measure recovery. Dilute the Labeled Toxics/LOC/window-defining stock solution (Section 7.9.1) with acetone to produce a concentration of the labeled compounds at 2 ng/mL, as shown in Table 3. When 1 mL of this solution is spiked into an IPR, OPR, blank, or sample and concentrated to a final extract volume of 20 µL, the concentration in the final extract volume will be 100 ng/mL (100 pg/µL). Prepare only the amount necessary for each reference matrix with each sample batch.

7.13 Labeled cleanup standard spiking solution—This solution is spiked into each extract prior to cleanup to measure the efficiency of the cleanup process. Dilute the Labeled cleanup standard stock solution (Section 7.9.2) in methylene chloride to produce a concentration of the cleanup standards at 2 ng/mL, as shown in Table 3. When 1 mL of this solution is spiked into a sample extract and concentrated to a final volume of 20 µL, the concentration in the final volume will be 100 ng/mL (100 pg/µL).

7.14 Labeled injection internal standard spiking solution—This solution is added to each concentrated extract prior to injection into the HRGC/HRMS. Dilute the Labeled injection internal standard stock solution (Section 7.9.3) in nonane to produce a concentration of the injection internal standards at 1000 ng/mL, as shown in Table 3. When 2 µL of this solution is spiked into a 20 µL extract, the concentration of each injection internal standard will be nominally 100 ng/mL (100 pg/µL).

Note: *The addition of 2 µL of the Labeled injection internal standard spiking solution to a 20 µL final extract has the effect of diluting the concentration of the components in the extract by 10%. Provided all calibration solutions and all extracts undergo this dilution as a result of adding the Labeled injection internal standard spiking solution, the effect of the 10% solution is compensated, and correction for this dilution should not be made.*

7.15 QC Check Sample—A QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified Standard Reference Material (SRM) containing the CBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has SRMs, and the Institute for National Measurement Standards of the National Research Council of Canada in Ottawa has certified reference materials (CRMs), for CBs in various matrices.

7.16 Stability of solutions—Standard solutions used for quantitative purposes (Sections 7.9 through 7.14) should be assayed periodically (e.g., every 6 months) against SRMs from NIST (if available), or certified reference materials from a source that will attest to the authenticity and concentration, to assure that the composition and concentrations have not changed.

8.0 Sample collection, preservation, storage, and holding times

8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 13).

8.2 Aqueous samples

8.2.1 Samples that flow freely are collected as grab samples or in refrigerated bottles using automatic sampling equipment.

8.2.2 If residual chlorine is present, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 14).

8.2.3 Maintain aqueous samples in the dark at <6 °C from the time of collection until receipt at the laboratory. If the sample will be frozen, allow room for expansion. Store in the dark at <6 °C.

8.3 Solid, mixed-phase, semi-solid, and oily samples, excluding tissue.

8.3.1 Collect samples as grab samples using wide-mouth jars.

8.3.2 Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <6 °C from the time of collection until receipt at the laboratory. Store solid, semi-solid, oily, and mixed-phase samples in the dark at less than -10 °C.

8.4 Fish and other tissue samples

8.4.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.4.2 Collect fish, wrap in aluminum foil, and maintain at <6 °C from the time of collection until receipt at the laboratory, to a maximum time of 24 hours. If a longer transport time is necessary, freeze the sample. Ideally, fish should be frozen upon collection and shipped to the laboratory under dry ice.

8.4.3 Freeze tissue samples upon receipt at the laboratory and maintain in the dark at less than -10 °C until prepared. Maintain unused sample in the dark at less than -10 °C.

8.5 Holding times

8.5.1 There are no demonstrated maximum holding times associated with the CBs in aqueous, solid, semi-solid, tissue, or other sample matrices. If stored in the dark at <6 °C, aqueous samples may be stored for up to one year. Similarly, if stored in the dark at less than -10 °C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.5.2 Store sample extracts in the dark at less than -10 °C until analyzed. If stored in the dark at less than -10 °C, sample extracts may be stored for one year.

9.0 Quality assurance/quality control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 15). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the Method.

If the Method is to be applied to sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate reference matrix (Sections 7.6.2 - 7.6.5 and 7.15) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.

9.1.1 The laboratory must make an initial demonstration of the ability to generate acceptable precision and recovery with this Method. This demonstration is given in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, and cleanup procedures, and changes in columns and detectors. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade Method performance, are not allowed. If an analytical technique other than the techniques specified in this Method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this Method for the analytes of interest.

9.1.2.1 Each time a modification is made to this Method, the laboratory is required to repeat the procedure in Section 9.2. If the detection limit of the Method will be affected by the change, the laboratory is required to demonstrate that the MDLs (40 CFR Part 136, Appendix B) are lower than one-third the regulatory compliance level or one-third the EMDLs in this Method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per Section 10. Once the modification is demonstrated to produce results equivalent or superior to results produced by this Method as written, that modification may be used routinely thereafter, so long as the other requirements in this Method are met (e.g., labeled compound recovery).

9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this Method, including:

a) Calibration (Section 10).
b) Calibration verification (Section 15.3).
c) Initial precision and recovery (Section 9.2).
d) Labeled compound recovery (Section 9.3).
e) Analysis of blanks (Section 9.5).
f) Accuracy assessment (Section 9.4).

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers.
b) Extraction dates.
c) Analysis dates and times.
d) Analysis sequence/run chronology.
e) Sample weight or volume (Section 11).
f) Extract volume prior to each cleanup step (Section 13).
g) Extract volume after each cleanup step (Section 13).
h) Final extract volume prior to injection (Section 14).
i) Injection volume (Section 14.3).
j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5).
k) Instrument and operating conditions.
l) Column (dimensions, liquid phase, solid support, film thickness, etc).
m) Operating conditions (temperatures, temperature program, flow rates).
n) Detector (type, operating conditions, etc).
o) Chromatograms, printer tapes, and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

9.1.2.3 Alternate HRGC columns and column systems—See Sections 6.9.1. If a column or column system alternate to those specified in this Method is used, that column or column system must meet the requirements in Section 6.9.1 - 6.9.1.1.3.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are described in Sections 9.5 and 15.6.

9.1.4 The laboratory must spike all samples with labeled compounds to monitor Method performance. This test is described in Section 9.3. When results of these spikes indicate atypical Method performance for samples, the samples are diluted to bring Method performance within acceptable limits. Procedures for dilution are given in Section 17.5.

9.1.5 The laboratory must, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery standard (OPR) and blanks that the analytical system is in control. These procedures are given in Sections 15.1 through 15.6.

9.1.6 The laboratory should maintain records to define the quality of data generated. Development of accuracy statements is described in Section 9.4.

9.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory must perform the following operations.

9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with 1 mL each of the Native Toxics/LOC spiking solution (Section 7.11), the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12), and the Labeled cleanup standard spiking solution (Section 7.13), according to the procedures in Sections 11 through 18. For an alternative sample matrix, four aliquots of the alternative reference matrix (Section 7.6) are used. All sample processing steps that are to be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), must be included in this test.

9.2.2 Using results of the set of four analyses, compute the average percent recovery (X) of the extracts and the relative standard deviation (RSD) of the concentration for each compound, by isotope dilution for CBs with a labeled analog, and by internal standard for CBs without a labeled analog and for the labeled compounds.

9.2.3 For each CB and labeled compound, compare RSD and X with the corresponding limits for initial precision and recovery in Table 6. If RSD and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual RSD exceeds the precision limit or any individual X falls outside the range for recovery, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).

9.3 To assess Method performance on the sample matrix, the laboratory must spike all samples with the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) and all sample extracts with the Labeled cleanup standard spiking solution (Section 7.13).

9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.

9.3.2 Compute the percent recovery of the labeled Toxics/LOC/window-defining congeners and the labeled cleanup congeners using the internal standard method (Section 17.2).

9.3.3 The recovery of each labeled compound must be within the limits in Table 6. If the recovery of any compound falls outside of these limits, Method performance is unacceptable for that compound in that sample. Additional cleanup procedures must then be employed to attempt to bring the recovery within the normal range. If the recovery cannot be brought within the normal range after all cleanup procedures have been employed, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are analyzed per Section 18.

9.4 It is suggested but not required that recovery of labeled compounds from samples be assessed and records maintained.

9.4.1 After the analysis of 30 samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (S_R) for the labeled compounds only. Express the assessment as a percent recovery interval from $R - 2S_R$ to $R + 2S_R$ for each matrix. For example, if R = 90% and S_R = 10% for five analyses of pulp, the recovery interval is expressed as 70 to 110%.

9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each five to ten new measurements).

9.5 Method blanks—A reference matrix Method blank is analyzed with each sample batch (Section 4.3) to demonstrate freedom from contamination. The matrix for the Method blank must be similar to the sample matrix for the batch, e.g., a 1-L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3); tissue blank (Section 7.6.4), or alternative reference matrix blank (Section 7.6.5).

9.5.1 Spike 1.0 mL each of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12), and the Labeled cleanup standard spiking solution (Section 7.13) into the Method blank, according to the procedures in Sections 11 through 18. Prepare, extract, clean up, and concentrate the Method blank. Analyze the blank immediately after analysis of the OPR (Section 15.5) to demonstrate freedom from contamination.

9.5.2 If any CB (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance limit, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each CB given in Table 2 (assuming a response factor of 1 relative to the quantitation reference in Table 2 at that level of chlorination for a potentially interfering compound; i.e., a compound not listed in this Method), analysis of samples must be halted until the sample batch is re-extracted and the extracts re-analyzed, and the blank associated with the sample batch shows no evidence of contamination at these levels. All samples must be associated with an uncontaminated Method blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes.

9.6 QC Check Sample—Analyze the QC Check Sample (Section 7.15) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.

9.7 The specifications contained in this Method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.5) precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for determination of CBs by this Method.

9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

10.0 Calibration

10.1 Establish the operating conditions necessary to meet the retention times (RTs) and relative retention times (RRTs) for the CBs in Table 2.

10.1.1 Suggested GC operating conditions:

Injector temperature:	270 °C
Interface temperature:	290 °C
Initial temperature:	75 °C
Initial time:	2 minutes
Temperature program:	75-150 °C at 15 °C/minute
	150-290 °C at 2.5 °C/minute
Final time:	1 minute

Note: *All portions of the column that connect the GC to the ion source should remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.*

The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR standards, and samples.

10.1.2 Retention time calibration for the CB congeners

10.1.2.1 Separately inject each of the diluted individual congener solutions (Section 7.10.2.1.2). Establish the beginning and ending retention times for the scan descriptors in Table 7. Scan descriptors other than those listed in Table 7 may be used provided the MLs in Table 2 are met. Store the retention time (RT) and relative retention time (RRT) for each congener in the data system.

10.1.2.2 The absolute retention time of CB 209 must exceed 55 minutes on the SPB-octyl column; otherwise, the GC temperature program must be adjusted and

this test repeated until the minimum retention time criterion is met. If a GC column or column system alternate to the SPB-octyl column is used, a similar minimum retention time specification must be established for the alternate column or column systems so that interferences that may be encountered in environmental samples will be resolved from the analytes of interest. This specification is deemed to be met if the retention time of CB 209 is greater than 55 minutes on such alternate column.

10.1.2.3 Inject the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 5). Adjust the chromatographic conditions and scan descriptors until the RT and RRT for all congeners are approximately within the windows in Table 2 and the column performance specifications in Sections 6.9.1 - 6.9.1.2 are met. If an alternate column is used, adjust the conditions for that column. If column performance is unacceptable, optimize the analysis conditions or replace the column and repeat the performance tests. Confirm that the scan descriptor changes at times when CBs do not elute.

10.1.2.4 After the column performance tests are passed (Section 10.1.2.2 - 10.1.2.3), calculate and store the RT and RRT for the resolved congeners and the RT and RRT for the isomeric congeners that co-elute. The windows in Table 2 were developed based on the GC conditions given in Section 10.1.1.

10.2 Mass spectrometer (MS) resolution

10.2.1 Using PFK (or other reference substance) and a molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at m/z 330.9792 or any other significant PFK fragment in the range of 300 to 350. For each descriptor (Table 7), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The level of PFK (or other reference substance) metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Note: *Different lots and types of PFK can contain varying levels of contamination, and excessive PFK (or other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.*

10.2.2 The analysis time for CBs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, mass-drift correction is mandatory and a lock-mass m/z from perfluorokerosene (PFK) or other reference substance is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 7. The deviation between each monitored exact m/z and the theoretical m/z (Table 7) must be less than 5 ppm.

10.2.3 Obtain a selected ion current profile (SICP) at the two exact m/z's specified in Table 7 and at ≥10,000 resolving power at each LOC for the native congeners and congener groups and for the labeled congeners. Because of the extensive mass range covered in each function, it may not be possible to maintain 10,000 resolution throughout the mass range during the function. Therefore, resolution must be ≥8,000 throughout the mass range and must be ≥10,000 in the center of the mass range for each function.

10.2.4 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below the minimum (Section 10.2.1.3) to save re-analysis time.

10.3 Ion abundance ratios, minimum levels, and signal-to-noise ratios. Choose an injection volume of either 1 or 2 µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 or 2 µL aliquot of the CS-1 calibration solution (Table 5) using the GC conditions in Section 10.1.1.

10.3.1 Measure the SICP areas for each congener or congener group, and compute the ion abundance ratios at the exact m/z's specified in Table 7. Compare the computed ratio to the theoretical ratio given in Table 8.

10.3.1.1 The exact m/z's to be monitored in each descriptor are shown in Table 7. Each group or descriptor must be monitored in succession as a function of GC retention time to ensure that the CBs of interest are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the descriptors listed in Table 7, provided that the laboratory is able to monitor the m/z's of all CBs that may elute from the GC in a given LOC window. The laboratory must also monitor exact m/z's for congeners at higher levels of chlorination to determine if fragments will compromise measurement of congeners at lower levels of chlorination.

10.3.1.2 The mass spectrometer must be operated in a mass-drift correction mode, using PFK (or other reference substance) to provide lock m/z's. The lock mass for each group of m/z's is shown in Table 7. Each lock mass must be monitored and must not vary by more than ± 20% throughout its respective retention time window. Variations of lock mass by more than 20% indicate the presence of co-eluting interferences that raise the source pressure and may significantly reduce the sensitivity of the mass spectrometer. Re-injection of another aliquot of the sample extract may not resolve the problem and additional cleanup of the extract may be required to remove the interference. A lock mass interference or suppression in a retention time region in which CBs and labeled compounds do not elute may be ignored.

10.3.2 All CBs and labeled compounds in the CS-1 standard must be within the QC limits in Table 8 for their respective ion abundance ratios; otherwise, the mass spectrometer must be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.2.1) prior to repeat of the test.

10.3.3 Verify that the HRGC/HRMS instrument meets the estimated minimum levels (EMLs) in Table 2. The peaks representing the CBs and labeled compounds in the CS-1 calibration standard must have signal-to-noise ratios (S/N) ≥ 10; otherwise, the mass spectrometer must be adjusted and this test repeated until the minimum levels in Table 2 are met.

Note: *The EMDLs and EMLs in Table 2 are based on the levels of contamination normally found in laboratories. Lower levels may be readily achievable if segregation and extensive cleaning of glassware is employed. If lower levels are achievable, these levels must be established as described in Section 17.6.1.4.1.*

10.4 Calibration by isotope dilution—Isotope dilution is used for calibration of the Toxics/LOC CBs. The reference compound for each native compound its labeled analog, as listed in Table 2. A 5- or 6-point calibration encompassing the concentration range is prepared for each native congener.

10.4.1 For the Toxics/LOC CBs determined by isotope dilution, the relative response (RR) (labeled to native) vs. concentration in the calibration solutions (Table 5) is computed over the calibration range according to the procedures described below. Five calibration points are employed for less-sensitive HRMS instruments (e.g., VG 70); five or six points may be employed for more-sensitive instruments (e.g., Micromass Autospec Ultima).

10.4.2 The response of each Toxics/LOC CB relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 7, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ C_n}$$

Where:

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the PCB.

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_l = The concentration of the labeled compound in the calibration standard (Table 4).

C_n = The concentration of the native compound in the calibration standard (Table 4).

10.4.3 To calibrate the analytical system by isotope dilution, inject calibration standards CS-1 through CS-5 (Section 7.10 and Table 5) for a less sensitive instrument or CS-0.2 through CS-5 for a more sensitive instrument. Use a volume identical to the volume chosen in Section 10.3, the procedure in Section 14, and the conditions in Section 10.1.1. Compute and store the relative response (RR) for each Native Toxics/LOC CB at each concentration. Compute the average (mean) RR and the RSD of the 5 (or 6) RRs.

10.4.4 Linearity—If the RR for any Native Toxics/LOC CB is constant (less than 20% RSD), the average RR may be used for that congener; otherwise, the complete calibration curve for that congener must be used over the calibration range.

10.5 Calibration by internal standard—Internal standard calibration is applied to determination of the native CBs for which a labeled compound is not available, to determination of the Labeled Toxics/LOC/window-defining congeners and Labeled cleanup congeners for performance tests and intra-laboratory statistics (Sections 9.4 and 15.5.4), and to determination of the Labeled injection internal standards except for CB 178. The reference compound for each compound is listed in Table 2. For the native congeners (other than the Native Toxics/LOC CBs), calibration is performed at a single point using the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 5). For the labeled compounds, calibration is performed using data from the 5 (or 6) points in the calibration for the Native Toxics/LOC CBs (Section 10.4).

10.5.1 Response factors—Internal standard calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ C_s}$$

Where:

$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the PCB.

$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard.

C_{is} = The concentration of the internal standard (Table 5).

C_s = The concentration of the compound in the calibration standard (Table 5).

10.5.2 To single-concentration calibrate the analytical system for native CBs other than the Native Toxics/LOC CBs by internal standard, inject the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 3). Use a volume identical to the volume chosen in Section 10.3, the procedure in Section 14, and the conditions in Section 10.1.1.

10.5.3 Compute and store the response factor (RF) for all native CBs except the Native Toxics/LOC CBs. Use the average (mean) response of the labeled compounds at each level of chlorination (LOC) as the quantitation reference, to a maximum of 5 labeled congeners, as shown in Table 2. For the combinations of isomeric congeners that co-elute, compute a combined RF for the co-eluted group. For example, for congener 122, the areas at the two exact m/z's for 104L, 105L, 114L, 118L, and 123L are summed and the total area is divided by 5 (because there are 5 congeners in the quantitation reference).

Note: *All labeled congeners at each LOC are used as reference to reduce the effect of an interference if a single congener is used as reference. Other quantitation references and procedures may be used provided that the results produced are as accurate as results produced by the quantitation references and procedures described in this Section.*

10.5.4 Compute and store the response factor (RF) for the labeled compounds, except CB 178. For the Labeled Toxics/LOC/window-defining compounds and the Labeled cleanup standards, use the nearest eluted Labeled injection internal standard as the quantitation reference, as given in Table 2. The Labeled injection internal standards are referenced to CB 178, as shown in Table 2.

11.0 Sample preparation

11.1 Sample preparation involves modifying the physical form of the sample so that the CBs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 9 lists the phases and suggested quantities for extraction of various sample matrices.

For samples known or expected to contain high levels of the CBs, the smallest sample size representative of the entire sample should be used (see Section 18). For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.

11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.

11.1.2 Aqueous samples—Because CBs may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.

11.1.2.1 Aqueous samples containing one percent solids or less are prepared per Section 11.4 and extracted directly using one of the extraction techniques in Section 12.2.

11.1.2.2 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.

11.1.3 Solid samples are prepared using the procedure described in Section 11.5 followed by extraction using the SDS procedure in Section 12.3.

11.1.4 Multi-phase samples—The phase(s) containing the CBs is separated from the non-CB phase using pressure filtration and centrifugation, as described in Section 11.6. The CBs will be in the organic phase in a multi-phase sample in which an organic phase exists.

11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.

11.1.6 Tissue samples—Preparation procedures for fish and other tissues are given in Section 11.8.

11.2 Determination of percent suspended solids

Note: *This aliquot is used for determining the solids content of the sample, not for determination of CBs.*

11.2.1 Aqueous liquids and multi-phase samples consisting of mainly an aqueous phase.

11.2.1.1 Desiccate and weigh a GF/D filter (Section 6.5.3) to three significant figures.

11.2.1.2 Filter 10.0 ±0.02 mL of well-mixed sample through the filter.

11.2.1.3 Dry the filter a minimum of 12 hours at 110 ±5 °C and cool in a desiccator.

11.2.1.4 Calculate percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying\ (g) - weight\ of\ filter\ (g)}{10\ g} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous; but not tissues.

11.2.2.1 Weigh 5 to 10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at 110 ±5 °C, and cool in a desiccator.

11.2.2.3 Calculate percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying}{weight\ of\ sample\ aliquot\ before\ drying} \times 100$$

11.3 Estimation of particle size

11.3.1 Spread the dried sample from Section 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of aqueous samples containing one percent suspended solids or less.

11.4.1 Aqueous samples containing one percent suspended solids or less are prepared using the procedure below and extracted using the one of the extraction techniques in Section 12.2.

11.4.2 Preparation of sample and QC aliquots

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to ± 1 g.

11.4.2.2 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for 1 to 2 hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0-L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into both reagent water aliquots. One of these aliquots will serve as the Method blank.

11.4.2.5 Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.5).

11.4.2.6 For extraction using SPE, add 5 mL of methanol to the sample and QC aliquots. Cap and shake the sample and QC aliquots to mix thoroughly, and proceed to Section 12.2 for extraction.

11.5 Preparation of samples containing greater than one percent solids

11.5.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar.

11.5.2 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the sample.

11.5.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12 hour shift, weigh two 10-g aliquots of the appropriate reference matrix (Section 7.6) into clean beakers or glass jars.

11.5.4 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into both reference matrix aliquots. Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into one reference matrix aliquot. This aliquot will serve as the OPR (Section 15.5). The other aliquot will serve as the Method blank.

11.5.5 Stir or tumble and equilibrate the aliquots for 1 to 2 hours.

11.5.6 Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

11.5.7 If particles >1 mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).

11.5.8 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.

11.6 Multi-phase samples

11.6.1 Using the percent solids determined in Section 11.2.1 or 11.2.2, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.

11.6.2 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the amount of sample determined in Section 11.6.1, and into the OPR and blank. Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into the OPR. Pressure filter the sample, blank, and OPR through Whatman GF/D glass-fiber filter paper (Section 6.5.3). If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration.

11.6.3 Discard any aqueous phase (if present). Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample (Section 11.6.1) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.5).

11.6.4 If particles >1 mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. Observe the precaution in Section 4.8.

11.6.5 After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced-size particles using the SDS procedure in Section 12.3. If particles >1 mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

11.7 Sample grinding, homogenization, or blending—Samples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.

11.7.1 Each size-reducing preparation procedure on each matrix must be verified by running the tests in Section 9.2 before the procedure is employed routinely.

11.7.2 The grinding, homogenization, or blending procedures must be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.7.3 Grinding—Certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Sections 11.5.7 or 11.6.5 in a clean grinder. Do not allow the sample temperature to exceed 50 °C. Grind the blank and reference matrix aliquots using a clean grinder.

11.7.4 Homogenization or blending—Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed

homogenization or blending. Homogenize and/or blend the particles or filter from Sections 11.5.7 or 11.6.5 for the sample, blank, and OPR aliquots.

11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.

11.8 Fish and other tissues—Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish-skin on, whole fish-skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.

11.8.1 Homogenization

11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.

11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extraction of a second aliquot of the same homogenized sample, if re-analysis is required. When whole fish analysis is necessary, the entire fish is homogenized.

11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.

11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400- to 500-mL beaker.

11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-lined lid. Seal the jar and store the tissue at less than -10 °C. Return any tissue that was not homogenized to its original container and store at less than -10 °C.

11.8.2 QC aliquots

11.8.2.1 Prepare a Method blank by adding approximately 1-2 g of the oily liquid reference matrix (Section 7.6.4) to a 400- to 500-mL beaker.

11.8.2.2 Prepare a precision and recovery aliquot by adding 1-2 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400- to 500-mL beaker. Record the weight to the nearest 10 mg. If the initial precision and recovery test is to be performed, use four aliquots; if the ongoing precision and recovery test is to be performed, use a single aliquot.

11.8.3 Spiking

11.8.3.1 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into the OPR aliquot.

11.8.4 Extract the aliquots using the procedures in Section 12.4.

12.0 Extraction and concentration

12.1 Extraction procedures include: solid-phase (Section 12.2.1), separatory funnel (Section 12.2.2), and continuous liquid/liquid (Section 12.2.3) for aqueous liquids; Soxhlet/Dean-Stark (Section 12.3) for solids and filters; and Soxhlet extraction (Section 12.4) for tissues. Acid/base back-extraction (Section 12.5) is used for initial cleanup of extracts.

Macro-concentration procedures include: rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish (K-D) evaporation (Section 12.6.3). Micro-concentration uses nitrogen evaporation (Section 12.7).

12.2 Extraction of aqueous liquids

12.2.1 Solid-phase extraction of samples containing less than one percent solids

12.2.1.1 Disk preparation

12.2.1.1.1 Remove the test tube from the suction flask (Figure 4). Place an SPE disk on the base of the filter holder and wet with methylene chloride. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with methylene chloride and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1-L glass reservoir and the vacuum filtration flask.

12.2.1.1.2 Rinse the sides of the reservoir with approx 15 mL of methylene chloride using a squeeze bottle or pipet. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the methylene chloride through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

12.2.1.2 Sample extraction

12.2.1.2.1 Pre-wet the disk by adding approx 20 mL of methanol to the reservoir. Pull most of the methanol through the filter/disk, retaining a layer of methanol approx 2 mm thick on the filter.

Do not allow the filter/disk to go dry from this point until the extraction is completed.

12.2.1.2.2 Add approx 20 mL of reagent water to the reservoir and pull most through, leaving a layer approx 2 mm thick on the filter/disk.

12.2.1.2.3 Allow the sample (Section 11.4.2.6) to stand for 1-2 hours, if necessary, to settle the suspended particles. Decant the clear layer of the sample, the blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into its respective reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10 minutes. For samples containing a high concentration of particles (suspended solids), the extraction time may be an hour or longer.

12.2.1.2.4 Before all of the sample has been pulled through the filter/disk, add approx 50 mL of reagent water to the sample bottle, swirl to suspend the solids (if present), and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all solids are removed.

12.2.1.2.5 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.

12.2.1.2.6 Partially dry the filter/disk under vacuum for approx 3 minutes.

12.2.1.3 Elution of the filter/disk

12.2.1.3.1 Release the vacuum, remove the entire filter/disk/reservoir assembly from the vacuum flask, and empty the flask. Insert a test tube for eluant collection into the flask. The test tube should have sufficient capacity to contain the total volume of the elution solvent (approx 50 mL) and should fit around the drip tip. The drip tip should protrude into the test tube to preclude loss of sample from spattering when vacuum is applied. Reassemble the filter/disk/reservoir assembly on the vacuum flask.

12.2.1.3.2 Wet the filter/disk with 4-5 mL of acetone. Allow the acetone to spread evenly across the disk and soak for 15-20 seconds. Pull the acetone through the disk, releasing the vacuum when approx 1 mm thickness remains on the filter.

12.2.1.3.3 Rinse the sample bottle with approx 20 mL of methylene chloride and transfer to the reservoir. Pull approx half of the solvent through the filter/disk and release the vacuum. Allow the filter/disk to soak for approx 1 minute. Pull all of the solvent through the disk. Repeat the bottle rinsing and elution step with

another 20 mL of methylene chloride. Pull all of the solvent through the disk.

12.2.1.3.4 Release the vacuum, remove the filter/disk/reservoir assembly, and remove the test tube containing the sample solution. Quantitatively transfer the solution to a 250-mL separatory funnel and proceed to Section 12.5 for back-extraction.

12.2.2 Separatory funnel extraction

12.2.2.1 Pour the spiked sample (Section 11.4.2.2) into a 2-L separatory funnel. Rinse the bottle or flask twice with 5 mL of reagent water and add these rinses to the separatory funnel.

12.2.2.2 Add 60 mL methylene chloride to the empty sample bottle. Seal the bottle and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms and is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation (see note below). Drain the methylene chloride extract through a solvent-rinsed glass funnel approximately one-half full of granular anhydrous sodium sulfate (Section 7.2.1) supported on clean glass-fiber paper into a solvent-rinsed concentration device (Section 12.6).

Note: *If an emulsion forms, the laboratory must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase (Section 12.2.1), CLLE (Section 12.2.3), or other extraction techniques may be used to prevent emulsion formation. Any alternative technique is acceptable so long as the requirements in Section 9.2 are met.*

12.2.2.3 Extract the water sample two more times with 60-mL portions of methylene chloride. Drain each portion through the sodium sulfate into the concentrator. After the third extraction, rinse the separatory funnel with at least 20 mL of methylene chloride, and drain this rinse through the sodium sulfate into the concentrator. Repeat this rinse at least twice. Set aside the funnel with sodium sulfate if the extract is to be combined with the extract from the particles.

12.2.2.4 Concentrate the extract using one of the macro-concentration procedures in Section 12.6 and proceed to back extraction in Section 12.5.

12.2.3 Continuous liquid/liquid extraction

12.2.3.1 Place 100-150 mL methylene chloride in each continuous extractor and 200-300 mL in each distilling flask.

12.2.3.2 Pour the sample(s), blank, and QC aliquots into the extractors. Rinse the sample containers with 50-100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

12.2.3.3 Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1-2 drops of methylene chloride per second will fall from the condenser tip into the water. Extract for 16-24 hours.

12.2.3.4 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate into a 500-mL K-D evaporator flask equipped with a 10-mL concentrator tube. Rinse the distilling flask with 30-50 mL of methylene chloride and pour through the drying column. Concentrate and exchange to hexane per Section 12.6 and back extract per Section 12.5.

12.3 SDS extraction of samples containing particles

12.3.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2).

Note: *Do not disturb the silica layer throughout the extraction process.*

12.3.2 Place the thimble in a clean extractor. Place 30 to 40 mL of toluene in the receiver and 200 to 250 mL of toluene in the flask.

12.3.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1 to 2 drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of 3 hours.

12.3.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

12.3.5 Load the wet sample and/or filter from Sections 11.5.8, 11.6.5, or 11.7.5 and any non-aqueous liquid from Section 11.6.3 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.

12.3.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of toluene to the receiver and reflux flask. Apply power to the heating mantle to begin re-fluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first 2 hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.3.7 Drain the water from the receiver at 1-2 hours and 8-9 hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

12.3.8 Remove the distilling flask. Drain the water from the Dean-Stark receiver and add any toluene in the receiver to the extract in the flask.

12.3.9 Concentrate the extracts from particles to approximately 10 mL using the rotary evaporator (Section 12.6.1) or heating mantle (Section 12.6.2), transfer to a 250-mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.4 Soxhlet extraction of tissue

Note: *This procedure includes determination of the lipid content of the sample (Sections 12.4.8 - 12.4.9), using the same sample extract that is analyzed by GC/MS. Alternatively, a separate sample aliquot may be used for the lipid determination. If a separate aliquot is used, use nitrogen to evaporate the main portion of the sample extract only to the extent necessary to effect the solvent exchange to n-hexane, so that loss of low molecular weight CBs is avoided, i.e., it is not necessary to dry the main portion of the sample to constant weight (Section 12.4.8).*

12.4.1 Add 30 to 40 g of powdered anhydrous sodium sulfate (Section 7.2.2) to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with aluminum foil and dry until the mixture becomes a free-flowing powder (30 minutes minimum). Remix prior to extraction to prevent clumping.

12.4.2 Assemble and pre-extract the Soxhlet apparatus per Sections 12.3.1-12.3.4, except use methylene chloride for the pre-extraction and rinsing and omit the quartz sand.

12.4.3 Reassemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride to the reflux flask.

12.4.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.

12.4.5 Rinse the beaker with several portions of solvent and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18-24 hours.

12.4.6 After extraction, cool and disassemble the apparatus.

12.4.7 Quantitatively transfer the extract to a macro-concentration device (Section 12.6), and concentrate to near dryness. Set aside the concentration apparatus for re-use.

12.4.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60 °C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.9 Percent lipid determination

12.4.9.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the Labeled cleanup standard spiking solution (Section 7.13) into the solution.

12.4.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.6), retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$Percent\ lipid = \frac{Weight\ of\ residue\ (g)}{Weight\ of\ tissue\ (g)} \times 100$$

12.4.9.4 The laboratory should determine the lipid content of the blank, IPR, and OPR to assure that the extraction system is working effectively.

12.5 Back-extraction with base and acid

12.5.1 Back-extraction may not be necessary for some samples. For some samples, the presence of color in the extract may indicate that back-extraction is necessary. If back-extraction is not performed, spike 1.0 mL of the Labeled cleanup standard spiking solution (Section 7.13) into the extract and concentrate the extract for cleanup or analysis (Section 12.7). If back-extraction is necessary, spike 1.0 mL of the Labeled cleanup standard spiking solution (Section 7.13) into the separatory funnels containing the sample and QC extracts from Section 12.2.3.4 or 12.3.9.

12.5.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1). Shake for 2 minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the CBs. Stronger potassium hydroxide solutions may be employed for back-extraction, provided that the laboratory meets the specifications for labeled compound recovery and demonstrates acceptable performance using the procedure in Section 9.2.

12.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with base. Discard the aqueous layer.

12.5.4 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.5.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.

12.5.6 Pour each extract through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30 to 50 mL of solvent, and pour through the drying column. Collect each extract in a round-bottom flask. Re-concentrate the sample and QC aliquots per Sections 12.6-12.7, and clean up the samples and QC aliquots per Section 13.

12.6 Macro-concentration—Extracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danish apparatus.

Note: *In the concentration procedures below, the extract must not be allowed to concentrate to dryness because the mono- through tri-chlorobiphenyls may be totally or partially lost.*

12.6.1 Rotary evaporation—Concentrate the extracts in separate round-bottom flasks.

12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45 °C. On a daily basis, pre-clean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2- to 3-mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.

12.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

Note: *If the rate of concentration is too fast, analyte loss may occur.*

12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

12.6.1.5 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.2 Heating mantle—Concentrate the extracts in separate round-bottom flasks.

12.6.2.1 Add one or two clean boiling chips to the round-bottom flask, and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottom flask in a heating mantle, and apply heat as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottom flask from the heating mantle and allow the solvent

to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.

12.6.2.3 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.3 Kuderna-Danish (K-D)—Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-D technique unless a water bath fed by a steam generator is used.

12.6.3.1 Add 1 to 2 clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of solvent. A 5-mL syringe is recommended for this operation.

12.6.3.4 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

12.6.3.7 Proceed to 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4 Preparation for back-extraction or micro-concentration and solvent exchange

12.6.4.1 For back-extraction (Section 12.5), transfer the extract to a 250-mL separatory funnel. Rinse the concentration vessel with small portions of hexane, adjust the hexane volume in the separatory funnel to 10 to 20 mL, and proceed to back-extraction (Section 12.5).

12.6.4.2 For determination of the weight of residue in the extract, or for clean-up procedures other than back-extraction, transfer the extract to a blowdown vial using 2-3 rinses of solvent. Proceed with micro-concentration and solvent exchange (Section 12.7).

12.7 Micro-concentration and solvent exchange

12.7.1 Extracts to be subjected to GPC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, carbon, Florisil, and/or HPLC are exchanged into hexane.

12.7.2 Transfer the vial containing the sample extract to a nitrogen evaporation device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

Note: *A large vortex in the solvent may cause analyte loss.*

12.7.3 Lower the vial into a 45 °C water bath and continue concentrating.

12.7.3.1 If the extract or an aliquot of the extract is to be concentrated to dryness for weight determination (Sections 12.4.8 and 13.6.4), blow dry until a constant weight is obtained.

12.7.3.2 If the extract is to be concentrated for injection into the GC/MS or the solvent is to be exchanged for extract cleanup, proceed as follows:

12.7.4 When the volume of the liquid is approximately 100 µL, add 2 to 3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other cleanups) and continue concentration to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, concentrate the extract to 1.0 mL. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.5, respectively).

12.7.6 If the extract is to be cleaned up by column chromatography (silica gel, Carbopak/Celite, or Florisil), bring the final volume to 1.0 mL with hexane. Proceed with column cleanup (Sections 13.3, 13.4, or 13.7).

12.7.7 If the extract is to be concentrated for injection into the GC/MS (Section 14), quantitatively transfer the extract to a 0.3-mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100 µL. Add 20 µL of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC/MS analysis. If GC/MS analysis will not be performed on the same day, store the vial at less than -10 °C.

13.0 Extract cleanup

13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure.

13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts. It may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids). It should also be used for tissue extracts after initial cleanup on the anthropogenic isolation column (Section 13.6).

13.1.2 Acid, neutral, and basic silica gel (Section 13.3) and Florisil (Section 13.7) are used to remove non-polar and polar interferences.

13.1.3 Carbopak/Celite (Section 13.4) can be used to separate CBs 77, 126, and 169 from the mono- and di- ortho-substituted CBs, if desired.

13.1.4 HPLC (Section 13.5) is used to provide specificity for certain congeners and congener groups.

13.1.5 The anthropogenic isolation column (Section 13.6) is used for removal of lipids from tissue samples.

13.2 Gel permeation chromatography (GPC)

13.2.1 Column packing

13.2.1.1 Place 70 to 75 g of SX-3 Bio-beads (Section 6.7.1.1) in a 400- to 500-mL beaker.

13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).

13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5 to 5.5 mL/minute prior to connecting the column to the detector.

13.2.1.4 After purging the column with solvent for 1 to 2 hours, adjust the column head pressure to 7 to 10 psig and purge for 4 to 5 hours to remove air. Maintain a head pressure of 7 to 10 psig. Connect the column to the detector (Section 6.7.1.4).

13.2.2 Column calibration

13.2.2.1 Load 5 mL of the GPC calibration solution (Section 7.4) into the sample loop.

13.2.2.2 Inject the GPC calibration solution and record the signal from the detector. The elution pattern will be corn oil, BEHP, methoxychlor, perylene, and sulfur.

13.2.2.3 Set the "dump time" to allow >85% removal of BEHP and >85% collection of methoxychlor.

13.2.2.4 Set the "collect time" to the time of the sulfur peak maximum.

13.2.2.5 Verify calibration with the GPC calibration solution after every 20 extracts. Calibration is verified if the recovery of the methoxychlor is greater than 85%. If calibration is not verified, the system must be recalibrated using the GPC calibration solution, and the previous sample batch must be re-extracted and cleaned up using the calibrated GPC system.

13.2.3 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this Method is designed to handle a maximum of 0.5 g of material from an aqueous, soil, or mixed-phase sample in a 5-mL extract, and has been shown to handle 1.5 g of lipid from a tissue sample in a 5-mL extract. If the extract is known or expected to contain more than these amounts, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50-µL aliquot.

13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove particles. Load the 5.0-mL extract onto the column.

13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400- to 500-mL beaker. Allow the system to rinse for additional 10 minutes before injecting the next sample.

13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

13.2.3.4 If an extract is encountered that could overload the GPC column to the extent that carry-over could occur, a 5.0-mL methylene chloride blank must be run through the system to check for carry-over.

13.2.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the GC/MS.

13.3 Silica gel cleanup

13.3.1 Place a glass-wool plug in a 15-mm ID chromatography column (Section 6.7.4.2). Pack the column bottom to top with: 1 g silica gel (Section 7.5.1.1), 4 g basic silica gel (Section 7.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.5.1.2), 2 g silica gel, and 4

g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

13.3.2 Pre-elute the column with 50 to 100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

13.3.4 Rinse the receiver twice with 1-mL portions of hexane, and apply separately to the column. Elute the CBs with 25 mL of hexane and collect the eluate.

13.3.5 Concentrate the eluate per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.3.6 For extracts of samples known to contain large quantities of other organic compounds, it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 40% w/w (6.7 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used.

Note: *The use of stronger acid silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of the CBs. Increasing the strengths of the acid and basic silica gel may also require different volumes of hexane than those specified above to elute the analytes from the column. The performance of the Method after such modifications must be verified by the procedure in Section 9.2.*

13.4 Carbon column (Reference 17)

13.4.1 Cut both ends from a 50-mL disposable serological pipet (Section 6.7.3.2) to produce a 20-cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 3.6 g of Carbopak/Celite (Section 7.5.2.3) to form an adsorbent bed 20 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

13.4.2 Pre-elute the column with 20 mL each in succession of toluene, methylene chloride, and hexane.

13.4.3 When the solvent is within 1 mm of the column packing, apply the n-hexane sample extract to the column. Rinse the sample container twice with 1-mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.

13.4.4 Elute the column with 25 mL of n-hexane and collect the eluate. This fraction will contain the mono- and di-ortho CBs. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.4.5 Elute the column with 15 mL of methanol and discard the eluate. The fraction discarded will contain residual lipids and other potential interferents, if present.

13.4.6 Elute the column with 15 mL of toluene and collect the eluate. This fraction will contain CBs 77, 126, and 169. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.4.7 Concentrate the fractions per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.5 HPLC (References 4 and 18)

13.5.1 Column calibration

13.5.1.1 Prepare a calibration standard containing the Toxics and other congeners of interest at the concentrations of the stock solution in Table 3, or at a concentration appropriate to the response of the detector.

13.5.1.2 Inject the calibration standard into the HPLC and record the signal from the detector. Collect the eluant for reuse. Elution will be in the order of the di-ortho, mono-ortho, and non-ortho congeners.

13.5.1.3 Establish the collection time for the congeners of interest. Following calibration, flush the injection system with solvent to ensure that residual CBs are removed from the system.

13.5.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the CBs is 75 to 125% compared to the calibration (Section 13.5.1.1). If calibration I s not verified, the system must be recalibrated using the calibration solution, and the previous 20 samples must be re-extracted and cleaned up using the calibrated system.

13.5.2 Extract cleanup—HPLC requires that the column not be overloaded. The column specified in this Method is designed to handle a maximum of 5-50 µg of a given CB, depending on the congener (Reference 18). If the amount of material in the extract will overload the column, split the extract into fractions and combine the fractions after elution from the column.

13.5.2.1 Rinse the sides of the vial containing the sample and adjust to the volume required for the sample loop for injection.

13.5.2.2 Inject the sample extract into the HPLC.

13.5.2.3 Elute the extract using the calibration data determined in Section 13.5.1. Collect the fraction(s) in clean 20-mL concentrator tubes.

13.5.2.4 If an extract containing greater than 500 µg of total CBs is encountered, a blank must be run through the system to check for carry-over.

13.5.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/MS.

13.6 Anthropogenic isolation column (Reference 3)—Used for removal of lipids from tissue extracts

13.6.1 Prepare the column as given in Section 7.5.3.

13.6.2 Pre-elute the column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

13.6.3 Load the sample and rinses (Section 12.4.9.2) onto the column by draining each portion to the top of the bed. Elute the CBs from the column into the apparatus used for concentration (Section 12.4.7) using 200 mL of hexane.

13.6.4 Remove a small portion (e.g, 50 µL) of the extract for determination of residue content. Estimate the percent of the total that this portion represents. Concentrate the small portion to constant weight per Section 12.7.3.1. Calculate the total amount of residue in the extract. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.

13.6.5 If necessary, exchange the extract to a solvent suitable for the additional cleanups to be used (Section 13.2-13.5 and 13.7).

13.6.6 Clean up the extract using the procedures in Sections 13.2-13.5 and 13.7. GPC (Section 13.2) and Florisil (Section 13.7) are recommended as minimum additional cleanup steps.

13.6.7 Following cleanup, concentrate the extract to 20 µL as described in Section 12.7 and proceed with the analysis in Section 14.

13.7 Florisil cleanup (Reference 19)

13.7.1 Begin to drain the n-hexane from the column (Section 7.5.4.1.2). Adjust the flow rate of eluant to 4.5-5.0 mL/min.

13.7.2 When the n-hexane is within 1 mm of the sodium sulfate, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1-mL portions of hexane and apply to the column.

13.7.3 Elute the mono-ortho and di-ortho CBs with approx 165 mL of n-hexane and collect the eluate. Elute the non-ortho co-planar CBs with approx 100 mL of 6% ether:hexane and collect the eluate. The exact volumes of solvents will need to be determined for each batch of Florisil. If the mono/di-ortho CBs are not to be separated from the non-ortho co-planar CBs, elute all CBs with 6% ether:hexane.

13.7.4 Concentrate the eluate(s) per Sections 12.6-12.7 for further cleanup or for injection into the HPLC or GC/MS.

14.0 HRGC/HRMS analysis

14.1 Establish the operating conditions given in Section 10.1.

14.2 Add 2 µL of the labeled injection internal standard spiking solution (Section 7.14) to the 20 µL sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more labeled injection internal standard spiking solution. Rather, bring the extract back to its previous volume (e.g., 19 µL) with pure nonane (18 µL if 2 µL injections are used).

14.3 Inject 1.0 or 2.0 µL of the concentrated extract containing the Labeled injection internal standards using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10.3).

14.3.1 Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes.

14.3.2 Monitor the exact m/z's at each LOC throughout the LOC retention time window. Where warranted, monitor m/z's associated with congeners at higher levels of chlorination to assure that fragments are not interfering with the m/z's for congeners at lower levels of chlorination. Also where warranted, monitor m/z's associated with interferents expected to be present.

14.3.3 Stop data collection after $^{13}C_{12}$-DeCB has eluted. Return the column to the initial temperature for analysis of the next extract or standard.

15.0 System and laboratory performance

15.1 At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all native CBs and labeled compounds. For these tests, analysis of the CS-3 calibration verification (VER) standard (Section 7.10.1 and Table 5) and the diluted combined 209 congener solution (Section 7.10.2.2 and Table 5) must be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) must be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.

15.2 MS resolution—Static resolving power checks must be performed at the beginning and at the end of each shift per Sections 10.2.1. If analyses are performed on successive shifts, only the beginning of shift static resolving power check is required. If the requirement in Section 10.2.1 cannot be met, the problem must be corrected before analyses can proceed. If any of the samples in the previous shift may be affected by poor resolution, those samples must be re-analyzed.

15.3 Calibration verification

15.3.1 Inject the VER (CS-3) standard using the procedure in Section 14.

15.3.2 The m/z abundance ratios for all CBs must be within the limits in Table 8; otherwise, the mass spectrometer must be adjusted until the m/z abundance ratios fall within the

limits specified when the verification test is be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.2.1) prior to repeat of the verification test.

15.3.3 The GC peak representing each native CB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer must be adjusted and the verification test repeated.

15.3.4 Compute the concentration of the Toxics/LOC CBs by isotope dilution (Section 17.1). These concentrations are computed based on the calibration data in Section 10.

15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 6. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly. In this event, prepare a fresh calibration standard or correct the problem and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10). If recalibration is required, recalibration for the 209 congeners (Section 10.5) must also be performed.

15.4 Retention times and GC resolution

15.4.1 Retention times.

15.4.1.1 Absolute—The absolute retention times of the Labeled Toxics/LOC/window defining standard congeners (Section 7.12) in the verification test (Section 15.3) must be within ± 15 seconds of the respective retention times in the calibration or, if an alternate column or column system is employed, within ± 15 seconds of the respective retention times in the calibration for the alternate column or column system (Section 6.9.1.2).

15.4.1.2 Relative—The relative retention times of native CBs and labeled compounds in the verification test (Section 15.3) must be within their respective RRT limits in Table 2 or, if an alternate column or column system is employed, within their respective RRT limits for the alternate column or column system (Section 6.9.1.2).

15.4.1.3 If the absolute or relative retention time of any compound is not within the limits specified, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.

15.4.2 GC resolution and minimum analysis time

15.4.2.1 As a final step in calibration verification, inject the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 5).

15.4.2.2 The resolution and minimum analysis time specifications in Sections 6.9.1.1.2 and 6.9.1.1.1, respectively, must be met for the SPB-octyl column or, if an alternate column or column system is employed, must be met as specified for the alternate column or column system (Section 6.9.1.2). If these specifications are not met, the GC analysis conditions must be adjusted until the specifications are met, or the column must be replaced and the calibration verification tests repeated Sections 15.4.1 through 15.4.2.2), or the system must be recalibrated (Section 10).

15.4.2.3 After the resolution and minimum analysis time specifications are met, update the retention times, relative retention times, and response factors for the all congeners except the Toxics and LOC CBs. For the Toxics and LOC CBs, the multi-point calibration data must be used (see Section 10.4 and 15.3).

15.5 Ongoing precision and recovery

15.5.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.4, 11.6.2, or 11.8.3.2) prior to analysis of samples from the same batch.

15.5.2 Compute the percent recovery of the Toxics/LOC CBs by isotope dilution (Section 10.4). Compute the percent recovery of each labeled compound by the internal standard method (Section 10.5).

15.5.3 For the Toxics/LOC CBs and labeled compounds, compare the recovery to the OPR limits given in Table 6. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/ concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.5).

15.5.4 If desired, add results that pass the specifications in Section 15.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each congener in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (S_R). Express the accuracy as a recovery interval from $R - 2S_R$ to $R + 2S_R$. For example, if R = 95% and S_R = 5%, the accuracy is 85 to 105%.

15.6 Blank—Analyze the Method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. If CBs will be carried from the OPR into the Method blank, analyze one or more aliquots of solvent between the OPR and the Method blank. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

16.0 Qualitative determination

A CB or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

16.1 The signals for the two exact m/z's in Table 7 must be present and must maximize within the same two scans.

16.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each CB detected in a sample extract, and greater than or equal to 10 for all CBs in the calibration and verification standards (Sections 10.3.3 and 15.3.3).

16.3 The ratio of the integrated areas of the two exact m/z's specified in Table 7 must be within the limit in Table 8, or within ± 15 percent of the ratio in the midpoint (CS-3) calibration or calibration verification (VER), whichever is most recent.

16.4 The relative retention time of the peak for a CB must be within the RRT QC limits specified in Table 2 or within similar limits developed from calibration data (Section 10.1.2)]. If an alternate column or column system is employed, the RRT for the CB must be within its respective RRT QC limits for the alternate column or column system (Section 6.9.1.2).

Note: *For native CBs determined by internal standard quantitation, a given CB congener may fall within more than RT window and be mis-identified unless the RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. Retention time regression analysis may aid in this identification.*

16.5 Because of congener overlap and the potential for interfering substances, it is possible that all of the identification criteria (Sections 16.1-16.4) may not be met. It is also possible that loss of one or more chlorines from a highly chlorinated congener may inflate or produce a false concentration for a less-chlorinated congener that elutes at the same retention time (see Section 18.5). If identification is ambiguous, an experienced spectrometrist (Section 1.4) must determine the presence or absence of the congener.

16.6 If the criteria for identification in Sections 16.1-16.5 are not met, the CB has not been identified and the result for that congener may not be reported or used for permitting or regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

17.0 Quantitative determination

17.1 Isotope dilution quantitation

17.1.1 By adding a known amount of the Labeled Toxics/LOC/window-defining compounds to every sample prior to extraction, correction for recovery of the CB can be made because the native compound and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative responses (RRs) are used

in conjunction with the calibration data in Section 10.4 to determine concentrations in the final extract, so long as labeled compound spiking levels are constant.

17.1.2 Compute the concentrations in the extract of the Native Toxics/LOC CBs using the RRs from the calibration data (Section 10.4) and following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

Where:

C_{ex} = The concentration of the PCB in the extract , and the other terms are as defined in Section 10.5.1

17.2 Internal standard quantitation and labeled compound recovery

17.2.1 Compute the concentrations in the extract of the native compounds other than those in the Native Toxics/LOC standard, in the Labeled cleanup standard, and in the Labeled injection internal standard (except for labeled CB 178) using the response factors determined from the calibration data (Section 10.5) and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ RF}$$

Where:

C_{ex} = The concentration of the labeled compound in the extract, and the opthers terms are as defined in Section 10.6.1.

17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the Labeled Toxics/LOC/window-defining CBs and the Labeled cleanup standard CBs using the following equation:

$$Recovery\ (\%) = \frac{Concentration\ found\ (ng/mL)}{Concentration\ spiked\ (ng/mL)} \times 100$$

17.3 The concentration of a native CB in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.2.2.3), as follows:

$$Concentration\ in\ solid\ (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

Where:

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
W_s = The sample weight (dry weight) in kg.

17.4 The concentration of a native CB in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4), as follows:

$$\textit{Concentration in aqueous phase (pg/L)} = 1000 \times \frac{(C_{ex} \times V_{ex})}{V_s}$$

Where:

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
V_s = The sample volume in liters.

17.5 If the SICP area at either quantitation m/z for any congener exceeds the calibration range of the system, dilute the sample extract by the factor necessary to bring the concentration within the calibration range, adjust the concentration of the Labeled injection internal standard to 100 pg/µL in the extract, and analyze an aliquot of this diluted extract. If the CBs cannot be measured reliably by isotope dilution, dilute and analyze an aqueous sample or analyze a smaller portion of a soil, tissue, or mixed-phase sample. Adjust the CB congener concentrations, detection limits, and minimum levels to account for the dilution.

17.6 Reporting of results—Results are reported to three significant figures for the CBs and labeled compounds found in all standards, blanks, and samples.

17.6.1 Reporting units and levels

17.6.1.1 Aqueous samples—Report results in pg/L (parts-per-quadrillion).

17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost)—Report results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be converted to aqueous units.

17.6.1.3 Tissues—Report results in ng/kg of wet tissue, not on the basis of the lipid content of the tissue. Report the percent lipid content, so that the data user can calculate the concentration on a lipid basis if desired.

17.6.1.4 Reporting level

17.6.1.4.1 Report results above the minimum level of quantitation (ML) for analyses of blanks, standards, and samples. The estimated minimum levels (EMLs) in Table 2 are based on common laboratory contamination levels. A laboratory may establish an ML for a CB lower than the EMLs in Table 2. MLs may be established as low as the lowest calibration point (Table 5) provided that the concentration of the congener in a minimum of 10 blanks for a sample medium (e.g., water, soil, sludge, tissue) is significantly below the EML in Table 2. Significant means that the ML for the congener is no less than 2 standard deviations above the average (mean) level in the minimum of 10 blanks (Reference 20). The blanks must be analyzed during the

same period that samples are analyzed, ideally over an approximately 1-month period.

17.6.1.4.2 Standards (VER, IPR, OPR) and samples—Report the result for each congener at or above the ML (or EML Table 2) to 3 significant figures. Report results below the ML (or EML) as <ML (where ML is the concentration at the ML) or as required by the regulatory authority or permit.

17.6.1.4.3 Blanks—Report results above the ML (or EML) to 3 significant figures. Report results below the ML but above the MDL (or EMDL) to 2 significant figures. Report results below the MDL as <MDL (where MDL is the concentration at the MDL) or as required by the regulatory authority or permit.

17.6.1.4.4 Blank correction—Blank-corrected results may be reported in addition to reporting of separate results for samples (Section 17.6.1.4.1) and blanks (Section 17.6.1.4.2). The recommended procedure for blank correction (Reference 20) is that a result is significantly above the blank level, and the level in the blank may be subtracted, if the result is 2 standard deviations above the mean (average) of results of analyses of 10 or more blanks for a sample medium.

17.6.2 Results for a CB in a sample that has been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5).

17.6.3 For a CB having a labeled analog, report results at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the Method (Section 9.3 and Table 6).

17.6.4 If requested, the total concentration of all congeners at a given level of chlorination (homolog; i.e., total TrCB, total PeCB, total HxCB) may be reported by summing the concentrations of all congeners identified at that LOC, including both the Toxics and other congeners. Also if requested, total CBs may be reported by summing all congeners identified at all LOCs.

18.0 Analysis of complex samples

18.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts may not concentrate to 20 µL (Section 12.7); others may overload the GC column and/or mass spectrometer. Fragment ions from congeners at higher levels of chlorination may interfere with determination of congeners at lower levels of chlorination.

18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to 20 µL after all cleanup procedures have been exhausted. If a smaller aliquot of soils or mixed-phase samples is analyzed, attempt to assure that the sample is representative.

18.3 Perform integration of peak areas and calculate concentrations manually when interferences preclude computerized calculations.

18.4 Several laboratories have reported that backgrounds of many of the CB congeners are difficult to eliminate, and that these backgrounds can interfere with the determination of the CBs in environmental samples. Backgrounds of Toxics with congener numbers 105, 114, 118, 123, 156, 157, and 167 are common. The effects of contamination on results for these congeners should be understood in order to make a reliable determination.

18.5 Interferences may pose a problem in the determination of congeners 81, 123, 126, and 169 in some environmental samples. Loss of one or more chlorines from a highly chlorinated congener may inflate or produce a false concentration for a less-chlorinated congener that elutes at the same retention time. If, upon inspection of the chromatogram, the possibility of interferences is evident (e.g., high concentrations of fragments from loss of one or two chlorines from higher chlorinated closely eluting congeners), carbon column fractionation (Section 13.4) and analysis is recommended.

18.6 Recovery of labeled compounds—In most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).

18.6.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 6), a diluted sample must be analyzed (Section 17.5).

18.6.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.10.1 and Table 5) must be analyzed and calibration verified (Section 15.3).

18.6.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.

18.6.4 If calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the Method does not apply to the sample being analyzed and the result may not be reported or used for permitting or regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this Method or an alternate GC column must be employed to resolve the interference. If all cleanup procedures in this Method and an alternate GC column have been employed and labeled compound recovery remains outside of the normal range, extraction and/or cleanup procedures that are beyond this scope of this Method will be required to analyze the sample.

19.0 Pollution prevention

19.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When wastes cannot be reduced feasibly at the source, the Agency recommends recycling as the next best option.

19.2 The CBs in this Method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

19.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477.

20.0 Waste management

20.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

20.2 Samples containing HCl or H_2SO_4 to pH <2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.

20.3 The CBs decompose above 800 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

20.4 Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the CBs can no longer be detected.

20.5 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better-Laboratory Chemical Management for Waste Reduction,* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

21.0 Method performance

Method 1668A was validated and preliminary data were collected in a single laboratory (Reference 21). The original version of Method 1668 was validated in two single-laboratory studies. Figure 8 is a chromatogram showing method performance at each level of chlorination.

22.0 References

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23.0 Tables and Figures

Table 1. Names, Congener numbers, and CAS Registry numbers for native and labeled chlorinated biphenyl (CB) congeners determined by isotope dilution and internal standard HRGC/HRMS.

CB congener[1]	Congener number	CAS registry number	Labeled analog	Congener analog	CAS registry number
2-MoCB	1	2051-60-7	$^{13}C_{12}$-2-MoCB[2]	1L	234432-85-0
3-MoCB	2	2051-61-8			
4-MoCB	3	2051-62-9	$^{13}C_{12}$-4-MoCB[2]	3L	208263-77-8
2,2'-DiCB	4	13029-08-8	$^{13}C_{12}$-2,2'-DiCB[2]	4L	234432-86-1
2,3-DiCB	5	16605-91-7			
2,3'-DiCB	6	25569-80-6			
2,4-DiCB	7	33284-50-3			
2,4'-DiCB[3]	8	34883-43-7			
2,5-DiCB	9	34883-39-1	$^{13}C_{12}$-2,5-DiCB[4]	9L	250694-89-4
2,6-DiCB	10	33146-45-1			
3,3'-DiCB	11	2050-67-1			
3,4-DiCB	12	2974-92-7			
3,4'-DiCB	13	2974-90-5			
3,5-DiCB	14	34883-41-5			
4,4'-DiCB	15	2050-68-2	$^{13}C_{12}$-4,4'-DiCB[2]	15L	208263-67-6
2,2',3-TrCB	16	38444-78-9			
2,2',4-TrCB	17	37680-66-3			
2,2',5-TrCB[3]	18	37680-65-2			
2,2',6-TrCB	19	38444-73-4	$^{13}C_{12}$-2,2',6-TrCB[2]	19L	234432-87-2
2,3,3'-TrCB	20	38444-84-7			
2,3,4-TrCB	21	55702-46-0			
2,3,4'-TrCB	22	38444-85-8			
2,3,5-TrCB	23	55720-44-0			
2,3,6-TrCB	24	55702-45-9			
2,3',4-TrCB	25	55712-37-3			
2,3',5-TrCB	26	38444-81-4			
2,3',6-TrCB	27	38444-76-7			
2,4,4'-TrCB[3]	28	7012-37-5	$^{13}C_{12}$-2,4,4'-TriCB[5]	28L	208263-76-7
2,4,5-TrCB	29	15862-07-4			
2,4,6-TrCB	30	35693-92-6			
2,4',5-TrCB	31	16606-02-3			
2,4',6-TrCB	32	38444-77-8			
2',3,4-TrCB	33	38444-86-9			
2',3,5-TrCB	34	37680-68-5			

CB congener[1]	Congener number	CAS registry number	Labeled analog	Congener analog	CAS registry number
3,3',4-TrCB	35	37680-69-6			
3,3',5-TrCB	36	38444-87-0			
3,4,4'-TrCB	37	38444-90-5	$^{13}C_{12}$-3,4,4'-TrCB[2]	37L	208263-79-0
3,4,5-TrCB	38	53555-66-1			
3,4',5-TrCB	39	38444-88-1			
2,2',3,3'-TeCB	40	38444-93-8			
2,2',3,4-TeCB	41	52663-59-9			
2,2',3,4'-TeCB	42	36559-22-5			
2,2',3,5-TeCB	43	70362-46-8			
2,2',3,5'-TeCB[3]	44	41464-39-5			
2,2',3,6-TeCB	45	70362-45-7			
2,2',3,6'-TeCB	46	41464-47-5			
2,2',4,4'-TeCB	47	2437-79-8			
2,2',4,5-TeCB	48	70362-47-9			
2,2',4,5'-TeCB	49	41464-40-8			
2,2',4,6-TeCB	50	62796-65-0			
2,2',4,6'-TeCB	51	68194-04-7			
2,2',5,5'-TeCB[3]	52	35693-99-3	$^{13}C_{12}$-2,2',5,5'-TeCB[4]	52L	208263-80-3
2,2',5,6'-TeCB	53	41464-41-9			
2,2',6,6'-TeCB	54	15968-05-5	$^{13}C_{12}$-2,2',6,6'-TeCB[2]	54L	234432-88-3
2,3,3',4'-TeCB	55	74338-24-2			
2,3,3',4'-TeCB	56	41464-43-1			
2,3,3',5-TeCB	57	70424-67-8			
2,3,3',5'-TeCB	58	41464-49-7			
2,3,3',6-TeCB	59	74472-33-6			
2,3,4,4'-TeCB	60	33025-41-1			
2,3,4,5-TeCB	61	33284-53-6			
2,3,4,6-TeCB	62	54230-22-7			
2,3,4',5-TeCB	63	74472-34-7			
2,3,4',6-TeCB	64	52663-58-8			
2,3,5,6-TeCB	65	33284-54-7			
2,3',4,4'-TeCB[3]	66	32598-10-0			
2,3',4,5-TeCB	67	73575-53-8			
2,3',4,5'-TeCB	68	73575-52-7			
2,3',4,6-TeCB	69	60233-24-1			
2,3',4',5-TeCB	70	32598-11-1			
2,3',4',6-TeCB	71	41464-46-4			
2,3',5,5'-TeCB	72	41464-42-0			

CB congener[1]	Congener number	CAS registry number	Labeled analog	Congener analog	CAS registry number
2,3',5',6-TeCB	73	74338-23-1			
2,4,4',5-TeCB	74	32690-93-0			
2,4,4',6-TeCB	75	32598-12-2			
2',3,4,5-TeCB	76	70362-48-0			
3,3',4,4'-TeCB[3,6]	77	32598-13-3	$^{13}C_{12}$-3,3',4,4'-TeCB[2,7]	77L	105600-23-5
3,3',4,5-TeCB	78	70362-49-1			
3,3',4,5'-TeCB	79	41464-48-6			
3,3',5,5'-TeCB	80	33284-52-5			
3,4,4',5-TeCB[6]	81	70362-50-4	$^{13}C_{12}$-3,4,4',5-TeCB[7]	81L	208461-24-9
2,2',3,3',4-PeCB	82	52663-62-4			
2,2',3,3',5-PeCB	83	60145-20-2			
2,2',3,3',6-PeCB	84	52663-60-2			
2,2',3,4,4'-PeCB	85	65510-45-4			
2,2',3,4,5-PeCB	86	55312-69-1			
2,2',3,4,5'-PeCB	87	38380-02-8			
2,2',3,4,6-PeCB	88	55215-17-3			
2,2',3,4,6'-PeCB	89	73575-57-2			
2,2',3,4',5-PeCB	90	68194-07-0			
2,2',3,4',6-PeCB	91	68194-05-8			
2,2',3,5,5'-PeCB	92	52663-61-3			
2,2',3,5,6-PeCB	93	73575-56-1			
2,2',3,5,6'-PeCB	94	73575-55-0			
2,2',3,5',6-PeCB	95	38379-99-6			
2,2',3,6,6'-PeCB	96	73575-54-9			
2,2',3',4,5-PeCB	97	41464-51-1			
2,2',3',4,6-PeCB	98	60233-25-2			
2,2',4,4',5-PeCB	99	38380-01-7			
2,2',4,4',6-PeCB	100	39485-83-1			
2,2',4,5,5'-PeCB[3]	101	37680-73-2	$^{13}C_{12}$-2,2',4,5,5'-PeCB[4]	101L	104130-39-4
2,2',4,5,6'-PeCB	102	68194-06-9			
2,2',4,5,'6-PeCB	103	60145-21-3			
2,2',4,6,6'-PeCB	104	56558-16-8	$^{13}C_{12}$-2,2',4,6,6'-PeCB[2]	104L	234432-89-4
2,3,3',4,4'-PeCB[3,6]	105	32598-14-4	$^{13}C_{12}$-2,3,3',4,4'-PeCB[7]	105L	208263-62-1
2,3,3',4,5-PeCB	106	70424-69-0			
2,3,3',4',5-PeCB	107	70424-68-9			
2,3,3',4,5'-PeCB	108	70362-41-3			
2,3,3',4,6-PeCB	109	74472-35-8			
2,3,3',4',6-PeCB	110	38380-03-9			

CB congener[1]	Congener number	CAS registry number	Labeled analog	Congener analog	CAS registry number
2,3,3',5,5'-PeCB	111	39635-32-0	$^{13}C_{12}$-2,3,3',5,5'-PeCB[5]	111 L	235416-29-2
2,3,3',5,6-PeCB	112	74472-36-9			
2,3,3',5',6-PeCB	113	68194-10-5			
2,3,4,4',5-PeCB[6]	114	74472-37-0	$^{13}C_{12}$-2,3,4,4',5-PeCB[7]	114 L	208263-63-2
2,3,4,4',6-PeCB	115	74472-38-1			
2,3,4,5,6-PeCB	116	18259-05-7			
2,3,4',5,6-PeCB	117	68194-11-6			
2,3',4,4',5-PeCB[3,6]	118	31508-00-6	$^{13}C_{12}$-2,3',4,4',5-PeCB[7]	118 L	104130-40-7
2,3',4,4',6-PeCB	119	56558-17-9			
2,3',4,5,5'-PeCB	120	68194-12-7			
2,3',4,5,'6-PeCB	121	56558-18-0			
2',3,3',4,5-PeCB	122	76842-07-4			
2',3,4,4',5-PeCB[6]	123	65510-44-3	$^{13}C_{12}$-2',3,4,4',5-PeCB[7]	123L	208263-64-3
2',3,4,5,5'-PeCB	124	70424-70-3			
2',3,4,5,6'-PeCB	125	74472-39-2			
3,3',4,4',5-PeCB[3,6]	126	57465-28-8	$^{13}C_{12}$-3,3',4,4',5-PeCB[2,7]	126L	208263-65-4
3,3',4,5,5'-PeCB	127	39635-33-1			
2,2',3,3',4,4'-HxCB[3]	128	38380-07-3			
2,2',3,3',4,5-HxCB	129	55215-18-4			
2,2',3,3',4,5'-HxCB	130	52663-66-8			
2,2',3,3',4,6-HxCB	131	61798-70-7			
2,2',3,3',4,6'-HxCB	132	38380-05-1			
2,2',3,3',5,5'-HxCB	133	35694-04-3			
2,2',3,3',5,6-HxCB	134	52704-70-8			
2,2',3,3',5,6'-HxCB	135	52744-13-5			
2,2',3,3',6,6'-HxCB	136	38411-22-2			
2,2',3,4,4',5-HxCB	137	35694-06-5			
2,2',3,4,4',5'-HxCB[3]	138	35065-28-2	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[4]	138L	208263-66-5
2,2',3,4,4',6-HxCB	139	56030-56-9			
2,2',3,4,4',6'-HxCB	140	59291-64-4			
2,2',3,4,5,5'-HxCB	141	52712-04-6			
2,2',3,4,5,6-HxCB	142	41411-61-4			
2,2',3,4,5,6'-HxCB	143	68194-15-0			
2,2',3,4,5',6-HxCB	144	68194-14-9			
2,2',3,4,6,6'-HxCB	145	74472-40-5			
2,2',3,4',5,5'-HxCB	146	51908-16-8			
2,2',3,4',5,6-HxCB	147	68194-13-8			
2,2',3,4',5,6'-HxCB	148	74472-41-6			

CB congener[1]	Congener number	CAS registry number	Labeled analog	Congener analog	CAS registry number
2,2',3,4',5',6-HxCB	149	38380-04-0			
2,2',3,4',6,6'-HxCB	150	68194-08-1			
2,2',3,5,5',6-HxCB	151	52663-63-5			
2,2',3,5,6,6'-HxCB	152	68194-09-2			
2,2',4,4',5,5'-HxCB[3]	153	35065-27-1			
2,2',4,4',5',6-HxCB	154	60145-22-4			
2,2',4,4',6,6'-HxCB	155	33979-03-2	$^{13}C_{12}$-2,2',4,4',6,6'-HxCB[2]	155L	234432-90-7
2,3,3',4,4',5-HxCB[6]	156	38380-08-4	$^{13}C_{12}$-2,3,3',4,4',5-HxCB[7]	156L	208263-68-7
2,3,3',4,4',5'-HxCB[6]	157	69782-90-7	$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[7]	157L	235416-30-5
2,3,3',4,4',6-HxCB	158	74472-42-7			
2,3,3',4,5,5'-HxCB	159	39635-35-3			
2,3,3',4,5,6-HxCB	160	41411-62-5			
2,3,3',4,5',6-HxCB	161	74472-43-8			
2,3,3',4',5,5'-HxCB	162	39635-34-2			
2,3,3',4',5,6-HxCB	163	74472-44-9			
2,3,3',4',5',6-HxCB	164	74472-45-0			
2,3,3',5,5',6-HxCB	165	74472-46-1			
2,3,4,4',5,6-HxCB	166	41411-63-6			
2,3',4,4',5,5'-HxCB[6]	167	52663-72-6	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[7]	167L	208263-69-8
2,3',4,4',5',6-HxCB	168	59291-65-5			
3,3',4,4',5,5'-HxCB[3,6]	169	32774-16-6	$^{13}C_{12}$-3,3',4,4',5,5'-HxCB[2,7]	169L	208263-70-1
2,2',3,3',4,4',5-HpCB[3]	170	35065-30-6	$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	160901-80-4
2,2'3,3',4,4',6-HpCB	171	52663-71-5			
2,2',3,3',4,5,5'-HpCB	172	52663-74-8			
2,2',3,3',4,5,6-HpCB	173	68194-16-1			
2,2',3,3',4,5,6'-HpCB	174	38411-25-5			
2,2',3,3',4,5',6-HpCB	175	40186-70-7			
2,2',3,3',4,6,6'-HpCB	176	52663-65-7			
2,2',3,3',4',5,6-HpCB	177	52663-70-4			
2,2',3,3',5,5',6-HpCB	178	52663-67-9	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[5]	178L	232919-67-4
2,2',3,3',5,6,6'-HpCB	179	52663-64-6			
2,2',3,4,4',5,5'-HpCB[3]	180	35065-29-3	$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	160901-82-6
2,2',3,4,4',5,6-HpCB	181	74472-47-2			
2,2',3,4,4',5,6'-HpCB	182	60145-23-5			
2,2',3,4,4',5',6-HpCB	183	52663-69-1			
2,2',3,4,4',6,6'-HpCB	184	74472-48-3			
2,2',3,4,5,5',6-HpCB	185	52712-05-7			
2,2',3,4,5,6,6'-HpCB	186	74472-49-4			

CB congener[1]	Congener number	CAS registry number	Labeled analog	Congener analog	CAS registry number
2,2',3,4',5,5',6-HpCB[3]	187	52663-68-0			
2,2',3,4',5,6,6'-HpCB	188	74487-85-7	$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB[2]	188L	234432-91-8
2,3,3',4,4',5,5'-HpCB[6]	189	39635-31-9	$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB[2,7]	189L	208263-73-4
2,3,3',4,4',5,6-HpCB	190	41411-64-7			
2,3,3',4,4',5',6-HpCB	191	74472-50-7			
2,3,3',4,5,5',6-HpCB	192	74472-51-8			
2,3,3',4',5,5',6-HpCB	193	69782-91-8			
2,2',3,3',4,4',5,5'-OcCB	194	35694-08-7	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB[4]	194L	208263-74-5
2,2',3,3',4,4',5,6-OcCB[3]	195	52663-78-2			
2,2',3,3',4,4',5,6'-OcCB	196	42740-50-1			
2,2',3,3',4,4',6,6'-OcCB	197	33091-17-7			
2,2',3,3',4,5,5',6-OcCB	198	68194-17-2			
2,2',3,3',4,5,5',6'-OcCB	199	52663-75-9			
2,2',3,3',4,5,6,6'-OcCB	200	52663-73-7			
2,2',3,3',4,5',6,6'-OcCB	201	40186-71-8			
2,2',3,3',5,5',6,6'-OcCB	202	2136-99-4	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB[2]	202L	105600-26-8
2,2',3,4,4',5,5',6-OcCB	203	52663-76-0			
2,2',3,4,4',5,6,6'-OcCB	204	74472-52-9			
2,3,3',4,4',5,5',6-OcCB	205	74472-53-0	$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB[2]	205L	234446-64-1
2,2',3,3',4,4',5,5',6-NoCB[3]	206	40186-72-9	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB[2]	206L	208263-75-6
2,2',3,3',4,4',5,6,6'-NoCB	207	52663-79-3			
2,2',3,3',4,5,5',6,6'-NoCB	208	52663-77-1	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB[2]	208L	234432-92-9
DeCB[3]	209	2051-24-3	$^{13}C_{12}$-DeCB[2]	209L	105600-27-9

1. Abbreviations for chlorination levels

MoCB	monochlorobiphenyl	HxCB	hexachlorobiphenyl
DiCB	dichlorobiphenyl	HpCB	heptachlorobiphenyl
TrCB	trichlorobiphenyl	OcCB	octachlorobiphenyl
TeCB	tetrachlorobiphenyl	NoCB	nonachlorobiphenyl
PeCB	pentachlorobiphenyl	DeCB	decachlorobiphenyl

2. Labeled level of chlorination (LOC) window-defining congener

3. National Oceanic and Atmospheric Administration (NOAA) congener of interest

4. Labeled injection internal standard

5. Labeled clean-up standard

7. Labeled analog of WHO toxic congener

6. World Health Organization (WHO) toxic congener

Table 2. Retention times (RT), RT references, relative retention times (RRTs), estimated method detection limits (EMDLs), and estimated minimum levels (EMLs) for the 209 CB congeners on SPB-octyl.

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
Compounds using 9L ($^{13}C_{12}$-2,5-DiCB) as Labeled injection internal standard												
CB congener												
Monochlorobiphenyls												
1	1	1L	13:44	1.0012	0.9988-1.0036	-1+3	1L	82	200	8	20	10
1	2	3L	16:08	0.9878	0.9847-0.9908	6	1L/3L	4	10	0.4	1	0.5
1	3	3L	16:21	1.0010	0.9990-1.0031	-1+3	3L	88	200	9	20	10
Dichlorobiphenyls												
2	4	4L	16:40	1.0010	0.9990-1.0030	-1+3	4L	172	500	17	50	20
2	10	4L	16:53	1.0140	1.0110-1.0170	6	4L/15L	22	50	2	5	2
2	9	4L	18:55	1.1361	1.1331-1.1391	6	4L/15L	20	50	2	5	2
2	7	4L	19:07	1.1481	1.1451-1.1512	6	4L/15L	15	50	2	5	2
2	6	4L	19:26	1.1672	1.1642-1.1702	6	4L/15L	13	50	1	5	2
2	5	4L	19:48	1.1892	1.1862-1.1922	6	4L/15L	11	50	1	5	2
2	8	4L	19:56	1.1972	1.1942-1.2002	6	4L/15L	121	500	12	50	20
2	14	15L	21:42	0.9267	0.9246-0.9288	6	4L/15L	31	100	3	10	5
2	11	15L	22:42	0.9694	0.9673-0.9715	6	4L/15L	105	200	10	20	10
2	13	15L	23:03	0.9843	0.9822-0.9865	6	4L/15L	28	100	3	10	5
2	12	15L	23:06	0.9865	0.9843-0.9886	6	4L/15L					
2	13/12	15L	23:04	0.9851	0.9829-0.9872	6	4L/15L					
2	15	15L	23:26	1.0007	0.9993-1.0021	-1+3	15L	183	500	18	50	20
Trichlorobiphenyls												
3	19	19L	20:19	1.0008	0.9992-1.0025	-1+3	19L	42	100	4	10	5
3	30	19L	22:15	1.0961	1.0936-1.0985	6	19L/37L	175	500	17	50	20

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
3	18	19L	22:23	1.1026	1.1002-1.1051	6	19L/37L					
3	30/18	19L	22:19	1.0993	1.0969-1.1018	6	19L/37L					
3	17	19L	22:49	1.1240	1.1215-1.1264	6	19L/37L	86	200	9	20	10
3	27	19L	23:06	1.1379	1.1355-1.1404	6	19L/37L	59	200	6	20	10
3	24	19L	23:14	1.1445	1.1420-1.1470	6	19L/37L	53	200	5	20	10
3	16	19L	23:25	1.1535	1.1511-1.1560	6	19L/37L	35	100	4	10	5
3	32	19L	24:57	1.2291	1.2266-1.2315	6	19L/37L	84	200	8	20	10
3	34	19L	25:17	1.2455	1.2430-1.2479	6	19L/37L	74	200	7	20	10
3	23	19L	25:26	1.2529	1.2504-1.2553	6	19L/37L	50	200	5	20	10
3	29	19L	25:47	1.2701	1.2660-1.2742	10	19L/37L					
3	26	19L	25:48	1.2709	1.2668-1.2750	10	19L/37L	83	200	8	20	10
3	26/29	19L	25:48	1.2709	1.2668-1.2750	10	19L/37L					
3	25	37L	26:04	0.8364	0.8348-0.8380	6	19L/37L	55	200	5	20	10
3	31	37L	26:25	0.8476	0.8460-0.8492	6	19L/37L	152	500	15	50	20
3	28	37L	26:44	0.8578	0.8551-0.8604	10	19L/37L					
3	20	37L	26:49	0.8604	0.8578-0.8631	10	19L/37L	192	500	19	50	20
3	28/20	37L	26:47	0.8594	0.8567-0.8620	10	19L/37L					
3	21	37L	26:58	0.8652	0.8626-0.8679	10	19L/37L					
3	33	37L	27:01	0.8668	0.8642-0.8695	10	19L/37L	51	200	5	20	10
3	21/33	37L	26:59	0.8658	0.8631-0.8684	10	19L/37L					
3	22	37L	27:29	0.8818	0.8802-0.8834	6	19L/37L	90	200	9	20	10
3	36	37L	29:05	0.9332	0.9316-0.9348	6	19L/37L	79	200	8	20	10
3	39	37L	29:30	0.9465	0.9449-0.9481	6	19L/37L	85	200	9	20	10
3	38	37L	30:10	0.9679	0.9663-0.9695	6	19L/37L	83	200	8	20	10
3	35	37L	30:42	0.9850	0.9834-0.9866	6	19L/37L	77	200	8	20	10
3	37	37L	31:11	1.0005	0.9995-1.0011	-1+3	37L	132	500	13	50	20

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
	Labeled Compounds											
1	1L	9L	13:43	0.7257	0.7125-0.7390	30	9L					
1	3L	9L	16:20	0.8642	0.8510-0.8774	30	9L					
2	4L	9L	16:39	0.8810	0.8677-0.8942	30	9L					
2	15L	9L	23:25	1.2390	1.2302-1.2478	20	9L					
3	19L	9L	20:18	1.0741	1.0608-1.0873	30	9L					
3	37L	52L	31:10	1.0841	1.0754-1.0928	30	52L					
Compounds using 52L ($^{13}C_{12}$-2,2',5,5'-TeCB) as Labeled injection internal standard												
	CB congener											
	Tetrachlorobiphenyls											
4	54	54L	23:51	1.0007	0.9993-1.0021	-1+3	54L	118	500	12	50	20
4	50	54L	26:07	1.0958	1.0923-1.0993	10	54L/81L/77L	58	200	6	20	10
4	53	54L	26:09	1.0972	1.0937-1.1007	10	54L/81L/77L					
4	50/53	54L	26:08	1.0965	1.0930-1.1000	10	54L/81L/77L					
4	45	54L	26:55	1.1294	1.1259-1.1329	10	54L/81L/77L	51	200	5	20	10
4	51	54L	26:58	1.1315	1.1280-1.1350	10	54L/81L/77L					
4	45/51	54L	26:57	1.1308	1.1273-1.1343	10	54L/81L/77L					
4	46	54L	27:18	1.1455	1.1434-1.1476	6	54L/81L/77L	101	200	10	20	10
4	52	54L	28:45	1.2063	1.2042-1.2084	6	54L/81L/77L	191	500	19	50	20
4	73	54L	28:52	1.2112	1.2091-1.2133	6	54L/81L/77L	160	500	16	50	20
4	43	54L	28:58	1.2154	1.2133-1.2175	6	54L/81L/77L	94	200	9	20	10
4	69	54L	29:08	1.2224	1.2189-1.2259	10	54L/81L/77L	115	500	11	50	20
4	49	54L	29:16	1.2280	1.2245-1.2315	10	54L/81L/77L					
4	69/49	54L	29:12	1.2252	1.2217-1.2287	10	54L/81L/77L					
4	48	54L	29:33	1.2399	1.2378-1.2420	6	54L/81L/77L	76	200	8	20	10

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
4	65	54L	29:49	1.2510	1.2476-1.2545	10	54L/81L/77L	195	500	19	50	20
4	47	54L	29:50	1.2517	1.2483-1.2552	10	54L/81L/77L					
4	44	54L	29:53	1.2538	1.2503-1.2573	10	54L/81L/77L					
4	44/47/65	54L	29:50	1.2517	1.2483-1.2552	10	54L/81L/77L					
4	62	54L	30:06	1.2629	1.2594-1.2664	10	54L/81L/77L	57	200	6	20	10
4	75	54L	30:08	1.2643	1.2608-1.2678	10	54L/81L/77L					
4	59	54L	30:12	1.2671	1.2636-1.2706	10	54L/81L/77L					
4	59/62/75	54L	30:09	1.2650	1.2615-1.2685	10	54L/81L/77L					
4	42	54L	30:26	1.2769	1.2748-1.2790	6	54L/81L/77L	61	200	6	20	10
4	41	54L	30:52	1.2951	1.2916-1.2986	10	54L/81L/77L	119	500	12	50	20
4	71	54L	30:58	1.2993	1.2958-1.3028	10	54L/81L/77L					
4	40	54L	31:01	1.3014	1.2979-1.3049	10	54L/81L/77L					
4	41/40/71	54L	30:58	1.2993	1.2958-1.3028	10	54L/81L/77L					
4	64	54L	31:12	1.3091	1.3070-1.3112	6	54L/81L/77L	70	200	7	20	10
4	72	81L	31:59	0.8336	0.8323-0.8349	6	54L/81L/77L	158	500	16	50	20
4	68	81L	32:18	0.8419	0.8406-0.8432	6	54L/81L/77L	149	500	15	50	20
4	57	81L	32:46	0.8540	0.8527-0.8553	6	54L/81L/77L	125	500	12	50	20
4	58	81L	33:05	0.8623	0.8610-0.8636	6	54L/81L/77L	127	500	13	50	20
4	67	81L	33:13	0.8658	0.8645-0.8671	6	54L/81L/77L	147	500	15	50	20
4	63	81L	33:30	0.8732	0.8719-0.8745	6	54L/81L/77L	138	500	14	50	20
4	61	81L	33:46	0.8801	0.8775-0.8827	12	54L/81L/77L	171	500	17	50	20
4	70	81L	33:53	0.8831	0.8805-0.8858	12	54L/81L/77L					
4	76	81L	33:55	0.8840	0.8814-0.8866	12	54L/81L/77L					
4	74	81L	33:57	0.8849	0.8827-0.8871	10	54L/81L/77L					
4	61/70/74/76	81L	33:55	0.8840	0.8814-0.8866	12	54L/81L/77L					
4	66	81L	34:15	0.8927	0.8914-0.8940	6	54L/81L/77L	162	500	16	50	20

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
4	55	81L	34:28	0.8983	0.8970-0.8997	6	54L/81L/77L	120	500	12	50	20
4	56	81L	35:03	0.9136	0.9123-0.9149	6	54L/81L/77L	98	200	10	20	10
4	60	81L	35:16	0.9192	0.9179-0.9205	6	54L/81L/77L	131	500	13	50	20
4	80	81L	35:32	0.9262	0.9248-0.9275	6	54L/81L/77L	175	500	18	50	20
4	79	81L	37:16	0.9713	0.9700-0.9726	6	54L/81L/77L	173	500	17	50	20
4	78	81L	37:52	0.9870	0.9857-0.9883	6	54L/81L/77L	171	500	17	50	20
4	81	81L	38:23	1.0004	0.9996-1.0013	-1+3	81L	177	500	18	50	20
4	77	77L	39:02	1.0004	0.9996-1.0013	-1+3	77L	169	500	17	50	20
	Labeled compounds											
4	54L	52L	23:50	0.8290	0.8232-0.8348	20	52L					
4	81L	52L	38:22	1.3345	1.3287-1.3403	20	52L					
4	77L	52L	39:01	1.3571	1.3513-1.3629	20	52L					
Compounds using 101L ($^{13}C_{12}$-2,2',4,5,5'-PeCB) as Labeled injection internal standard												
	CB congener											
	Pentachlorobiphenyls											
5	104	104L	29:46	1.0000	0.9994-1.0017	-1+3	104L	228	500	23	50	20
5	96	104L	30:17	1.0174	1.0146-1.0202	10	104L/123L/114L/118L/105L	210	500	21	50	20
5	103	104L	32:11	1.0812	1.0795-1.0829	6	104L/123L/114L/118L/105L	225	500	23	50	20
5	94	104L	32:29	1.0913	1.0896-1.0929	6	104L/123L/114L/118L/105L	121	500	12	50	20
5	95	104L	33:00	1.1086	1.1058-1.1114	10	104L/123L/114L/118L/105L	221	500	22	50	20
5	100	104L	33:06	1.1120	1.1092-1.1148	10	104L/123L/114L/118L/105L					
5	93	104L	33:14	1.1165	1.1137-1.1193	10	104L/123L/114L/118L/105L					
5	102	104L	33:21	1.1204	1.1176-1.1232	10	104L/123L/114L/118L/105L					
5	98	104L	33:26	1.1232	1.1204-1.1260	10	104L/123L/114L/118L/105L					
5	95/100/93/102/98	104L	33:13	1.1159	1.1131-1.1187	15	104L/123L/114L/118L/105L					

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
5	88	104L	33:48	1.1355	1.1321-1.1389	12	104L/123L/114L/118L/105L	118	500	12	50	20
5	91	104L	33:55	1.1394	1.1366-1.1422	10	104L/123L/114L/118L/105L					
5	88/91	104L	33:52	1.1377	1.1344-1.1411	12	104L/123L/114L/118L/105L					
5	84	104L	34:14	1.1501	1.1484-1.1517	6	104L/123L/114L/118L/105L	124	500	12	50	20
5	89	104L	34:44	1.1669	1.1652-1.1685	6	104L/123L/114L/118L/105L	195	500	19	50	20
5	121	104L	34:57	1.1741	1.1725-1.1758	6	104L/123L/114L/118L/105L	209	500	21	50	20
5	92	123L	35:26	0.8639	0.8627-0.8651	6	104L/123L/114L/118L/105L	115	500	12	50	20
5	113	123L	36:01	0.8781	0.8761-0.8801	10	104L/123L/114L/118L/105L	241	1000	24	100	50
5	90	123L	36:03	0.8789	0.8769-0.8809	10	104L/123L/114L/118L/105L					
5	101	123L	36:04	0.8793	0.8773-0.8813	10	104L/123L/114L/118L/105L					
5	113/90/101	123L	36:03	0.8789	0.8769-0.8809	10	104L/123L/114L/118L/105L					
5	83	123L	36:39	0.8935	0.8911-0.8960	12	104L/123L/114L/118L/105L	217	500	22	50	20
5	99	123L	36:41	0.8944	0.8923-0.8964	10	104L/123L/114L/118L/105L					
5	83/99	123L	36:40	0.8939	0.8915-0.8964	12	104L/123L/114L/118L/105L					
5	112	123L	36:51	0.8984	0.8972-0.8996	6	104L/123L/114L/118L/105L	245	1000	25	100	50
5	119	123L	37:12	0.9069	0.9037-0.9102	16	104L/123L/114L/118L/105L	149	500	15	50	20
5	108	123L	37:12	0.9069	0.9037-0.9102	16	104L/123L/114L/118L/105L					
5	86	123L	37:17	0.9090	0.9057-0.9122	16	104L/123L/114L/118L/105L					
5	97	123L	37:17	0.9090	0.9057-0.9122	16	104L/123L/114L/118L/105L					
5	125	123L	37:21	0.9106	0.9074-0.9139	16	104L/123L/114L/118L/105L					
5	87	123L	37:25	0.9122	0.9102-0.9143	10	104L/123L/114L/118L/105L					
5	108/119/86/97/125/87	123L	37:19	0.9098	0.9065-0.9130	16	104L/123L/114L/118L/105L					
5	117	123L	37:57	0.9252	0.9228-0.9277	12	104L/123L/114L/118L/105L	104	200	10	20	10
5	116	123L	38:02	0.9273	0.9248-0.9297	12	104L/123L/114L/118L/105L					
5	85	123L	38:05	0.9285	0.9265-0.9305	10	104L/123L/114L/118L/105L					
5	117/116/85	123L	38:00	0.9265	0.9240-0.9289	12	104L/123L/114L/118L/105L					

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
5	110	123L	38:16	0.9330	0.9309-0.9350	10	104L/123L/114L/118L/105L	243	1000	24	100	50
5	115	123L	38:18	0.9338	0.9317-0.9358	10	104L/123L/114L/118L/105L					
5	110/115	123L	38:17	0.9334	0.9313-0.9354	10	104L/123L/114L/118L/105L					
5	82	123L	38:40	0.9427	0.9415-0.9439	6	104L/123L/114L/118L/105L	133	500	13	50	20
5	111	123L	38:52	0.9476	0.9464-0.9488	6	104L/123L/114L/118L/105L	243	1000	24	100	50
5	120	123L	39:21	0.9594	0.9581-0.9606	6	104L/123L/114L/118L/105L	147	500	15	50	20
5	107	123L	40:39	0.9911	0.9890-0.9931	10	104L/123L/114L/118L/105L	200	1000	27	100	50
5	124	123L	40:40	0.9915	0.9894-0.9935	10	104L/123L/114L/118L/105L					
5	107/124	123L	40:39	0.9911	0.9890-0.9931	10	104L/123L/114L/118L/105L					
5	109	123L	40:54	0.9972	0.9959-0.9984	6	104L/123L/114L/118L/105L	103	200	10	20	10
5	123	123L	41:02	1.0004	0.9996-1.0012	-1+3	123L	150	500	15	50	20
5	106	123L	41:10	1.0037	1.0024-1.0049	6	104L/123L/114L/118L/105L	143	500	14	50	20
5	118	118L	41:22	1.0004	0.9996-1.0012	-1+3	118L	193	500	19	50	20
5	122	118L	41:49	1.0113	1.0101-1.0125	6	104L/123L/114L/118L/105L	117	500	12	50	20
5	114	114L	41:58	1.0004	0.9999-1.0012	-1+3	114L	120	500	12	50	20
5	105	105L	42:43	0.9996	0.9992-1.0012	-2+3	105L	109	200	11	20	10
5	127	105L	44:09	1.0332	1.0320-1.0343	6	104L/123L/114L/118L/105L	278	1000	28	100	50
5	126	126L	45:58	1.0004	0.9996-1.0011	-1+3	126L	136	500	14	50	20
Labeled compounds												
5	104L	101L	29:46	0.8257	0.8211-0.8303	20	101L					
5	123L	101L	41:01	1.1378	1.1331-1.1424	20	101L					
5	118L	101L	41:21	1.1470	1.1424-1.1516	20	101L					
5	114L	101L	41:57	1.1637	1.1590-1.1683	20	101L					
5	105L	101L	42:44	1.1854	1.1808-1.1900	20	101L					
5	126L	101L	45:57	1.2746	1.2700-1.2792	20	101L					
Compounds using 138L ($^{13}C_{12}$-2,2',3,4,4',5'-HxCB) as Labeled injection internal standard												

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
	CB congener											
	Hexachlorobiphenyls											
6	155	155L	35:44	1.0000	0.9995-1.0014	-1+3	155L	339	1000	34	100	50
6	152	155L	36:07	1.0107	1.0093-1.0121	6	155L/156L/157L/167L/169L	238	1000	24	100	50
6	150	155L	36:15	1.0145	1.0131-1.0159	6	155L/156L/157L/167L/169L	328	1000	33	100	50
6	136	155L	36:44	1.0280	1.0266-1.0294	6	155L/156L/157L/167L/169L	91	200	9	20	10
6	145	155L	37:00	1.0354	1.0340-1.0368	6	155L/156L/157L/167L/169L	317	1000	32	100	50
6	148	155L	34:26	1.0756	1.0742-1.0770	6	155L/156L/157L/167L/169L	324	1000	32	100	50
6	151	155L	39:10	1.0961	1.0938-1.0984	10	155L/156L/157L/167L/169L	112	500	11	50	20
6	135	155L	39:17	1.0993	1.0970-1.1017	10	155L/156L/157L/167L/169L					
6	154	155L	39:21	1.1012	1.0989-1.1035	10	155L/156L/157L/167L/169L					
6	151/135/154	155L	39:15	1.0984	1.0961-1.1007	10	155L/156L/157L/167L/169L					
6	144	155L	39:47	1.1133	1.1119-1.1147	6	155L/156L/157L/167L/169L	167	500	17	50	20
6	147	155L	40:09	1.1236	1.1213-1.1259	10	155L/156L/157L/167L/169L	179	500	18	50	20
6	149	155L	40:12	1.1250	1.1227-1.1273	10	155L/156L/157L/167L/169L					
6	147/149	155L	40:10	1.1241	1.1217-1.1264	10	155L/156L/157L/167L/169L					
6	134	155L	40:27	1.1320	1.1297-1.1343	10	155L/156L/157L/167L/169L	134	500	13	50	20
6	143	155L	40:30	1.1334	1.1311-1.1357	10	155L/156L/157L/167L/169L					
6	134/143	155L	40:29	1.1329	1.1306-1.1353	10	155L/156L/157L/167L/169L					
6	139	155L	40:47	1.1413	1.1390-1.1437	10	155L/156L/157L/167L/169L	196	500	20	50	20
6	140	155L	40:48	1.1418	1.1395-1.1441	10	155L/156L/157L/167L/169L					
6	139/140	155L	40:47	1.1413	1.1390-1.1437	10	155L/156L/157L/167L/169L					
6	131	155L	41:03	1.1488	1.1474-1.1502	6	155L/156L/157L/167L/169L	121	500	12	50	20
6	142	155L	41:13	1.1535	1.1521-1.1549	6	155L/156L/157L/167L/169L	311	1000	31	100	50
6	132	155L	41:36	1.1642	1.1618-1.1665	10	155L/156L/157L/167L/169L	125	500	12	50	20
6	133	155L	41:57	1.1740	1.1726-1.1754	6	155L/156L/157L/167L/169L	169	500	17	50	20

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
6	165	167L	42:23	0.8864	0.8853-0.8874	6	155L/156L/157L/167L/169L	361	1000	36	100	50
6	146	167L	42:38	0.8916	0.8906-0.8926	6	155L/156L/157L/167L/169L	182	500	18	50	20
6	161	167L	42:47	0.8947	0.8937-0.8958	6	155L/156L/157L/167L/169L	352	1000	35	100	50
6	153	167L	43:17	0.9052	0.9035-0.9069	10	155L/156L/157L/167L/169L	130	500	13	50	20
6	168	167L	43:21	0.9066	0.9048-0.9083	10	155L/156L/157L/167L/169L					
6	153/168	167L	43:19	0.9059	0.9041-0.9076	10	155L/156L/157L/167L/169L					
6	141	167L	43:34	0.9111	0.9101-0.9122	6	155L/156L/157L/167L/169L	93	200	9	20	10
6	130	167L	44:01	0.9205	0.9195-0.9216	6	155L/156L/157L/167L/169L	136	500	14	50	20
6	137	167L	44:14	0.9251	0.9240-0.9261	6	155L/156L/157L/167L/169L	300	1000	30	100	50
6	164	167L	44:22	0.9278	0.9268-0.9289	6	155L/156L/157L/167L/169L	136	500	14	50	20
6	138	167L	44:42	0.9348	0.9324-0.9373	14	155L/156L/157L/167L/169L	211	500	21	50	20
6	163	167L	44:42	0.9348	0.9324-0.9373	14	155L/156L/157L/167L/169L					
6	129	167L	44:47	0.9366	0.9341-0.9390	14	155L/156L/157L/167L/169L					
6	160	167L	44:53	0.9387	0.9369-0.9404	10	155L/156L/157L/167L/169L					
6	138/163/129/160	167L	44:47	0.9366	0.9341-0.9390	14	155L/156L/157L/167L/169L					
6	158	167L	45:05	0.9428	0.9418-0.9439	6	155L/156L/157L/167L/169L	96	200	10	20	10
6	166	167L	45:59	0.9617	0.9599-0.9634	10	155L/156L/157L/167L/169L	124	500	12	50	20
6	128	167L	46:09	0.9651	0.9634-0.9669	10	155L/156L/157L/167L/169L					
6	128/166	167L	46:04	0.9634	0.9617-0.9651	10	155L/156L/157L/167L/169L					
6	159	167L	46:59	0.9826	0.9815-0.9836	6	155L/156L/157L/167L/169L	348	1000	35	100	50
6	162	167L	47:18	0.9892	0.9881-0.9902	6	155L/156L/157L/167L/169L	355	1000	35	100	50
6	167	167L	47:49	1.0000	0.9997-1.0010	-1+3	167L	115	500	11	50	20
6	156	156L/157L	49:05	0.9993	0.9983-1.0003	6	156L/157L	132	500	13	50	20
6	157	156L/157L	49:09	1.0007	0.9990-1.0024	10	156L/157L					
6	156/157	156L/157L	45:07	1.0000	0.9990-1.0010	6	156L/157L					
6	169	169L	52:31	1.0003	0.9997-1.0010	-1+3	169L	161	500	16	50	20

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
	Labeled compounds											
6	155L	138L	35:44	0.7997	0.7960-0.8034	20	138L					
6	167L	138L	47:49	1.0701	1.0664-1.0739	20	138L					
6	156L	138L	49:05	1.0985	1.0974-1.0996	20	138L					
6	157L	138L	49:08	1.0996	1.0959-1.1033	20	138L					
6	156L/157L	138L	49:07	1.0992	1.0981-1.1003	20	138L					
6	169L	138L	52:30	1.1749	1.1738-1.1761	20	138L					
Compounds using 194L($^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB) as Labeled injection internal standard												
	CB congener											
	Heptachlorobiphenyls											
7	188	188L	41:51	1.0000	0.9996-1.0012	-1+3	188L	235	500	23	50	20
7	179	188L	42:19	1.0112	1.0100-1.0123	6	188L/189L	229	500	23	50	20
7	184	188L	42:45	1.0215	1.0203-1.0227	6	188L/189L	403	1000	40	100	50
7	176	188L	43:15	1.0335	1.0323-1.0346	6	188L/189L	385	1000	39	100	50
7	186	188L	43:45	1.0454	1.0442-1.0466	6	188L/189L	407	1000	41	100	50
7	178	188L	45:06	1.0777	1.0765-1.0789	6	188L/189L	221	500	22	50	20
7	175	188L	45:46	1.0936	1.0924-1.0948	6	188L/189L	383	1000	38	100	50
7	187	188L	46:02	1.1000	1.0988-1.1012	6	188L/189L	191	500	19	50	20
7	182	188L	46:14	1.1047	1.1035-1.1059	6	188L/189L	398	1000	40	100	50
7	183	188L	46:42	1.1159	1.1147-1.1171	6	188L/189L	401	1000	40	100	50
7	185	188L	46:53	1.1203	1.1191-1.1215	6	188L/189L					
7	183/185	188L	46:47	1.1179	1.1167-1.1191	6	188L/189L					
7	174	188L	47:02	1.1239	1.1227-1.1251	6	188L/189L	186	500	19	50	20
7	177	188L	47:30	1.1350	1.1338-1.1362	6	188L/189L	141	500	14	50	20
7	181	188L	47:52	1.1438	1.1426-1.1450	6	188L/189L	396	1000	40	100	50

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
7	171	188L	48:10	1.1509	1.1489-1.1529	10	188L/189L	374	1000	37	100	50
7	173	188L	48:11	1.1513	1.1501-1.1525	6	188L/189L					
7	171/173	188L	48:10	1.1509	1.1489-1.1529	10	188L/189L					
7	172	189L	49:47	0.9035	0.9026-0.9044	6	188L/189L	377	1000	38	100	50
7	192	189L	50:06	0.9093	0.9083-0.9102	6	188L/189L	420	1000	42	100	50
7	193	189L	50:26	0.9153	0.9144-0.9162	6	188L/189L	136	500	14	50	20
7	180	189L[11]	50:27	0.9156	0.9147-0.9165	6	188L/189L[11]					
7	180/193	189L	50:26	0.9153	0.9144-0.9162	6	188L/189L					
7	191	189L	50:51	0.9229	0.9220-0.9238	6	188L/189L	418	1000	42	100	50
7	170	189L[11]	51:54	0.9419	0.9410-0.9428	6	188L/189L[11]	162	500	16	50	20
7	190	189L	52:26	0.9516	0.9507-0.9525	6	188L/189L	234	500	23	50	20
7	189	189L	55:07	1.0003	0.9997-1.0009	-1+3	189L	177	500	18	50	20
Octachlorobiphenyls												
8	202	202L	47:32	1.0004	0.9996-1.0011	-1+3	202L	442	1000	44	100	50
8	201	202L	48:31	1.0210	1.0193-1.0228	10	202L/205L	440	1000	44	100	50
8	204	202L	49:11	1.0351	1.0340-1.0361	6	202L/205L	447	1000	45	100	50
8	197	202L	49:27	1.0407	1.0396-1.0417	6	202L/205L	245	1000	25	100	50
8	200	202L	49:40	1.0452	1.0442-1.0463	6	202L/205L					
8	197/200	202L	49:33	1.0428	1.0417-1.0438	6	202L/205L					
8	198	202L	52:30	1.1049	1.1031-1.1066	10	202L/205L	203	500	20	50	25
8	199	202L	52:32	1.1056	1.1045-1.1066	6	202L/205L					
8	198/199	202L	52:31	1.1052	1.1035-1.1070	10	202L/205L					
8	196	205L	53:13	0.9207	0.9198-0.9216	6	202L/205L	429	1000	43	100	50
8	203	205L	53:26	0.9245	0.9236-0.9253	6	202L/205L	444	1000	44	100	50
8	195	205L	54:55	0.9501	0.9493-0.9510	6	202L/205L	427	1000	43	100	50
8	194	205L	57:19	0.9916	0.9908-0.9925	6	202L/205L	170	500	17	50	20

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
8	205	205L	57:49	1.0003	0.9997-1.0009	-1+3	205L	449	1000	45	100	50
Nonachlorobiphenyls												
9	208	208L	54:33	1.0003	0.9997-1.0009	-1+3	208L	455	1000	46	100	50
9	207	208L	55:32	1.0183	1.0174-1.0193	6	208L/206L	453	1000	45	100	50
9	206	206L	59:37	1.0003	0.9997-1.0008	-1+3	206L	451	1000	45	100	50
Decachlorobiphenyl												
10	209	209L	61:15	1.0003	0.9997-1.0008	-1+3	209L	153	500	15	50	20
Labeled compounds												
7	188L	194L	41:51	0.7304	0.7275-0.7333	20	194L					
7	180L	194L	50:27	0.8805	0.8775-0.8834	20	194L					
7	170L	194L	51:53	0.9055	0.9026-0.9084	20	194L					
7	189L	194L	55:06	0.9616	0.9587-0.9645	20	194L					
8	202L	194L	47:31	0.8293	0.8264-0.8322	20	194L					
8	205L	194L	57:48	1.0087	1.0044-1.0131	30	194L					
9	208L	194L	54:32	0.9517	0.9488-0.9546	20	194L					
9	206L	194L	59:36	1.0401	1.0358-1.0445	30	194L					
10	209L	194L	61:14	1.0686	1.0643-1.0730	30	194L					
Labeled clean-up standards												
3	28L	52L	26:44	0.9266	0.9209-0.9324	20	52L					
5	111L	101L	38:51	1.0777	1.0730-1.0823	20	101L					
7	178L	138L	45:05	1.0090	1.0052-1.0127	20	138L					
Labeled injection internal standards												
2	9L	138L	18:54	0.4230	0.4183-0.4276	25	138L					
4	52L	138L	28:45	0.6434	0.6388-0.6481	25	138L					
5	101L	138L	36:03	0.8068	0.8021-0.8115	25	138L					
6	138L	138L	44:41	1.0000	0.9996-1.0011	100	138L					

Cl No.[1]	Congener No. [2,3]	RT Ref[4]	RT[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/µL)
								EMDL	EML	EMDL	EML	EML
8	194L	138L	57:18	1.2824	1.2777-1.2870	25	138L					

1. Number of chlorines on congener.

2. Suffix "L" indicates labeled compound.

3. Multiple congeners in a box indicates a group of congeners that co-elute or may not be adequately resolved on a 30-m SPB-octyl column. Congeners included in the group are listed as the last entry in the box.

4. Retention time (RT) reference used to locate target congener.

5. Retention time of target congener.

6. Relative retention time (RRT) between the RT for the congener and RT for the reference.

7. RRT limits based on RT window.

8. RT window width necessary to attempt to unambiguously identify the congener in the presence of other congeners.

9. Labeled congeners that form the quantitation reference. Areas from the exact m/z's of the congeners listed in the quantitation reference are summed, and divided by the number of congeners in the quantitation reference. For example, for congener 10, the areas at the exact m/z's for 4L and 15L are summed and the sum is divided by 2 (because there are 2 congeners in the quantitation reference).

10. EMDLs and EMLs with common laboratory interferences present. Without interferences, EMDLs and EMLs will be, respectively, 5 and 10 pg/L for aqueous samples, 0.5 and 1.0 ng/kg for soil, tissue, and mixed-phase samples, and EMLs for extracts will be 0.5 pg/uL.

11. If congeners 170L and 180L are included in the calibration and spiking solutions, these congeners should be used as RT and quantitation references.

Table 3. Concentrations of native and labeled chlorinated biphenyls in stock solutions, spiking solutions, and final extracts

CB congener	Solution concentrations		
	Stock (µg/mL)	Spiking (ng/mL)	Extract (ng/mL)
Native Toxics/LOC[1]			
1	20	1.0	50
3	20	1.0	50
4	20	1.0	50
15	20	1.0	50
19	20	1.0	50
37	20	1.0	50
54	20	1.0	50
77	20	1.0	50
81	20	1.0	50
104	20	1.0	50
105	20	1.0	50
114	20	1.0	50
118	20	1.0	50
123	20	1.0	50
126	20	1.0	50
155	20	1.0	50
156	20	1.0	50
157	20	1.0	50
167	20	1.0	50
169	20	1.0	50
188	20	1.0	50
189	20	1.0	50
202	20	1.0	50
205	20	1.0	50
206	20	1.0	50
208	20	1.0	50
209	20	1.0	50
Native congener mix stock solutions[2]			
MoCB thru TrCB	2.5		
TeCB thru HpCB	5.0		
OcCB thru DeCB	7.5		

CB congener	Solution concentrations		
	Stock (µg/mL)	Spiking (ng/mL)	Extract (ng/mL)
Labeled Toxics/LOC/window-defining[3]			
1L	1.0	2.0	100
3L	1.0	2.0	100
4L	1.0	2.0	100
15L	1.0	2.0	100
19L	1.0	2.0	100
37L	1.0	2.0	100
54L	1.0	2.0	100
77L	1.0	2.0	100
81L	1.0	2.0	100
104L	1.0	2.0	100
105L	1.0	2.0	100
114L	1.0	2.0	100
118L	1.0	2.0	100
123L	1.0	2.0	100
126L	1.0	2.0	100
155L	1.0	2.0	100
156L	1.0	2.0	100
157L	1.0	2.0	100
167L	1.0	2.0	100
169L	1.0	2.0	100
188L	1.0	2.0	100
189L	1.0	2.0	100
202L	1.0	2.0	100
205L	1.0	2.0	100
206L	1.0	2.0	100
208L	1.0	2.0	100
209L	1.0	2.0	100
Labeled clean-up[4]			
28L	1.0	2.0	100
111L	1.0	2.0	100
178L	1.0	2.0	100
Labeled injection internal[5]			
9L	5	1000	100
52L	5	1000	100
101L	5	1000	100
138L	5	1000	100
194L	5	1000	100

CB congener	Solution concentrations		
	Stock (µg/mL)	**Spiking (ng/mL)**	**Extract (ng/mL)**
Diluted combined 209 congener[6]			
	Solution concentration (ng/mL)		
Standard	Native	Labeled	
Native congeners			
MoCB thru TrCB	25		
TeCB thru HpCB	50		
OcCB thru DeCB	75		
Labeled Toxics/LOC/window-defining			100
Labeled Cleanup			100
Labeled Injection internal			100

1. Stock solution: Section 7.8.1; Spiking solution: Section 7.11

2. Section 7.8.1.2

3. Stock solution: Section 7.9.1; Spiking solution: Section 7.12

4. Stock solution: Section 7.9.2; Spiking solution: Section 7.13

5. Stock solution: Section 7.9.3; Spiking solution: Section 7.14

6. Section 7.10.2.2.2

Table 4. Composition of individual native CB congener solutions[1]

Solution identifier				
A2	**B2**	**C2**	**D2**	**E2**
Accu-Standard part number				
M-1668A-1	**M-1668A-2**	**M-1668A-3**	**M-1668A-4**	**M-1668A-5**
2	7	13	25	1
10	5	17	21	3
9	12	29	69	4
6	18	20	47	15
8	24	46	42	19
14	23	65	64	16
11	28	59	70	37
30	22	40	102	54
27	39	67	97	43
32	53	76	115	44
34	51	80	123	74
26	73	93	134	56
31	48	84	131	77
33	62	101	163	104
36	71	112	180	98
38	68	86		125
35	58	116		110
50	61	109/107		126
45	55	154		155
52	60	147		138
49	94	140		169
75	100	146		188
41	91	141		189
72	121	164		202
57	90	158		205
63	99	182		208
66	108/109	174		206
79	117	173		209
78	111	193		
81	107/108			
96	118			
103	114			
95	150			
88	145			

Solution identifier				
A2	**B2**	**C2**	**D2**	**E2**
Accu-Standard part number				
M-1668A-1	**M-1668A-2**	**M-1668A-3**	**M-1668A-4**	**M-1668A-5**
89	135			
92	149			
113	139			
83	132			
119	165			
87	168			
85	137			
82	160			
120	128			
124	162			
106	157			
122	184			
105	186			
127	187			
152	185			
136	181			
148	192			
151	197			
144	199/201			
143	203			
142				
133				
161				
153				
130				
129				
166				
159				
167				
156				
179				
176				
178				
175				
183				
177				

Solution identifier				
A2	**B2**	**C2**	**D2**	**E2**
Accu-Standard part number				
M-1668A-1	**M-1668A-2**	**M-1668A-3**	**M-1668A-4**	**M-1668A-5**
171				
172				
191				
170				
190				
201/200				
204				
200/199				
198				
196				
195				
194				
207				
Total number of congeners				
83	54	29	15	28

1. Congeners present in each standard solution are listed in elution order for each level of chlorination. Congener number (Table 1) listed first; BZ number listed second where ambiguous. See Table 3 for concentrations of congeners in stock solutions and Table 5 for concentrations in calibration standard.

Table 5. Concentration of CB congeners in calibration and calibration verification standards

		Solution concentration (ng/mL)					
CB congener	**Congener[1]**	**CS-0.2 (Hi sens)[2]**	**CS-1**	**CS-2**	**CS-3 (VER)**	**CS-4**	**CS-5**
Native Toxics/LOC							
2-MoCB	1	0.2	1.0	5.0	50	400	2000
4-MoCB	3	0.2	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.2	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.2	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.2	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.2	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.2	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.2	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.2	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.2	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.2	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.2	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.2	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.2	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.2	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.2	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.2	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.2	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.2	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.2	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.2	1.0	5.0	50	400	2000
DeCB	209	0.2	1.0	5.0	50	400	2000
Labeled Toxics/LOC/window-defining							
$^{13}C_{12}$-2-MoCB	1L	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6'-TrCB	19L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100

		Solution concentration (ng/mL)					
CB congener	**Congener[1]**	**CS-0.2 (Hi sens)[2]**	**CS-1**	**CS-2**	**CS-3 (VER)**	**CS-4**	**CS-5**
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Labeled clean-up							
$^{13}C_{12}$-2,4,4'-TrCB	28L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100	100
Labeled injection internal							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100

1. Suffix "L" indicates labeled compound

2. Additional concentration used for calibration of high sensitivity HRGC/HRMS systems

Table 6. QC acceptance criteria for chlorinated biphenyls in VER, IPR, OPR, and samples[1]

Congener	Congener number[2]	Test conc (ng/mL)[3]	VER[4] (%)	IPR		OPR (%)	Labeled compound recovery in samples (%)
				RSD (%)	X (%)		
2-MoCB	1	50	70-130	40	60-140	50-150	
4-MoCB	3	50	70-130	40	60-140	50-150	
2,2'-DiCB	4	50	70-130	40	60-140	50-150	
4,4'-DiCB	15	50	70-130	40	60-140	50-150	
2,2'6-TrCB	19	50	70-130	40	60-140	50-150	
3,4,4'-TrCB	37	50	70-130	40	60-140	50-150	
2,2'6,6'TeCB	54	50	70-130	40	60-140	50-150	
3,3',4,4'-TeCB	77	50	70-130	40	60-140	50-150	
3,4,4',5-TeCB	81	50	70-130	40	60-140	50-150	
2,2',4,6,6'-PeCB	104	50	70-130	40	60-140	50-150	
2,3,3',4,4'-PeCB	105	50	70-130	40	60-140	50-150	
2,3,4,4',5-PeCB	114	50	70-130	40	60-140	50-150	
2,3',4,4',5-PeCB	118	50	70-130	40	60-140	50-150	
2',3,4,4',5-PeCB	123	50	70-130	40	60-140	50-150	
3,3',4,4',5-PeCB	126	50	70-130	40	60-140	50-150	
2,2',4,4',6,6'-HxCB	155	50	70-130	40	60-140	50-150	
2,3,3',4,4',5-HxCB[5]	156	50	70-130	40	60-140	50-150	
2,3,3',4,4',5'-HxCB[5]	157	50	70-130	40	60-140	50-150	
2,3',4,4',5,5'-HxCB	167	50	70-130	40	60-140	50-150	
3,3',4,4',5,5'-HxCB	169	50	70-130	40	60-140	50-150	
2,2',3,4',5,6,6'-HpCB	188	50	70-130	40	60-140	50-150	
2,3,3',4,4',5,5'-HpCB	189	50	70-130	40	60-140	50-150	
2,2',3,3',5,5',6,6'-OcCB	202	50	70-130	40	60-140	50-150	
2,3,3',4,4',5,5',6-OcCB	205	50	70-130	40	60-140	50-150	

Congener	Congener number[2]	Test conc (ng/mL)[3]	VER[4] (%)	IPR		OPR (%)	Labeled compound recovery in samples (%)
				RSD (%)	X (%)		
2,2',3,3',4,4',5,5',6-NoCB	206	50	70-130	40	60-140	50-150	
2,2',3,3,'4,5,5',6,6'-NoCB	208	50	70-130	40	60-140	50-150	
DeCB	209	50	70-130	40	60-140	50-150	
$^{13}C_{12}$-2-MoCB	1L	100	50-150	50	20-135	15-140	15-150
$^{13}C_{12}$-4-MoCB	3L	100	50-150	50	20-135	15-140	15-150
$^{13}C_{12}$-2,2'-DiCB	4L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-4,4'-DiCB	15L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',6-TrCB	19L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	50-150	50	35-135	30-140	25-150
13C12-3,3',4,4'-TeCB	77L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5 -HxCB[5]	156L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[5]	157L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB	189L	100	50-150	50	35-135	30-140	25-150

Congener	Congener number[2]	Test conc (ng/mL)[3]	VER[4] (%)	IPR		OPR (%)	Labeled compound recovery in samples (%)
				RSD (%)	X (%)		
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	50-150	50	35-135	30-140	25-150
Cleanup standard							
$^{13}C_{12}$-2,4,4'-TrCB	28L	100	60-130	45	45-120	40-125	30-135
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	45	45-120	40-125	30-135
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	45	45-120	40-125	30-135

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume

2. Suffix "L" indicates labeled compound.

3. See Table 5.

4. Section 15.3.

5. PCBs 156 and 157 are tested as the sum of two concentrations

Table 7. Scan descriptors, levels of chlorination, m/z information, and substances monitored by HRGC/HRMS

Function and chlorine level	m/z[1]	m/z type	m/z formula	Substance
Fn-1; Cl-1	188.0393	M	$^{12}C_{12}H_9{}^{35}Cl$	Cl-1 CB
	190.0363	M+2	$^{12}C_{12}H_9{}^{37}Cl$	Cl-1 CB
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	$^{13}C_{12}$ Cl-1 CB
	202.0766	M+2	$^{13}C_{12}H_9{}^{37}Cl$	$^{13}C_{12}$ Cl-1 CB
	218.9856	lock	C_4F_9	PFK
Fn-2; Cl-2,3	222.0003	M	$^{12}C_{12}H_8{}^{35}Cl_2$	Cl-2 PCB
	223.9974	M+2	$^{12}C_{12}H_8{}^{35}Cl\,{}^{37}Cl$	Cl-2 PCB
	225.9944	M+4	$^{12}C_{12}H_8{}^{37}Cl_2$	Cl-2 PCB
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	$^{13}C_{12}$ Cl-2 PCB
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl\,{}^{37}Cl$	$^{13}C_{12}$ Cl-2 PCB
	242.9856	lock	C_6F_9	PFK
	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB
	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	$^{13}C_{12}$ Cl-3 PCB
Fn-3	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB
Cl-3,4,5	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB
	259.9554	M+4	$^{12}C_{12}H_7{}^{35}Cl\,{}^{37}Cl_2$	Cl-3 PCB
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	$^{13}C_{12}$ Cl-3 PCB
	280.9825	lock	C_6F_{11}	PFK
	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB
	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{13}C_{12}H5{}^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}H5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB

Function and chlorine level	m/z[1]	m/z type	m/z formula	Substance
Fn-4	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB
Cl-4,5,6	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	330.9792	lock	C_7F_{15}	PFK
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	359.8415	M+2	$^{12}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{12}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
Fn-5	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB
Cl-5,6,7	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	354.9792	lock	C_9F_{13}	PFK
	359.8415	M+2	$^{12}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{12}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
	393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB
	395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB
	397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	Cl-7 PCB
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB
	454.9728	QC	$C_{11}F_{17}$	PFK

Function and chlorine level	m/z[1]	m/z type	m/z formula	Substance
Fn-6	393.8025	M+2	$^{12}C_{12}$ H_3 $^{35}Cl_6$ ^{37}Cl	Cl-7 PCB
Cl-7,8,9,10	395.7995	M+4	$^{12}C_{12}$ H_3 $^{35}Cl_5$ $^{37}Cl_2$	Cl-7 PCB
	397.7966	M+6	$^{12}C_{12}$ H_3 $^{35}Cl_4$ $^{37}Cl_3$	Cl-7 PCB
	405.8428	M+2	$^{13}C_{12}$ H_3 $^{35}Cl_6$ ^{37}Cl	$^{13}C_{12}$ Cl-7 PCB
	407.8398	M+4	$^{13}C_{12}$ H_3 $^{35}Cl_5$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB
	427.7635	M+2	$^{12}C_{12}$ H_2 $^{35}Cl_7$ ^{37}Cl	Cl-8 PCB
	429.7606	M+4	$^{12}C_{12}$ H_2 $^{35}Cl_6$ $^{37}Cl_2$	Cl-8 PCB
	431.7576	M+6	$^{12}C_{12}$ H_2 $^{35}Cl_5$ $^{37}Cl_3$	Cl-8 PCB
	439.8038	M+2	$^{13}C_{12}$ H_2 $^{35}Cl_7$ ^{37}Cl	$^{13}C_{12}$ Cl-8 PCB
	441.8008	M+4	$^{13}C_{12}$ H_2 $^{35}Cl_6$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB
	442.9728	QC	C_{10} F_{13}	PFK
	454.9728	lock	C_{11} F_{13}	PFK
	461.7246	M+2	$^{12}C_{12}$ H_1 $^{35}Cl_8$ ^{37}Cl	Cl-9 PCB
	463.7216	M+4	$^{12}C_{12}$ H_1 $^{35}Cl_7$ $^{37}Cl_2$	Cl-9 PCB
	465.7187	M+6	$^{12}C_{12}$ H_1 $^{35}Cl_6$ $^{37}Cl_3$	Cl-9 PCB
	473.7648	M+2	$^{13}C_{12}$ H_1 $^{35}Cl_8$ ^{37}Cl	$^{13}C_{12}$ Cl-9 PCB
	475.7619	M+4	$^{13}C_{12}$ H_1 $^{35}Cl_7$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-9 PCB
	495.6856	M+2	$^{12}C_{12}$ H_4 $^{35}Cl_9$ ^{37}Cl	Cl-10 PCB
	497.6826	M+4	$^{12}C_{12}$ $^{35}Cl_8$ $^{37}Cl_2$	Cl-10 PCB
	499.6797	M+6	$^{12}C_{12}$ $^{35}Cl_7$ $^{37}Cl_3$	Cl-10 PCB
	507.7258	M+2	$^{13}C_{12}$ $^{35}Cl_9$ ^{37}Cl	$^{13}C_{12}$ Cl-10 PCB
	509.7229	M+4	$^{13}C_{12}$ $^{35}Cl_8$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-10 PCB
	511.7199	M+6	$^{13}C_{12}$ $^{35}Cl_7$ $^{37}Cl_3$	$^{13}C_{12}$ Cl-10 PCB

1. Isotopic masses used for accurate mass calculation

^{1}H	1.0078
^{12}C	12.0000
^{13}C	13.0034
^{35}Cl	34.9689
^{37}Cl	36.9659
^{19}F	18.9984

Table 8. Theoretical ion abundance ratios and QC limits

Chlorine atoms	m/zs forming ratio	Theoretical ratio	Lower QC limit	Upper QC limit
1	m/m+2	3.13	2.66	3.60
2	m/(m+2)	1.56	1.33	1.79
3	m/(m+2)	1.04	0.88	1.20
4	m/(m+2)	0.77	0.65	0.89
5	(m+2)/(m+4)	1.55	1.32	1.78
6	(m+2)/(m+4)	1.24	1.05	1.43
7	(m+2)/(m+4)	1.05	0.89	1.21
8	(m+2)/(m+4)	0.89	0.76	1.02
9	(m+2)/(m+4)	0.77	0.65	0.89
10	(m+4)(m+6)]	1.16	0.99	1.33

Table 9. Suggested Sample Quantities to be Extracted for Various Matrices[1]

Sample matrix[2]	Example	Percent solids	Phase	Quantity extracted
Single-phase				
Aqueous	Drinking water	<1	—[3]	1000 mL
	Groundwater			
	Treated wastewater			
Solid	Dry soil	>20	Solid	10 g
	Compost			
	Ash			
Organic	Waste solvent	<1	Organic	10 g
	Waste oil			
	Organic polymer			
Tissue	Fish	—	Organic	10 g
	Human adipose			
Multi-phase				
Liquid/Solid				
Aqueous/Solid	Wet soil	1-30	Solid	10 g
	Untreated effluent			
	Digested municipal sludge			
	Filter cake			
	Paper pulp			
Organic/solid	Industrial sludge	1-100	Both	10 g
	Oily waste			
Liquid/Liquid				
Aqueous/organic	In-process effluent	<1	Organic	10 g
	Untreated effluent			
	Drum waste			
Aqueous/organic/solid	Untreated effluent	>1	Organic & solid	10 g
	Drum waste			

1. The quantity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing one percent solids will contain 10 grams of solids. For aqueous samples containing greater than one percent solids, a lesser volume is used so that 10 grams of solids (dry weight) will be extracted.
2. The sample matrix may be amorphous for some samples. In general, when the CBs are in contact with a multi-phase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.
3. Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

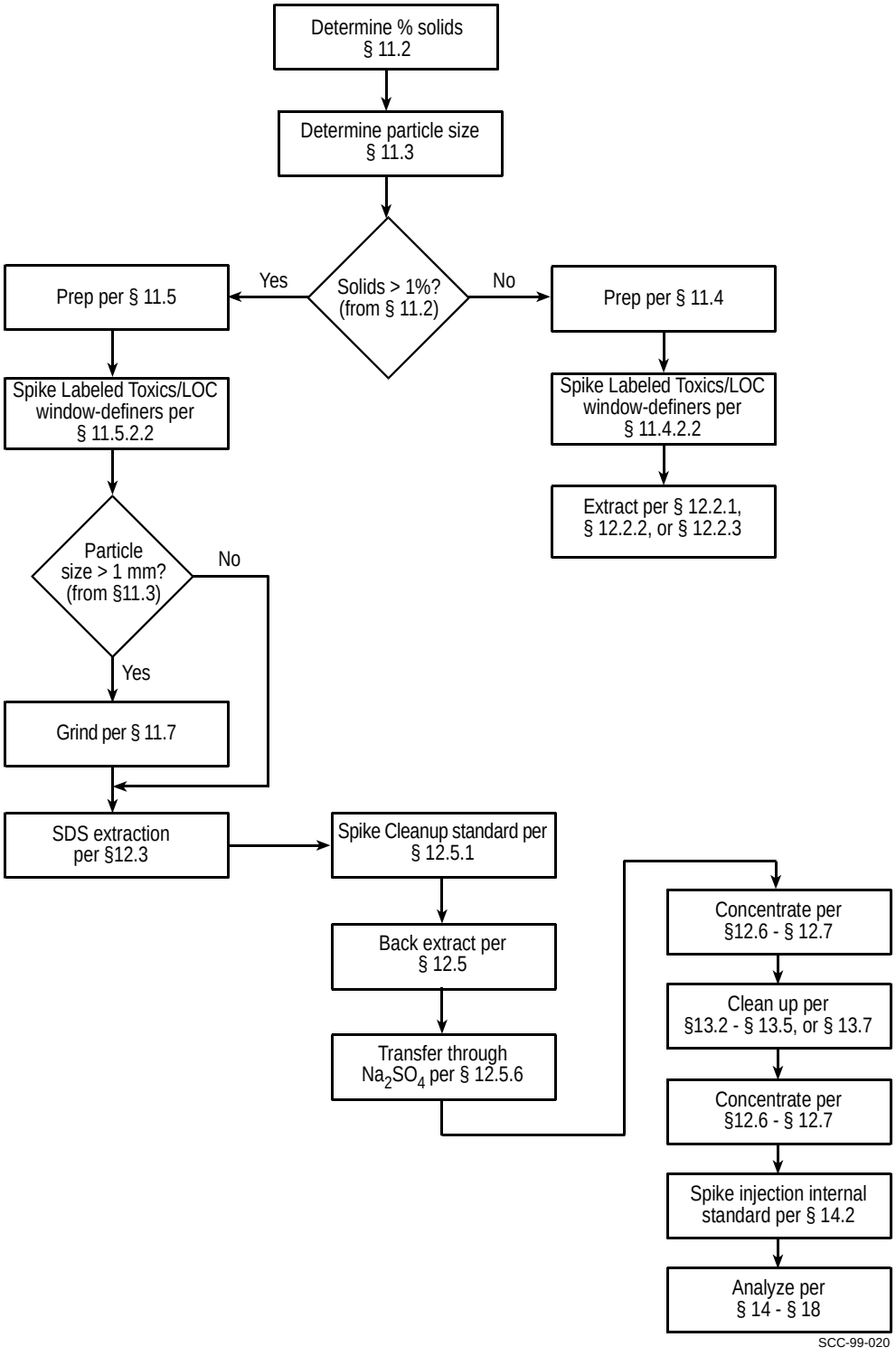


Figure 1 Flow Chart for Analysis of Aqueous and Solid Samples

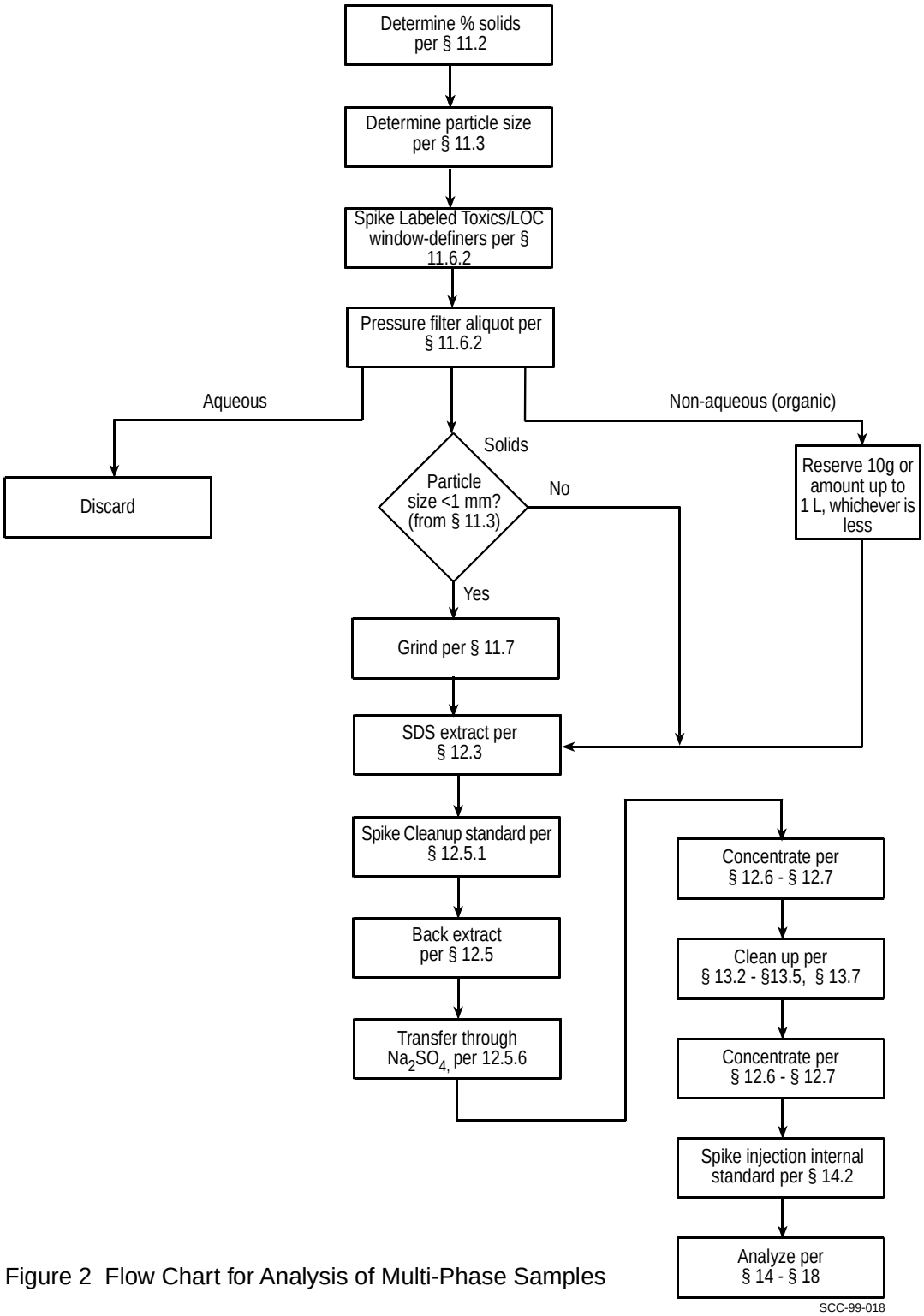


Figure 2 Flow Chart for Analysis of Multi-Phase Samples

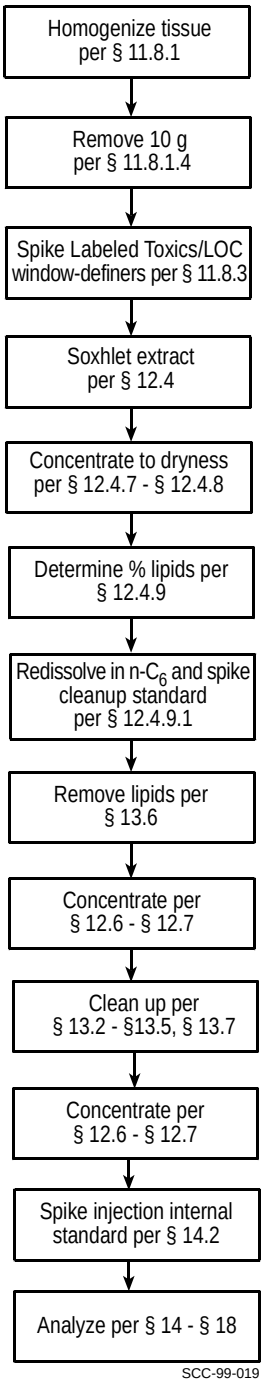


Figure 3 Flow Chart for Analysis of Tissue Samples

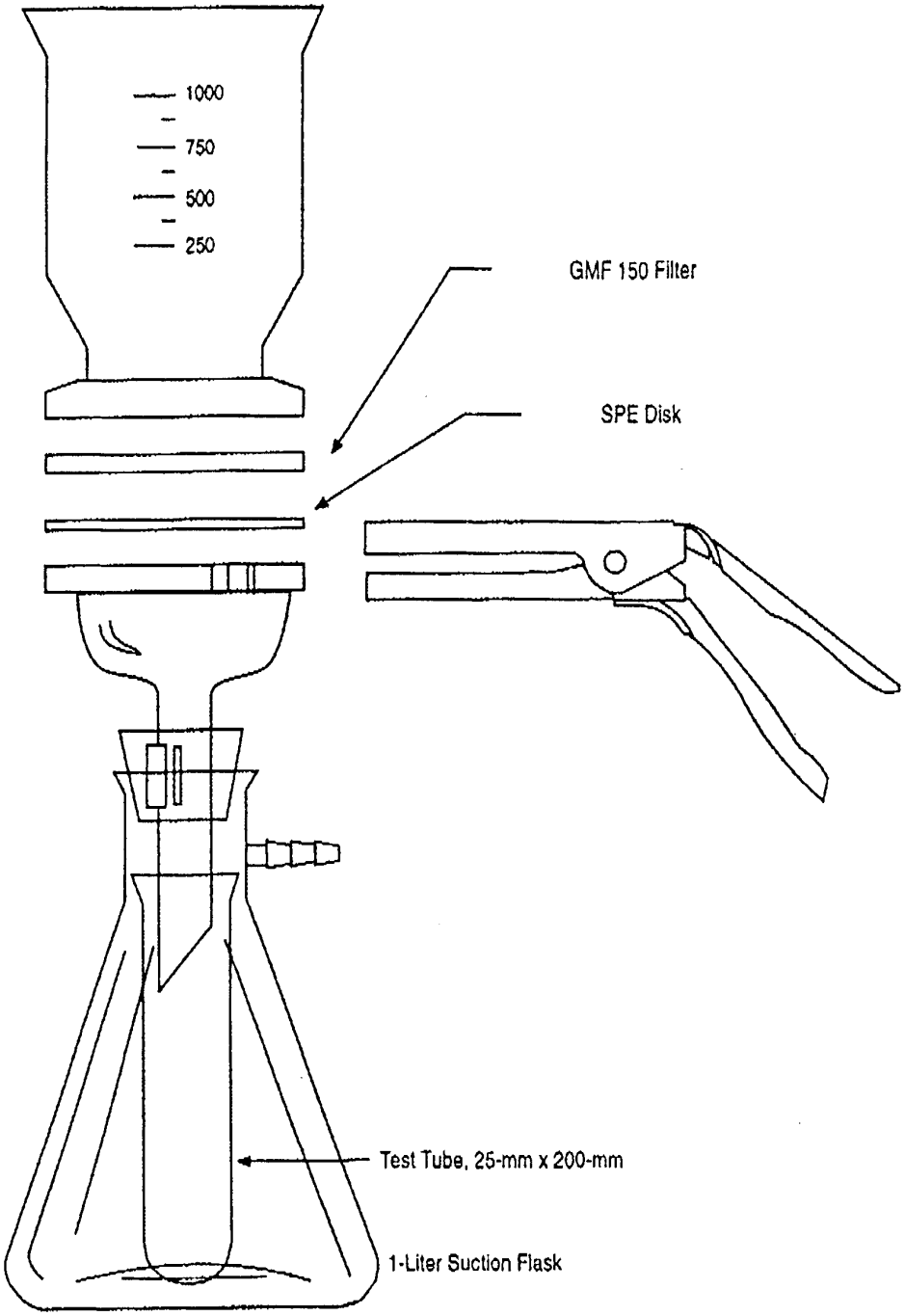
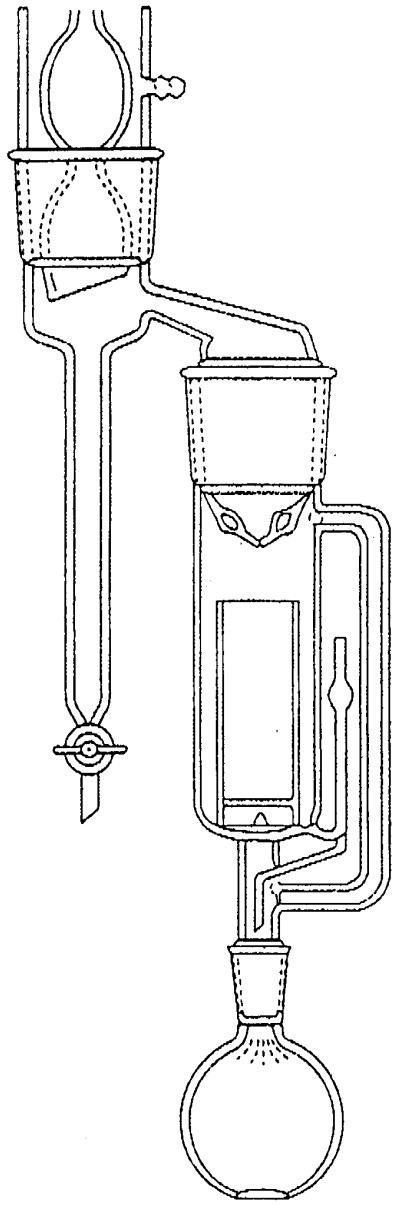


Figure 4 Solid-phase Extraction Apparatus



52-027-02

Figure 5 Soxhlet/Dean-Stark Extractor

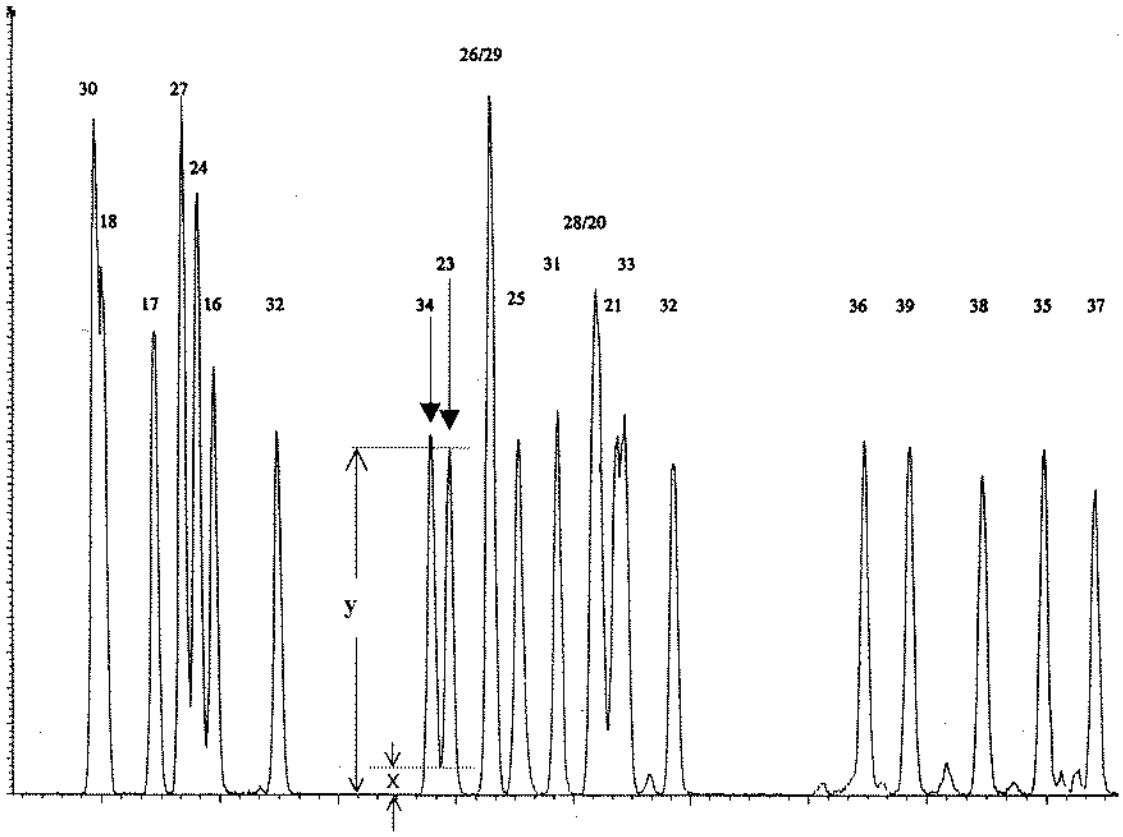


Figure 6 Octyl column resolution test #1: Separation of Cl-3 congeners 34 and 23 with valley <40% (i.e. 100x/y < 40%)

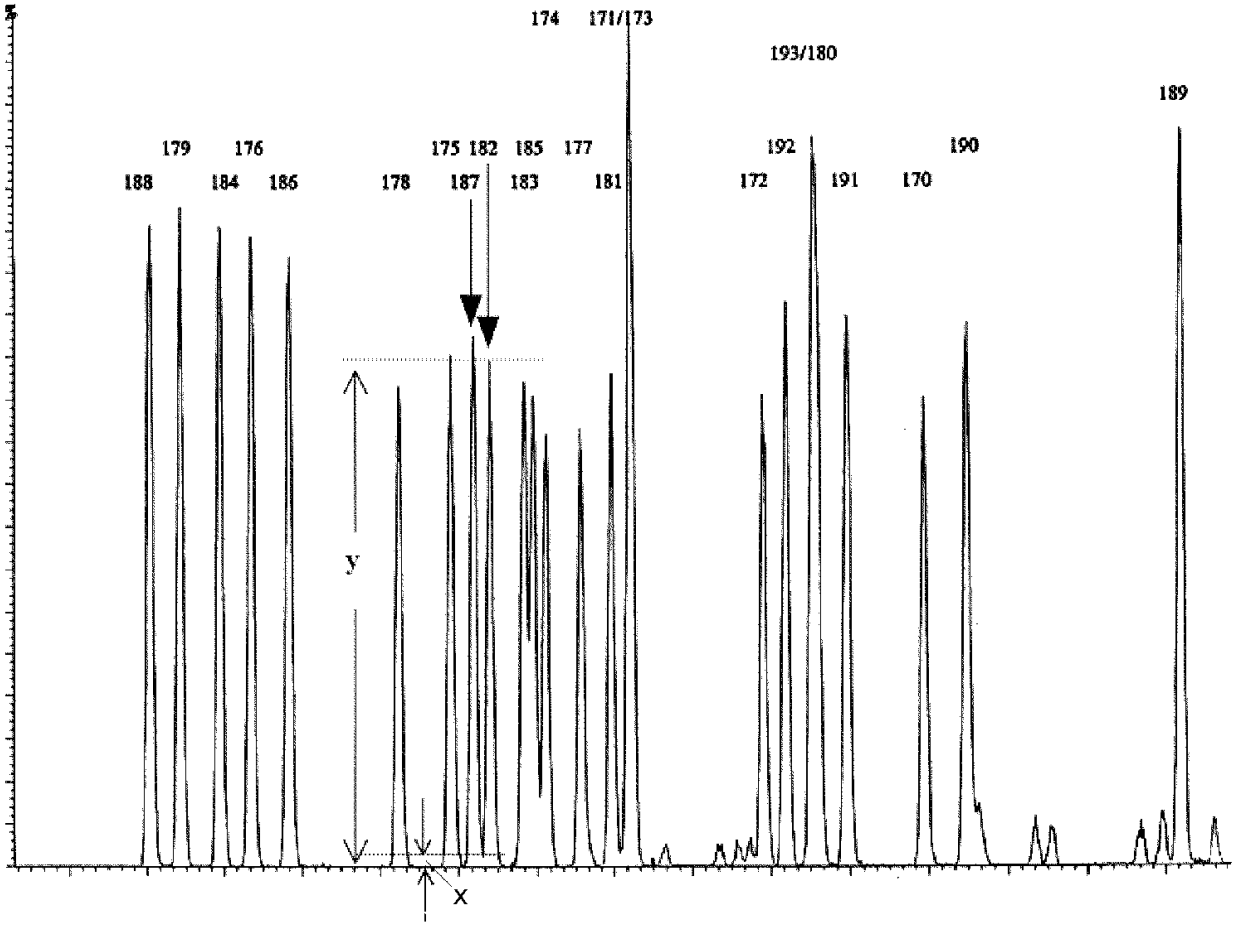


Figure 7 Octyl column resolution test #2: Separation of Cl-7 congeners 187 and 182 with valley < 40% (i.e. 100 x/y < 40%)

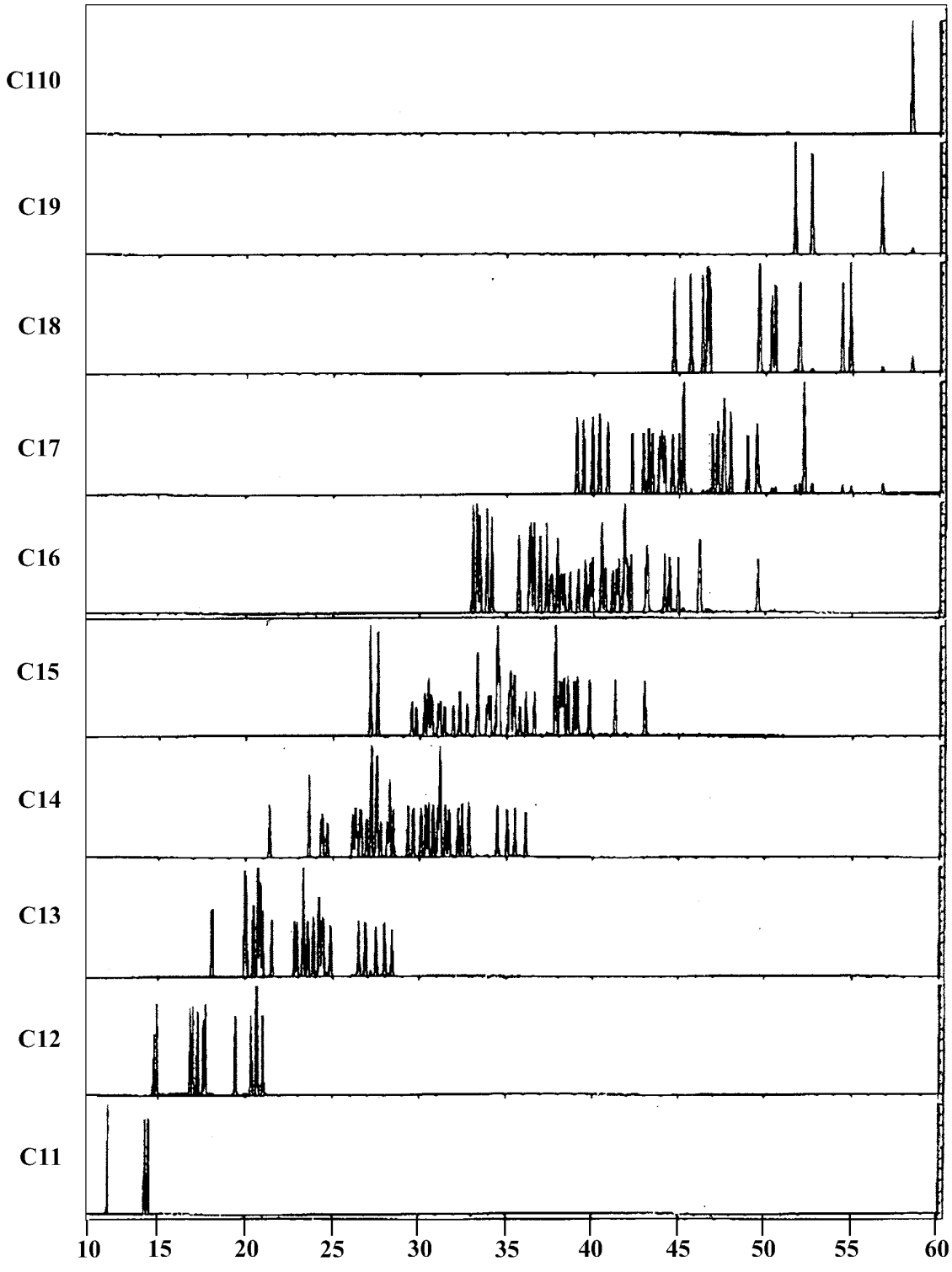


Figure 8. CB congeners at each level of chlorination on the SPB-octyl column

24.0 Glossary

These definitions and purposes are specific to this Method but have been conformed to common usage to the extent possible.

24.1 Units of weight and measure and their abbreviations

24.1.1 Symbols

°C	degrees Celsius
µL	microliter
µm	micrometer
<	less than
>	greater than
%	percent

24.1.2 Alphabetical abbreviations

cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppq	part-per-quadrillion
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

24.2 Definitions and acronyms (in alphabetical order)

Analyte—A CB tested for by this Method. The analytes are listed in Table 1.

Calibration standard (CAL)—A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the HRGC/HRMS instrument.

Calibration verification standard (VER)—The mid-point calibration standard (CS-3) that is used to verify calibration. See Table 5.

CB—chlorinated biphenyl congener. One of the 209 individual chlorinated biphenyl congeners determined using this Method. The 209 CBs are listed in Table 1.

CS-0.2, CS-1, CS-2, CS-3, CS-4, CS-5—See Calibration standards and Table 5.

DeCB—decachlorobiphenyl (PCB 209)

DiCB—dichlorobiphenyl

Estimated method detection limit (EMDL)—The lowest concentration at which a CB can be detected with common laboratory interferences present. EMDLs are listed in Table 2.

Estimated minimum level (EML)—The lowest concentration at which a CB can be measured reliably with common laboratory interferences present. EMLs are listed in Table 2.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography

GPC—Gel permeation chromatograph or gel permeation chromatography

HpCB—heptachlorobiphenyl

HPLC—High performance liquid chromatograph or high performance liquid chromatography

HRGC—High resolution GC

HRMS—High resolution MS

HxCB—hexachlorobiphenyl

Labeled injection internal standard—All five, or any one of the five, $^{13}C_{12}$-labeled CB congeners spiked into the concentrated extract immediately prior to injection of an aliquot of the extract into the HRGC/HRMS. The five Labeled injection internal standards in this Method are CBs with congener numbers 9, 52, 101, 138, and 194.

Internal standard—a labeled compound used as a reference for quantitation of other labeled compounds and for quantitation of native CB congeners other than the congener of which it is a labeled analog. See Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of (1) a naturally occurring (native) compound by reference to a compound other than its labeled analog and (2) a labeled compound by reference to another labeled compound.

IPR—Initial precision and recovery; four aliquots of a reference matrix spiked with the analytes of interest and labeled compounds and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IPR is performed prior to the first time this Method is used and any time the Method or instrumentation is modified.

Isotope dilution quantitation—A means of determining a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched. In this Method, all 12 carbon atoms in the biphenyl molecule are enriched with carbon-13 to produce $^{13}C_{12}$-labeled analogs of the chlorinated biphenyls. The $^{13}C_{12}$-labeled CBs are spiked into each sample and allow identification and correction of the concentration of the native compounds in the analytical process.

K-D—Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent

Laboratory blank—See Method blank

Laboratory control sample (LCS)—See Ongoing precision and recovery standard (OPR)

Laboratory reagent blank—See Method blank

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The Method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum level of quantitation (ML)—The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all Method-specified sample weights, volumes, and cleanup procedures have been employed.

MoCB—monochlorobiphenyl

MS—Mass spectrometer or mass spectrometry

Must—This action, activity, or procedural step is required.

NoCB-nonachlorobiphenyl

OcCB—octachlorobiphenyl

OPR—Ongoing precision and recovery standard (OPR); a method blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this Method for precision and recovery.

Perfluorokerosene (PFK)—A mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation blank—See Method blank

Quality control check sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

PeCB—pentachlorobiphenyl

PCB—polychlorinated biphenyl

Reagent water—water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RF—Response factor. See Section 10.5

RR—Relative response. See Section 10.4

RSD—See Relative standard deviation

SDS—Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials (Reference 11 and Figure 5).

Signal-to-noise ratio (S/N)—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

Should—This action, activity, or procedural step is suggested but not required.

SICP—Selected ion current profile; the line described by the signal at an exact m/z.

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TeCB—tetrachlorobiphenyl

TEF—Toxicity equivalency factor; an estimate of the toxicity of a specific congener relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

TEQ—the toxicity equivalent concentration in an environmental sample. It is the sum of the concentrations of each individual toxic PCB and each individual 2,3,7,8-substituted, tetra-through octachlorinated, dibenzo-*p*-dioxin and dibenzofuran multiplied by their respective TEFs (Reference 1).

TEQ_{PCB}—the portion of the TEQ attributable to the toxic PCBs.

TrCB—trichlorobiphenyl

Unique GC resolution or uniquely resolved—Two adjacent chromatographic peaks in which the height of the valley is less than 40 percent of the height of the shorter peak (See section 6.9.1.1.2 and Figures 6 and 7 for unique resolution specific to the SPB-octyl column).

VER—See Calibration verification.

Appendix A—Preliminary information for determination of 209 CBs on the DB-1 Column

1.0 Column and Conditions

1.1 Column—30 ± 5-m long x 0.25 ± 0.02-mm ID; 0.25 µm film DB-1 (J&W, or equivalent).

1.2 Suggested GC operating conditions:

Injector temperature:	270 °C
Interface temperature:	290 °C
Initial temperature:	75 °C
Initial time:	2 minutes
Temperature program:	75-150 °C at 15 °C/minute
	150-270 °C at 2.5 °C/minute
Final time:	7 minutes
Carrier gas velocity:	40 cm/sec at 200 °C

Note: *The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.*

2.0 Operating Information

2.1 Congener solutions—Mixes of individual congene4rs that will allow separation of all w09 congeners on the DB-1 column had not been developed at the date of writing of these corrections to Method 1668A.

2.2 Elution order data—The congener mixes developed for the SPB-octyl column (Table 4 of Method 1668A) were run on the DB-1 column. Although some congeners in these mixes co-elute, the mixes allow determination of retention times for many congeners on the DB-1 column. These retention times are shown in Appendix Table A-1.

2.3 Window-defining congeners—The beginning and ending congeners at each level of chlorination are the same as for the SPB-octyl column. See Table 2 in Method 1668A.

2.4 Scan descriptors—The 6-function scan descriptors are shown in Appendix Table A-2.

Table A-1. Retention time (RT) references, quantitation references, and relative retention times (RRTs) for CB congeners using a DB-1 column.

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
$^{13}C_{12}$-2-MoCB[4]	1L	$^{13}C_{12}$-4-MoCB[4,5]	3L	09:17	0.8855	0.8776-0.8935
2-MoCB	1	$^{13}C_{12}$-2-MoCB[4]	1L	09:17	1.0000	0.9964-1.0072
3-MoCB	2	$^{13}C_{12}$-4-MoCB[4,5]	3L	10:22	0.9889	0.9809-0.9968
$^{13}C_{12}$-4-MoCB[4,5]	3L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	10:29	0.5561	0.5473-0.5650
4-MoCB	3	$^{13}C_{12}$-4-MoCB[4,5]	3L	10:29	1.0000	0.9968-1.0064
$^{13}C_{12}$-2,2'-DiCB[4]	4L	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	11:08	0.7591	0.7477-0.7705
2,2'-DiCB	4	$^{13}C_{12}$-2,2'-DiCB[4]	4L	11:08	1.0000	0.9925-1.0075
2,6-DiCB	10	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	11:10	0.7614	0.7500-0.7727
2,5-DiCB	9	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:08	0.8273	0.8216-0.8330
2,4-DiCB	7	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:09	0.8284	0.8227-0.8341
2,3'-DiCB	6	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:31	0.8534	0.8477-0.8591
2,4'-DiCB[6]	8	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:43	0.8670	0.8614-0.8727
2,3-DiCB	5	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:46	0.8705	0.8648-0.8761
$^{13}C_{12}$-2,2',6-TrCB[4]	19L	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	13:31	0.7990	0.7892-0.8089
2,2',6-TrCB	19	$^{13}C_{12}$-2,2',6-TrCB[4]	19L	13:31	1.0000	0.9975-1.0049
3,5-DiCB	14	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	13:36	0.9273	0.9216-0.9330
2,4,6-TrCB	30	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	14:06	0.8335	0.8286-0.8384
3,3'-DiCB	11	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:11	0.9670	0.9614-0.9727
3,4'-DiCB	13	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:26	0.9841	0.9784-0.9898
3,4-DiCB	12	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:27	0.9852	0.9795-0.9909
2,2',5-TrCB[6]	18	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	14:36	0.8631	0.8581-0.8680
$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	14:40	0.7781	0.7692-0.7869
4,4'-DiCB	15	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:40	1.0000	0.9977-1.0043
2,2',4-TrCB	17	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	14:43	0.8700	0.8650-0.8749
2,3',6-TrCB	27	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:06	0.8926	0.8877-0.8975

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,3,6-TrCB	24	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:06	0.8926	0.8877-0.8975
2,2',3-TrCB	16	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:26	0.9123	0.9074-0.9172
2,4',6-TrCB	32	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:29	0.9153	0.9103-0.9202
$^{13}C_{12}$-2,2',6,6'-TeCB[4]	54L	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	16:02	0.6139	0.6075-0.6203
2,2',6,6'-TeCB	54	$^{13}C_{12}$-2,2',6,6'-TeCB[4]	54L	16:02	1.0000	0.9979-1.0042
2',3,5-TrCB	34	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:03	0.9488	0.9438-0.9537
2,3,5-TrCB	23	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:07	0.9527	0.9478-0.9576
2,4,5-TrCB	29	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:18	0.9635	0.9586-0.9685
2,3',5-TrCB	26	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:29	0.9744	0.9695-0.9793
2,3',4-TrCB	25	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:36	0.9813	0.9764-0.9862
2,4',5-TrCB	31	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:52	0.9970	0.9921-1.0020
$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	16:55	0.8974	0.8930-0.9019
2,4,4'-TrCB[6]	28	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:55	1.0000	0.9980-1.0039
2,2',4,6-TeCB	50	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	16:55	0.6477	0.6414-0.6541
2,3,4-TrCB	21	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:21	1.0256	1.0207-1.0305
2,2',5,6'-TeCB	53	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	17:26	0.6675	0.6611-0.6739
2,3,3'-TrCB	20	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:22	1.0266	1.0217-1.0315
2',3,4-TrCB	33	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:24	1.0286	1.0236-1.0335
2,2',4,6'-TeCB	51	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	17:42	0.6777	0.6713-0.6841
2,3,4'-TrCB	22	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:43	1.0473	1.0424-1.0522
2,2',3,6-TeCB	45	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:00	0.6892	0.6828-0.6956
3,3',5-TrCB	36	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	18:16	1.0798	1.0749-1.0847
2,2',3,6'-TeCB	46	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:24	0.7045	0.6981-0.7109
3,4',5-TrCB	39	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	18:37	1.1005	1.0956-1.1054
$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	18:51	1.0000	0.9956-1.0044
2,2',5,5'-TeCB[6]	52	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:51	0.7218	0.7154-0.7281
2,3',4,6-TeCB	69	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:52	0.7224	0.7160-0.7288

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,3',5',6-TeCB	73	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:57	0.7256	0.7192-0.7320
2,2',4,5'-TeCB	49	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:00	0.7275	0.7211-0.7339
2,2',3,5-TeCB	43	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:04	0.7301	0.7237-0.7364
3,4,5-TrCB	38	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	19:12	1.1350	1.1300-1.1399
2,2',4,4'-TeCB	47	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:15	0.7371	0.7307-0.7435
2,4,4',6-TeCB	75	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:20	0.7403	0.7339-0.7466
2,2',4,5-TeCB	48	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:20	0.7403	0.7339-0.7466
2,3,5,6-TeCB	65	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:31	0.7473	0.7409-0.7537
2,3,4,6-TeCB	62	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:36	0.7505	0.7441-0.7569
3,3',4-TrCB	35	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	19:41	1.1635	1.1586-1.1685
$^{13}C_{12}$-2,2',4,6,6'-PeCB[4]	104L	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	19:45	0.7037	0.6977-0.7096
2,2',4,6,6'-PeCB	104	$^{13}C_{12}$-2,2',4,6,6'-PeCB[4]	104L	19:45	1.0000	0.9983-1.0034
2,2',3,5'-TeCB[6]	44	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	19:55	0.7626	0.7562-0.7690
$^{13}C_{12}$-3,4,4'-TrCB[4]	37L	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	20:03	1.1852	1.1803-1.1901
3,4,4'-TrCB	37	$^{13}C_{12}$-3,4,4'-TrCB[4]	37L	20:03	1.0000	0.9983-1.0033
2,3,3',6-TeCB	59	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:05	0.7690	0.7626-0.7754
2,2',3,4'-TeCB	42	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:07	0.7703	0.7639-0.7766
2,3',5,5'-TeCB	72	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:36	0.7888	0.7824-0.7951
2,3',4',6-TeCB	71	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:36	0.7888	0.7824-0.7951
2,3,4',6-TeCB	64	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:37	0.7894	0.7830-0.7958
2,2',3,4-TeCB	41	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:39	0.7907	0.7843-0.7971
2,2',3,6,6'-PeCB	96	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	20:48	0.7411	0.7352-0.7470
2,3',4,5'-TeCB	68	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:52	0.7990	0.7926-0.8054
2,2',3,3'-TeCB	40	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	20:58	0.8028	0.7996-0.8060
2,3,3',5-TeCB	57	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	21:21	0.8175	0.8143-0.8207
2,2',4,5,'6-PeCB	103	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	21:22	0.7613	0.7553-0.7672
2,3',4,5-TeCB	67	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	21:38	0.8283	0.8251-0.8315

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,2',4,4',6-PeCB	100	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	21:41	0.7726	0.7666-0.7785
2,3,3',5'-TeCB	58	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	21:43	0.8315	0.8283-0.8347
2,3,4',5-TeCB	63	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	21:51	0.8366	0.8334-0.8398
2,2',3,5,6'-PeCB	94	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:05	0.7868	0.7809-0.7928
2,4,4',5-TeCB	74	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:07	0.8468	0.8437-0.8500
2,3,4,5-TeCB	61	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:11	0.8494	0.8462-0.8526
2,3',4',5-TeCB	70	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:20	0.8551	0.8519-0.8583
2',3,4,5-TeCB	76	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:25	0.8583	0.8551-0.8615
2,2',3',4,6-PeCB	98	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:28	0.8005	0.7975-0.8034
2,3',4,4'-TeCB[6]	66	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:29	0.8609	0.8577-0.8641
2,2',4,5,6'-PeCB	102	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:32	0.8029	0.7999-0.8058
2,2',3,5',6-PeCB	95	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:34	0.8040	0.8011-0.8070
2,2',3,5,6-PeCB	93	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:36	0.8052	0.8023-0.8082
3,3',5,5'-TeCB	80	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:45	0.8711	0.8679-0.8743
2,2',3,4,6-PeCB	88	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:49	0.8129	0.8100-0.8159
2,2',3,4',6-PeCB	91	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:55	0.8165	0.8135-0.8195
2,3,3',4'-TeCB	55	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	22:57	0.8787	0.8756-0.8819
2,3',4,5,'6-PeCB	121	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:04	0.8219	0.8189-0.8248
2,3,3',4'-TeCB	56	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	23:24	0.8960	0.8928-0.8992
2,3,4,4'-TeCB	60	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	23:24	0.8960	0.8928-0.8992
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB[4]	155L	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	23:43	0.7104	0.7054-0.7154
2,2',4,4',6,6'-HxCB	155	$^{13}C_{12}$-2,2',4,4',6,6'-HxCB[4]	155L	23:43	1.0000	0.9986-1.0028
2,2',3,3',6-PeCB	84	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:44	0.8456	0.8426-0.8486
2,2',3,5,5'-PeCB	92	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:50	0.8492	0.8462-0.8521
2,2',3,4,6'-PeCB	89	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:53	0.8510	0.8480-0.8539
2,2',3,4',5-PeCB	90	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:07	0.8593	0.8563-0.8622
$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	24:11	1.0000	0.9966-1.0034

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,2',4,5,5'-PeCB[6]	101	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:11	0.8616	0.8587-0.8646
2,3,3',5',6-PeCB	113	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:23	0.8688	0.8658-0.8717
3,3',4,5'-TeCB	79	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	24:27	0.9362	0.9330-0.9394
2,2',4,4',5-PeCB	99	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:28	0.8717	0.8688-0.8747
2,2',3,4',6,6'-HxCB	150	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	24:52	0.7449	0.7399-0.7499
2,3',4,4',6-PeCB	119	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:54	0.8872	0.8842-0.8901
2,3,3',5,6-PeCB	112	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:00	0.8907	0.8878-0.8937
2,3,3',4,5'-PeCB	108	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:09	0.8961	0.8931-0.8990
2,2',3,5,6,6'-HxCB	152	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	25:17	0.7574	0.7524-0.7624
2,2',3,3',5-PeCB	83	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:20	0.8919	0.8890-0.8949
2,2',3',4,5-PeCB	97	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:22	0.9038	0.9008-0.9068
2,2',3,4,5-PeCB	86	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:27	0.9068	0.9038-0.9097
$^{13}C_{12}$-3,4,4',5-TeCB[9]	81L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	25:32	1.3546	1.3457-1.3634
3,4,4',5-TeCB[10]	81	$^{13}C_{12}$-3,4,4',5-TeCB[4,5,9]	77L	25:32	1.0000	0.9987-1.0026
2',3,4,5,6'-PeCB	125	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:36	0.9121	0.9091-0.9151
2,3,4',5,6-PeCB	117	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:37	0.9127	0.9097-0.9157
2,2',3,4,5'-PeCB	87	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:38	0.9133	0.9103-0.9163
3,3',4,5-TeCB	78	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	25:40	0.9598	0.9566-0.9630
2,2',3,4,6,6'-HxCB	145	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	25:42	0.7698	0.7649-0.7748
2,3,4,4',6-PeCB	115	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:44	0.9169	0.9139-0.9198
$^{13}C_{12}$-2,3,3',5,5'-PeCB[8]	111L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	25:51	1.0689	1.0655-1.0724
2,3,3',5,5'-PeCB	111	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:51	0.9210	0.9181-0.9240
2,2',3,4,4'-PeCB	85	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:51	0.9210	0.9181-0.9240
2,3,4,5,6-PeCB	116	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:48	0.9192	0.9163-0.9222
$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	26:07	1.3855	1.3767-1.3943
3,3',4,4'-TeCB[6,10]	77	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	26:07	1.0000	0.9987-1.0026
2,2',3,3',6,6'-HxCB	136	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	26:10	0.7793	0.7743-0.7843

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,3',4,5,5'-PeCB	120	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	26:12	0.9335	0.9305-0.9365
2,2',3,4',5,6'-HxCB	148	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	26:14	0.7858	0.7808-0.7908
2,3,3',4',6-PeCB	110	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	26:16	0.9359	0.9329-0.9388
2,2',4,4',5,6'-HxCB	154	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	26:44	0.8008	0.7983-0.8033
2,2',3,3',4-PeCB	82	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	26:48	0.9549	0.9519-0.9578
2,2',3,5,5',6-HxCB	151	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:18	0.8178	0.8153-0.8203
2,2',3,3',5,6'-HxCB	135	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:31	0.8243	0.8218-0.8268
2',3,4,5,5'-PeCB	124	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	27:36	0.9834	0.9804-0.9863
2,2',3,4,5',6-HxCB	144	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:38	0.8278	0.8253-0.8303
2,3,3',4',5-PeCB	107	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	27:40	0.9857	0.9828-0.9887
2,2',3,4',5,6-HxCB	147	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:44	0.8308	0.8283-0.8333
2,3,3',4,6-PeCB	109	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	27:45	0.9887	0.9857-0.9917
2,2',3,4',5',6-HxCB	149	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:01	0.8392	0.8367-0.8417
2,2',3,3',5,6-HxCB	134	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:35	0.8562	0.8537-0.8587
2,2',3,4,5,6'-HxCB	143	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:34	0.8557	0.8532-0.8582
$^{13}C_{12}$-2',3,4,4',5-PeCB[9]	123L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	27:53	1.1530	1.1496-1.1564
2',3,4,4',5-PeCB[10]	123	$^{13}C_{12}$-2',3,4,4',5-PeCB[9]	123L	27:53	1.0000	0.9988-1.0024
2,2',3,4,4',6-HxCB	139	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:01	0.8392	0.8367-0.8417
2,3,3',4,5-PeCB	106	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	28:04	1.0000	0.9970-1.0030
$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	28:04	1.1606	1.1571-1.1640
2,3',4,4',5-PeCB[6,10]	118	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	28:04	1.0000	0.9988-1.0024
2,2',3,4,4',6'-HxCB	140	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:12	0.8447	0.8422-0.8472
$^{13}C_{12}$-2,3,4,4',5-PeCB[9]	114L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	28:38	1.1840	1.1806-1.1875
2,3,4,4',5-PeCB[10]	114	$^{13}C_{12}$-2,3,4,4',5-PeCB[9]	114L	28:38	1.0000	0.9988-1.0023
2',3,3',4,5-PeCB	122	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	28:48	1.0261	1.0232-1.0291
2,2',3,3',4,6-HxCB	131	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:52	0.8647	0.8622-0.8672
2,2',3,4,5,6-HxCB	142	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:59	0.8682	0.8657-0.8707

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,2',3,3',5,5'-HxCB	133	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:59	0.8682	0.8657-0.8707
2,2',3,3',4,6'-HxCB	132	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:32	0.8847	0.8822-0.8872
2,3,3',5,5',6-HxCB	165	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:21	0.8792	0.8767-0.8817
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB[4]	188L	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	29:22	0.9511	0.7327-0.7411
2,2',3,4',5,6,6'-HpCB	188	$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB[4]	188L	29:22	1.0000	0.9989-1.0023
2,2',3,4',5,5'-HxCB	146	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:24	0.8807	0.8782-0.8832
$^{13}C_{12}$-2,3,3',4,4'-PeCB[9]	105L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	29:30	1.2198	1.2130-1.2267
2,3,3',4,4'-PeCB[6,10]	105	$^{13}C_{12}$-2,3,3',4,4'-PeCB[9]	105L	29:30	1.0000	0.9989-1.0023
2,3,3',4,5',6-HxCB	161	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:32	0.8847	0.8822-0.8872
2,2',4,4',5,5'-HxCB[6]	153	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:48	0.8927	0.8902-0.8952
2,2',3,4,4',6,6'-HpCB	184	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	29:49	0.7482	0.7440-0.7524
3,3',4,5,5'-PeCB	127	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	29:57	1.0671	1.0641-1.0701
2,3',4,4',5',6-HxCB	168	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:59	0.8982	0.8957-0.9006
2,2',3,4,5,5'-HxCB	141	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	30:31	0.9141	0.9116-0.9166
2,2',3,3',5,6,6'-HpCB	179	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	30:33	0.7666	0.7624-0.7708
2,2',3,4,4',5-HxCB	137	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	30:51	0.9241	0.9216-0.9266
2,2',3,3',4,5'-HxCB	130	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	30:57	0.9271	0.9246-0.9296
2,2',3,3',4,6,6'-HpCB	176	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	31:01	0.7783	0.7742-0.7825
$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	31:20	1.0000	0.9973-1.0027
2,2',3,4,4',5'-HxCB[6]	138	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:20	0.9386	0.9361-0.9411
2,3,3',4',5',6-HxCB	164	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:22	0.9396	0.9371-0.9421
2,3,3',4',5,6-HxCB	163	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:28	0.9426	0.9401-0.9451
2,3,3',4,5,6-HxCB	160	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:33	0.9451	0.9426-0.9476
2,3,3',4,4',6-HxCB	158	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:35	0.9461	0.9436-0.9486
2,2',3,4,5,6,6'-HpCB	186	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	31:36	0.7930	0.7888-0.7972
2,2',3,3',4,5-HxCB	129	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:48	0.9526	0.9501-0.9551
$^{13}C_{12}$-3,3',4,4',5-PeCB[4,9]	126L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	31:49	1.3156	1.3088-1.3225

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
3,3',4,4',5-PeCB[6,10]	126	$^{13}C_{12}$-3,3',4,4',5-PeCB[4,9]	126L	31:49	1.0000	0.9990-1.0021
2,3,4,4',5,6-HxCB	166	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	32:13	0.9651	0.9626-0.9675
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	32:14	1.0000	0.9974-1.0026
2,2',3,3',5,5',6-HpCB	178	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:14	0.8089	0.8068-0.8110
2,2',3,3',4,5',6-HpCB	175	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:33	0.8168	0.8147-0.8189
2,3,3',4,5,5'-HxCB	159	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	32:43	0.9800	0.9775-0.9825
2,2',3,4',5,5',6-HpCB[6]	187	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:46	0.8223	0.8202-0.8243
2,2',3,4,4',5,6'-HpCB	182	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:47	0.8227	0.8206-0.8248
2,2',3,3',4,4'-HxCB[6]	128	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	32:52	0.9845	0.9820-0.9870
2,3,3',4',5,5'-HxCB	162	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	33:00	0.9885	0.9860-0.9910
2,2',3,4,4',5',6-HpCB	183	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	33:06	0.8306	0.8285-0.8327
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	33:23	1.0654	1.0628-1.0681
2,3',4,4',5,5'-HxCB[10]	167	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	33:23	1.0000	0.9990-1.0020
2,2',3,4,5,5',6-HpCB	185	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	33:43	0.8461	0.8440-0.8482
2,2',3,3',4,5,6'-HpCB	174	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:07	0.8561	0.8540-0.8582
2,2',3,4,4',5,6-HpCB	181	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:11	0.8578	0.8557-0.8599
2,2',3,3',4',5,6-HpCB	177	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:22	0.8624	0.8603-0.8645
2,2'3,3',4,4',6-HpCB	171	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:40	0.8699	0.8678-0.8720
$^{13}C_{12}$-2,3,3',4,4',5 -HxCB[9]	156L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	34:40	1.1064	1.1037-1.1090
2,3,3',4,4',5-HxCB[10]	156	$^{13}C_{12}$-2,3,3',4,4',5 -HxCB[9]	156L	34:40	1.0000	0.9990-1.0019
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB[4]	202L	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	34:56	0.8265	0.8245-0.8285
2,2',3,3',5,5',6,6'-OcCB	202	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB[4]	202L	34:56	1.0000	0.9990-1.0019
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[9]	157L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	34:57	1.1154	1.1128-1.1181
2,3,3',4,4',5'-HxCB[10]	157	$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[9]	157L	34:57	1.0000	0.9990-1.0019
2,2',3,3',4,5,6-HpCB	173	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	35:04	0.8800	0.8779-0.8821
2,2',3,3',4,5',6,6'-OcCB	201	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	35:25	0.8379	0.8360-0.8399
2,2',3,4,4',5,6,6'-OcCB	204	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	35:36	0.8423	0.8403-0.8442

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
2,2',3,3',4,5,5'-HpCB	172	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	35:41	0.8954	0.8934-0.8975
2,3,3',4,5,5',6-HpCB	192	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	35:51	0.8996	0.8975-0.9017
2,2',3,3',4,4',6,6'-OcCB	197	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	35:55	0.8498	0.8478-0.8517
2,2',3,4,4',5,5'-HpCB[6]	180	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	36:07	0.9063	0.9042-0.9084
2,3,3',4',5,5',6-HpCB	193	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	36:20	0.9118	0.9097-0.9138
2,3,3',4,4',5',6-HpCB	191	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	36:34	0.9176	0.9155-0.9197
2,2',3,3',4,5,6,6'-OcCB	200	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	36:49	0.8711	0.8691-0.8730
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB[4,9]	169L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	37:19	1.1910	1.1883-1.1936
3,3',4,4',5,5'-HxCB[6,10]	169	$^{13}C_{12}$-3,3',4,4',5,5'-HxCB[4,9]	169L	37:19	1.0000	0.9991-1.0018
2,2',3,3',4,4',5-HpCB[6]	170	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	37:44	0.9469	0.9448-0.9490
2,3,3',4,4',5,6-HpCB	190	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	37:56	0.9519	0.9498-0.9540
2,2',3,3',4,5,5',6-OcCB	198	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	38:34	0.9125	0.9105-0.9144
2,2',3,3',4,5,5',6'-OcCB	199	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	38:43	0.9160	0.9140-0.9180
2,2',3,3',4,4',5,6'-OcCB	196	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	39:05	0.9247	0.9227-0.9267
2,2',3,4,4',5,5',6-OcCB	203	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	39:05	0.9247	0.9227-0.9267
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	39:51	1.2363	1.2311-1.2415
2,3,3',4,4',5,5'-HpCB[10]	189	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	39:51	1.0000	0.9992-1.0017
2,2',3,3',4,4',5,6-OcCB[6]	195	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	40:45	0.9641	0.9621-0.9661
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB[4]	208L	$^{13}C_{12}$-Cl9-PCB-206[4,5]	206L	41:03	0.9149	0.9131-0.9168
2,2',3,3',4,5,5',6,6'-NoCB	208	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB[4]	208L	41:03	1.0000	0.9992-1.0016
2,2',3,3',4,4',5,6,6'-NoCB	207	$^{13}C_{12}$-Cl9-PCB-206[4,5]	206L	41:32	0.9257	0.9238-0.9276
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB[5]	194L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	42:16	1.3113	1.3061-1.3164
2,2',3,3',4,4',5,5'-OcCB	194	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	42:16	1.0000	0.9992-1.0016
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB[4]	205L	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	42:44	1.0110	1.0091-1.0130
2,3,3',4,4',5,5',6-OcCB	205	$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB[4]	205L	42:44	1.0000	0.9992-1.0016
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB[4,5]	206L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	44:52	1.3919	1.3868-1.3971
2,2',3,3',4,4',5,5',6-NoCB[6]	206	$^{13}C_{12}$-Cl9-PCB-206[4,5]	206L	44:52	1.0000	0.9993-1.0015

Labeled or native CB[1]	Congener number[2]	Retention time and quantitation references	Congener number	RT	RRT	RRT QC limits[3]
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB[4,5]	209L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	46:55	1.4555	1.4504-1.4607
2,2',3,3',4,4',5,5',6,6'-DeCB[6]	209	$^{13}C_{12}$-Cl10-PCB-209[4,5]	209L	46:55	1.0000	0.9993-1.0014

1. Abbreviations for chlorination levels

MoCB	monochlorobiphenyl	HxCB	hexachlorobiphenyl
DiCB	dichlorobiphenyl	HpCB	heptachlorobiphenyl
TrCB	trichlorobiphenyl	OcCB	octachlorobiphenyl
TeCB	tetrachlorobiphenyl	NoCB	nonachlorobiphenyl
PeCB	pentachlorobiphenyl	DeCB	decachlorobiphenyl

2. Suffix "L" indicates labeled compound.

3. For native CBs determined by isotope dilution quantitation, RRT QC limits were constructed using -2 to +4 seconds around the retention time for the labeled analog. For native CBs determined by internal standard quantitation, RRT QC limits were constructed using a ± 2 percent window around the retention time for retention times in the range of 0.8-1.2 and a ± 4 percent window around the retention time for retention times <0.8 and >1.2. These windows may not be adequate for analyte identification (See the note in Section 16.4)

4. Labeled level of chlorination (LOC) window-defining congener

5. Labeled level of chlorination (LOC) quantitation congener

6. National Oceanic and Atmospheric Administration (NOAA) congener of interest

7. Instrument internal standard

8. Clean-up standard

9. Labeled internal standard for World Health Organization (WHO) toxic congener

10. WHO toxic congener

Table A-2. Scan descriptors, levels of chlorination, m/z information, and substances monitored by HRGC/HRMS

Function and chlorine level	m/z	m/z type	m/z formula	Substance
Fn-1	188.0393	M	$^{12}C_{12}$ H_9 ^{35}Cl	Cl-1 PCB
Cl-1	190.0363	M+2	$^{12}C_{12}$ H_9 ^{37}Cl	Cl-1P CB
	200.0795	M	$^{13}C_{12}$ H_9 ^{35}Cl	$^{13}C_{12}$ Cl-1 PCB
	202.0766	M+2	$^{13}C_{12}$ H_9 ^{37}Cl	$^{13}C_{12}$ Cl-1 PCB
	218.9856	lock	C_4 F_9	PFK
Fn-2	222.0003	M	$^{12}C_{12}$ H_8 $^{35}Cl_2$	Cl-2 PCB
Cl-2,3	223.9974	M+2	$^{12}C_{12}$ H_8 ^{35}Cl ^{37} Cl	Cl-2 PCB
	225.9944	M+4	$^{12}C_{12}$ H_8 $^{37}Cl_2$	Cl-2 PCB
	234.0406	M	$^{13}C_{12}$ H_8 $^{35}Cl_2$	$^{13}C_{12}$ Cl-2 PCB
	236.0376	M+2	$^{13}C_{12}$ H_8 ^{35}Cl ^{37} Cl	$^{13}C_{12}$ Cl-2 PCB
	242.9856	lock	C_6 F_9	PFK
	255.9613	M	$^{12}C_{12}$ H_7 $^{35}Cl_3$	Cl-3 PCB
	257.9584	M+2	$^{12}C_{12}$ H_7 $^{35}Cl_2$ ^{37}Cl	Cl-3 PCB
Fn-3	255.9613	M	$^{12}C_{12}$ H_7 $^{35}Cl_3$	Cl-3 PCB
Cl-3,4,5	257.9584	M+2	$^{12}C_{12}$ H_7 $^{35}Cl_2$ ^{37}Cl	Cl-3 PCB
	259.9554	M+4	$^{12}C_{12}$ H_7 ^{35}Cl $^{37}Cl_2$	Cl-3 PCB
	268.0016	M	$^{13}C_{12}$ H_7 $^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB
	269.9986	M+2	$^{13}C_{12}$ H_7 $^{35}Cl_2$ ^{37}Cl	$^{13}C_{12}$ Cl-3 PCB
	280.9825	lock	C_6 F_{11}	PFK
	289.9224	M	$^{12}C_{12}$ H_6 $^{35}Cl_4$	Cl-4 PCB
	291.9194	M+2	$^{12}C_{12}$ H_6 $^{35}Cl_3$ ^{37}Cl	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}$ H_6 $^{35}Cl_2$ $^{37}Cl_2$	Cl-4 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	301.9626	M	$^{13}C_{12}$ H_6 $^{35}Cl_4$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+2	$^{13}C_{12}$ H_6 $^{35}Cl_3$ ^{37}Cl	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}$ H_5 $^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}$ H_5 $^{35}Cl_4$ ^{37}Cl	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}$ H_5 $^{35}Cl_3$ $^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}$ H_5 $^{35}Cl_4$ ^{37}Cl	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}$ H_5 $^{35}Cl_3$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
Fn-4	289.9224	M	$^{12}C_{12}$ H_6 $^{35}Cl_4$	Cl-4 PCB
Cl-4,5,6	291.9194	M+2	$^{12}C_{12}$ H_6 $^{35}Cl_3$ ^{37}Cl	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}$ H_6 $^{35}Cl_2$ $^{37}Cl_2$	Cl-4 PCB
	301.9626	M+2	$^{13}C_{12}$ H_6 $^{35}Cl_3$ ^{37}Cl	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+4	$^{13}C_{12}$ H_6 $^{35}Cl_2$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}$ H_5 $^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}$ H_5 $^{35}Cl_4$ ^{37}Cl	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}$ H_5 $^{35}Cl_3$ $^{37}Cl_2$	Cl-5 PCB
	330.9792	lock	C_7 F_{15}	PFK
	337.9207	M+2	$^{13}C_{12}$ H_5 $^{35}Cl_4$ ^{37}Cl	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}$ H_5 $^{35}Cl_3$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	359.8415	M+2	$^{13}C_{12}$ H_4 $^{35}Cl_5$ ^{37}Cl	Cl-6 PCB
	361.8385	M+4	$^{13}C_{12}$ H_4 $^{35}Cl_4$ $^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{13}C_{12}$ H_4 $^{35}Cl_3$ $^{37}Cl_2$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}$ H_4 $^{35}Cl_5$ ^{37}Cl	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}$ H_4 $^{35}Cl_4$ $^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
Fn-5	323.8834	M	$^{12}C_{12}$ H_5 $^{35}Cl_5$	Cl-5 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
Cl-5,6,7,8	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	354.9792	lock	C_9F_{13}	PFK
	359.8415	M+2	$^{12}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{12}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
	393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB
	395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB
	397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	Cl-7 PCB
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB
	427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB
	429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB
	431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB
	454.9728	QC	$C_{11}F_{17}$	PFK
Fn-6	427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB
Cl-8,9,10	429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB
	431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB
	442.9728	QC	$C_{10}F_{13}$	PFK
	454.9728	lock	$C_{11}F_{13}$	PFK
	461.7246	M+2	$^{12}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	Cl-9 PCB
	463.7216	M+4	$^{12}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	Cl-9 PCB
	465.7187	M+6	$^{12}C_{12}H_1{}^{35}Cl_6{}^{37}Cl_3$	Cl-9 PCB
	473.7648	M+2	$^{13}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	$^{13}C_{12}$ Cl-9 PCB
	475.7619	M+4	$^{13}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	$^{13}C_{12}$ Cl-9 PCB
	495.6856	M+2	$^{13}C_{12}H_4{}^{35}Cl_9{}^{37}Cl$	Cl-10 PCB
	499.6797	M+4	$^{12}C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Cl-10 PCB
	501.6767	M+6	$^{12}C_{12}{}^{35}Cl_6{}^{37}Cl_4$	Cl-10 PCB
	507.7258	M+2	$^{13}C_{12}H_4{}^{35}Cl_9{}^{37}Cl$	$^{13}C_{12}$ Cl-10 PCB
	509.7229	M+4	$^{13}C_{12}H_4{}^{35}Cl_8{}^{37}Cl_2$	$^{13}C_{12}$ Cl-10 PCB
	511.7199	M+6	$^{13}C_{12}H_4{}^{35}Cl_8{}^{37}Cl_4$	$^{13}C_{12}$ Cl-10 PCB

1. Isotopic masses used for accurate mass calculation

^{1}H	1.0078
^{12}C	12.0000
^{13}C	13.0034
^{35}Cl	34.9689
^{37}Cl	36.9659
^{19}F	18.9984

No. L-3

TAL Metals

SW-846 Method 6020 / 1-P-QM-WI-9015160

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests (Refs. 1 and 2). When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-soluble) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of this method in a multi-laboratory study on solid and aqueous wastes are listed below.

Element		CASRN[a]
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0

Element		CASRN[a]
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

Acceptability of this method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectrophotometry or inductively coupled plasma-atomic emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988 and advances in ICP-MS instrumentation and software have been made since that time and additional studies have been added with validation and improvements in performance of the method. Performance, in general, exceeds the multi-laboratory performance data for the listed elements. It is expected that current performance will exceed the multi-laboratory performance data for the listed elements (and others) that are provided in Sec. 13.0. The lower limit of quantitation and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, quantitation limits will generally be below 0.1 µg/L. Less sensitive elements (like Se and As) and desensitized major elements may be 1.0 µg/L or higher.

1.3 If this method is used to determine any analyte not listed in Sec. 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Sec. 9.0). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{74}Ge, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standards.

1.5 Prior to employing this method, analysts are advised to consult the each preparative method that may be employed in the overall analysis (e.g., a 3000 series method) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel, including spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples should be solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater or other aqueous samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis (refer to Sec. 1.1).

2.2 This method describes the multi-elemental determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and extracted through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a channel electron multiplier or Faraday detector and the ion information is processed by the instrument's data handling system. Interferences must be assessed and valid corrections applied or the data qualified to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be applicable to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

4.3 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature (Refs. 3 and 4). Examples include $^{75}ArCl^+$ ion on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature (Ref. 5), the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z.

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [Ref. 6]).

Similarly:

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =
(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

where last 2 terms adjust for any $^{114}Sn^+$ or $^{114}MoO^+$ contributions at m/z 114.

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting precision.

The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found (Ref. 7) to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported (Ref. 7) for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences (Ref. 8). These techniques can be used provided that the lower limits of quantitation, accuracy, and precision requirements for analysis of the samples can be met.

4.4 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both element and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid decomposed samples. Acid decomposed samples refer to samples decomposed by methods similar to Methods 3052, 3051, 3050 or 3015. Samples with percent levels of iron and aluminum should be avoided. The

method also provides a method for preconcentration to enhance quantitation limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as imminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences can not occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs (Refs. 13 through 15). The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

4.5 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement (Ref. 9). Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) are recommended (Ref. 10) to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes (Ref. 11). When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30% of the signals in the calibrations standard) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Sec. 9.5).

4.6 Memory interferences or carry-over can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of observed memory interferences. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer -- A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.2 Argon gas supply -- High-purity grade (99.99%).

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2% (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used (Refs. 3 and 4). Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

7.3 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

7.4 Standard stock solutions for each analyte may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010 for instructions on preparing standard solutions from solids.

7.4.1 Bismuth internal standard stock solution (1 mL = 100 µg of Bi) -- Dissolve 0.1115 g of Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.2 Germanium internal standard stock solution (1 mL = 100 µg of Ge) -- Dissolve 0.2954 g of $GeCl_4$ in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.3 Holmium internal standard stock solution (1 mL = 100 µg of Ho) -- Dissolve 0.1757 g of $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.4 Indium internal standard stock solution (1 mL = 100 µg of In) -- Dissolve 0.1000 g of indium metal in 10 mL of conc. HNO_3. Dilute to 1,000 mL with reagent water.

7.4.5 Lithium internal standard stock solution (1 mL = 100 µg of ^6Li) -- Dissolve 0.6312 g of 95-atom-% ^6Li, Li_2CO_3 in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.6 Rhodium internal standard stock solution (1 mL = 100 µg of Rh) -- Dissolve 0.3593 g of ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL of conc. HCl and dilute to 1,000 mL with reagent water.

7.4.7 Scandium internal standard stock solution (1 mL = 100 µg of Sc) -- Dissolve 0.15343 g of Sc_2O_3 in 10 mL (1+1) of hot HNO_3. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.8 Terbium internal standard stock solution (1 mL = 100 µg of Tb) -- Dissolve 0.1828 g of $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) of HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.9 Yttrium internal standard stock solution (1 mL = 100 µg of Y) -- Dissolve 0.2316 g of $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL (1+1) of HNO_3. Add 5 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.10 Titanium interference stock solution (1 mL = 100 µg of Ti) -- Dissolve 0.4133 g of $(NH_4)_2TiF_6$ in reagent water. Add 2 drops of conc. HF and dilute to 1,000 mL with reagent water.

7.4.11 Molybdenum interference stock solution (1 mL = 100 µg of Mo) -- Dissolve 0.2043 g of $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

7.4.12 Gold preservative stock solution for mercury (1 mL = 100 µg) -- Recommend purchasing as high purity prepared solution of $AuCl_3$ in dilute hydrochloric acid matrix.

7.5 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{74}Ge and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.)

7.6 Blanks -- Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for

possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration. The rinse blank is used to flush the system between all samples and standards.

7.6.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1% HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Sec. 7.2.

7.6.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.9).

7.6.3 The rinse blank consists of 1 to 2% of HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the rinse blank should also contain 2 µg/mL (ppm) of $AuCl_3$ solution.

7.7 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Sec. 1.2. If this method is used to determine an element not listed in Sec. 1.2, the analyst should modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Sec. 9.7).

7.7.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

7.7.1.1 Mixed ICS solution I may be prepared by adding 13.903 g of $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g of $CaCO_3$ (dried at 180 EC for 1 hr before weighing), 1.000 g of Fe, 1.658 g of MgO, 2.305 g of Na_2CO_3, and 1.767 g of K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

7.7.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g of 85 % H_3PO_4, 6.373 g of 96% H_2SO_4, 40.024 g of 37% HCl, and 10.664 g of citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

7.7.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, selenium, chromium, cobalt, copper, manganese, nickel, silver, vanadium, and zinc stock solutions to about 50 mL of

reagent water. Add 2.0 mL of concentrated HNO_3, and dilute to 100.0 mL with reagent water.

7.7.1.4 Working ICS solutions

7.7.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), and 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

7.7.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2), and 2.0 mL of mixed ICS solution III (Sec. 7.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

7.8 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.4.3 for use). This standard may also be purchased.

7.9 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.4.4 for use).

7.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Sec. 10.2). This solution is also used to verify that the instrument has reached thermal stability (see Sec. 11.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material in Chapter Three, "Inorganic Analytes."

8.2 Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in this method.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to a 3000 series method (Method 3005, 3010, 3015, 3031, 3040, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are a useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limits of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.2.3.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book. Refer to Chapter One for additional guidance.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

9.6 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 70% of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. As an example, if the initial calibration internal standard response is 100,000 cps, anything below 70,000 cps in the sample would be unacceptable. Under these conditions, the established lower limit of quantitation has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed -- First, make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank, Sec. 7.6.1). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise to the minimum 70% limit. Reported results must be corrected for all dilutions.

9.7 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxide moleculars can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Sec. 4.2) for each instrument system are acceptable corrections for use in Method 6020.

9.8 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process, as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

9.9 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and,

if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 - 120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.10 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.11 should be conducted.

9.10.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{\left(\frac{|D_1 + D_2|}{2}\right)} \times 100$$

where:

RPD = relative percent difference.

D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.10.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.11 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.11.1 and 9.11.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These test will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.11.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.11.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.11.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

9.12 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with proper operating parameters established as detailed below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

10.2 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.

10.2.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of the appropriate correction equations or other routines for correcting spectral interferences. These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

10.2.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

10.2.3 The lower limits of quantitation should be established for all isotope masses utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.2.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.2.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

10.2.4 Specific recommended isotopes for the analytes noted in Sec. 1.2 are provided in Table 2. Other isotopes may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of mass spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

10.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 2.

10.4 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.5), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument standardization by analyzing appropriate QC samples as follows.

10.4.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

10.4.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

10.4.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses may not proceed or the previous ten samples need to be reanalyzed.

10.4.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.5. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. Flush the system with the rinse blank (Sec. 7.6.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.4.3.

Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated

sample concentration range. For all multi-point calibration scenarios, the lowest non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4.4 for recommendations on how to determine the linear dynamic range, while the guidance in this section and Sec. 10.4.3 provide options for defining the lower limit of quantitation.

10.4.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multi-point calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

10.4.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined by the lowest standard in the calibration curve.

10.4.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ±30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification, with the exception that analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's

quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

10.4.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data.

The low level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

10.5 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hr, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Sec. 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed.

NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 min before the calibration blank is run.

10.6 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach.

The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply a spectral correction, the correction may not be valid and those analytes where the spectral correction has been applied may be inaccurately reported.

NOTE: Some metals may exhibit non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ±30% of its true value should be achieved for the lowest concentration standard.

10.7 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metals determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must be matrix-matched with the standards. Solubilization and digestion procedures are presented in Chapter Three, "Inorganic Analytes."

CAUTION: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L (use 2.0 mL of 7.4.12 per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

11.2 Initiate appropriate operating configuration of the instrument’s computer according to the instrument manufacturer's instructions.

11.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

11.4 Operating conditions -- The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 min for the instrument to equilibrate before analyzing any samples. This must be verified by an analysis of the tuning solution (Sec. 7.10) at least four integrations with relative standard deviations of #5% for the analytes contained in the tuning solution.

CAUTION: The instrument should have features that protect itself from high ion currents. If not, precautions must be taken to protect the detector from high ion currents. A channel electron multiplier or active film multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

11.5 Calibrate the instrument following the procedure outlined in Sec. 10.0.

11.6 Flush the system with the rinse blank solution (Sec. 7.6.3) until the signal levels return to the DQO or method's levels of quantitation (usually about 30 sec) before the analysis of each sample (see Sec. 10.0). Nebulize each sample until a steady-state signal is achieved (usually about 30 sec) prior to collecting data. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

11.7 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.4.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.4.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.4.4) be analyzed after every ten samples and at the end of the analysis batch.

11.8 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.2 and 10.4). Alternatively apply solid phase chelation chromatography to eliminate the matrix as described in Sec. 4.4.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All results should be reported with up to three significant figures.

12.2 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Sec. 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In an EPA multi-laboratory study (Ref. 12), twelve laboratories applied the ICP-MS technique to both aqueous and solid samples. Table 3 summarizes the method performance data for aqueous samples. Performance data for solid samples are provided in Table 4. These data are provided for guidance purposes only.

13.3 Table 5 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 6 summarizes the performance data for a simulated drinking water standard. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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U.S. Patent Office, March 1989, 31 pages, Granted June 30, 1992, Patent held by US Government.

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16. D. E. Dobb, J. T. Rowan, and D. Cardenas, Lockheed Environmental Systems and Technologies Co., Las Vegas, NV; and L. C. Butler, and E. M. Heithmar, E.M., U.S.EPA, Las Vegas, NV; "Determination of Mercury by ICP-MS."

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

These data are provided for guidance purposes only.

TABLE 2
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass(es)
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Germanium (IS)	74
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

[a] These masses are also useful for interference correction (Sec. 4.2).
[b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

NOTE: Method 6020 is recommended for only those analytes listed in Sec.1.2. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

TABLE 3

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	16 - 16	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique (ICP-AES or GFAA).

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). A larger number gives a more reliable comparison.

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 4

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	19 - 34	15 - 16	7
Beryllium	50 - 87	8.6 - 14	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE METHOD PERFORMANCE DATA FOR AQUEOUS AND SEA WATER SAMPLES[A]
WITH INTERFERING ELEMENTS REMOVED
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]		
		9.0 mL	27.0 mL	CERTFIED
Manganese	55	1.8±0.05	1.9±0.2	1.99±0.15
Nickel	58	0.32±0.018	0.32±0.04	0.30±0.04
Cobalt	59	0.033±0.002	0.028±0.003	0.025±0.006
Copper	63	0.68±0.03	0.63±0.03	0.68±0.04
Zinc	64	1.6±0.05	1.8±0.15	1.97±0.12
Copper	65	0.67±0.03	0.6±0.05	0.68±0.04
Zinc	66	1.6±0.06	1.8±0.2	1.97±0.12
Cadmium	112	0.020±0.0015	0.019±0.0018	0.019±0.004
Cadmium	114	0.020±0.0009	0.019±0.002	0.019±0.004
Lead	206	0.013±0.0009	0.019±0.0011	0.019±0.006
Lead	207	0.014±0.0005	0.019±0.004	0.019±0.006
Lead	208	0.014±0.0006	0.019±0.002	0.019±0.006

Data obtained from Ref. 12.
[A] The dilution of the sea-water during the adjustment of pH produced 10 mL samples containing 9 mL of sea-water and 30 mL samples containing 27 mL of sea-water. Samples containing 9.0 mL of CASS-2, n=5; samples containing 27.0 mL of CASS-2, n=3.
[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

TABLE 6

ANALYSIS OF NIST SRM 1643b, TRACE METALS IN WATER[A]
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]	
		DETERMINED	CERTFIED
Manganese	55	30±1.3	28±2
Nickel	58	50±2	49±3
Cobalt	59	27±1.3	26±1
Nickel	60	51±2	49±3
Copper	63	23±1.0	21.9±0.4
Zinc	64	67±1.4	66±2
Copper	65	22±0.9	21.9±0.4
Zinc	66	67±1.8	66±2
Cadmium	111	20±0.5	20±1
Cadmium	112	19.9±0.3	20±1
Cadmium	114	19.8±0.4	20±1
Lead	206	23±0.5	23.7±0.7
Lead	207	23.9±0.4	23.7±0.7
Lead	208	24.2±0.4	23.7±0.7

Data obtained from Ref. 12.

[A] 5.0 mL samples, n=5.
[B] Concentration (ng/mL) ± 95% confidence limits.

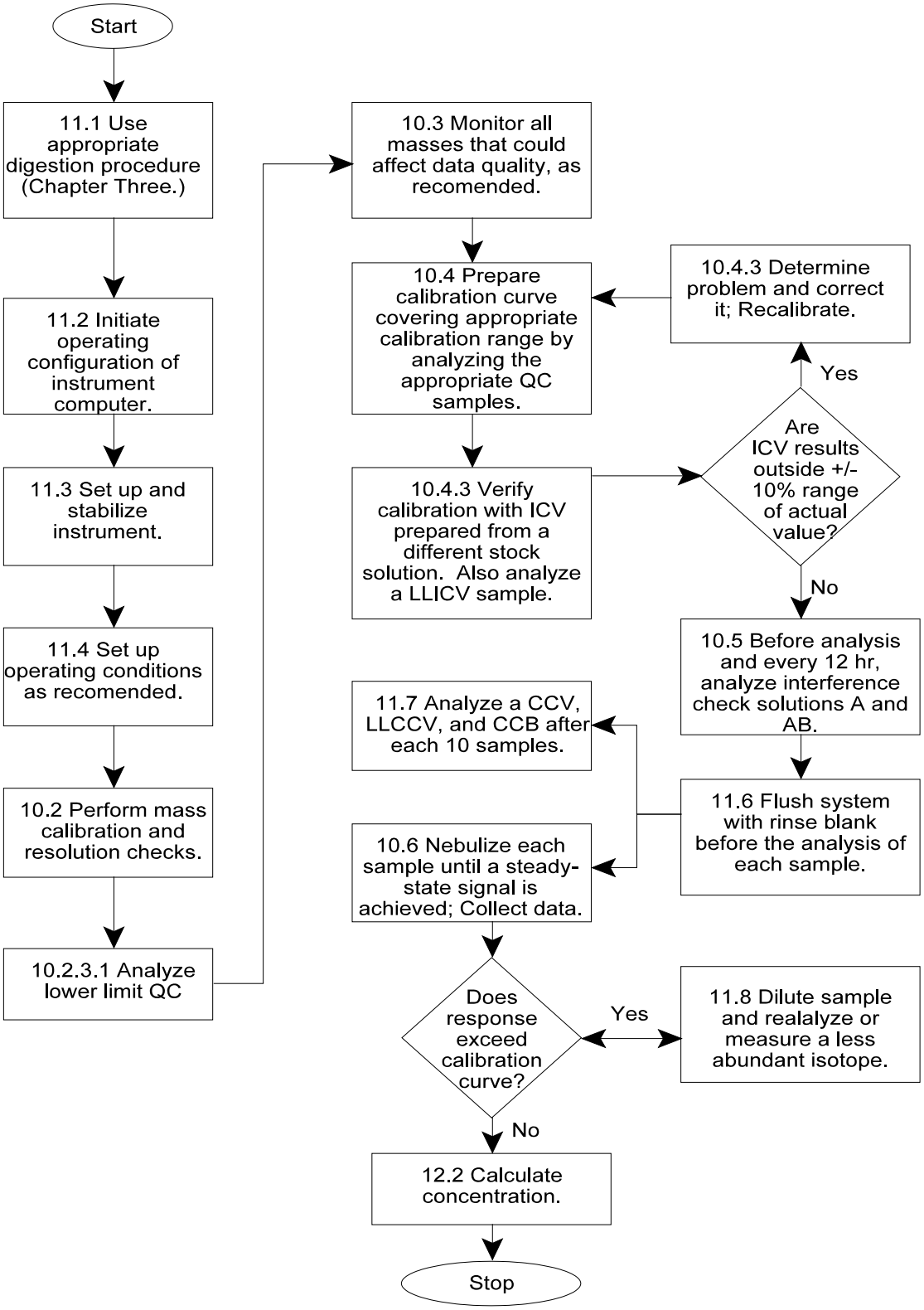
These data are provided for guidance purposes only.

TABLE 7

COMPARISON OF TOTAL MERCURY RESULTS IN HEAVILY CONTAMINATED SOILS

Soil Sample	Mercury in µg/g	
	ICP-MS	CVAA
1	27.8	29.2
2	442	376
3	64.7	58.2
4	339	589
5	281	454
6	23.8	21.4
7	217	183
8	157	129
9	1670	1360
10	73.5	64.8
11	2090	1830
12	96.4	85.8
13	1080	1190
14	294	258
15	3300	2850
16	301	281
17	2130	2020
18	247	226
19	2630	2080

Source: Ref. 16.
These data are provided for guidance purposes only.


Start
11.1 Use appropriate digestion procedure (Chapter Three.)
11.2 Initiate operating configuration of instrument computer.
11.3 Set up and stabilize instrument.
11.4 Set up operating conditions as recomended.
10.2 Perform mass calibration and resolution checks.
10.2.3.1 Analyze lower limit QC
10.3 Monitor all masses that could affect data quality, as recomended.
10.4 Prepare calibration curve covering appropriate calibration range by analyzing the appropriate QC samples.
10.4.3 Verify calibration with ICV prepared from a different stock solution. Also analyze a LLICV sample.
Are ICV results outside +/- 10% range of actual value?
Yes
10.4.3 Determine problem and correct it; Recalibrate.
No
10.5 Before analysis and every 12 hr, analyze interference check solutions A and AB.
11.6 Flush system with rinse blank before the analysis of each sample.
11.7 Analyze a CCV, LLCCV, and CCB after each 10 samples.
10.6 Nebulize each sample until a steady-state signal is achieved; Collect data.
Does response exceed calibration curve?
Yes
11.8 Dilute sample and realalyze or measure a less abundant isotope.
No
12.2 Calculate concentration.
Stop

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Revision Log:

Revision: 21		**Effective Date:** This version
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Cross Reference	Reflect current procedure	Added reference Analysis #6142, 6123, 6125, 10801…
Scope	Clarification	Reworded section.
Sample Collection, Preservation and Handling	Reflect current procedure	Changed sample storage temperature to 0° to 6°C, but not frozen.
Reagents and Standards	Reflect current procedure	Added reference to 1-P-QM-FOR-9009182.
Procedure	Reflect current procedure	Add boiling stones to the batch blank and LCS for the fish samples.
Block Digestor Instructions	Reflect current procedure No longer used	Hold and press the star key. Deleted test pertaining to the control panel grey buttons.
Quality Assurance/Quality Control	Reflect current procedure	Added reference to ICP/MS Analysis #6142, 6123, 6125, 10801, …. for batch requirements.

Revision: 20		**Effective Date:** Jan 22, 2013
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Throughout Document	Reflect re-identification of documents in EtQ	Replaced all prior Level 1, 2, 3, and 4 document numbers (analyses excluded) with EDR numbers
Safety Precautions and Waste Handling	Reflect current procedure	Added the use of designated dispensing equipment for HNO3 and HCL Added test pertaining to hazardous flags
Procedure	Reflects current procedure	Removed paint chip section. Deleted text pertaining to reducing the weight of paint chips. Paint chips will be digested as normal digestion per this procedure.
Procedure 2	Reflects current procedure	Added text pertaining to adding PTFE boiling stones to the LCS. Added text pertaining to entering the weights of the Blank and LCS in the LLENS.

Reference:

1. Test Methods for Evaluating Solid Wastes, SW-846 Method 3050B, December 1996.

2. *Chemical Hygiene Plan*, current version.

Cross Reference:

Document	Document Title
Analysis #6142, 6123, 6125, 10801, 6126, 6127, 6129, 6128, 6132, 6131, 6133, 6134, 6140, 6136, 6137, 6138, 6143, 6139, 6135, 6124, 6141, 6146, 6144, 6147, 6145, …	Metals by Inductively Coupled Plasma Mass Spectrometry for SW-846 Methods 6020/6020A (aqueous, solid, tissue), CLP 5.2 (aqueous, solid, tissue) and EPA 200.8 (aqueous)
Analysis #6966, 1643, 6935, 7914, 6946, 6947, 1650, 6949, 6952, 6951, 6953, 1654, 1662, 1656, 1657, 6958, 6960, 1667, 6961,10145, 6955, 6944, 6936, 6969, 7968, …	Metals by Inductively Coupled Plasma Atomic Emissions Spectroscopy for SW-846 Methods 6010A/B/C (aqueous, solid, tissue), CLP 2.1(water/solid/tissue), CLP 4.0(water/solid/tissue), CLP 5.2 (water/solid/tissue) and EPA 200.7(aqueous)
1-P-QM-FOR-9009182	Working Instructions for Prep Solutions and Standards

Purpose:

This digestion procedure is for the preparation of solid samples for analysis by ICP and ICP/MS following SW-846 protocol.

Scope:

This method is used for preparation of metals in solid samples for analysis by ICP and ICP/MS.

Basic Principles:

A representative sample is digested with repeated additions of nitric acid (HNO3) and hydrogen peroxide (H2O2). Hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. The resultant digestate is diluted and analyzed.

This method is not a total digestion technique for most samples; it is a very strong acid digestion that dissolves almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure.

Definitions:

1. ACS – American Chemical Society
2. D – Sample Duplicate
3. DOC – Demonstration of Capability
4. IDOC – Initial Demonstration of Capability
5. LCS/LCSD – Laboratory Control Sample/ Laboratory Control Sample Duplicate
6. LCSW– Laboratory Control Sample Water
7. LLENS - the computer program that integrates a PC with an analytical balance to collect data directly from the balance. The program organizes the data and transmits the readings to the LIMS.
8. LIMS – Laboratory Information Management Systems
9. LLI Sample ID – unique 7-digit number assigned to a client sample.
10. LOQ – Limit of Quantitation
11. MDL – Method Detection Limit
12. MS (R) – Matrix Spike
13. MSD (M) – Matrix spike duplicate

14. PB/PBW–Preparation Blank/ Preparation Blank Water

15. QC – Quality Control

16. Method Blank - equivalent to a Preparation Blank. A designated sample designed to monitor for sample contamination during the analysis process. A volume of reagent laboratory water is typically used to monitor water sample analysis, while solids blanks consist of a purified solid matrix or just the reagents used in the test. The blank demonstrates that no artifacts were introduced during the analysis process.

17. SOP- Standard Operating Procedure

18. U or US – unspiked background sample

Interferences:

When analyzing sample by ICP-MS using this digestion procedure we follow the instrument manufacturer's guidelines to eliminate polyatomic interferences typically caused by Chlorine. The process we follow involves the use of a collision/reaction cell on the ICP-MS. Below is a description of how the collision/reaction cell works.

Reaction Process - The primary method of interference removal is through a reaction event. When using a reaction gas, either the target interference is more reactive than the target analyte, leading to preferential removal of the interferent or (less commonly) the target analyte is more reactive and is converted to a new species at a different mass which is free from any existing or newly-formed overlap

Collision Process - The primary method of interference removal is through a non-reactive event. This process of interference removal is kinetic energy discrimination (KED). Energy Discrimination is most commonly used with an inert gas, which means the interference removal process is not affected by reactions in the cell.

Safety Precautions and Waste Handling:

All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state and local laws and regulations.

See *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

Preparing samples for inorganic analysis involves working with concentrated acids and other chemicals which are dangerous if not handled carefully:

Nitric acid (HNO3) – This acid can cause skin burns. Add nitric acid to samples in a hood or use the designated dispensing equipment to avoid exposure to toxic fumes.

Hydrochloric acid (HCl) – This acid can cause skin burns. Never mix HCI with concentrated H2SO4 to avoid a violent reaction. Always use in a fume hood or use the designated dispensing equipment.

Hydrogen peroxide (H2O2) - This is a strong oxidizing agent and causes severe burns. Avoid contact with skin.

When diluting strong acids, never add water to acid; always add acid to water.

Store concentrated acids in the prep room acid lockers. Only acids are to be stored in these lockers. (Store solvents in the flammable liquid storage cabinet.) Some concentrated acids are kept in the acid reagent bottles on prep room counters. Fill reagent bottles in an operating fume hood using caution to avoid spills.

Perform acid digestions in hoods that are turned on and have active alarms. Notify a supervisor immediately if the hood is malfunctioning or the alarm sounds.

Samples that contain dust may be hazardous. Open in a fume hood.

When a hazardous flag is added indicating possible cyanide, special precautions are required to avoid exposure to hydrogen cyanide gas. Contact your supervisor prior to adding acid. Always open these samples and add the acid in a hood.

Use spill pillows to absorb large acid spills (small spills are cleaned with wet paper towels.) Use SPILL-X-A powder or equivalent to neutralize any remaining acid and then rinse the area thoroughly with water. Spill pillows and SPILL-X-A are stored on the prep room shelf.

Dispose of acid waste properly. Collect all acid digestions, waste solutions, and expired reagent solutions in waste containers. When the acid waste containers are full, a designated acid waste handler transfers the waste to the acid neutralization tank.

Personnel Training and Qualifications:

All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and a documented Demonstration of Capability (DOC).

Initially, each employee performing this digestion procedure must work with an experienced employee for a period of time until they can independently set up batches and perform the necessary steps outlined in this procedure. Proficiency is measured through documentation of the critical steps in this procedure, over checking of data as well as an IDOC.

The IDOC and the DOC consists of four laboratory control samples that are carried through all steps of the analysis and meet the defined acceptance criteria. The criteria include the calculation of mean accuracy and standard deviation.

Sample Collection, Preservation, and Handling:

Solid samples require no chemical preservation.

Samples must be submitted in glass or plastic containers and stored at 0° to 6°C, but not frozen, prior to digestion. Samples must be digested within 6 months (180 days) of sample collection.

Digested samples are stored in polypropylene bottles at room temperature.

Apparatus and Equipment:

1. Polypropylene containers and covers (digestion vessels) - certified clean and Class A equivalent

2. Whatman No. 41 filter paper or equivalent

3. Funnels

4. Environmental Express HotBlock (block digestor) - adjustable and capable of maintaining a temperature of 90 to 95°C

5. Balance capable of reading 0.01 g

6. Chemware Ultra-Pure PTFE boiling stones, or equivalent.

7. Computer and software LLENS (Lancaster Laboratories Electronic Notebook System)

Reagents and Standards:

For reagent preparation, shelf life, and storage conditions, see Form 1-P-QM-FOR-9009182.

1. Nitric acid (HNO_3) _ Fisher, Trace Metal Grade, or equivalent. Store at room temperature. Re-evaluate annually.

2. Nitric acid (1:1) – Add 500 mL of HNO_3 to 500 mL of reagent water. Store in polypropylene at room temperature. Expires 6 months from date of preparation. (Different volumes are acceptable but ratios must stay the same.)

3. Hydrogen peroxide, 30% (H_2O_2) – Fisher, Certified ACS or equivalent. Store at room temperature. Re-evaluate annually.

4. Hydrochloric acid (HCl) – Baker Instra-Analyzed, or equivalent. Store at room temperature. Re-evaluate annually.

   NOTE: It is acceptable to prepare using multiples of indicated weights and volumes if ratios are maintained.

Calibration:

Not applicable.

Procedure:

1. Turn block digestor on and allow block to reach the Control Point setting that provides 90° to 95°C sample temperature. (The block temperature setting is not necessarily the sample temperature.) See below for **Block Digestor Instructions** section.

2. Weigh 1.00 to 1.05 g (to the nearest 0.01 g) of a well mixed sample into a polypropylene digestion vessel. (If the sample is watery use 5.00 to 5.05 grams for analysis. Additional information on non-standard matrices is found at the end of the procedure section.) Add 1.00 to 1.49 g of Chemware Ultra-Pure PTFE boiling stones to the digestion vessel for the blank and LCS. Enter the blank and LCS weight as 1.0000 to 100.0000 final volume in the LLENS. For sample batch spiking procedures see 1-P-QM-FOR-9009182. All spiking must be performed prior to starting the digestion procedure.

3. Add 10 mL of (1:1) HNO_3, swirl to mix, and cover with a polypropylene cover.

4. Place sample vessel in block digestor. Heat (reflux) the sample at 90° to 95°C for 10 to 15 minutes without boiling.

5. Remove vessel from digestion block and allow sample to cool.

6. Add 5 mL of concentrated HNO_3. Replace cover, return vessel to digestion block and heat for 30 minutes.

   NOTE: If brown fumes are generated (indicating oxidation of the sample by HNO_3) continue the process of adding 5 mL HNO3 and heating until no brown fumes are given off by the sample. This indicates that the reaction with HNO_3 is complete. Add the same amount of HNO_3 to the entire digestion batch.

7. With cover on, heat at 90° to 95°C without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times (add reagent water if necessary).

8. Remove vessel from digestion block and allow sample to cool.

9. Add 2 mL of reagent water and 3 mL of 30% H_2O_2. With cover on, return vessel to digestion block and heat until effervescence subsides. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

10. Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

    NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

11. With cover on, continue heating the acid-peroxide digestate at 90° to 95°C without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times (add reagent water if necessary).

12. Remove sample vessel from digestion block and allow to cool.

13. Add 10 mL of HCl. With the cover on, return vessel to digestion block and heat at 90° to 95°C for 15 minutes.

14. Remove sample vessel from digestion block.

15. If floating particulate is evident after digestion, the sample must be filtered.

    a. Filter through Whatman No. 41 filter paper into a polypropylene container.

    b. Wash sample vessel, residue, and paper thoroughly with reagent water.

    c. If any samples are filtered, the prep blank and LCS must also be filtered.

16. Adjust volume to the 100mL mark on the digestion vessel with reagent water and mix. Seal vessel with a screw cap. The sample is now ready for analysis.

NOTE: When special limits of quantitation are required by the client, use more sample weight.

For wipe samples:

When wipes are digested by this method, one blank media each must be used for the batch preparation blank, the laboratory control sample (LCS), and the laboratory control sample duplicate (LCSD). Refer to Form 1-P-QM-FOR-9009182 for the spiking of the LCS and LCSD. Digest wipes in their own batch. Use reagent water to rinse any particulate matter from the wipe container into the vessel containing the wipe before digesting. If brown fumes are evolved during wipe sample digestion, perform only two 5 mL HNO_3 additions with 30-minute refluxing each; add the same amount of HNO_3 to the entire batch. Proceed with digestion.

For fish tissue samples:

When fish tissues are digested by this method, refer to Form 1-P-QM-FOR-9009182 for the spiking of the LCS, LCSD (if needed), R (matrix spike), and M (matrix spike duplicate). Add 1.00 to 1.49 g of Chemware Ultra-Pure PTFE boiling stones to the digestion vessel for the blank and LCS. Digest fish tissues in their own batch.

Block Digestor Instructions:

1. Turn block digestor on by pressing rocker switch located on the cord.

2. Wait about 8 seconds until controller display indicates current block temperature.

3. PRESS and hold STAR (*) key.

4. The display shows Control Point temperature.

5. The digits can be changed to the desired value by pressing the up and down arrow keys while holding the (*) key.

6. Confirm Control Point temperature is set to the block temperature that provides 90° to 95°C.

   NOTE: See HotBlock Control Point Temperature Logbook to obtain control point temperature setting for the HotBlock being used. If necessary, adjust Control Point temperature to the proper setting as instructed below.

   NOTE: Polypropylene containers must not be heated above 130°C.

Calculations:

Not applicable

Statistical Information/Method Performance:

Not applicable to this procedure. See analysis method.

Quality Assurance/Quality Control:

For sample batch spiking instructions see form 1-P-QM-FOR-9009182. Refer to ICP section when prepping ICP analysis. Refer to ICP/MS section when prepping ICP/MS analysis. Prepare a method blank, sample duplicate, sample matrix spike, sample matrix spike duplicate, and laboratory control sample with every digestion batch (20 samples or less). Each piece of batch QC is digested following the procedure in this SOP. If any samples are filtered the prep blank and LCS must also be filtered.

Refer to ICP Analysis #6966, 1643, 6935, … for sample batch quality control requirements, acceptance criteria and corrective action.

Refer to ICP/MS Analysis #6142, 6123, 6125, 10801, 6126, … for sample batch quality control requirements, acceptance criteria and corrective action.

No. L-4

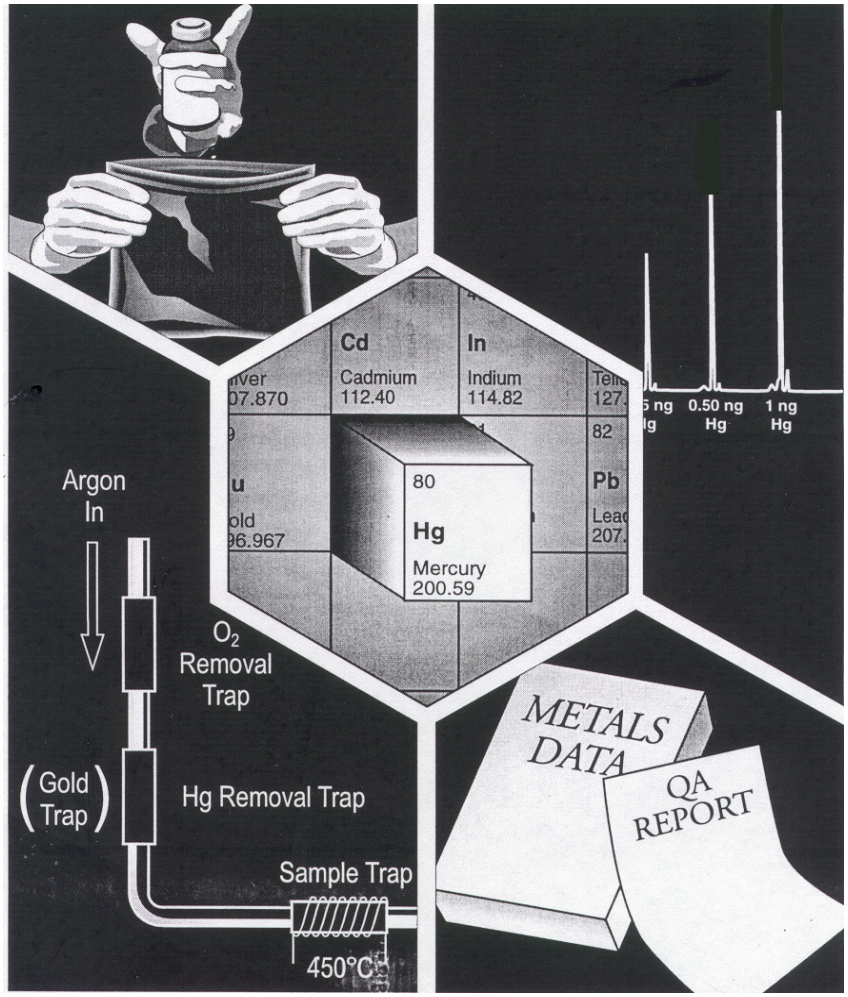
Mercury

USEPA Method 1631

United States
Environmental Protection
Agency

Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

August 2002



United States Environmental Protection Agency
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Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

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Disclaimer

This Method has been reviewed and approved for publication by the Statistics and Analytical Support Branch within EPA's Engineering and Analysis Division. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table of Contents

Introduction

Method 1631 (the "Method") supports technology-based and water quality-based monitoring programs authorized under the Clean Water Act (CWA; the "Act").

CWA Sections 301 and 306 require EPA to publish effluent standards that restrict the direct discharge of pollutants to the nations waters, and CWA Sections 307(b) and (c) require EPA to promulgate nationally applicable pretreatement standards which restrict pollutant discharges into sewers flowing to publicly owned treatment works (POTWs). The effluent limitations guidelines are published at CFR parts 401-503.

CWA Section 303 requires each State to set a water quality standard for each body of water within its boundaries. A State water quality standard consists of a designated use or uses of a water body or a segment of a water body, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. CWA Section 304(a) requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific water body, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by CWA Sections 301(b) and 306.

In 1987, amendments to the CWA required States to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses. Method 1631 was specifically developed to provide reliable measurements of mercury at EPA WQC levels.

In developing methods for determination of trace metals, EPA found that one of the greatest difficulties was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. Method 1631 is designed to preclude contamination in nearly all situations. It also contains procedures necessary to produce reliable results at the lowest WQC levels published by EPA. In recognition of the variety of situations to which this Method may be applied, and in recognition of continuing technological advances, Method 1631 is performance based. Alternative procedures may be used so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this draft Method should be directed to:

U.S. EPA Sample Control Center
6101 Stevenson Avenue
Alexandria, VA 22304-3540
703/461–2100

Note: This Method is performance based. The laboratory is permitted to omit steps or modify procedures provided that all performance requirements in this Method are met. The laboratory must not omit or modify any procedure defined by the term "shall" or "must" and must perform all quality control tests.

Method 1631, Revision E

Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

1.0 Scope and Application

1.1 Method 1631, Revision E (the "Method") is for determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). This Method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The Method is based on a contractor-developed procedure (Reference 16.1) and on peer-reviewed, published procedures for the determination of mercury in aqueous samples, ranging from sea water to sewage effluent (References 16.2–16.5).

1.2 This Method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Sampling Method). The Sampling Method guidance document is recommended to preclude contamination during the sampling process.

1.3 This Method is for determination of Hg in the range of 0.5–100 ng/L. Application may be extended to higher levels by selection of a smaller sample size or by calibration of the analytical system across a higher range. For measurement of blank samples, the Method may be extended to a lower level by calibration to a lower calibration point. Section 10.4 gives requirements for extension of the calibration range.

1.4 The ease of contaminating ambient water samples with mercury and interfering substances cannot be overemphasized. This Method includes suggestions for improvements in facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable trace metals determinations. Certain sections of this Method contain suggestions and other sections contain requirements to minimize contamination.

1.5 The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrument limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be 0.2 ng/L when no interferences are present. The minimum level of quantitation (ML) has been established as 0.5 ng/L. An MDL as low as 0.05 ng/L can be achieved for low Hg samples by using a larger sample volume, a lower BrCl level (0.2%), and extra caution in sample handling.

1.6 Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this Method because they lack an exact definition. However, the information provided in this Method is consistent with the summary guidance on clean and ultraclean techniques (References 16.6-16.7).

1.7 This Method follows the EPA Environmental Methods Management Council's "Guidelines and Format for Methods to Be Proposed at 40 CFR, part 136 or part 141."

1.8 This Method is "performance based." The laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurements if all performance criteria are met. Section 9.1.2.1 gives the requirements for establishing method equivalency.

1.9 Any modification of this Method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.10 This Method should be used only by analysts experienced in the use of CVAFS techniques and who are trained thoroughly in the sample handling and instrument techniques described in this Method. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedures in Section 9.2.

1.11 This Method is accompanied by a data verification and validation guidance document, *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for CWA Compliance Monitoring* (Reference 16.8), that can be used for verification and validation of the data obtained.

1.12 This Method uses either a bubbler or flow-injection system for determination of mercury in water. Separate calibration, analysis, and calculation procedures are provided for a bubbler system (Sections 10.2, 11.2.1, and 12.2) and for a flow-injection system (Sections 10.3, 11.2.2, and 12.3).

2.0 Summary of Method

2.1 A 100- to 2000-mL sample is collected directly into a cleaned, pretested, fluoropolymer or glass bottle using sample handling techniques designed for collection of mercury at trace levels (Reference 16.9).

2.2 For dissolved Hg, the sample is filtered through a 0.45-µm capsule filter prior to preservation.

2.3 The sample is preserved by adding either pretested 12N hydrochloric acid (HCl) or bromine monochloride (BrCl) solution. If a sample will also be used for the determination of methyl mercury, it should be preserved according to procedures in the method that will be used for determination of methylmercury.

2.4 Prior to analysis, all Hg in a 100-mL sample aliquot is oxidized to Hg(II) with BrCl.

2.5 After oxidation, the sample is sequentially reduced with $NH_2OH{\cdot}HCl$ to destroy the free halogens, then reduced with stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0).

2.6 The Hg(0) is separated from solution either by purging with nitrogen, helium, or argon, or by vapor/liquid separation. The Hg(0) is collected onto a gold trap (Figures 1, 2, and 3).

2.7 The Hg is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) to a second gold (analytical) trap. The Hg is desorbed from the analytical trap into a gas stream that carries the Hg into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection (Figures 2 and 3).

2.8 Quality is assured through calibration and testing of the oxidation, purging, and detection systems.

3.0 Definitions

3.1 Total mercury—all BrCl-oxidizable mercury forms and species found in an unfiltered aqueous solution. This includes, but is not limited to, Hg(II), Hg(0), strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg, and several tested covalently bound organo-mercurials (e.g., CH_3HgCl, $(CH_3)_2Hg$, and $C_6H_5HgOOCCH_3$). The recovery of Hg bound within microbial cells may require the additional step of UV photo-oxidation. In this Method, total mercury and total recoverable mercury are synonymous.

3.2 Dissolved mercury—all BrCl-oxidizable mercury forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45-µm filter.

3.3 Apparatus—Throughout this Method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis that come in contact with the sample and therefore require careful cleaning will be referred to collectively as the Apparatus.

3.4 Definitions of other terms used in this Method are given in the glossary (Section 17.0).

4.0 Contamination and Interferences

4.1 Preventing samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing samples for trace metals.

4.2 Samples may become contaminated by numerous routes. Potential sources of trace metals contamination during sampling include: metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned or stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples directly exposed to exhalation (Reference 16.9).

4.3 Contamination Control

4.3.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain mercury.

4.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. This Method and the Sampling Method give requirements and suggestions for control of sample contamination.

4.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. This Method gives requirements and suggestions for protecting the laboratory.

4.3.1.3 Although contamination control is essential, personnel health and safety remain the highest priority. The Sampling Method and Section 5 of this Method give suggestions and requirements for personnel safety.

4.3.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done. Therefore, it is imperative that the procedures described in this Method be carried out by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class-100 clean room. If a clean room is not available, all sample preparation should be performed in a class-100 clean bench or a nonmetal glove box fed by mercury-and particle-free air or nitrogen. Digestion should be performed in a nonmetal fume hood equipped with HEPA filtration and ideally situated in a clean room.

4.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags. Minimizing the time between cleaning and use will also minimize contamination.

4.3.5 Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

4.3.6 Wear gloves—Sampling personnel must wear clean, non-talc gloves during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.3.7 Use metal-free Apparatus—All Apparatus used for determination of mercury at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both.

4.3.7.1 Construction materials—Only fluoropolymer or glass containers must be used for collection of samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, leading to results that are biased low or high. Polyethylene and/or polypropylene labware may be used for digestion and other purposes because the time of sample exposure to these materials is relatively short. All materials, regardless of construction, that will directly or

indirectly contact the sample, must be known to be clean and free of Hg at the levels specified in this Method before proceeding.

4.3.7.2 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of reusable Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to introduction into the instrument. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected.

4.3.7.3 The laboratory or cleaning facility is responsible for cleaning the Apparatus used by the sampling team. If there are any indications that the Apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.3.8 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.3.8.1 Contamination by carryover—Contamination may occur when a sample containing a low concentration of mercury is processed immediately after a sample containing a relatively high concentration of mercury. The Hg concentration at which the analytical system (purge, traps, detector) will carry greater than 0.5 ng/L of Hg into a succeeding bubbler or system blank must be determined by analyzing calibration solutions containing successively larger concentrations of Hg. This test must be run prior to first use of the analytical system and whenever a change is made that would increase the amount of carryover. When a sample contains ½ or greater of this determined Hg concentration, a bubbler blank (bubbler system) or system blank (flow injection system) must be analyzed to demonstrate no carryover at the blank criteria level. For the bubbler system, the blank must be run using the same bubbler and sample trap used to run the high concentration sample. Samples analyzed following a sample that has been determined to result in carryover must be reanalyzed. Samples that are known or suspected to contain the lowest concentration of mercury should be analyzed first followed by samples containing higher levels.

4.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other undiluted samples containing concentrations of mercury greater than 100 ng/L are processed and analyzed. Samples known or suspected to contain Hg concentrations greater than 100 ng/L should be diluted prior to bringing them into the clean room or laboratory dedicated for processing trace metals samples.

4.3.8.3 Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. It is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of water samples be thoroughly cleaned (Section 6.1.2).

4.3.8.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination.

4.3.8.5 Contamination from reagents— Contamination can be introduced into samples from method reagents used during processing and analysis. Reagent blanks must be analyzed for contamination prior to use (see Section 9.4.3). If reagent blanks are contaminated, a new batch of reagents must be prepared (see Section 9.4.3.2).

4.4 Interferences

4.4.1 At the time of promulgation of this Method, gold and iodide were known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent. At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with $SnCl_2$ (to remove the brown color) and additional or more concentrated $SnCl_2$ should be added. To preclude loss of Hg, the additional $SnCl_2$ should be added in a closed vessel or analysis should proceed immediately. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis (Reference 16.10).

4.4.2 The potential exists for destruction of the gold traps if free halogens are purged onto them, or if they are overheated (>500 °C). When the instructions in this Method are followed, neither of these outcomes is likely.

4.4.3 Water vapor may collect in the gold traps and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by predrying the gold trap. Traps that tend to absorb large quantities of water vapor should not be used.

4.4.4 The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The dual amalgamation technique eliminates quenching due to trace gases, but it remains the laboratory's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Organo-mercurials may cause permanent brain damage. Because of the toxicological and physical properties of Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase a dilute standard solution of the Hg in this Method. If primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator shall be worn.

5.2 This Method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current file of OSHA regulations for safe handling of the chemicals specified in this Method. OSHA rules require that a reference file of material safety data sheets (MSDSs) must be made available to all personnel involved in these analyses (29 CFR 1917.28, Appendix E). It also is suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this Method and that the results of this monitoring be made available to the analyst. Personal hygiene monitoring should be performed using OSHA or NIOSH approved personal hygiene monitoring methods. Additional information on laboratory safety can be found in References 16.11-16.14. The references and bibliography included in Reference 16.14 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 Samples suspected to contain concentrations of Hg at µg/L or higher levels are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a safety program for handling Hg.

5.3.1 Facility—When samples known or suspected of containing high concentrations of mercury are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak-tight or in a fume hood demonstrated to have adequate airflow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluent from the CVAFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react mercury vapors.

5.3.7 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Sulfur powder will react with Hg to produce mercuric sulfide, thereby eliminating the possible volatilization of Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with sulfur powder, then washing with any detergent and water.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons that convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this Method can achieve a limit of detection of less than 1 ng per wipe. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

6.0 Apparatus and Materials

Disclaimer: The mention of trade names or commercial products in this Method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus, materials, or cleaning procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

6.1 Sampling equipment

6.1.1 Sample collection bottles-fluoropolymer or glass, 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.

6.1.2 Cleaning

6.1.2.1 New bottles are cleaned by heating to 65–75 °C in 4 N HCl or concentrated HNO_3 for at least 48 h. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70°C overnight. After cooling, they are rinsed three more times with reagent water, filled with reagent water containing 0.4% (v/v) HCl, and placed in a mercury-free Class-100 clean bench until the outside surfaces are dry. The bottles are tightly capped (with a wrench), double-bagged in new polyethylene zip-type bags until needed, and stored in wooden or plastic boxes until use. The bottles may be shipped to the sampling site containing dilute HCl solution (e.g., 0.04%), containing reagent water, or empty.

6.1.2.2 Used bottles known not to have contained mercury at high (>100 ng/L) levels are cleaned as above, except for only 6–12 h in hot 4 N HCl.

6.1.2.3 Bottle blanks must be analyzed as described in Section 9.4.7. To verify the effectiveness of the cleaning procedures, bottle blanks must be demonstrated to be free of mercury at the ML of this Method.

6.1.2.4 As an alternative to cleaning by the laboratory, bottles may be purchased from a commercial supplier and each lot certified to be clean. Bottles from the lot must be tested as bottle blanks (Section 9.4.7) and demonstrated to be free of mercury at the ML of this Method. If mercury is present above this level in any bottle, either the lot must be rejected or the bottles must be re-cleaned.

6.1.3 Filtration Apparatus

6.1.3.1 Filter—0.45-µm, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)

6.1.3.2 Peristaltic pump—115-V a.c., 12-V d.c., internal battery, variable-speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. 07570-10 drive with Quick Load pump head, Catalog No. 07021-24, or equivalent).

6.1.3.3 Tubing—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approx 3/8-in ID by approximately 3 ft (Cole-Parmer size 18, Catalog No. 06424-18, or approximately 1/4-in OD, Cole-Parmer size 17, Catalog No. 06424-17, or equivalent). Tubing is cleaned by soaking in 5–10% HCl solution for 8–24 h, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

6.2 Equipment for bottle and glassware cleaning

6.2.1 Vat, 100–200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

6.2.2 Panel immersion heater, 500-W, all-fluoropolymer coated, 120 vac (Cole-Parmer H-03053-04, or equivalent)

WARNING: *Read instructions carefully!! The heater will maintain steady state, without temperature feedback control, of 60–75°C in a vat of the size described. However, the equilibrium temperature will be higher (up to boiling) in a smaller vat. Also, the heater plate MUST be maintained in a vertical position, completely submerged and away from the vat walls to avoid melting the vat or burning out!*

6.2.3 Laboratory sink—in Class-100 clean area, with high-flow reagent water (Section 7.1) for rinsing.

6.2.4 Clean bench—Class-100, for drying rinsed bottles.

6.2.5 Oven—stainless steel, in Class-100 clean area, capable of maintaining ± 5°C in the 60–70°C temperature range.

6.3 Cold vapor atomic fluorescence spectrometer (CVAFS): The CVAFS system used may either be purchased from a supplier, or built in the laboratory from commercially available components.

6.3.1 Commercially available CVAFS—Tekran (Toronto, ON) Series 2600 CVAFS, Brooks-Rand (Seattle, WA) Model III CVAFS, Leeman Labs Hydra AF Gold*plus* CVAFS, or equivalent

6.3.2 Custom-built CVAFS (Reference 16.15). Figure 2 shows the schematic diagram. The system consists of the following:

6.3.2.1 Low-pressure 4-W mercury vapor lamp

6.3.2.2 Far UV quartz flow-through fluorescence cell—12 mm x 12 mm x 45 mm, with a 10-mm path length (NSG Cells, or equivalent).

6.3.2.3 UV-visible photomultiplier (PMT)—sensitive to < 230 nm. This PMT is isolated from outside light with a 253.7-nm interference filter (Oriel Corp., Stamford, CT, or equivalent).

6.3.2.4 Photometer and PMT power supply (Oriel Corp. or equivalent), to convert PMT output (nanoamp) to millivolts

6.3.2.5 Black anodized aluminum optical block—holds fluorescence cell, PMT, and light source at perpendicular angles, and provides collimation of incident and fluorescent beams (Frontier Geosciences Inc., Seattle, WA, or equivalent).

6.3.2.6 Flowmeter—with needle valve capable of reproducibly keeping the carrier gas flow rate at 30 mL/min

6.4 Hg purging system—Figure 2 shows the schematic diagram for the purging system. The system consists of the following:

6.4.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min.

6.4.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm OD fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm OD fluoropolymer tubing because of its greater flexibility.

6.4.3 Acid fume pretrap—10-cm long x 0.9-cm ID fluoropolymer tube containing 2–3 g of reagent grade, nonindicating, 8–14 mesh soda lime chunks, packed between wads of silanized glass wool. This trap is cleaned of Hg by placing on the output of a clean cold vapor generator (bubbler) and purging for 1 h with N_2 at 350 mL/min.

6.4.4 Cold vapor generator (bubbler)—200-mL borosilicate glass (15 cm high x 5.0 cm diameter) with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc. or equivalent).

6.5 The dual-trap Hg(0) preconcentrating system

6.5.1 Figures 2 and 3 show the dual-trap amalgamation system (Reference 16.5).

6.5.2 Gold-coated sand traps—10-cm long x 6.5-mm OD x 4-mm ID quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., Seattle, WA, or equivalent). The ends are plugged with quartz wool.

6.5.2.1 Traps are fitted with 6.5-mm ID fluoropolymer friction-fit sleeves for making connection to the system. When traps are not in use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination.

6.5.2.2 At least six traps are needed for efficient operation, one as the "analytical" trap, and the others to sequentially collect samples.

6.5.3 Heating of gold-coated sand traps—To desorb Hg collected on a trap, heat for 3.0 min to 450–500 °C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 10-14 vac. Potential is applied and finely adjusted with an autotransformer.

6.5.4 Timers—The heating interval is controlled by a timer-activated 120-V outlet (Gralab, or equivalent), into which the heating coil autotransformer is plugged. Two timers are required, one each for the "sample" trap and the "analytical" trap.

6.5.5 Air blowers—After heating, traps are cooled by blowing air from a small squirrel-cage blower positioned immediately above the trap. Two blowers are required, one each for the "sample" trap and the "analytical" trap.

6.6 Recorder—Any multi-range millivolt chart recorder or integrator with a range compatible with the CVAFS is acceptable. By using a two-pen recorder with pen sensitivity offset by a factor of 10, the dynamic range of the system is extended to 10^3.

6.7 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10 µL to 5.0 mL.

6.8 Analytical balance capable of weighing to the nearest 0.01 g

7.0 Reagents and Standards

Note: The quantities of reagents and the preparation procedures in this section are for illustrative purposes. Equivalent performance may be achievable using quantities of reagents and procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

7.1 Reagent water—18-MΩ minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

7.2 Air—It is very important that the laboratory air be low in both particulate and gaseous mercury. Ideally, mercury work should be conducted in a new laboratory with mercury-free paint on the walls. A source of air that is very low in Hg should be brought directly into the Class-100 clean bench air intake. If this is not possible, air coming into the clean bench can be cleaned for mercury by placing a gold-coated cloth prefilter over the intake. Gold-coated cloth filter: Soak 2 m^2 of cotton gauze in 500 mL of 2% gold chloride solution at pH 7. In a hood, add 100 mL of 30% $NH_2OH{\cdot}HCl$ solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to set for several hours, then rinse

with copious amounts of deionized water. Squeeze-dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake prefilter of the laminar flow hood.

CAUTION: Great care should be taken to avoid contaminating the laboratory with gold dust. This could cause interferences with the analysis if gold becomes incorporated into the samples or equipment. The gilding procedure should be done in a remote laboratory if at all possible.

7.3 Hydrochloric acid—trace-metal purified reagent-grade HCl containing less than 5 pg/mL Hg. The HCl should be analyzed for Hg before use.

7.4 Hydroxylamine hydrochloride—Dissolve 300 g of $NH_2OH \cdot HCl$ in reagent water and bring to 1.0 L. This solution may be purified by the addition of 1.0 mL of $SnCl_2$ solution and purging overnight at 500 mL/min with Hg-free N_2. Flow injection systems may require the use of less $SnCl_2$ for purification of this solution.

7.5 Stannous chloride—Bring 200 g of $SnCl_2 \cdot 2H_2O$ and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with mercury-free N_2 at 500 mL/min to remove all traces of Hg. Store tightly capped.

7.6 Bromine monochloride (BrCl)—In a fume hood, dissolve 27 g of reagent grade KBr in 2.5 L of low-Hg HCl. Place a clean magnetic stir bar in the bottle and stir for approximately 1 h in the fume hood. Slowly add 38 g reagent grade $KBrO_3$ to the acid while stirring. When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid.

WARNING: *This process generates copious quantities of free halogens (Cl_2, Br_2, BrCl), which are released from the bottle. Add the $KBrO_3$ slowly in a fume hood!*

7.7 Stock mercury standard—NIST-certified 10,000-ppm aqueous Hg solution (NIST-3133). This solution is stable at least until the NIST expiration date.

7.8 Secondary Hg standard—Add approx 0.5 L of reagent water and 5 mL of BrCl solution (Section 7.6) to a 1.00-L Class A volumetric flask. Add 0.100 mL of the stock mercury standard (Section 7.7) to the flask and dilute to 1.00 L with reagent water. This solution contains 1.00 µg/mL (1.00 ppm) Hg. Transfer the solution to a fluoropolymer bottle and cap tightly. This solution is considered stable until the NIST expiration date.

7.9 Working Hg Standard A—Dilute 1.00 mL of the secondary Hg standard (Section 7.8) to 100 mL in a Class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 7.6). This solution contains 10.0 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

7.10 Working Hg Standard B—Dilute 0.10 mL of the secondary Hg standard (Section 7.8) to 1000 mL in a Class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 7.6). This solution contains 0.10 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

7.11 Initial Precision and Recovery (IPR) and Ongoing Precision and Recovery (OPR) solutions—Using the working Hg standard A (Section 7.9), prepare IPR and OPR solutions at a

concentration of 5 ng/L Hg in reagent water. IPR/OPR solutions are prepared using the same amounts of reagents used for preparation of the calibration standards.

7.12 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.

7.13 Argon—Grade 5.0 (ultra high-purity, GC grade) argon that has been further purified by the removal of Hg using a gold-coated sand trap.

8.0 Sample Collection, Preservation, and Storage

8.1 Before samples are collected, consideration should be given to the type of data required (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be taken. An excess of BrCl should be confirmed either visually (presence of a yellow color) or with starch iodide indicating paper, using a separate sample aliquot, prior to sample processing or direct analysis to ensure the sample has been properly preserved.

8.2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Glass bottles may be used if Hg is the only target analyte. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Reference 16.4). Polyethylene sample bottles must not be used (Reference 16.15).

8.3 Collect samples using guidance provided in the Sampling Method (Reference 16.9). Procedures in the Sampling Method are based on rigorous protocols for collection of samples for mercury (References 16.4 and 16.15).

NOTE: *Discrete samplers have been found to contaminate samples with Hg at the ng/L level. Therefore, great care should be exercised if this type of sampler is used. It may be necessary for the sampling team to use other means of sample collection if samples are found to be contaminated using the discrete sampler.*

8.4 Sample filtration—For dissolved Hg, a sample is filtered through a 0.45-µm capsule filter (Section 6.1.3.1) in a mercury-free clean area prior to preservation. If the sample is filtered, it must be accompanied by a blank that has been filtered under the same conditions. The Sampling Method describes sample filtration procedures.

8.5 Preservation—Samples are preserved by adding either 5 mL/L of pretested 12N HCl or 5 mL/L BrCl solution to the sample bottle. If a sample will be used also for the determination of methyl mercury, it should be collected and preserved according to procedures in the method that will be used for determination of methyl mercury (e.g., HCl or H_2SO_4 solution). Preserved samples are stable for up to 90 days of the date of collection.

8.5.1 Samples to be analyzed for total or dissolved Hg only may be shipped to the laboratory unpreserved and unrefrigerated if they are collected in fluoropolymer or glass bottles and capped tightly. Samples must be either preserved or analyzed within 48 hours of collection. If a sample is oxidized in the sample bottle, the time to preservation can be extended to 28 days.

8.5.2 Samples that are acid-preserved may lose Hg to coagulated organic materials in the water or condensed on the walls (Reference 16.16). The best approach is to add BrCl directly to the sample bottle at least 24 hours before analysis. If other Hg species are to be analyzed, these aliquots must be removed prior to the addition of BrCl. If BrCl

cannot be added directly to the sample bottle, the bottle must be shaken vigorously prior to sub-sampling.

8.5.3 Handling of the samples in the laboratory should be undertaken in a mercury-free clean bench, after rinsing the outside of the bottles with reagent water and drying in the clean air hood.

NOTE: *Because of the potential for contamination, it is recommended that filtration and preservation of samples be performed in the clean room in the laboratory. However, if circumstances prevent overnight shipment of samples, samples should be filtered and preserved in a designated clean area in the field in accordance with the procedures given in Method 1669 (Reference 16.9). If filtered in the field, samples ideally should be filtered into the sample bottle.*

8.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until sample analysis.

8.7 Sample preservation, storage, and holding time requirements also are given at 40 CFR part 136.3(e) Table II.

9.0 Quality Control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 16.17). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess precision and recovery. Laboratory performance is compared to established performance criteria to determine that the results of analyses meet the performance characteristics of the Method.

9.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable accuracy and precision. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve results or lower the cost of measurements. These options include automation of the dual-amalgamation system, single-trap amalgamation (Reference 16.18), direct electronic data acquisition, calibration using gas-phase elemental Hg standards, use of the bubbler or flow-injection systems, or changes in the detector (i.e., CVAAS) when less sensitivity is acceptable or desired. Changes in the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this Method is used, that technique must have a specificity for mercury equal to or better than the specificity of the technique in this Method.

9.1.2.1 Each time this Method is modified, the laboratory is required to repeat the procedure in Section 9.2 to demonstrate that an MDL (40 CFR part 136, Appendix B) less than or equal to one-third the regulatory compliance limit or less than or equal to the MDL of this Method (Table 1), whichever is greater, can be achieved. If the change will affect calibration, the instrument must be recalibrated according to Section 10.

Note: If the compliance limit is greater than the concentration of Hg in the OPR/OPR (5 ng/L), the acceptance criteria for blanks and the concentrations of mercury spiked into quality control samples may be increased to support measurements at the compliance limit. For example, if the compliance limit is 12

ng/L (National Toxics Rule, 40 CFR 131.36), the MDL must be less than or equal to 4 ng/L; concentrations of the calibration standards may be 5, 10, 20, 50 , and 100 ng/L; concentrations of the IPR/OPR samples may be 10 ng/L; spike concentrations and acceptance criteria for MS/MSD samples would remain as specified in Section 9.3; and an appropriate blank acceptance criterion would be 5 ng/L.

9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and the quality control officer who witnessed and will verify the analyses and modification

9.1.2.2.2 A narrative stating the reason(s) for the modification(s)

9.1.2.2.3 Results from all quality control (QC) tests demonstrating the performance of the modified method, including the following:

(a) Calibration (Section 10)
(b) Initial precision and recovery (Section 9.2.2)
(c) Analysis of blanks (Section 9.4)
(d) Matrix spike/matrix spike duplicate analysis (Section 9.3)
(e) Ongoing precision and recovery (Section 9.5)
(f) Quality control sample (Section 9.6)
(g) Method detection limit (Section 9.2.1)

9.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result. These data are to include the following:

(a) Sample numbers and other identifiers
(b) Processing dates
(c) Analysis dates
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Copies of logbooks, chart recorder, or other raw data output
(g) Calculations linking raw data to the results reported

9.1.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 9.3 describes the procedure and QC criteria for spiking.

9.1.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 9.4 describes the procedures and criteria for analyzing blanks.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 9.5 and 9.6 describe these procedures, respectively.

9.1.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 9.3.7 and 9.5.3 describe the development of accuracy statements.

9.1.7 Quality of the analyses is controlled by an analytical batch. An analytical batch is a set of samples oxidized with the same batch of reagents, and analyzed during the same 12-hour shift. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by 3 system blanks (Section 9.4.2 for the flow-injection system), a

minimum of 3 bubbler blanks (Section 9.4.1 for the bubbler system), 1 OPR sample at the beginning and end of the batch (Section 9.5), a QCS (Section 9.6), and at least 3 method blanks (Section 9.4.4). In addition, there must be 1 MS and 1 MSD sample for every 10 samples (a frequency of 10%). A typical analytical sequence would be:

(a) Three system blanks (Section 9.4.2) or a minimum of 3 bubbler blanks (Section 9.4.1)
(b) A minimum of five, non-zero calibration standards (Section 10.2.2.1)
(c) On-going precision and recovery (Section 9.5)
(d) Quality control sample (Section 9.6)
(e) Method blank (Section 9.4.4)
(f) Seven samples
(g) Method blank (Section 9.4.4)
(h) Three samples
(i) Matrix spike (Section 9.3)
(j) Matrix spike duplicate (Section 9.3)
(k) Four samples
(l) Method blank (Section 9.4.4)
(m) Six samples
(n) Matrix spike (Section 9.3)
(o) Matrix spike duplicate (Section 9.3)
(p) Ongoing precision and recovery (Section 9.5)

The above sequence includes calibration. If system performance is verified at the end of the sequence using the OPR, analysis of samples and blanks may proceed without recalibration (i.e., the analytical sequence would be entered at Step (d) above), unless more than 12 hours has elapsed since verification of system performance. If more than 12 hours has elapsed, the sequence would be initiated at Step (c) above.

9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect Hg, the laboratory shall achieve an MDL that is less than or equal to the MDL listed in Section 1.5 or one-third the regulatory compliance limit, whichever is greater. The MDL shall be determined according to the procedure at 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this Method. This MDL shall be used for determination of laboratory capability only, and should be determined when a new operator begins work or whenever, in the judgment of the laboratory, a change in instrument hardware or operating conditions would dictate reevaluation of capability.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:

9.2.2.1 Analyze four replicates of the IPR solution (5 ng/L, Section 7.11) according to the procedure beginning in Section 11.

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for Hg.

9.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the

precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test (Section 9.2.2.1).

9.3 Matrix spike (MS) and matrix spike duplicate (MSD)—To assess the performance of the Method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge. Therefore, an analytical batch of 20 samples would require two pairs of MS/MSD samples (four spiked samples total).

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit, the spiking level shall be at that limit or at 1–5 times the background concentration of the sample (as determined in Section 9.3.2), whichever is greater.

9.3.1.2 If the concentration of Hg in a sample is not being checked against a limit, the spike shall be at 1–5 times the background concentration or at 1-5 times the ML in Table 1, whichever is greater.

9.3.2 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established *a priori*.

9.3.2.1 If necessary, prepare a standard solution to produce an appropriate level in the sample (Section 9.3.1).

9.3.2.2 Spike two additional sample aliquots with identical amounts of the spiking solution and analyze these aliquots as described in Section 11.1.2 to determine the concentration after spiking (A).

9.3.3 Calculate the percent recovery (R) in each aliquot using the following equation:

$$\%\ R = 100\ \frac{(A-B)}{T}$$

where:

A = *Measured concentration of analyte after spiking*
B = *Measured concentration of analyte before spiking*
T = *True concentration of the spike*

9.3.4 Compare percent recovery (R) with the QC acceptance criteria in Table 2.

9.3.4.1 If results of the MS/MSD are similar and fail the acceptance criteria, and recovery for the OPR standard (Section 9.5) for the analytical batch is within the acceptance criteria in Table 2, an interference is present and the results may not be reported or otherwise used for permitting or regulatory compliance purposes. If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the laboratory must modify the method, repeat the test required in Section 9.1.2, and repeat analysis of the sample and MS/MSD. However, during the development

of Method 1631, very few interferences have been noted in the determination of Hg using this Method. (See Section 4.4 for information on interferences.)

9.3.4.2 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be not in control, and the results may not be reported or used for permitting or regulatory compliance purposes. The laboratory must identify and correct the problem and reanalyze all samples in the sample batch.

9.3.5 Relative percent difference (RPD)—Compute the RPD between the MS and MSD results according to the following equation using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.3.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD = 200 \times \frac{(|D1-D2|)}{(D1+D2)}$$

Where:
D1 = concentration of Hg in the MS sample
D2 = concentration of Hg in the MSD sample

9.3.6 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2. If the criterion is not met, the system is judged to be out of control. The problem must be identified and corrected, and the MS/MSD and corresponding samples reanalyzed.

9.3.7 As part of the QC program for the laboratory, method precision and recovery for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (R_a) and the standard deviation of the percent recovery (s_r). Express the accuracy assessment as a percent recovery interval from $R_a - 2s_r$ to $R_a + 2s_r$. For example, if $R_a = 90\%$ and $s_r = 10\%$ for five analyses, the accuracy interval is expressed as 70–110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).

9.4 Blanks—Blanks are critical to the reliable determination of Hg at low levels. The sections below give the minimum requirements for analysis of blanks. Analysis of additional blanks is recommended as necessary to pinpoint sources of contamination in, and external to, the laboratory.

9.4.1 Bubbler blanks—Bubbler blanks are analyzed to demonstrate that bubbler systems are free from contamination at levels that could affect data quality. At least three bubbler blanks must be run during calibration and with each analytical batch.

9.4.1.1 To analyze a bubbler blank, place a clean gold trap on the bubbler. Purge and analyze previously purged water using the procedure in Section 11, and determine the amount of Hg remaining in the system.

9.4.1.2 If the bubbler blank is found to contain more than 50 pg Hg, the system is out of control. The problem must be investigated and remedied, and the samples run on that bubbler must be reanalyzed. If the blanks from other bubblers contain less than 50 pg Hg, the data associated with those bubblers remain valid, provided that all other criteria in Section 9 also are met.

9.4.1.3 The mean result for all bubbler blanks (from bubblers passing the specification in Section 9.4.1.2) must be < 25 pg (0.25 ng/L) Hg with a standard deviation (n-1) of <10 pg (0.10 ng/L). If the mean is < 25 pg, the average peak area or height is subtracted from all raw data before results are calculated (Section 12.2).

9.4.1.4 If Hg in the bubbler blank exceeds the acceptance criteria in Section 9.4.1.3, the system is out of control. The problem must be resolved and the system recalibrated. Usually, the bubbler blank is too high for one of the following reasons:

(a) Bubblers need rigorous cleaning;
(b) Soda-lime is contaminated; or
(c) Carrier gas is contaminated.

9.4.2 System blanks— System blanks are analyzed to demonstrate that flow injection systems are free from contamination at levels that could affect data quality. Three system blanks must be run during calibration and with each analytical batch.

9.4.2.1 To analyze a system blank, analyze reagent water containing the same amount of reagents used to prepare the calibration standards.

9.4.2.2 If a system blank is found to contain ≥ 0.50 ng/L Hg, the system is out of control. The problem must be investigated and remedied, and the system recalibrated. If the blanks contain < 0.50 ng/L Hg, the data associated with the blanks remain valid, provided that all other criteria in Section 9 also are met.

9.4.2.3 The mean result for the three system blanks must be <0.5 ng/L Hg with a standard deviation (n-1) <0.1 ng/L. If the mean exceeds these criteria, the system is out of control, and the problem must be resolved and the system recalibrated. If the mean is <0.5 ng/L, the average peak height or area is subtracted from all raw data before results are calculated (Section 12.3).

9.4.3 Reagent blanks—Reagent blanks are used to demonstrate that the reagents used to prepare samples for Hg analyses are free from contamination. The Hg concentration in reagent blanks is determined by analyzing the reagent solutions using either the bubbler or flow-injection system. For the bubbler system, reagent may be added directly to previously purged water in the bubbler.

9.4.3.1 Reagent blanks are required when the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are prepared. The amount of Hg in a reagent blank containing 0.5% (v/v) BrCl solution (Section 7.6) and 0.2% (v/v) hydroxylamine hydrochloride solution (Section 7.4) must be < 20 pg (0.2 ng/L).

9.4.3.2 The presence of more than 20 pg (0.2 ng/L) of Hg indicates a problem with the reagent solution. The purging of certain reagent solutions, such as $SnCl_2$ or NH_2OH, with mercury-free nitrogen or argon can reduce Hg to acceptable levels. Because BrCl cannot be purified, a new batch must be prepared and tested if the BrCl is contaminated.

9.4.4 Method blanks— Method blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Method blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples.

9.4.4.1 A minimum of three method blanks per analytical batch are required for both the bubbler and flow-injection systems.

9.4.4.2 If the result for any method blank containing the nominal amount of reagent used to prepare a sample (Section 11.1.1) is found to contain ≥ 0.50 ng/L (50 pg) Hg, the system is out of control. Mercury in the analytical system must be reduced until a method blank is free from contamination at the 0.50 ng/L level. Samples associated with a contaminated method blank must be reanalyzed.

9.4.4.3 Because method blanks are analyzed using procedures identical to those used to analyze samples, any sample requiring an increased amount of reagent must be accompanied by at least one method blank that includes an identical amount of reagent.

9.4.5 Field blanks–Field blanks are used to demonstrate that samples have not been contaminated by the sample collection and transport activities.

9.4.5.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples). Analyze the blank immediately before analyzing the samples in the batch.

9.4.5.2 If Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

9.4.5.3 Alternatively, if sufficient multiple field blanks (a minimum of three) are collected, and the average concentration (of the multiple field blanks) plus two standard deviations is equal to or greater than the regulatory compliance limit or equal to or greater than one-half of the level in the associated sample, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

9.4.5.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

9.4.6 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks on all sampling equipment that will be used to demonstrate that the sampling equipment is free from contamination.

9.4.6.1 Equipment blanks are generated in the laboratory or at the equipment cleaning facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility for low level mercury measurements. If grab samples are to be collected using any ancillary equipment, e.g., an extension pole or a dipper, an equipment blank

is generated by submersing this equipment into the reagent water and analyzing the resulting reagent water collected.

9.4.6.2 The equipment blank must be analyzed using the procedures in this Method. If mercury or any potentially interfering substance is detected in the blank at or above the level specified for the field blank (Section 9.4.5), the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from mercury and interferences before the equipment may be used in the field.

9.4.7 Bottle blanks— Bottles must be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles (Section 6.1.2) should be filled with reagent water acidified to pH <2 and allowed to stand for a minimum of 24 h. At least 5% of the bottles from a given lot should be tested, and the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water must be analyzed for any signs of contamination. If a bottle shows contamination at or above the level specified for the field blank (Section 9.4.5), the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles re-cleaned.

9.5 Ongoing precision and recovery (OPR)—To demonstrate that the analytical system is within the performance criteria of this Method and that acceptable precision and recovery is being maintained within each analytical batch, the laboratory shall perform the following operations:

9.5.1 Analyze the OPR solution (5 ng/L, Section 7.11) prior to the analysis of each analytical batch according to the procedure beginning in Section 11. An OPR also must be analyzed at the end of an analytical sequence or at the end of each 12-hour shift.

9.5.2 Compare the recovery with the limits for ongoing precision and recovery in Table 2. If the recovery is in the range specified, the analytical system is in control and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not in control. Correct the problem and repeat the ongoing precision and recovery test. All reported results must be associated with an OPR that meets the Table 2 performance criteria at the beginning and end of each batch.

9.5.3 The laboratory should add results that pass the specification in Section 9.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory also should develop a statement of laboratory data quality by calculating the average percent recovery (R_a) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from $R_a - 2s_r$ to $R_a + 2s_r$. For example, if $R_a = 95\%$ and $s_r = 5\%$, the accuracy is 85–105%.

9.6 Quality control sample (QCS) – The laboratory must obtain a QCS from a source different from the Hg used to produce the standards used routinely in this Method (Sections 7.7–7.10). The QCS should be analyzed as an independent check of system performance.

9.7 Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

10.0 Calibration and Standardization

10.1 Calibration and standardization— Separate calibration procedures are provided for a bubbler system (Section 10.2) and flow-injection system (Section 10.3). Both systems are calibrated using standards traceable to NIST Standard Reference Materials. If system performance is verified at the end of an analytical batch using the OPR, analysis of samples and blanks may proceed without recalibration, unless more than 12 hours has elapsed since verification of system performance.

10.2 Bubbler system calibration

10.2.1 Establish the operating conditions necessary to purge Hg from the bubbler and to desorb Hg from the traps in a sharp peak. Further details for operation of the purge-and-trap, desorption, and analysis systems are given in Sections 11.2.1 and 11.2.2.

10.2.2 The calibration must contain a minimum of five non-zero points and the results of analysis of three bubbler blanks. The lowest calibration point must be at the Minimum Level (ML).

NOTE: *The purge efficiency of the bubbler system is 100% and is independent of volume at the volumes used in this Method. Calibration of this system is typically performed using units of mass. For purposes of working in concentration, the volume is assumed to be 100 mL.*

10.2.2.1 Standards are analyzed by the addition of aliquots of Hg working standard A (Section 7.9) and Hg working standard B (Section 7.10) directly into the bubblers. Add 0.50 mL of working standard B and 0.5 mL $SnCl_2$ to the bubbler. Swirl to produce a standard containing 50 pg of Hg (0.5 ng/L). Purge under the optimum operating conditions (Section 10.2.1). Sequentially follow with the addition of aliquots of 0.05, 0.25, 0.50 and 1.0 mL of working standard A to produce standards of 500, 2500, 5000, and 10,000 pg Hg (5.0, 25.0, 50.0 and 100.0 ng/L).

NOTE: *If calibration to the higher levels results in carryover (Section 4.3.8.1), calibrate the system across a narrower range (Section 10.4)*

10.2.2.2 Analyze the standards beginning with the lowest concentration and proceeding to the highest. Tabulate the height or area for each peak.

10.2.2.3 Prepare and analyze a minimum of 3 bubbler blanks. If multiple bubblers are used, there must be 1 bubbler blank per bubbler (to a maximum of 4 bubblers). Calculate the mean peak area or height for the bubbler blanks.

10.2.2.4 For each calibration point, subtract the mean peak height or area of the bubbler blanks from the peak height or area for each standard. Calculate the calibration factor (CF_x) for Hg in each of the five standards using the mean bubbler-blank-subtracted peak height or area and the following equation:

$$CF_x = \frac{(A_x) - (\overline{A}_{BB})}{(C_x)}$$

Where:

A_x = *peak height or area for Hg in standard*

$\overline{A}_{BB}$ = *mean peak height or area for Hg in bubbler blank*

C_x = *mass in standard analyzed (ng)*

10.2.2.5 Calculate the mean calibration factor (CF_m), the standard deviation of the calibration factor (SD; n-1), and the relative standard deviation (RSD) of the calibration factor, where RSD = 100 x SD/CF_m.

10.2.2.6 If RSD ≤ 15%, calculate the recovery for the lowest standard using CF_m. If the RSD ≤ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CF_m may be used to calculate the concentration of Hg in samples. If RSD > 15% or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

10.2.2.7 Calculate the concentration of Hg in the bubbler blanks (Section 10.2.2.1) using CF_m. The bubbler blanks must meet the criteria in Section 9.4.1; otherwise, mercury in the system must be reduced and the calibration repeated until the bubbler blanks meet the criteria.

10.3 Flow-injection system calibration

10.3.1 Establish the operating conditions necessary to purge Hg from the gas-liquid separator and dryer tube and desorb Hg from the traps in a sharp peak. Further details for operating the analytical system are given in Section 11.2.1.

10.3.2 The calibration must contain a minimum of 5 non-zero points and the results of analysis of 3 system blanks. The lowest calibration point must be at the minimum level (ML).

10.3.2.1 Place 25-30 mL of reagent water and 250 µL of concentrated BrCl solution (Section 7.6) in each of 5 calibrated 50-mL autosampler vials. Prepare the 0.5 ng/L calibration standard by adding 250 µL of working standard B (Section 7.10) to the vial. Dilute to the mark with reagent water. Sequentially follow with the addition of aliquots of 25, 125, 250 and 500 µL of working standard A (Section 7.9) to produce standards of 5.0, 25.0, 50.0 and 100.0 ng/L, respectively. Cap the vials and invert once to mix.

10.3.2.2 Immediately prior to analysis, remove the caps and add 125 µL of NH_2OH solution (Section 7.4). Re-cap, invert once to mix, and allow to stand until the yellow color disappears. Remove all caps and place vials into the analysis rack.

10.3.2.3 Analyze the standards beginning with the lowest concentration and proceeding to the highest. Tabulate the height or area for the Hg peak.

10.3.2.4 Prepare and analyze a minimum of 3 system blanks and tabulate the peak heights or areas. Calculate the mean peak area or height for the system blanks.

10.3.2.5 For each calibration point, subtract the mean peak height or area of the system blanks (Section 9.4.2) from the peak height or area for each standard. Calculate

the calibration factor (CF_x) for Hg in each of the five standards using the mean reagent-blank-subtracted peak height or area and the following equation:

$$CF_x = \frac{(A_x) - (\bar{A}_{SB})}{(C_x)}$$

Where:

A_x = *peak height or area for Hg in standard*
$\bar{A}_{SB}$ = *mean peak height or area for Hg in calibration blanks*
C_x = *concentration of standard analyzed (ng/L)*

10.3.2.6 Calculate the mean calibration factor (CF_m), the standard deviation of the calibration factor (SD; n-1), and the relative standard deviation (RSD) of the calibration factor, where RSD = 100 x SD/CF_m.

10.3.2.7 If RSD ≤ 15%, calculate the recovery for the lowest standard (0.5 ng/L) using CF_m. If the RSD ≤ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CF_m may be used to calculate the concentration of Hg in samples, blanks, and OPRs. If RSD > 15% or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

10.3.2.8 Calculate the concentration of Hg in the system blanks (Section 9.4.2) using CF_m. The system blanks must meet the criteria in Section 9.4.2; otherwise, mercury in the system must be reduced and the calibration repeated until the system blanks meet the criteria.

10.4 Calibration to a range other than 0.5 to 100 ng/L—This Method may be calibrated to a range other than 0.5 to 100 ng/L, provided that the following requirements are met:

(a) There must be a minimum of five non-zero calibration points.
(b) The difference between successive calibration points must be no greater than a factor of 10 and no less than a factor of 2 and should be approximately evenly spaced on a logarithmic scale over the calibration range.
(c) The relative standard deviation (RSD) of the calibration factors for all calibration points must be less than 15%.
(d) The calibration factor for any calibration point at a concentration greater than 100 ng/L must be within ±15% of the average calibration factor for the points at or below 100 ng/L.
(e) The calibration factor for any point <0.5 ng/L must be within 25% of the average calibration factor for all points.
(f) If calibration is to a higher range and this Method is used for regulatory compliance, the ML must be less than one-third the regulatory compliance limit

11.0 Procedure

NOTE: *The following procedures for analysis of samples are provided as guidelines. Laboratories may find it necessary to optimize the procedures, such as drying time or potential applied to the Nichrome wires, for the laboratory's specific instrument set-up.*

11.1 Sample Preparation

11.1.1 Pour a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL fluoropolymer bottle. If BrCl was not added as a preservative (Section 8.5), add the amount of BrCl solution (Section 7.6) given below, cap the bottle, and digest at room temperature for a 12 h minimum.

11.1.1.1 For clear water and filtered samples, add 0.5 mL of BrCl; for brown water and turbid samples, add 1.0 mL of BrCl. If the yellow color disappears because of consumption by organic matter or sulfides, more BrCl should be added until a permanent (12-h) yellow color is obtained.

11.1.1.2 Some highly organic matrices, such as sewage effluent, will require high levels of BrCl (e.g., 5 mL/100 mL of sample) and longer oxidation times, or elevated temperatures (e.g., place sealed bottles in oven at 50 °C for 6 h). The oxidation must be continued until it is complete. Complete oxidation can be determined by either observation of a permanent yellow color remaining in the sample or the use of starch iodide indicating paper to test for residual free oxidizer. The sample also may be diluted to reduce the amount of BrCl required, provided that the resulting level of mercury is sufficient for reliable determination.

11.1.2 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour 2 additional 100-mL aliquots from a selected sample (see Section 9.3), spike at the level specified in Section 9.3, and process in the same manner as the samples. There must be a minimum of 2 MS/MSD pairs for each analytical batch of 20 samples.

11.2 Hg reduction and purging—Separate procedures are provided for the bubbler system (Section 11.2.1) and flow-injection (Section 11.2.2).

11.2.1 Hg reduction and purging for the bubbler system

11.2.1.1 Add 0.2-0.25 mL of NH_2OH solution to the BrCl-oxidized sample in the 125-mL sample bottle. Cap the bottle and swirl the sample. The yellow color will disappear, indicating the destruction of the BrCl. Allow the sample to react for 5 min with periodic swirling to be sure that no traces of halogens remain.

NOTE: *Purging of free halogens onto the gold trap will result in damage to the trap and low or irreproducible results.*

11.2.1.2 Connect a fresh trap to the bubbler, pour the reduced sample into the bubbler, add 0.5 mL of $SnCl_2$ solution, and purge the sample onto a gold trap with N_2 at 350 ± 50 mL/min for 20 min.

11.2.1.3 When analyzing Hg samples, the recovery is quantitative, and organic interferents are destroyed. Thus, standards, bubbler blanks, and small amounts of high-level samples may be run directly in previously purged water. After very high samples (Section 4.3.8.1), a small degree of carryover (<0.01%) may occur. Bubblers that contain such samples must be demonstrated to be clean prior to proceeding with low level samples. Samples run immediately following a sample that has been determined to result in carryover must be reanalyzed using a bubbler that is demonstrated to be clean as per Section 4.3.8.1.

11.2.2 Hg reduction and purging for the flow-injection system

11.2.2.1 Add 0.2-0.25 mL of NH_2OH solution (Section 7.4) to the BrCl-oxidized sample in the 125-mL sample bottle or in the autosampler tube (the amount of NH_2OH required will be approximately 30 percent of the BrCl volume). Cap the bottle and swirl the sample. The yellow color will disappear, indicating the destruction of the BrCl. Allow the sample to react for 5 minutes with periodic swirling to be sure that no traces of halogens remain.

NOTE: *Purging of free halogens onto the gold trap will result in damage to the trap and low or irreproducible results.*

11.2.2.2 Pour the sample solution into an autosampler vial and place the vial in the rack.

11.2.2.3 Carryover may occur after analysis of a sample containing a high level of mercury. Samples run immediately following a sample that has been determined to result in carryover (Section 4.3.8.1) must be reanalyzed using a system demonstrated to be clean as per Section 4.3.8.1.

11.3 Desorption of Hg from the gold trap

11.3.1 Remove the sample trap from the bubbler, place the Nichrome wire coil around the trap and connect the trap into the analyzer train between the incoming Hg-free argon and the second gold-coated (analytical) sand trap (Figure 2).

11.3.2 Pass argon through the sample and analytical traps at a flow rate of approximately 30 mL/min for approximately 2 min to drive off condensed water vapor.

11.3.3 Apply power to the coil around the sample trap for 3 minutes to thermally desorb the Hg (as Hg(0)) from the sample trap onto the analytical trap.

11.3.4 After the 3-min desorption time, turn off the power to the Nichrome coil, and cool the sample trap using the cooling fan.

11.3.5 Turn on the chart recorder or other data acquisition device to start data collection, and apply power to the Nichrome wire coil around the analytical trap. Heat the analytical trap for 3 min (1 min beyond the point at which the peak returns to baseline).

11.3.6 Stop data collection, turn off the power to the Nichrome coil, and cool the analytical trap to room temperature using the cooling fan.

11.3.7 Place the next sample trap in line and proceed with analysis of the next sample.

NOTE: *Do not heat a sample trap while the analytical trap is still warm; otherwise, the analyte may be lost by passing through the analytical trap.*

11.4 Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 minute and has a width at half-height of about 5 seconds.

11.4.1 Broad or asymmetrical peaks indicate a problem with the desorption train, such as improper gas flow rate, water vapor on the trap(s), or an analytical trap damaged by chemical fumes or overheating.

11.4.2 Damage to an analytical trap is also indicated by a sharp peak, followed by a small, broad peak.

11.4.3 If the analytical trap has been damaged, the trap and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration onto downstream surfaces.

11.4.4 Gold-coated sand traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded.

12.0 Data Analysis and Calculations

12.1 Separate procedures are provided for calculation of sample results using the bubbler system (Section 12.2) and the flow-injection system (Section 12.3), and for method blanks (Section 12.4).

12.2 Calculations for the bubbler system

12.2.1 Calculate the mean peak height or area for Hg in the bubbler blanks measured during system calibration or with the analytical batch (A_{BB}; n = 3 minimum).

12.2.2 Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each sample according to the following equation:

$$[Hg]\ (ng/L) = \frac{A_s - \overline{A}_{BB}}{CF_m \times V}$$

where:
A_s = *peak height (or area) for Hg in sample*
$\overline{A}_{BB}$ = *peak height (or area) for Hg in bubbler blank*
CF_m = *mean calibration factor (Section 10.2.2.5)*
V = *Volume of sample (L)*

12.3 Calculations for the flow-injection system

12.3.1 Calculate the mean peak height or area for Hg in the system blanks measured during system calibration or with each analytical batch (A_{SB}; n = 3)

12.3.2 Calculate the concentration of Hg in ng/L in each sample according to the following equation:

$$[Hg]\ (ng/L) = \frac{(A_s - \overline{A}_{SB})}{CF_m} \times \frac{V_{std}}{V_{sample}}$$

where:
A_s = *peak height (or area) for Hg in sample*
$\overline{A}_{SB}$ = *mean peak height (or area) for Hg in system blanks*
CF_m = *mean calibration factor (Section 10.3.2.6)*
V_{std} = *volume (mL) used for standards – volume (mL) reagent used in standards*
V_{sample} = *volume (mL) of sample – volume (mL) reagent used in sample*

12.4 Calculations for concentration of Hg in method blanks, field blanks, and reagent blanks.

12.4.1 Calculate the concentration of Hg in the method blanks (C_{MB}), field blanks (C_{FB}), or reagent blanks (C_{RB}) in ng/L, using the equation in Section 12.2.2 (if bubbler system is used) or Section 12.3.2 (if flow injection system is used) and substituting the peak height or area resulting from the method blank, field blank, or reagent blank for A_s.

12.4.2 Determine the mean concentration of Hg in the method blanks associated with the analytical batch (a minimum of three). If a sample requires additional reagent(s) (e.g., BrCl), a corresponding method blank containing an identical amount of reagent must be analyzed (Section 9.4.4.3). The concentration of Hg in the corresponding method blank may be subtracted from the concentration of Hg in the sample per Section 12.5.2.

12.5 Reporting

12.5.1 Report results for Hg at or above the ML, in ng/L, to three significant figures. Report results for Hg in samples below the ML as <0.5 ng/L, or as required by the regulatory authority or in the permit. Report results for Hg in reagent blanks and field blanks at or above the ML, in ng/L, to three significant figures. Report results for Hg in reagent blanks, method blanks, or field blanks below the ML but at or above the MDL to two significant figures. Report results for Hg not detected in reagent blanks, method blanks, or field blanks as <0.2 ng/L, or as required by the regulatory authority or in the permit.

12.5.2 Report results for Hg in samples, method blanks and field blanks separately. In addition to reporting results for the samples and blank(s) separately, the concentration of Hg in the method blanks or field blanks associated with the sample may be subtracted from the results for that sample, or must be subtracted if requested or required by a regulatory authority or in a permit.

12.5.3 Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results.

13.0 Method Performance

13.1 This Method was tested in 12 laboratories using reagent water, freshwater, marine water and effluent (Reference 16.19). The quality control acceptance criteria listed in Table 2 were verified by data gathered in the interlaboratory study, and the method detection limit (MDL) given in Section 1.5 was verified in all 12 laboratories. In addition, the techniques in this Method have been compared with other techniques for low-level mercury determination in water in a variety of studies, including ICES-5 (Reference 16.20) and the International Mercury Speciation Intercomparison Exercise (Reference 16.21).

13.2 Precision and recovery data for reagent water, freshwater, marine water, and secondary effluent are given in Table 3.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

14.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872–4477.

15.0 Waste Management

15.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

15.2 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

15.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

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17.0 Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

17.1 **Ambient Water**—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

17.2 **Analytical Batch**—A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).

17.3 **Bottle Blank**—The bottle blank is used to demonstrate that the bottle is free from contamination prior to use. Reagent water known to be free of mercury at the MDL of this Method is added to a bottle, acidified to pH <2 with BrCl or HCl, and allowed to stand for a minimum of 24 hours. The time that the bottle is allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water is analyzed.

17.4 **Bubbler Blank**—For this Method, the bubbler blank is specific to the bubbler system and is used to determine that the analytical system is free from contamination. After analysis of a standard, blank, or sample, the solution in the bubbler is purged and analyzed. A minimum of three bubbler blanks is required for system calibration.

17.5 **Equipment Blank**—Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility.

17.6 **Field Blank**—Reagent water that has been transported to the sampling site and exposed to the same equipment and operations as a sample at the sampling site. The field blank is used to demonstrate that the sample has not been contaminated by the sampling and sample transport systems.

17.7 **Intercomparison Study**—An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.

17.8 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.

17.9 **May**—This action, activity, or procedural step is allowed but not required.

17.10 **May not**—This action, activity, or procedural step is prohibited.

17.11 **Method blank**— Method blanks are used to determine the concentration of mercury in the analytical system during sample preparation and analysis, and consist of a volume of reagent water that is carried through the entire sample preparation and analysis. Method blanks are prepared by placing reagent water in a sample bottle and analyzing the water using reagents and procedures identical to those used to prepare and analyze the corresponding samples. A minimum of three method blanks is required with each analytical batch.

17.12 **Minimum Level (ML)**—The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10^n, where n is an integer (See Section 1.5).

17.13 **Must**—This action, activity, or procedural step is required.

17.14 **Quality Control Sample (QCS)**—A sample containing Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration.

17.15 **Reagent blank**—Reagent blanks are used to determine the concentration of mercury in the reagents (BrCl, $NH_2OH{\cdot}HCl$, and $SnCl_2$) that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of reagents is prepared.

17.16 **Reagent Water**—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MΩ ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as trip and field blanks, and in the preparation of standards and reagents.

17.17 **Regulatory Compliance Limit**—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.

17.18 **Shall**—This action, activity, or procedure is required.

17.19 **Should**—This action, activity, or procedure is suggested, but not required.

17.20 **Stock Solution**— A solution containing an analyte that is prepared from a reference material traceable to NIST, or a source that will attest to the purity and authenticity of the reference material.

17.21 **System Blank**— For this Method, the system blank is specific for the flow-injection system and is used to determine contamination in the analytical system and in the reagents used to prepare the calibration standards. A minimum of three system blanks is required during system calibration.

17.22 **Ultraclean Handling**— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

18.0 Tables and Figures

Table 1

Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Mercury (Hg)	1.3 ng/L	0.2 ng/L	0.5 ng/L

1. Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
2. Method detection limit (40 CFR 136, Appendix B)
3. Minimum level of quantitation (see Glossary)

Table 2

Quality Control Acceptance Criteria for Performance Tests in EPA Method 1631

Acceptance Criteria	Section	Limit (%)
Initial Precision and Recovery (IPR)	9.2.2	
Precision (RSD)	9.2.2.3	21
Recovery (X)	9.2.2.3	79-121
Ongoing Precision and Recovery (OPR)	9.5.2	77-123
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	9.3	
Recovery	9.3.4	71-125
Relative Percent Difference (RPD)	9.3.5	24

Table 3

Precision and Recovery for Reagent Water, Fresh Water, Marine Water, and Effluent Water Using Method 1631

Matrix	*Mean Recovery (%)	*Precision (% RSD)
Reagent Water	98.0	5.6
Fresh Water (Filtered)	90.4	8.3
Marine Water (Filtered)	92.3	4.7
Marine Water (Unfiltered)	88.9	5.0
Secondary Effluent (Filtered)	90.7	3.0
Secondary Effluent (Unfiltered)	92.8	4.5

*Mean percent recoveries and RSDs are based on expected Hg concentrations.

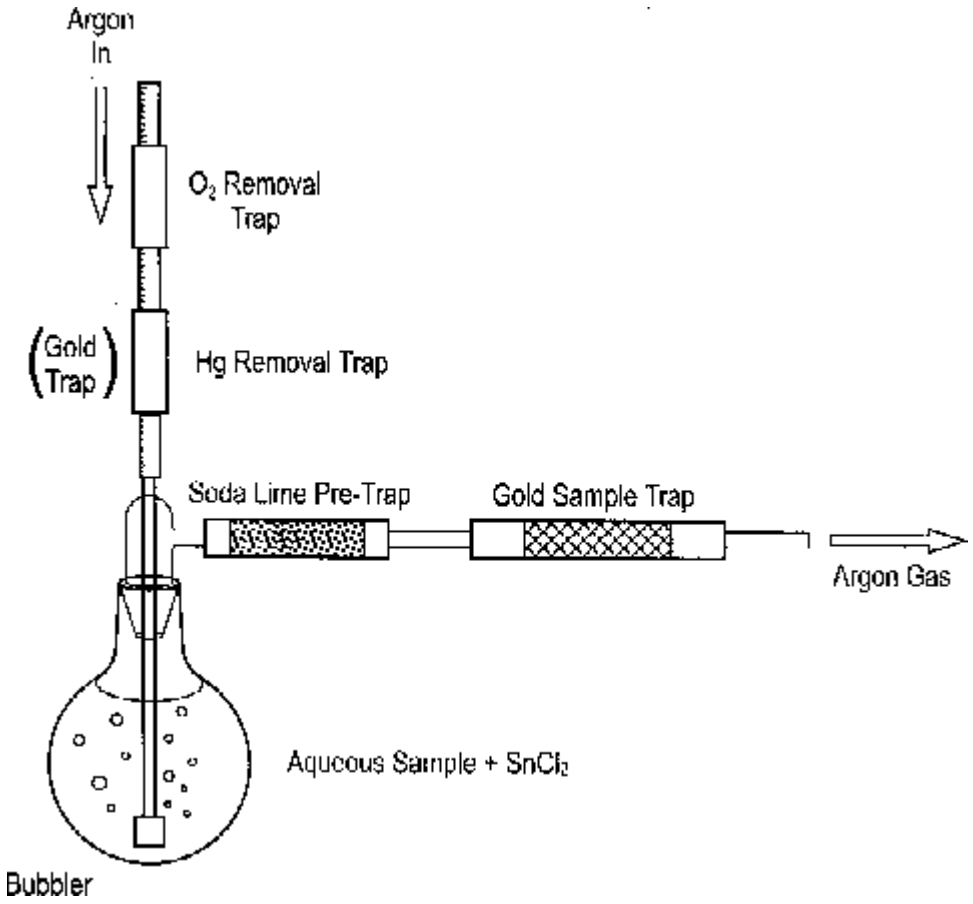

Figure 1. Schematic Diagram of Bubbler Setup

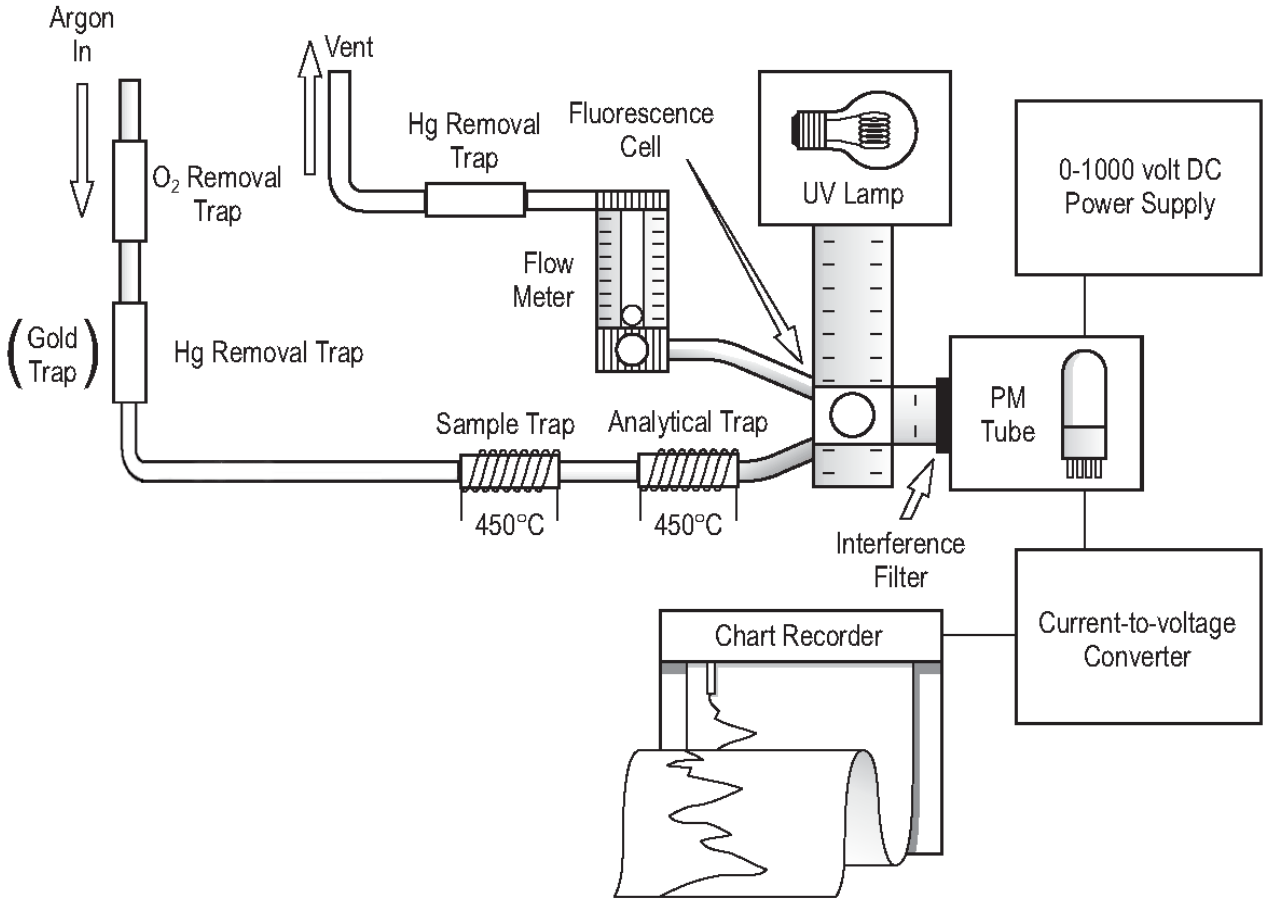

Figure 2. Schematic Diagram of the Bubbler, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System

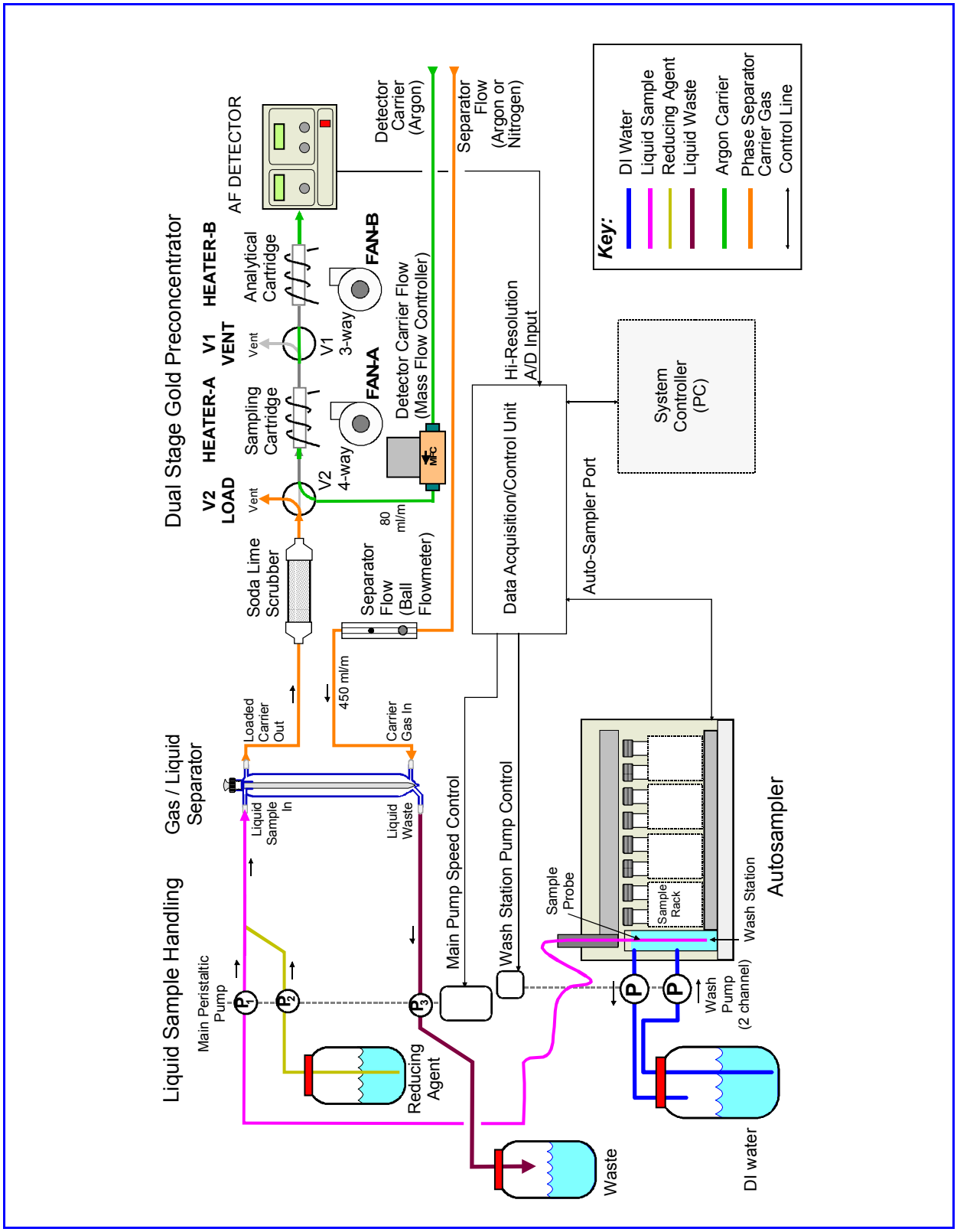

Figure 3. Schematic Diagram of the Flow-Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System

No. L-5

Methylmercury

USEPA Method 1630

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Method 1630

Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS

Draft
January 2001

U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
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Disclaimer

This method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. This method version contains minor editorial changes to the August 1998 version.

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Introduction

This analytical method supports water quality monitoring programs authorized under the Clean Water Act (CWA, the "Act"). CWA Section 304(a) requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

CWA Section 303 requires each state to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a water body or a segment of a water body, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific water body, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by CWA Sections 301(b) and 306.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to CWA required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, EPA developed new sampling and analysis methods to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (58 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 FR 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which the new sampling and analysis methods are based. Method 1630 was specifically developed to provide reliable measurements of methyl mercury at EPA WQC levels.

In developing methods for determination of trace metals, EPA found that one of the greatest difficulties was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method is designed to preclude contamination in nearly all situations. It also contains procedures necessary to produce reliable results at the lowest ambient water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, Method 1630 is performance based. Alternative procedures may be used so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

U.S. EPA NCEPI
11209 Kenwood Road
Cincinnati, OH 45242
513/489-8190

Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met. The laboratory may not omit any quality control analyses. The terms "shall," "must," and "may not" define procedures required for producing reliable data at water quality criteria levels. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this method.

Method 1630

Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS

1.0 Scope and Application

1.1 This method is for determination of methyl mercury (CH_3Hg) in filtered and unfiltered water by distillation, aqueous ethylation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). This method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a contractor-developed method (Reference 1) and on peer-reviewed, published procedures for the determination of CH_3Hg in aqueous samples, ranging from sea water to sewage effluent (References 2-7).

1.2 This method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Sampling Method). The Sampling Method is necessary to preclude contamination during the sampling process.

1.3 This method is designed for determination of CH_3Hg in the range of 0.02-5 ng/L and may be extended to higher levels by selection of a smaller sample size.

1.4 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metal determinations and minimize contamination (Section 4.0).

1.5 The detection limit and minimum level of quantitation in this method are usually dependent on the level of background elements rather than instrumental limitations. The method detection limit (MDL; 40 *CFR* 136, Appendix B) for CH_3Hg has been determined to be 0.02 ng/L when no background elements or interferences are present. The minimum level (ML) has been established as 0.06 ng/L. An MDL as low as 0.009 ng/L can be achieved for low CH_3Hg samples by using extra caution in sample handling and reagent selection, particularly the use of “for ultra-low level only” distillation equipment.

1.6 Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metal determinations. These terms are not used in this method because they lack an exact definition. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques.

1.7 This method follows the EPA Environmental Methods Management Council's "Format for Method Documentation."

1.8 This method is "performance based." The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements if all performance criteria are met. Section 9.1.2 gives the requirements for establishing method equivalency.

1.9 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 *CFR* 136.4 and 136.5.

1.10 This method should be used only by analysts who are experienced in the use of CVAFS techniques and who are thoroughly trained in the sample handling and instrumental techniques described in this method. Each analyst who uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.11 This method is accompanied by a data verification and validation guidance document, *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for CWA Compliance Monitoring*. Data users should state data quality objectives (DQOs) required for a project before this method is used.

2.0 Summary of Method

2.1 A 100-2000 mL sample is collected directly into specially cleaned, pretested, fluoropolymer or borosilicate bottle(s) using sample handling techniques specially designed for collection of metals at trace levels (Reference 6).

2.2 For dissolved CH_3Hg, samples are filtered through a 0.45-µm capsule filter.

2.3 Fresh water samples are preserved by adding 4 mL/L of pretested 11.6 M HCl, while saline samples ($[Cl^-] > 500$ ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution, to avoid distillation interferences caused by excess chloride.

2.4 Prior to analysis, a 45-mL sample aliquot is placed in a specially designed fluoropolymer distillation vessel, and 35 mL of the water is distilled into the receiving vessel at 125ºC under N_2 flow.

2.5 After distillation, the sample is adjusted to pH 4.9 with an acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate ($NaBEt_4$).

2.6 The ethyl analog of CH_3Hg, methylethyl mercury ($CH_3CH_3CH_2Hg$), is separated from solution by purging with N_2 onto a graphitic carbon (Carbotrap®) trap.

2.7 The trapped methylethyl mercury is thermally desorbed from the Carbotrap® trap into an inert gas stream that carries the released methylethyl mercury first through a pyrolytic decomposition column, which converts organo mercury forms to elemental mercury (Hg^0), and then into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.

2.8 Quality is ensured through calibration and testing of the distillation, ethylation, purging, and detection systems.

3.0 Definitions

3.1 Apparatus: Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis that come in contact with the sample and therefore require careful cleaning will be referred to collectively as the Apparatus.

3.2 Dissolved methyl mercury: All distillable CH_3Hg forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45 micron filter.

3.3 Methyl mercury: All acid-distillable Hg, which, upon reaction with $NaBEt_4$ yields methylethyl mercury. This includes, but is not limited to, CH_3Hg^+, strongly organo-complexed CH_3Hg compounds, adsorbed particulate CH_3Hg, and CH_3Hg bound in microorganisms. In freshly collected samples, dimethyl mercury ($(CH_3)_2Hg$) will not be recovered as CH_3Hg, but in samples which have been acidified for several days, most $(CH_3)_2Hg$ has broken down to CH_3Hg. In this method, CH_3Hg and total recoverable CH_3Hg are synonymous.

3.4 Definitions of other terms used in this method are given in the glossary at the end of the method.

4.0 Contamination and Interferences

4.1 Preventing ambient water samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.2 Samples may become contaminated by numerous routes. Potential sources of trace metal contamination during sampling include: metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metal contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 5).

4.3 Contamination control

4.3.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain Hg or CH_3Hg.

4.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. This method and the Sampling Method give requirements and suggestions for control of sample contamination.

4.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. This method gives requirements and suggestions for protecting the laboratory.

4.3.1.3 Although contamination control is essential, personnel health and safety remain the highest priority. The Sampling Method and Section 5 of this method give requirements and suggestions for personnel safety.

4.3.2 Avoid contamination—The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to the work being done. Therefore, it is imperative that the procedures described in this method be carried out by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class 100 clean room. If a clean room is not available, all sample preparation should be performed in a class 100 clean bench or a nonmetal glove box fed by mercury-free and particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally in the clean room.

4.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized. When not in use, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags. Minimizing the time between cleaning and use will also minimize contamination.

4.3.5 Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

4.3.6 Wear gloves—Sampling personnel must wear clean, non talc gloves during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.3.7 Use metal-free Apparatus—All Apparatus used for determination of CH_3Hg at ambient water quality criteria levels must be nonmetallic and free of material that may contain metals.

4.3.7.1 Construction materials—Only fluoropolymer or borosilicate glass containers should be used for samples that will be analyzed for Hg because Hg vapors can diffuse in or out of other materials, resulting in results that are biased low or high. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures in this method and must be known to be clean and mercury free before proceeding.

4.3.7.2 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to introduction into the instrument. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected.

4.3.7.3 The laboratory or cleaning facility is responsible for cleaning the Apparatus used by the sampling team. If there are any indications that the Apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.3.8 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.3.8.1 Contamination by carryover—Contamination may occur when a sample containing a low concentration of CH_3Hg is processed immediately after a sample containing a relatively high concentration. When an unusually concentrated sample is encountered, a ethylation blank should be analyzed immediately following the sample to check for carryover. Samples known or suspected to contain the lowest concentration of CH_3Hg should be analyzed first followed by samples containing higher levels.

4.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other samples containing high concentrations of Hg or CH_3Hg are processed and analyzed. This method is not intended for application to these samples, and samples containing high concentrations

of trace metals should not be permitted into the clean room and laboratory dedicated for processing trace metals samples.

4.3.8.3 Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of samples be thoroughly cleaned (see Section 6.1.2).

4.3.8.4 Contamination by airborne particulate matter—Airborne particles are less obvious substances capable of contaminating samples. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination.

4.4 Interferences

4.4.1 When the method is properly applied, no significant interferences have been observed in the analysis of ambient waters.

4.4.2 Distillation of CH_3Hg from solution requires a carefully controlled level of HCl in solution. Distillation will not be quantitative if too little HCl is added, but too much HCl results in co-distillation of HCl fumes, which interfere with the ethylation procedure. Therefore fresh water samples must be preserved only with between 0.3% and 0.5% (v/v) 11.6 M HCl, and salt water samples with between 0.1% and 0.2% (v/v) 9 M H_2SO_4.

4.4.3 Samples preserved with nitric acid (HNO_3) cannot be analyzed for CH_3Hg as the analyte is partially decomposed in the distillation step by this reagent.

4.4.4 The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The Carbotrap® trap eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train. In some rare cases (such as oil polluted water) low molecular weight organic compounds may purge with the methylethyl mercury and collect on the Carbotrap® trap, subsequently resulting in signal quenching during elution. Such cases are best treated by sample dilution prior to distillation.

4.4.5 Recent investigations have shown that a positive artifact is possible with the distillation procedure in cases where high inorganic Hg concentrations are present (Reference 7). In natural waters, approximately 0.01 to 0.05% of the ambient inorganic Hg in solution may be methylated by ambient organic matter during the distillation step. In most waters, where the percent CH_3Hg is 1-30% of the total, this effect is trivial. However, the analyst

should be aware that in inorganic Hg contaminated waters, the fraction CH_3Hg can be < 1% of the total, and so flagging of the data (as representing a maximum estimate of CH_3Hg concentration) may be warranted. In samples with high levels of divalent mercury (Hg(II)), solvent extraction may be preferable to distillation (Reference 7).

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.

5.1.1 Chronic Hg exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of the toxicological and physical properties of CH_3Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase a dilute standard solution of CH_3Hg for this method. If primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator shall be worn when high concentrations are handled.

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 7-10. The references and bibliography at the end of Reference 10 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 Samples suspected of containing high concentrations of CH_3Hg are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a strict safety program for handling CH_3Hg.

5.3.1 Facility—When samples known or suspected to contain high concentrations of CH_3Hg are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leakproof or in a fume hood demonstrated to have adequate airflow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazard except in an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluent from the CVAFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react with Hg vapors.

5.3.7 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Activated carbon powder will adsorb CH_3Hg, eliminating the possible volatilization of CH_3Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with activated carbon powder, then washing with any detergent and water.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this method can achieve a limit of detection of less than 1 ng per wipe. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard, requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

6.0 Equipment and Supplies

NOTE*: The mention of trade names or commercial products in this method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus, materials, or cleaning procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.*

6.1 Sampling equipment

6.1.1 Sample collection bottles-fluoropolymer or borosilicate glass, 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.

6.1.2 Cleaning

6.1.2.1 New bottles are cleaned by heating to 65-75°C in 4 N HCl for at least 48 h. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70°C overnight. After cooling, they are rinsed three more times with reagent water, filled with reagent water containing 0.4% (v/v) HCl, capped, and placed in a mercury-free class 100 clean bench until the outside of the bottle is dry. The caps are then tightened with a wrench and the bottles are double-bagged in new polyethylene zip-type bags. The capped bottles are stored in wooden or plastic boxes until use.

6.1.2.2 To avoid long-term accumulation of Hg or CH_3Hg on the bottle walls due to trace organic coatings, used bottles are filled with reagent water containing 0.02 N BrCl solution and allowed to stand over night. The BrCl is neutralized with the addition of 0.2 mL of 20% NH_2OH solution. The bottles are then cleaned exactly as in Section 6.1.2.1, except that they soak only 6-12 h in hot 4 N HCl.

6.1.2.3 Bottle blanks should be analyzed as described in Section 9.4.4.1 to verify the effectiveness of the cleaning procedures.

6.1.3 Filtration Apparatus

6.1.3.1 Filter—0.45-µm, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)

6.1.3.2 Peristaltic pump—115-V a.c., 12-V d.c., internal battery, variable-speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent).

6.1.3.3 Tubing—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approx 3/8-in i.d. by approximately 3 ft (Cole-Parmer size 18, Catalog No. G-06464-18, or approximately 1/4-in i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent). Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 h. It is rinsed with reagent water on a clean bench in a clean room and dried on the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

6.2 Equipment for bottle and glassware cleaning

6.2.1 Vat, 100-200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

6.2.2 Panel immersion heater, 500-W, all-fluoropolymer coated, 120 vac (Cole-Parmer H-03053-04, or equivalent)

NOTE*: Read instructions carefully!! The heater will maintain steady state, without temperature feedback control, of 60-75°C in a vat of the size described. However, the equilibrium temperature will be higher (up to boiling) in a smaller vat. Also, the heater plate MUST be maintained in a vertical position, completely submerged and away from the vat walls to avoid melting the vat or burning out!*

6.2.3 Laboratory sink in class 100 clean area, with high-flow reagent water (Section 7.1) for rinsing.

6.2.4 Clean bench, class 100, for drying rinsed bottles.

6.2.5 Oven, stainless steel, in class 100 clean area, capable of maintaining ± 5°C in the 60-70°C temperature range.

6.3 Cold vapor atomic fluorescence spectrometer (CVAFS): The CVAFS system used may either be purchased from a supplier, or built in the laboratory from commercially available components.

6.3.1 Commercially available: Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent

6.3.2 Custom-built CVAFS (Reference 11). Figure 1 shows the schematic diagram. The system consists of the following:

6.3.2.1 Low-pressure 4-W mercury vapor lamp

6.3.2.2 Far UV quartz flow-through fluorescence cell—12 mm x 12 mm x 45 mm, with a 10-mm path length (NSG Cells, or equivalent).

6.3.2.3 UV-visible photomultiplier (PMT)—sensitive to < 230 nm. This PMT is isolated from outside light with a 253.7-nm interference filter (Oriel Corp., or equivalent).

6.3.2.4 Photometer and PMT power supply (Oriel Corp., or equivalent), to convert PMT output (nanoamp) to millivolts

6.3.2.5 Black anodized aluminum optical block—holds fluorescence cell, PMT, and light source at perpendicular angles, and provides collimation of incident and fluorescent beams (Frontier Geosciences Inc., or equivalent).

6.3.2.6 Flowmeter, with needle valve capable of keeping the carrier gas at a reproducible flow rate of 30 mL/min

6.3.2.7 Ultra high-purity argon (grade 5.0)

6.4 Equipment for CH_3Hg purging system—Figure 2a shows the schematic diagram for the purging system. The system consists of the following:

6.4.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 350 (± 50) mL/min.

6.4.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm o.d. fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm o.d. fluoropolymer tubing because of its greater flexibility.

6.4.3 Cold vapor generator (bubbler)—200-mL borosilicate glass (15 cm high x 5.0 cm diameter) with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc., or equivalent).

6.5 Equipment for the isothermal gas chromatography (GC) system.

6.5.1 Figure 1 shows the schematic for the interface of the GC with the CVAFS detector (Reference 6).

6.5.2 Figure 2b shows the orientation consideration for purging and desorbing CH_3Hg from the Carbotrap® traps.

6.5.3 Carbotrap® traps—10-cm x 6.5-mm o.d. x 4-mm i.d. quartz tubing. The tube is filled with 3.4 cm of 30/45 mesh Carbotrap® graphitic carbon adsorbant (Supelco, Inc., or equivalent). The ends are plugged with silanized glass wool.

6.5.3.1 Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for making connection to the system. When traps are not in use,

fluoropolymer end plugs are inserted in trap ends to eliminate contamination.

6.5.3.2 At least six traps are needed for efficient operation.

6.5.3.3 Because the direction of flow is important in this analysis, the crimped end of the Carbotrap® trap will be referred to as "side A," while the uncrimped end will be referred to as "side B."

6.5.4 Heating of Carbotrap® traps—To desorb CH_3Hg collected on a trap, heat for 45 sec to 450-500°C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 16-20 vac. Potential is applied and finely adjusted with an autotransformer.

6.5.5 Timer—The heating interval is controlled by a timer-activated 120-V outlet, into which the heating coil autotransformer is plugged.

6.5.6 Isothermal GC—Consists of two parts, a custom fabricated packed GC column, and a custom fabricated constant temperature oven.

6.5.6.1 The column is 1 m long, made from 0.25 inch OD by 4 mm ID borosilicate glass GC column tubing. The column is formed into an 8 cm diameter coil, with 15 cm straight extensions from each end. The column is silanized, packed in the coiled portion with 60/80 mesh 15% OV-3 on acid-washed Chromasorb W, and then conditioned under inert gas flow at 200°C. A column meeting these specifications may be custom fabricated (Supelco Inc., or equivalent).

6.5.6.2 The GC oven consists of a 500-watt aluminum jacketed heating mantle, fitted with a custom machined fluoropolymer lid (14 cm OD by 1 cm thick). The lid is attached with stainless steel screws and contains three threaded holes (0.25 inch female NPT) in a triangular pattern in the top. The spacing of the holes conforms exactly to the spacing between the two 15 cm glass extensions of the GC column.

6.5.6.3 Fluoropolymer fittings, with 0.25-inch male NPT threads on the bottom and 0.25-inch compression fittings on top, are placed into the threaded holes. The GC column is secured into the oven by passing the glass extensions through two of the fluoropolymer fittings, so that 3 cm of the glass extensions protrude from the top, and tightening the compression fittings. The fluoropolymer lid holding the GC column is then screwed to the top of the oven.

6.5.6.4 Temperature feedback control (110 ± 2°C) is achieved through a thermocouple temperature controller. The oven is plugged into the controller and the thermocouple probe is inserted through the third

fluoropolymer fitting in the lid, such that the sensor is located near the center of the GC coil.

6.5.6.5 Several research groups have successfully interfaced the Carbotrap®/CVAFS system directly to a commercial gas chromatograph. The use of capillary column GC will result in better peak separation, although at higher cost.

6.5.7 Pyrolytic column—The output from the GC oven is connected directly to a high temperature column to decompose eluted organo-mercurial compounds to Hg^o. The output of the pyrolytic column is connected to the inlet of the CVAFS system.

6.5.7.1 The column consists of a 20-cm length of quartz tubing, packed over the central 10 cm with quartz wool.

6.5.7.2 The column is heated to orange heat (~ 700ºC) by a 1 m length of 22 gauge Nichrome wire, tightly wrapped around the quartz wool packed portion of the tube. The temperature of the coil is adjusted by visual inspection of the color, using a 0-120 volt autotransformer.

6.6 Recorder—Any multi-range millivolt chart recorder or integrator with a range compatible with the CVAFS is acceptable. By using a two pen recorder with pen sensitivity offset by a factor of 10, the dynamic range of the system is extended to 10^3.

6.7 Distillation unit—The distillation unit is a custom made temperature controlled aluminum block heater, as shown schematically in Figure 3 (Frontier Geosciences Inc., or equivalent).

6.7.1 Heating block insulation—Each heating block is encased first in refractory spun rock insulation (1 inch thickness) and then an exterior wood shell for rigidity.

6.7.2 Each heating block (10 cm wide x 20 cm long x 15 cm high) is bored with five 31 mm diameter holes (evenly spaced), 120 mm deep. A 3/8 inch diameter hole is bored to 90% of the block length, perpendicular to and behind the distillation tube holes, to accommodate a cylindrical heating element. A 2 mm diameter hole is bored parallel to the heating element hole, and 2 cm above it, to accommodate the temperature sensor.

6.7.3 Heating element—Each heating block is equipped with a 750 watt cylindrical heating element, 6 inches long by 3/8 inch diameter (Omega Inc.), immobilized in its respective hole by a dab of silicone glue.

6.7.4 Type J thermocouple probe—Each heating block is equipped with a type J thermocouple probe immobilized in its respective hole by a dab of silicone glue.

6.7.5 Digital temperature controller—The heating element and thermocouple are connected to a digital temperature controller.

6.7.6 Fluoropolymer vials with caps—The distillation unit is designed to accommodate 60-mL fluoropolymer vials (part number 0202, Savillex, or equivalent). The original caps are used to close the vials when distillate is to be stored until analysis.

6.7.6.1 For each distillation, two identical vials are needed: a distillation vessel and a receiving vessel. For convenience, each vial should be engraved with a line at 40.0 mL (obtained by weighing 40 g of water in the vial), and a unique identification number, both on the vial and the cap.

6.7.6.2 Fluoropolymer vials are acid cleaned initially as described for other fluoropolymer ware and stored filled with 0.5% HCl. After use, receiving vials are rinsed with reagent water and filled with 0.5% HCL. The tubing is looped around the cap as described in Section 6.7.7.1, and the vials are placed in a 70°C (± 5°C) oven overnight. Cleaning is the same for the distillation vials, with the exception that first the vials, caps, and tubing are thoroughly scrubbed with an alkaline detergent and test tube brush to remove any residues from the samples.

6.7.7 Purge caps—The standard caps on the fluoropolymer vials are replaced with purge caps (part number 33-2-2, Savillex, or equivalent) for distillation purposes.

6.7.7.1 Fluoropolymer tubing—each purge cap is threaded with a piece of 1/8 inch fluoropolymer tubing, approximately 30-40 cm long. One end is pulled through one of the holes in the cap, down to a length that will allow it to reach the bottom of the distillation vial when the vial is screwed onto the cap. The bottom end of this tubing is cut at a 45° angle. The outside end of the tubing is cut perpendicularly and is looped around and inserted into the second cap hole when not in use (to keep the system closed and clean).

6.7.8 Aluminum distillation cover—The cover for the heating block consists of a 5 cm high aluminum block of the same cross section as the heating block (10 cm wide x 20 cm long), which has been milled out completely except for a 0.5 cm shell all around. In this lid is placed a series of 5 slots, 0.5 cm wide by 3 cm high, on each of the long sides, to allow passage of the distillation tubing in and out of the distillation vessels.

NOTE: *It is very important that the heating block have an aluminum top covering the vessels, to avoid condensation and refluxing of the sample in the distillation vessels.*

6.7.9 Polyethylene container—Distillate is received and cooled in a fluoropolymer receiving vial supported in an ice bath in a polyethylene container. A box approximately 15 cm wide x 25 cm long x 10 cm high is a convenient container, and holes to accommodate the receiving vials can be cut into the lid of each box. Suitable boxes are generally available at sundries stores as storage containers.

6.7.10 Rotometer/needle valve—Five needle valve/rotometer (0-300 mL/min N_2) assemblies are required, one for each distillation vessel in the heating block. These rotometers can be mounted in banks of 5 for each distillation block, with all rotometers connected to a common gas manifold.

6.7.10.1 Fluoropolymer tubing–Inert gas(N_2 or Ar at 0.5-1 atm) is brought from the regulator to the manifold and from the rotometer outlets to the distillation vials by 1/8 inch fluoropolymer tubing.

6.7.11 The entire distillation set-up can be mounted on a stepped structure or shelving unit, such that the banks of rotometers are on the top and easily adjustable. Below the rotometers are the distillation blocks, and lower still, the ice baths for the receiving vessels.

6.8 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10-uL to 5.0-mL.

6.9 Analytical balance capable of weighing to the nearest 0.01 g.

7.0 Reagents and Standards

7.1 Reagent water—18-MΩ minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

7.2 Air—It is very important that the laboratory air be low in both particulate and gaseous Hg. Ideally, Hg work should be conducted in a new laboratory with mercury-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class 100 clean bench air intake. If this is impossible, air coming into the clean bench can be cleaned for Hg by placing a gold-coated cloth prefilter over the intake.

7.2.1 Gold-coated cloth filter: Soak 2 m^2 of cotton gauze in 500 mL of 2% gold chloride solution at pH 7. In a hood, add 100 mL of 30% $NH_2OH{\cdot}HCl$ solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to set for several hours, then rinse with copious amounts of reagent water. Squeeze-dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake prefilter of the laminar flow hood.

NOTE: *Great care should be taken to avoid contaminating the laboratory with gold dust. This could cause interferences with the analysis if gold becomes incorporated into the samples or equipment. The gilding procedure should be done in a remote laboratory if at all possible.*

7.3 Hydrochloric acid—Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH_3Hg.

7.4 Sulfuric acid—Trace-metal purified reagent H_2SO_4 containing less than 5 pg/mL Hg. CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH_3Hg.

7.5 1% APDC solution—To 100 mL of reagent water, add 1.0 g of reagent grade APDC (ammonium pyrrolidine dithiocarbamate), and shake to dissolve. The solution is purified by extraction with three 10 mL aliquots of methylene chloride.

7.6 Glacial acetic acid—Reagent grade

7.7 2 M Acetate buffer—2 moles of reagent grade sodium acetate (272 g) and 2 moles of reagent grade glacial acetic acid (118 mL) dissolved in reagent water to give a final volume of 1.0 L. To purify the buffer of traces of CH_3Hg, add 0.5 mL of 1% $NaBEt_4$ and purge the solution overnight with Hg-free N_2 or Ar. This solution has an indefinite lifetime when stored in a fluoropolymer bottle at room temperature.

7.8 1% Sodium tetraethyl borate—This reagent is purchased in 1.0-g air-sealed bottles (Strem Chemical, or equivalent. One hundred milliliters of 2% KOH in reagent water is prepared in a fluoropolymer bottle and chilled to 0ºC. The bottle of $NaBEt_4$ is rapidly opened and approximately 5 mL of the KOH solution poured in. The reagent bottle is capped and shaken to dissolve the $NaBEt_4$. This is poured into the 100 mL bottle of KOH solution, and shaken to mix. Immediately, the 1% $NaBEt_4$ solution in 2% KOH is poured into fifteen (15) 7-mL fluoropolymer bottles, which are capped and placed in a low temperature freezer. For use, one of these bottles is removed and thawed until it starts to form a liquid layer. The reagent is then used until just before all of the ice is melted. Usually this lasts about 3 h if the bottle is placed in the refrigerator between uses.

NOTE: *It is imperative that this reagent be exposed to air a minimum length of time. Thus, when removing reagent, open and close the lid quickly and tightly!*

Frozen bottles of $NaBEt_4$ will keep for at least one week. If any doubt arises about the quality of the ethylating reagent, make a new batch, as the old material often gives good results for reagent water spikes, but not for environmental samples. Do not use $NaBEt_4$ solid or solutions if they have a yellow color.

WARNING: *$NaBEt_4$ is toxic, gives off toxic gases (triethylboron), and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of 1N HCl in the hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Leave the acid beaker in the hood indefinitely, or boil down to 1/2 volume to destroy residues before discarding as any acid waste.*

7.9 Methyl mercuric chloride(s)—A 5-g bottle of methyl mercuric chloride (s), reagent grade (Strem Chemical, or equivalent).

7.10 Stock methyl mercury standard—Either procure certified CH_3Hg solution (Frontier Geosciences Inc., or equivalent) or prepare the stock solutions in the laboratory. Dissolve the contents of an entire 5-g bottle of methyl mercuric chloride in reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl in a fluoropolymer bottle. This solution contains 4000-5000 mg/L

CH_3Hg as Hg. It does not have a specific titre because, due to the contamination danger, the methyl mercuric chloride is not weighed. The stock solution has an indefinite lifetime when stored in an amber glass bottle with an fluoropolymer lid at room temperature. Do not make or keep this concentrated stock solution in the trace mercury laboratory.

NOTE: *Making a CH_3Hg standard rather than purchasing one requires the laboratory to have available the technology to perform analyses with Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. Total Hg and labile Hg (II) determinations, made with Method 1631, are necessary to accurately determine the CH_3Hg concentration of the standards. Additionally, laboratories must be cautioned against assuming that purchased CH_3Hg stock solution will remain constant in concentration. Purchased stock solution has been seen to degrade occasionally, in one case from 1000 mg/L to 4 mg/L.*

7.11 Secondary methyl mercury standard—Dilute 1.00 mL of stock solution (B) to 1000.0 mL with reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. This solution contains approximately 4-5 mg/L (5.00 ng/mL) CH_3Hg as Hg.. The exact CH_3Hg titre is determined as indicated in Sections 7.11.1-7.11.4. The secondary CH_3Hg standard solution has been observed to maintain its titre over a year when stored in a fluoropolymer bottle in the refrigerator.

7.11.1 Dilute the secondary standard 1:10 with concentrated BrCl solution (0.100 mL of secondary stock solution added to 0.900 mL BrCl in a small FEP vial). Allow the solution to oxidize for at least 4 h. The total Hg in the dilution may then be analyzed using dual amalgamation/CVAFS, by comparison to a dilution of NIST-3133 (as in Method 1631). A mean of at least seven replicate analyses of the secondary stock solution is necessary to accurately quantify the total Hg concentration of the solution.

7.11.2 Analyze the secondary standard for labile Hg(II) using Method 1631 by directly reducing an aliquot of standard solution with $SnCl_2$, but without prior BrCl oxidation as performed in Section 7.11.1. At least two determinations of labile Hg(II) must be made of the stock solution.

7.11.3 Calculate the CH_3Hg in the secondary CH_3Hg standard solution by subtracting the mean labile Hg(II) concentration from the mean total Hg concentration.

7.11.4 If the secondary CH_3Hg stock solution drops below 98.0% CH_3Hg, discard the solution and make a fresh secondary solution.

7.12 Working methyl mercury standard—Prepare a dilution of the secondary CH_3Hg standard using reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. A convenient concentration for this standard is 1.00 ng/mL CH_3Hg as Hg. This solution will maintain its titre for more than one month when kept in a fluoropolymer bottle on the lab bench top. Refrigeration is not necessary.

7.13 IPR and OPR solutions—Using the working CH_3Hg standard (Section 7.9), prepare IPR and OPR solutions at a concentration of 0.5 ng/L as Hg in reagent water.

7.14 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap (Section 7.16).

7.15 Argon—Grade 5.0 (ultra high-purity, GC grade) that has been further purified by the removal of Hg using a gold-coated sand trap (Section 7.16).

7.16 Gold-coated sand trap—The trap is made from 10-cm x 6.5-mm o.d. x 4-mm i.d. quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., or equivalent). The ends are plugged with quartz wool. Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for connection to the system.

8.0 Sample Collection, Preservation, and Storage

8.1 Before samples are collected, consideration should be given to the type of data required, (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately before removing an aliquot for processing or direct analysis to ensure the sample has been properly preserved.

NOTE: *Do not dip pH paper or pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot pH.*

8.2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Borosilicate glass bottles may be used if Hg and Hg species are the only target analytes. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads. Polyethylene sample bottles must not be used (Reference 13).

8.3 Collect samples using the Sampling Method (Reference 8). Procedures in the Sampling Method are based on rigorous protocols for collection of samples for Hg (Reference 13).

NOTE: *Discrete samplers have been found to contaminate samples with Hg at the ng/L level; therefore, great care should be exercised if this type of sampler is used to collect samples. It may be necessary for the sampling team to use other means of sample collection if samples are found to be contaminated using the discrete sampler.*

8.4 Sample filtration—For dissolved CH_3Hg, samples and field blanks are filtered through a 0.45-µm capsule filter (Section 6.1.3.1). The Sampling Method describes filtering procedures.

8.5 Preservation—Samples are preserved by adding 4 mL/L of concentrated HCL (to allow both CH_3Hg and total Hg determination). Saline samples ($[Cl^-]$>500 ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution. Acid-preserved samples are stable for at least six months, if kept dark and cool.

8.5.1 Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0-4°C from the time of collection until preservation. The samples must be acid-preserved within 48 h of sampling.

8.5.2 Handling of the samples in the laboratory should be undertaken on a mercury-free clean bench, after rinsing the outside of the bottles with reagent water and drying in the clean air hood.

NOTE: *Due to the potential for contamination, it is recommended that filtration and preservation of samples be performed in the clean room in the laboratory. However, if circumstances in the field prevent overnight shipment of samples, the samples should be filtered and preserved in a designated clean area in the field in accordance with the procedures given in Sections 8.3 and 8.4 of Method 1669.*

8.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until analysis. To maintain CH_3Hg concentrations without degradation, it is necessary to keep acid-preserved samples dark and cool. If properly preserved, samples can be held up at least six months before analysis.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 14). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine whether the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted certain options to improve results or lower the cost of measurements. These options include automation of the system, solvent extraction in place of distillation (Reference 2), direct electronic data acquisition, or changes in the detector (i.e., CVAAS, AES, ICP/MS). Changes in the principle of the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this method is used, that technique must have a specificity for CH_3Hg equal to or better than the specificity of the technique in this method.

9.1.2.1 Each time this method is modified, the analyst is required to repeat the procedure in Section 9.2. If the change will affect the detection limit of the method, the laboratory is required to demonstrate that the MDL (40 *CFR* Part 136, Appendix B) is lower than one-third the regulatory compliance level or lower than the MDL of this method, whichever is higher. If the change will affect calibration, the analyst must recalibrate the instrument according to Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and the

quality control officer who witnessed and will verify the analyses and modification

9.1.2.2.2 A narrative stating the reason(s) for the modification(s)

9.1.2.2.3 Results from all quality control (QC) tests comparing the modified method to this method, including the following:

(a) Calibration (Section 10)
(b) Initial precision and recovery (Section 9.2)
(c) Analysis of blanks (Section 9.4)
(d) Matrix spike/matrix spike duplicate analysis (Section 9.3)
(e) Ongoing precision and recovery (Section 9.5)
(f) Quality control sample (Section 9.6)

9.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result. These data are to include the following:

(a) Sample numbers and other identifiers
(b) Processing dates
(c) Analysis dates
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Copies of logbooks, chart recorder, or other raw data output
(g) Calculations linking raw data to the results reported

9.1.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 9.3 describes the procedure and QC criteria for spiking.

9.1.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 9.4 describes the procedures and criteria for analyzing blanks.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 9.5 and 9.6 describe these procedures, respectively.

9.1.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 9.3.7 and 9.5.3 describe the development of accuracy statements.

9.1.7 The determination of CH_3Hg in water is controlled by an analytical batch. An analytical batch is a set of samples distilled with the same batch of reagents, and analyzed during the same 12-hour shift. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by at least three method blanks (Section 9.4), an OPR sample, and a QCS. In addition, there must be one MS and one MSD sample for every 10 samples (a frequency of 10%).

9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect CH_3Hg, the analyst shall determine the MDL according to the procedure at 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Section 1.5 or one-third the regulatory compliance limit, whichever is greater. The MDL should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that the MDL be redetermined.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations:

9.2.2.1 Analyze four replicates of the IPR solution (0.5 ng/L, Section 7.10) according to the procedure beginning in Section 11.

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for CH_3Hg.

9.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test (Section 9.2.2.1).

9.3 Method accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform either matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 10% of the samples from each site being monitored, or at least one MS/MSD sample analysis for each sample set, whichever is more frequent.

9.3.1 The concentration of the CH_3Hg in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of CH_3Hg in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample (as determined in Section 9.3.2), whichever is greater.

9.3.1.2 If the concentration of CH_3Hg in a sample is not being checked against a limit, the spike shall be at 1-5 times the background concentration or at 1-5 times the ML in Table 1, whichever is greater.

9.3.2 Assessing spike recovery

9.3.2.1 Determine the background concentration (B) by analyzing one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priori.

9.3.2.2 If necessary, prepare a spiking solution to produce an appropriate level in the sample (Section 9.3.1).

9.3.2.3 Spike two sample aliquots with the spiking solution and analyze these aliquots as described in Section 11.1.2 to determine the concentration after spiking (A).

9.3.2.4 Calculate the percent recovery (P) in each aliquot using Equation 1:

Equation 1

$$P = 100 * \frac{A - B}{T}$$

Where:

A=Measured concentration of analyte after spiking
B=Measured concentration of analyte before spiking
P=Percent recovery
T=True concentration of the spike

9.3.3 Compare the percent recovery (P) with the QC acceptance criteria in Table 2.

9.3.3.1 If P falls outside the designated range for recovery in Table 2, the CH_3Hg analysis has failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard (Section 9.5). If the OPR is within established performance criteria (Table 2), the analytical system is within specification and the problem can be attributed to interference by the sample matrix.

9.3.3.2 If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the analyst must modify the method, repeat the test required in Section 9.1.2, and repeat analysis of the sample and MS/MSD. However, when this method was written, there were no known interferences in the determination of CH_3Hg using this method. If such a result is observed, the analyst should investigate it thoroughly.

9.3.3.3 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and reanalyze the sample batch.

9.3.4 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 2 using the CH_3Hg concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.3.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 2

$$RPD = 200 * \frac{|D_1 - D_2|}{D_1 + D_2}$$

Where:

RPD=Relative percent difference
D_1=Concentration of CH_3Hg in the MS sample
D_2=Concentration of CH_3Hg in the MSD sample

9.3.5 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2. If the criterion is not met, the system performance is unacceptable. The problem must immediately be identified and corrected, and the analytical batch reanalyzed.

9.3.6 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 9.3.2, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if $P_a = 90\%$ and $s_p = 10\%$ for five analyses, the accuracy interval is expressed as 70-110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).

9.4 Blanks—Blanks are critical to the reliable determination of CH_3Hg at low levels. The sections below give the minimum requirements for analysis of blanks. However, it is suggested that additional blanks be analyzed as necessary to pinpoint sources of contamination in, and external to, the laboratory.

9.4.1 Ethylation blanks—Reagent water typically contains no CH_3Hg. The reagent (ethylation) blank may conveniently be determined by adding 0.3 mL of acetate buffer and 0.040 mL of 1% $NaBEt_4$ solution to 50 mL of reagent water in the reaction vessel.

NOTE: *Do not ever use a previously ethylated water sample, as a build-up of the gas triethyl boron will occur, which results in a negative interference and poor chromatography.*

9.4.1.1 A single ethylation blank is analyzed with each analytical run, as part of the calibration sequence. This value is used to blank correct the standard curve.

9.4.1.2 The presence of more than 2 pg of CH_3Hg indicates a problem with the reagent water or one of the reagent solutions. An investigation of the cause of the high blank can be made by varying, one at a time, the amounts of buffer, reagent water, and $NaBEt_4$. Because $NaBEt_4$ cannot be purified, a new batch should be made from different reagents and should be tested for Hg levels if the level of CH_3Hg is too high. If the reagent water is found high, this can be remedied by replacing the purification cartridges.

9.4.2 Method blanks—The method blanks (distillation blanks) are prepared by the distillation and analysis of 45 mL aliquots of 0.4% HCl acidified reagent water, exactly as if they were samples.

9.4.2.1 Three method blanks should accompany each analytical batch. The mean blank value should be less than 0.045 ng/L of CH_3Hg, and the variability should be less than 0.015 ng/L of CH_3Hg. A mean blank value greater than 0.045 ng/L CH_3Hg or a variability greater than 0.015 ng/L of CH_3Hg is unacceptable for low level ambient analysis.

9.4.3 Field blanks

9.4.3.1 Analyze the field blank(s) shipped with each sample set. Analyze the blank immediately before analyzing the samples in the batch.

9.4.3.2 If CH_3Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.4.3.3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blanks, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.

9.4.3.4 If contamination of the field blank(s) and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

9.4.4 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that the

sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.

9.4.4.1 Bottle blanks—After undergoing the cleaning procedures in this method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to 0.4% HCL and allowed to stand for a minimum of 24 h. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

9.4.4.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or cleaning facility.

9.4.4.2.1 Sampler check blanks are generated by filling a large carboy (Section 7.17) or other container with reagent water (Section 7.1) and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method). For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the submersible pump or intake tubing into the water and pumping water into a sample container.

9.4.4.2.2 The sampler check blank must be analyzed using the procedures in this method. If CH_3Hg or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from CH_3Hg and interferences before the equipment may be used in the field.

9.4.4.2.3 Sampler check blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

9.5 Ongoing precision and recovery (OPR)—To demonstrate that the analysis system is within specified limits and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations:

9.5.1 Analyze the OPR solution (0.5 ng/L, Section 7.10) followed by a ethylation blank prior to the analysis of each analytical batch according to the procedure in Section 11. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift. Subtract the peak height (or peak area) of the ethlyation blank from the peak height (or area) for the OPR and compute the concentration for the blank-subtracted OPR.

9.5.2 Compare the computed OPR concentration with the limits in Table 2. If the concentration is in the range specified, the analysis system is within specification and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not within the specified limits. Correct the problem and repeat the OPR test.

9.5.3 The laboratory should add results that pass the specification in Section 9.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from R - $2s_r$ to R + $2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85-105%.

9.6 Quality control sample (QCS)—The laboratory must obtain a QCS from a source different from the CH_3Hg used to produce the standards used routinely in this method (Sections 7.7-7.10). The QCS should be analyzed as an independent check of instrument calibration in the middle of the analytical batch (e.g., for a batch of 14 samples, the QCS should be analyzed after the seventh sample). Good QCS samples may be made by KOH/methanol digestion (Reference 2) of CH_3Hg certified tissue CRMs. CH_3Hg certified CRMs are available through the National Institute of Standards Technology (NIST), National Research Council of Canada (NRCC), and International Atomic Energy Agency (IAEA).

9.7 Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 35%. If the RPD of the field duplicates exceeds 35%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

10.0 Calibration and Standardization

10.1 Establish the operating conditions necessary to purge Hg species from the bubbler and to desorb Hg species from the traps so that sharp peaks are given. The system is calibrated using CH_3Hg standards ultimately traceable to NIST standard total Hg reference material, as follows:

10.1.1 Calibration

10.1.1.1 The calibration must contain five or more non-zero points and the results of analysis of one ethylation blank. The lowest calibration point must be at the minimum level (ML).

10.1.1.2 Standards are analyzed by the addition of aliquots of the CH_3Hg working standard (Section 7.9) directly into the bubblers (Section 6.4.3). Add 50 mL of fresh reagent water, a 0.005 ng aliquot of the standard, 0.3 mL of acetate buffer, and 0.04 mL of $NaBEt_4$ to the bubbler, swirling to mix. Allow to react for 17 min, and then purge and analyze as below (Section 11). Sequentially follow with aliquots of 0.05, 0.1, 0.2, and 0.01 ng CH_3Hg in separate bubblers.

10.1.1.3 For each point, correct the standard peak height or area by subtracting the peak height or area of the ethylation blank for the analytical batch. Calculate the calibration factor (CF) for CH_3Hg for each of the five standards using the mean ethylation-blank-corrected peak height or area (Equation 3).

Equation 3

$$CF = \frac{R_s - R_e}{C_s}$$

where:

R_s*=Peak height or area of the standard*
R_e*=Peak height or area of the ethylation blank*
C_s*=Concentration of the standard (ng/L)*

10.1.1.4 Calculate the mean calibration factor (CF_m), the standard deviation of the CF_m (SD), and the relative standard deviation (RSD) of the calibration, where RSD = 100 x SD/CF_m. If the RSD is $\leq$ 15%, the CF_m may be used to calculate sample concentrations. If RSD > 15%, recalibrate the analytical system and repeat the test.

10.1.1.5 The net concentration recovery (minus ethylation blank) for the lowest standard must be in the range of 65-135% of the expected value to continue with sample analysis.

10.2 Ongoing precision and recovery—Perform the ongoing precision and recovery test to verify calibration prior to analysis of samples in each analytical batch. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift.

11.0 Procedure

NOTE: *The following procedures for analysis of samples are provided as guidelines. Analysts may find it necessary to optimize the procedures, such as drying time or potential applied to the Nichrome wires, for the laboratory's specific instrumental set-up.*

11.1 Sample Distillation

11.1.1 Weigh a 45-mL aliquot from a thoroughly shaken, acidified sample, into a 60-mL fluoropolymer distillation vial. Add 200 µL of 1% APDC solution, and replace the distillation cap, such that the tubing extends to the bottom of the vial.

11.1.1.1 Repeat this procedure for all samples to be distilled in a set, including three reagent water blanks and spiked samples.

11.1.1.2 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour two additional 45-mL aliquots from a randomly selected sample. Spike the aliquots at the level specified in Section 9.3 and process them in the same manner as the samples. There should be two MS/MSD pairs for each analytical batch of 20 samples.

11.1.1.3 For each sample, prepare a 60-mL distillate receiving vial. Add 5.0 mL reagent water to each receiving vial and replace the cap so that the tubing extends into the water layer.

11.1.1.4 Record the sample ID associated with each distillation and receiving vial. It is important to develop an unambiguous tracking system, such as the use of engraved vial numbers, because the distillation vials themselves cannot be labeled (due to the heat).

11.1.2 Place each prepared distillation vial into one of the holes in the heating block and attach the fluoropolymer tubing to the incoming gas supply from the rotometer manifold. Adjust the gas flow rate through the bubbler to 60 ± 20 mL/min.

11.1.3 As each distillation vial with sample is placed into the heating block, place the corresponding labeled distillation vial into the ice bath immediately adjacent to the heating block. Attach the tubing from the receiving vessel to the port of the distillation vessel.

11.1.4 Once all the holes in a heating block are filled, place the aluminum lid over the vessel caps in such a way that all tubing is passing without crimps through the slots, and the lid is making metal-to-metal contact with the block (to provide proper heating of the lid).

11.1.5 Turn on the temperature controllers to the heating blocks to a pre-set block temperature of 125 ± 3°C.

11.1.6 Distill the samples until each receiving vial fills to the engraved 40 mL line. This time period will be approximately 2.5 h to 4 h depending upon exact temperatures, gas flow rates, and water characteristics.

11.1.6.1 Different samples and locations on the block will distill at somewhat different rates, so after about 2 h, all of the tubes should be monitored frequently to avoid over-distillation. As the individual samples fill to the line, they should be removed from the distillation unit.

11.1.6.2 Over-distillation is the greatest potential risk for poor recoveries by this method. If more than the prescribed amount of sample distills over, the risk of HCl fumes co-distilling increases. Chloride and low pH are interferences with the ethylation procedure.

11.1.6.3 If any samples are suspected of over-distillation, they should be checked with pH paper. If the distillate has a pH of less than 3.5, it should be discarded, rather than analyzed.

11.1.7 Once all of the vials are distilled, the distillates may be stored at room temperature and in the dark for up to 48 h before analysis (loop the fluoropolymer tube around to close off the second port on the receiving vial). Do not refrigerate or store longer than 48 h.

11.1.8 The distillation-side (dirty) vials must be scrubbed thoroughly with a test-tube brush and alkaline detergent, then rinsed in reagent water, to remove organics prior to acid cleaning. To acid-clean between uses, the vials are filled with 10% HCl, recapped with the tubing looped around to close off the port, and placed in an oven at 80°C overnight.

11.2 Ethylation and purging of the distillates

11.2.1 Immediately before analysis, add 0.3 mL of acetate buffer to the sample in the receiving vial, and then add another 10 mL of reagent water to the vial (so that the total sample volume is > 50 mL; the vial is almost full).

11.2.2 Pour the buffered sample into the reaction vessel/bubbler, and add 0.04 mL of freshly thawed 1% $NaBEt_4$ solution. Close the reaction vessel with the bubbler cap, and swirl gently to mix.

11.2.3 If standards, ethylation blanks, or QCS are being analyzed, pour 50 mL of reagent water into the bubbler, add 0.3 mL of acetate buffer, the appropriate spike, etc., and 0.04 mL 1% $NaBEt_4$ solution.

11.2.4 Allow the contents of the bubbler to react for 17 min. All CH_3Hg in the sample is converted to volatile methylethyl mercury.

11.2.5 After reaction, attach a Carbotrap® trap to each bubbler with the 1/4" fluoropolymer fitting, and purge the sample with N_2 (200 mL/min) for 17 min.

NOTE: *The Carbotrap® trap must be attached such that the gas from the bubbler enters the trap on side A.*

11.2.6 Once the sample has been purged for 17 min, any adsorbed water must be dried from the Carbotrap® trap. Disconnect the Carbotrap® trap from the bubbler and attach the N_2 flow directly to the trap. Use the same orientation (i.e., N_2 entering from side A), and purge the trap for 7 min.

11.2.7 The sample is now ready for analysis. The methylethyl mercury collected on the trap is quantitatively stable for up to 6 h and must be analyzed within that period.

11.3 Desorption of methylethyl mercury from the Carbotrap® trap

11.3.1 Close the argon stopcock on the GC, and allow 30 sec for the pressure in the system to dissipate. Remove the previous Carbotrap® trap from the GC.

11.3.2 Attach the Carbotrap® trap containing the new sample to the GC column using a 1/4" fluoropolymer friction fit connector, *such that side A is facing toward the GC column.*

11.3.3 Place the Nichrome wire heating coil around the Carbotrap® trap, centered over, and extending beyond the packing material on side A. Re-connect the argon gas to side B of the Carbotrap® trap.

11.3.4 Open the argon stopcock, and allow gas to flow for 30 sec prior to heating the column. Make sure that the post GC pyrolytic column is on and red-hot (~700°C).

11.3.5 Apply power to the coil around the sample trap for 45 sec (using an automatic timer) to thermally desorb the ethylated species from the sample trap into the GC column.

11.3.6 Turn on the chart recorder or other data acquisition device to start data collection.

11.3.7 Three peaks should emerge during the analytical run. The first peak (~1 min) is Hg^o, which is residual, and non-quantitative. This peak signifies the start of the peak set. Usually, the second peak to emerge (~2.5 min) is methylethyl mercury, the peak of interest. Following this (~4 min) is the peak for diethyl mercury ($(CH_3CH_2)_2Hg$), which is the ethylation product of Hg(II). If $(CH_3)_2Hg$ were present in the sample, it would appear as a second peak between Hg^o and methylethyl mercury-not fully resolved from the Hg^o. See appendix for advice on the quantitation of $(CH_3)_2Hg$.

11.3.8 Allow the GC run to proceed at least 1 min beyond the point that the diethyl mercury (Hg(II)) peak returns to base line. Place the next sample Carbotrap® trap in line and proceed with analysis of the next sample.

11.4 Peaks generated using this technique should be very sharp and almost symmetrical. Methylethyl mercury elutes at approximately 2.5 min and has a width at half-height of about 10 sec. Earlier peaks (Hg^o, $(CH_3)_2Hg$) are sharper, while later peaks (diethyl mercury) are broader.

11.4.1 The appearance of only one peak (Hg^o) usually signifies either that the pyrolytic column is not turned on, or that $NaBEt_4$ was not added to the sample.

11.4.2 Normally the Hg^o peak is quite small. However, some Hg^o is generated by thermal degradation of diethyl mercury during the desorption step. Thus, when samples contain a high concentration of Hg(II), both the Hg^o and the diethyl mercury peaks will be bigger. The ratio of the two peaks is indicative of the quality of the Carbotrap® trap. As the Carbotrap® trap degrades, the amount of thermal breakdown of organo-mercurials increases. Since the diethyl mercury is much more sensitive to thermal breakdown than the methylethyl mercury, monitoring the latter peak can serve as an early warning for Carbotrap® trap replacement. Generally, the Carbotrap® traps should be replaced any time the Hg^o peak grows to be as large as the diethyl mercury peak. As a rule of thumb for samples with significant Hg(II), use 1.0 ng Hg(II) from a non-acidified solution deliberately added to the reaction vessel as a trap check. For samples very low in Hg(II), such as blanks, the Hg^o peak is generally higher than the diethyl mercury peak, due to residual sources.

11.4.3 In the event that samples with large Hg(II) content are analyzed, some of the diethyl mercury generated breaks down to monoethyl mercury (CH_3CH_2Hg) during thermal desorption. If this occurs, a very broad peak (width of several minutes) will appear at some long time after the run is over (5-20 min). Such occurrences result in a confusing and messy increase and then decrease in the baseline. Such peaks can be hurried through the system by turning the GC column to 140°C until the peak emerges, and then reducing the temperature back to 110°C before resuming analysis.

12.0 Data Analysis and Calculations

12.1 Calculate the following parameters for each analytical batch:

12.1.1 Ethylation blank (n = 1) or the mean ethylation blank (n > 1)

12.1.2 Ethylation-blank subtracted calibration factor for each standard (Cf_x, Section 10.1.3) and peak measurement for each sample (R_s)

12.1.3 The mean calibration factor (Cf_m), standard deviation of the calibration factor (SD), and relative standard deviation (RSD) of the calibration factor (Section 10.1.1.4).

12.2 Compute the concentration of CH_3Hg in ng/L (parts-per-trillion; ppt) according to Equation 4:

Equation 4

$$[CH_3Hg](ng/L) = \frac{R_s - R_{EB}}{CF_m * V}$$

Where:

R_s=gross peak height (or area) of signal for CH_3Hg in sample
R_e=peak height (or area) of signal for CH_3Hg in ethylation blank (n = 1) or mean ethylation blank (n > 1)
CF_m=mean calibration factor
V=Sample volume (L)

12.3 The CH_3Hg concentration of the mean (n=3 or more) method blank (ng/L, Equation 4) should be subtracted from the sample concentration calculated above to obtain the net in situ CH_3Hg concentration (Equation 5).

Equation 5

$$\left[CH_3Hg\right]_{MB}(ng/L) = \frac{R_{MB} - R_{EB}}{CF_m * V_{MB}} * \frac{V_{MB}}{V_s}$$

where:

R_{MB}=gross peak height (or area) of signal for CH_3Hg in the mean method blank
R_{EB}=gross peak height (or area) of signal for CH_3Hg in the ethylation blank (n = 1) or the mean ethylation blank (n > 1)
CF_m=Mean calibration factor
V_{MB}=Volume of the method blank
V_s=Volume of the sample

Equation 6

$$\left[CH_3Hg\right]_{net} = \left[CH_3Hg\right]_{sample} - \left[CH_3Hg\right]_{MB}$$

where:

$[CH_3Hg]_{net}$=net in situ CH3Hg concentration (ng/L)
$[CH_3Hg]_{sample}$=ethylation-blank corrected concentration of CH3Hg in the sample (ng/L, Equation 3)
$[CH_3Hg]_{MB}$=concentration of CH3Hg in the mean method blank (ng/L, Equation 4)

12.4 Reporting

12.4.1 All results are reported after subtraction of mean method blanks (Equation 6).

12.4.2 Under the conditions described here, the distillation procedure not 100% efficient in recovering CH_3 Hg because not all of the sample volume can be distilled, to avoid co-

distillation of HCl. Laboratories should calculate the efficiency of the distillation for their laboratory. This calculation is done by keeping a running mean of the last 30 recoveries calculated for precision and recovery samples (IPR and OPR), excluding all values that are more than two standard deviations from the mean. Since the distillation technique is inherently and reproducibly non-quantitative, all results should be recovery corrected by an empirically derived factor (Equation 7).

Equation 7

$$F = \frac{100}{R}$$

where:

F=Empirically derived correction factor
R=Recovery (the running mean of the last 30 IPR and OPR samples)

12.4.3 Report all values in ng/L to three significant figures. Report results below the ML as <0.06 ng/L, or as required by the permitting authority or in the permit. If the laboratory achieved an MDL lower than 0.02 ng/L (Section 1.5), a new ML may be calculated by multiplying the laboratory-determined MDL by 3.18 and rounding the result to the nearest multiple of 1, 2, 5, 10, etc. in accordance with procedures described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994. Results below this level should be reported as less than the calculated ML.

13.0 Method Performance

13.1 The method detection limit (MDL) listed in Table 1 and the quality control acceptance criteria listed in Table 2 were validated in four laboratories. In addition, the techniques in this method have been intercompared with other techniques for low-level CH_3Hg determination in water in the International Mercury Speciation Intercomparison Exercise (Reference 15).

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option. The acids used in this method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

14.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*,

available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477.

15.0 Waste Management

15.1 The laboratory is responsible for complying with all federal, state, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

15.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

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16.4 Horvat, M., Bloom, N.S., and Liang, L. "A Comparison of Distillation with other Current Isolation Methods for the Determination of Methyl Mercury Compounds in Low Level Environmental Samples Part 2, Water" *Anal. Chim. Acta,* 1993, **282:** 153.

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16.6 Liang, L., Horvat, M., and Bloom, N.S. 1994. "An Improved Speciation Method for Mercury by GC/CVAFS After Aqueous Phase Ethylation and Room Temperature Precollection," *Talanta* 1994, **41:** 371.

16.7 Bloom, N.S., Coleman, J.A., and Barber, L. "Artifact Formation of Methyl Mercury During Extraction of Environmental Samples by Distillation." *Fres. Anal. Chem.* 1997, (in press).

16.8 Method 1669, "Method for Sampling Ambient Water for Determination of Metals at EPA Ambient Criteria Levels," U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460, April 1995 with January 1996 revisions.

16.9 "Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service. Centers for Disease Control. NIOSH Publication 77-206, Aug. 1977, NTIS PB-277256.

16.10 "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 *CFR* 1910.

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16.12 "Standard Methods for the Examination of Water and Wastewater," 18th ed. and later revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-35: Section 1090 (Safety), 1992.

16.13 Bloom, N.S. "Trace Metals & Ultra-Clean Sample Handling," *Environ. Lab.* **1995,** *7*, 20.

16.14 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.15 Bloom, N.S.; Horvat, M.; Watras, C.J. "Results of the International Mercury Speciation Intercomparison Exercise," *Wat. Air. Soil Pollut.*, **1995**, *80*, 1257.

17.0 Tables and Diagrams

Table 1 Methyl Mercury Analysis Using Method 1630: Lowest Water Quality Criterion, Method Detection Limit, and Minimum Level

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[(2)]	ML[(3)]
Methyl Mercury (CH_3Hg)	none	0.02 ng/L	0.06 ng/L

NOTES:

1. Lowest of the freshwater, marine, and human health ambient water quality criteria promulgated by EPA for 9 States and the District of Columbia at 40 *CFR* Part 131 on May 4, 1995 (60 *FR* 22229)
2. Method Detection Limit as determined by the procedure in 40 *CFR* Part 136, Appendix B.
3. Minimum Level (ML)

Table 2 Quality Control Acceptance Criteria for Performance Tests In EPA Method 1630

Metal	IPR (Section 9.2)		OPR (Section 9.5)	Method Blanks (Section 9.4)		MS/MSD[1] (Section 9.3)	
	s	X		Max	Mean	%R	RPD
Methyl Mercury (CH_3Hg)	31%	69-131%	67-133%	< 0.1 ng/L	< 0.05 ng/L	65-135%	35%

NOTES:

1. Recovery corrected

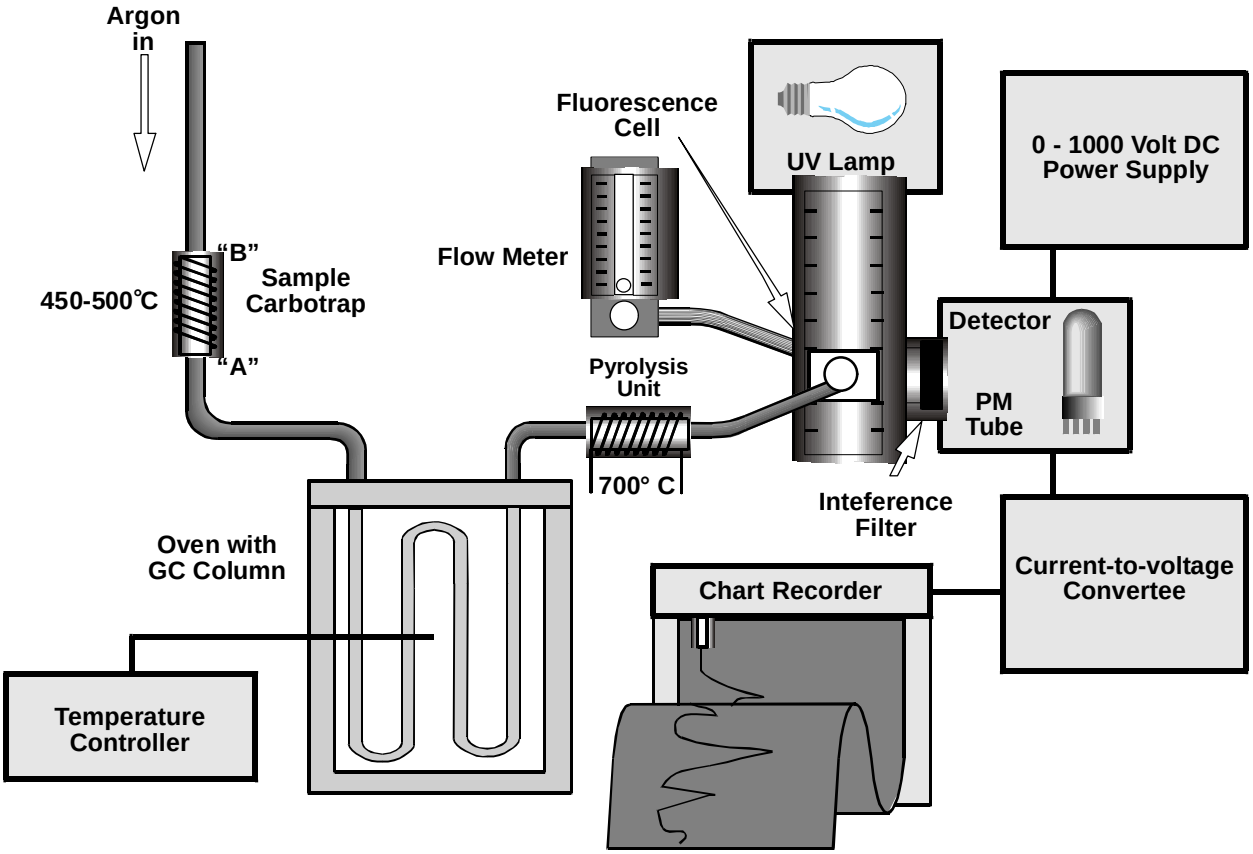

Figure 1 Schematic Diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) Detector interfaced with the isothermal GC and pyrolytic decomposition column.

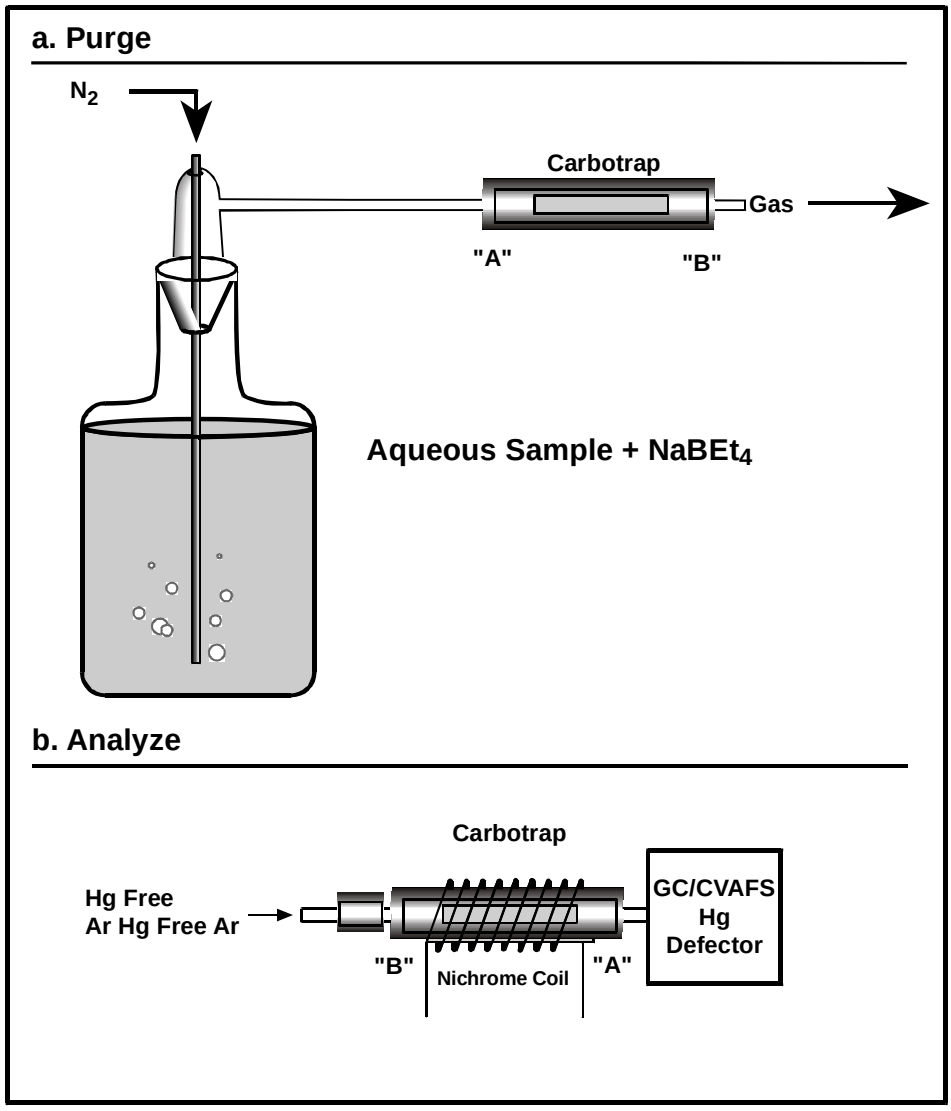

Figure 2 Schematic Diagram of Bubbler Setup (a), and Carbotrap® trap orientation (b).

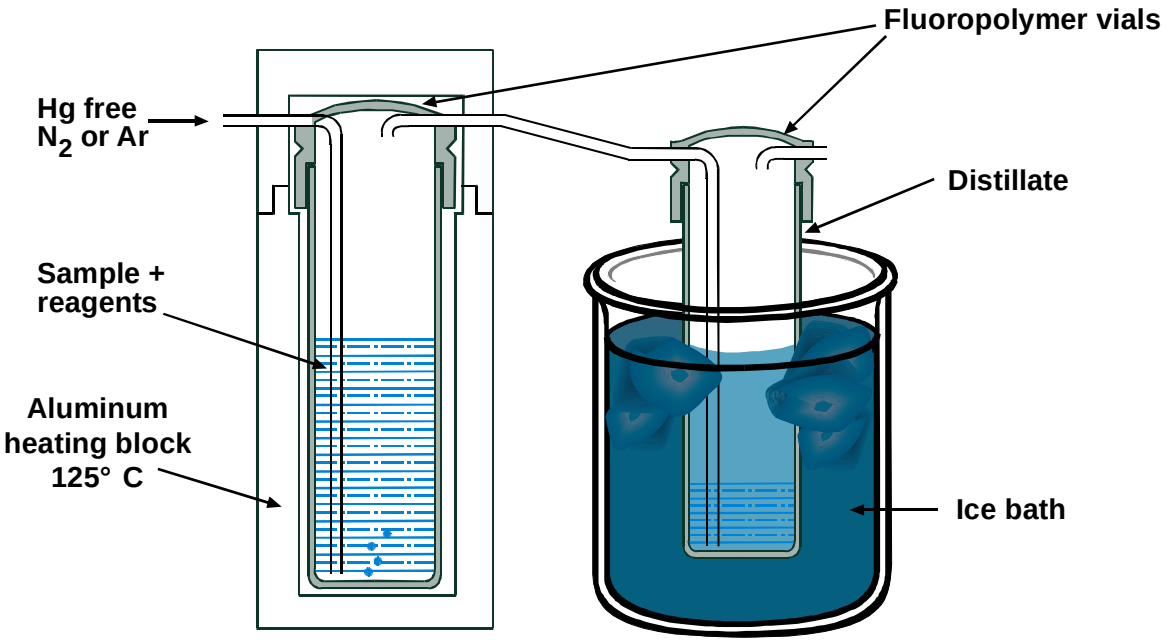

Figure 3 Schematic diagram showing the CH_3Hg distillation set-up.

18.0 Glossary

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

18.1 Ambient Water: Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

18.2 Analytical Batch: A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include an OPR and a QCS. MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).

18.3 Intercomparison Study: An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.

18.4 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentration(s) of the analyte(s) in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.

18.5 May: This action, activity, or procedural step is allowed but not required.

18.6 May not: This action, activity, or procedural step is prohibited.

18.7 Minimum Level (ML): The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10^n, where n is an integer.

18.8 Must: This action, activity, or procedural step is required.

18.9 Quality Control Sample (QCS): A sample containing CH_3Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration.

18.10 Reagent Water: Prepared from 18 MΩ ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as source water for trip and field blanks, and in the preparation of standards and reagents.

18.11 Sample set: Samples collected from the same site or, if for compliance monitoring, from a given discharge. This term applies to samples collected at the same time, to a maximum of ten samples.

18.12 Shall: This action, activity, or procedure is required.

18.13 Should: This action, activity, or procedure is suggested, but not required.

18.14 Stock Solution: A solution containing an analyte that is prepared from a reference material traceable to EPA, NIST, or a source that will attest to the purity and authenticity of the reference material.

18.15 Ultraclean Handling: A series of established procedures designed to ensure that samples are not contaminated for CH_3Hg during sample collection, storage, or analysis.

Appendix A :

Determination of Dimethyl Mercury

1.0 Scope and Application

1.1 This method is for determination of dimethyl mercury ($(CH_3)_2Hg$) in unfiltered water by direct purge and trap, isothermal GC separation, and CVAFS detection.

1.2 The method described in this appendix is not supportable by the full range of QC samples, so the method is to be considered for research purposes only.

1.3 The method described in this appendix is subsidiary to Method 1630 (Methyl Mercury in Aqueous Samples by Aqueous Phase Ethylation, Purge and Trap, and CVAFS). As such, only the major differences between the $(CH_3)_2Hg$ method and the CH_3Hg method will be described.

1.4 This method is designed for the determination of in the range of 0.0002 to 0.1 ng/L, and may be extended to higher levels by selection of a smaller sample size.

1.5 Since no reagents are added to the sample, the MDL is not ethylation blank limited, but is only limited by the instrumental noise. With the Tekran analyzer, the MDL for a 1 L sample volume is approximately 0.0002 ng/L as Hg (based on 7 replicates of a 0.0015 ng/L solution).

2.0 Summary of Method Changes

2.1 The analysis is performed using fresh, unfiltered, unpreserved samples. To minimize analyte losses, all efforts must be extended to speed the time between sample collection and sample analysis, and to minimize the contact of the sample with the atmosphere prior to purging.

2.2 Samples should be purged and analyzed in the field, but if this is not possible, samples may be collected directly into headspace-free 1-L glass bottles with fluoropolymer-lined caps, and sent via express to the laboratory for analysis. If kept unpreserved, dark, and cool, the $(CH_3)_2Hg$ present in the sample is found to be stable for up to 48 h from the time of collection.

2.3 Under no circumstances can plastic bottles of any kind (including fluoropolymer) be used for the collection of samples for the determination of $(CH_3)_2Hg$. The half-life of dissolved $(CH_3)_2Hg$ in fluoropolymer bottles is only about 6 h.

2.4 The entire 1 L sample is purged directly onto a Carbotrap® trap, using N_2 at a flow rate of 300 mL/min for 30 min. A specially constructed 1 L bottle with 24/40 ground glass fitting and fritted bubbler cap must be utilized for this purpose. After purging, the trap must be dried with N_2 and analyzed within 6 h, as described in method 1630.

2.5 The analyzer set-up for $(CH_3)_2Hg$ is exactly as in Method 1630, with the exception that the GC oven must be set at 80°C rather than 110°C, to facilitate separation of Hg^o from $(CH_3)_2Hg$.

2.6 Upon desorption of the Carbotrap® trap into the GC column, up to two peaks will appear. The first is usually Hg^o, which appears at approximately 1.0 min. The second is $(CH_3)_2Hg$, which appears approximately at 1.5 min.

NOTE: *Because these peaks are so close to each other, and either one or the other, or neither may be present, it is imperative that an event marker be triggered to signal the start of the GC run, so that the peak may be positively identified by its retention time.*

2.7 Calibration is performed by spiking appropriate aliquots of a $(CH_3)_2Hg$ standard into the same volume of reagent water as the samples, and purging onto Carbotrap® traps. A good calibration range is from 1 to 100 pg as Hg.

2.8 The stock solution for $(CH_3)_2Hg$ is a 1.0 parts per million solution in methanol, custom prepared by Strem Chemical (Newburyport, MA). A working stock (1 ng/mL) is prepared by 1:1000 dilution of the stock solution with methanol. These solutions have been found to be stable for over 4 years, when kept refrigerated, and dark, in glass bottles.

2.9 The stock solution as supplied by Strem is only approximate in its concentration. To exactly calibrate the solution, an aliquot of the working stock equal to approximately 1 ng is spiked into a bubbler of pre-purged reagent water, and then purged onto a gold coated sand trap. The trap is analyzed for total Hg according to EPA Method 1631. In this case, total Hg purged onto the trap equals $(CH_3)_2Hg$. Pre-calibrated working standards of $(CH_3)_2Hg$ in methanol are available for purchase (Frontier Geosciences Inc., or equivalent).

3.0 QC Measures

3.1 Not all QC measures available for method 1630 are available for use with the $(CH_3)_2Hg$ technique.

3.1.1 For each set of samples (or batch of 20), three method blanks, and two MS/MSD pairs should be measured. Since $(CH_3)_2Hg$ is rarely detected in the environment, matrix spikes should be low (i.e., 1-5 pg), to assure the ability to measure near the MDL.

3.1.2 No certified reference materials (CRMs) or second source LCSWs are available for $(CH_3)_2Hg$.

3.2 No interferences have been observed for this method, although volatile organic compounds, as might be present in waste waters and effluents could diminish the observed $(CH_3)_2Hg$ signal by co-eluting, and quenching the atomic fluorescence.

3.3 Separate field samples should be collected for replicates, and matrix spikes, since once the sample is opened, $(CH_3)_2Hg$ will rapidly be lost from solution by diffusion to the air.

3.4 Samples must not be filtered prior to analysis, or $(CH_3)_2Hg$ will be lost to the air.

3.5 Samples must not be stored acidified, or $(CH_3)_2Hg$ will decompose to CH_3Hg. Samples may be acidified just prior to analysis, if Hg^o and $(CH_3)_2Hg$ are to be both purged simultaneously (as in Method 1631 Appendix).

3.6 Samples should be kept out of light, or $(CH_3)_2Hg$ will decompose to CH_3Hg.

3.7 Samples must not be stored in plastic containers, or $(CH_3)_2Hg$ will rapidly be lost by diffusion into the plastic matrix.

4.0 Performance

4.1 This method is not often used, and so has not been rigorously tested. However, experience indicates that the following QC objectives can be met in ambient water samples, when using 1 L samples.

5.0 Tables

Table 1 Dimethyl Mercury Analysis Using Method 1630 Appendix: Lowest Water Quality Criterion, Method Detection Limit, and Minimum Level

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[(2)]	ML[(3)]
Dimethyl Mercury ($(CH_3)_2Hg$)	none	0.0002 ng/L	0.0006 ng/L

NOTES:

1. Lowest of the freshwater, marine, and human health ambient water quality criteria promulgated by EPA for nine States and the District of Colubia at 40 *CFR* Part 136 on May 4, 1995 (60 *FR* 22229).

2. Method Detection Limit as determined by the procedure in 40 *CFR* Part 136, Appendix B.

3. Minimum Levels (ML).

Table 2 Quality Control Acceptance Criteria for Performance Tests In EPA Method 1630 Appendix

Metal	**IPR (Section 9.2)**	**OPR (Section 9.5)**	**Method Blanks (Section 9.4)**	**MS/MSD[1] (Section 9.3)**	
	s	**S**	Max Mean	%R	RPD
CH_3Hg	79-121%	77-123%	< 0.0001 ng/L	75-125%	25%

NOTES:

1. Recovery corrected.

No. L-6

Butyltins

Title: Organotins by Gas Chromatography (GC)

Approval Signatures:

Kirstin Daigle
Laboratory Director

Kristine Dusablon
Department Manager

Brad Chirgwin
Technical Manager

Sara Goff
Quality Assurance Manager

Dan Helfrich
EH&S Coordinator

Approval Date: April 29, 2014

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure used to determine the concentration of organotins in environmental samples using dual column gas chromatography with flame photometric detectors (GC/FPD).

1.1 Analytes, Matrices, and Reporting Limits

This procedure may be used for a variety of matrices including: water, soil, sediment, waste and tissue.

The list of target compounds that can be determined from this method along with the associated reporting limits (RL) is provided in Table 1.

2.0 Summary of Method

3 uL of extract is injected into a dual capillary column gas chromatograph equipped with flame photometric detectors (GC/FPD). Organotins are quantified using internal standard technique.

This procedure is a laboratory developed method derived from the NOAA Status and Trends Program Document: Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Vol. IV, NOAA Technical Memorandum, NOS ORCA 71.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

- Method interference may be caused by contaminants in the extraction solvent. Solvents should be stored away from possible sources of contamination.

- Matrix interferences may be caused by contaminants co-extracted from the sample. The extent of the interferences will vary depending on the nature and diversity of the samples.

- Each lot of hexyl-magnesium bromide used during the extraction procedure for derivitization should be tested by the GC department prior to its use to ensure that it is free of contamination.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

Table 2 lists materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- Autosampler Vials, National Scientific or equivalent.
- Volume limiting inserts
- Volumetric Syringes, Class “A” (10µl, 25µl, 50µl, 100µl, 250µl and 500µl), Hamilton or equivalent.

6.2 Analytical System

- Computer Hardware/Software: GC Acquisition Platform - ChemStation. Data Processing - Hewlett-Packard 9000-series computers, an HP 9000 K200 (Chemsvr5)/ HP-UX 10.20 and Chrom integrated with TALS.
- GC/FPD: with dual columns, dual FPDs, and auto-sampler capable of a 3-µl injection split onto two columns: HP 7673A, HP 7673A Autosampler.
- GC Columns: A dual fused silica capillary column system that will provide simultaneous primary and confirmation analyses:
    - RTX-35, (30m x 0.32 mmID x 0.25um)
    - RTX-5, (30m x 0.32 mmID x 0.25um)

Equivalent columns may be used, provided the elution orders are documented and compound separations are maintained.

7.0 Reagents and Standards

7.1 Reagents

- Hexane, Ultra-Resi Analyzed, JT Baker or equivalent.

7.2 Standards

Purchase stock standard solutions from commercial vendors and from these prepare calibration and working standards by diluting a known volume of stock standard in an appropriate solvent to the final volume needed to achieve the desired concentration. The extractions laboratory prepares all calibration standards, CCVs and ICVs. The recommended formulation for the standards used in this procedure is provided in the extraction SOP. The final concentration of each calibration level is provided in Appendix B of this SOP.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are the recommended sample amounts needed for analysis and size, preservation and holding time requirements:

Matrix	Sample Container	Recommended Sample Size	Preservation	Extract Holding Time[1]	Reference
Water	Glass	1 L	Chilled to 4℃ (±2℃)	40 Days	Lab
Solid	Glass	50 g	Chilled to 4℃ (±2℃)	40 Days	Lab
Tissue	Glass	50 g	-15℃ (±5℃)	40 Days	Lab

[1]Analytical holding time is determined from date of initiation of extraction.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Table 3
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Table 3
Matrix Spike(s) MS/MSD	1 pair per extraction batch when sufficient sample volume is provided or per client request	See Table 3
Sample Duplicate (SD)	Client Request	See Table 3

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initially; when ICV or CCV fail	See Table 3
Second Source Calibration Verification (ICV)	Once, after each ICAL	See Table 3
Continuing Calibration Verification (CCV)	Daily, every 10 samples, end of sequence	See Table 3
Retention Time Windows	As Needed	See Table 3

10.0 Procedure

10.1 Instrument Operating Conditions

Install a five meter deactivated guard column into the injection port and connect the guard column to the separate analytical columns using a glass "Y". The analytical columns are installed into independent FPD detectors.

The recommended instrument operating conditions are as follows:

Initial Temperature:	100°C for 2 minutes
Temperature Program:	20°C per minute to 290°C Hold for 1 minute.
Detector Temperature	300°C
Injector Temperature:	190°C
Injection volume:	3µL
Carrier Gas:	Helium flow set at 6.0-10.0 mL/min
Makeup Gas:	Hydrogen (supplied by tank) and zero air (supplied by gas generators) should be optimized for sensitivity, but is generally set at approximately 175 mL/min total flow

10.2 Retention Time Window Establishment

An RT window of ± 0.05 minutes is used. The center of the RT window is set at the midpoint calibration level in the initial calibration sequence.

10.3 Instrument Calibration

10.3.1 Initial Calibration (ICAL)

Before initial or daily calibration, inject at least one instrument blank (IBLK) consisting of 100 µL hexane and 10µL Internal standard to bring the GC/FPD system online. A conditioning of two more instrument blanks may be needed.

The instrument is calibrated using a minimum of five different concentration levels for each target analyte. The calibration standards are prepared and derivatized following the procedures given in the extraction SOP. Prepare calibration standards for analysis by adding 10 µL of internal standard (tetra-n-propyltin) to 100 µL of standard in an autosampler vial insert. Cap the vials and place on the autosampler tray. Enter the Chrom ID numbers into the acquisition software. Set

the autosampler to inject 3-µl of each calibration standard. Start the acquisition process and autosampler.

The data processing system calculates the Response Factor (RF), mean RF and Percent Relative Standard Deviation (%RSD) for each analyte on both columns. The %RSD for each target analyte must be less than or equal to 20% in order to use the mean RF for quantification. If this criterion is not met, use another suitable quantification method for that analyte or correct the problem and repeat the calibration. Once a method of quantification is chosen for a specific compound, it must be consistent throughout the entire analytical sequence until a new initial calibration is performed.

Alternate Quantification Option:

Linear Regression & Weighted Linear Regression: Generate a curve of concentration vs. response for each analyte and calculate the correlation coefficient. The calibration must have a correlation coefficient (r) $\geq$ 0.995 (or $r^2 \geq 0.990$). If this criterion is not met, correct the problem and repeat the calibration. The use of linear regression requires a minimum of 5 calibration points.

10.3.2 Second Source Calibration Verification (ICV)

Immediately after each calibration and prior to the analysis of QC or field samples, verify the accuracy of the initial calibration by analyzing a second source ICV.

The ICV is prepared and derivatized following the procedures given in the extraction SOP. Prepare the ICV for analysis by adding 10 µL of internal standard (tetra-n-propyltin) to 100 µL of ICV in an autosampler vial insert. Inject 3 µl of the ICV standard onto the instrument in the same manner as performed for the initial calibration standards.

The percent recovery of each analyte must be within $\pm$ 25% of the expected value (%R: 75 -125). If this criterion is not met, correct the problem and reanalyze the ICV. If the reanalysis fails, remake the calibration standards or ICV standard and/or perform instrument maintenance and recalibrate. The QC acceptance criteria must be met on both columns.

10.3.3 Continuing Calibration Verification (CCV)

CCVs are prepared and derivatized following the procedures given in the extraction SOP. Prepare CCVs for analysis by adding 10 µL of internal standard (tetra-n-propyltin) to 100 µL of CCV in an autosampler vial insert. Inject 3 µl of the CCV standard onto the instrument in the same manner as performed for the initial calibration standards.

Analyze a CCV at or below mid-calibration level each day before sample analysis, after every ten injections and at the end of each analytical batch to monitor instrument drift. Calculate the RF and percent difference or drift (Appendix C) for each analyte on both columns. The percent difference or drift must be within ±25% for each analyte. Compare the RT of each analyte in the CCV with the established RT windows; the RT must be within the established window (refer to section 10.2). The acceptance criteria must be met on both columns.

If the CCV fails, it may be repeated once. If repeat analysis fails, corrective action must be taken. Samples must be bracketed by passing CCVs. Samples analyzed before and after CCV failure must be reanalyzed, unless the CCV is high and there are no detects in the associated samples.

10.4 Troubleshooting

Check the following items in case of calibration failures:

- ICAL Failure – Perform injection port maintenance, install new guard column, check detector ends to see if detector jet has slipped. In extreme cases, install new columns, particularly if the chromatography has degraded as evidenced by peak shapes.
- CCV Failure – Perform Injection port maintenance; if injection port maintenance does not restore CCV, install a new guard column and remove one or more loops from each analytical column.
- Needle crushed during injection - Replace the needle and check the injection port for obstructions and check the autosampler for misalignment.
- Auto-sampler failure - Reset the auto-sampler.
- Power failure - Reset run in ChemStation and re-acquire or re-initiate run sequence.

10.5 Sample Preparation

Remove the sample extract from refrigerated storage and warm to room temperature.

Prepare samples for analysis by adding 10 µL of internal standard (tetra-n-propyltin) to 100 µL of sample in an autosampler vial insert. Cap the vials and place on the autosampler tray. Enter the sample ID's into the data acquisition program.

10.6 Sample Analysis

Arrange the samples in a sequence that begins with the calibration standards and ICV followed by the analysis of QC samples, field samples and continuing calibration verification standards (CCVs).

Enter the standard and sample names into the data acquisition program in the order the samples were placed in the autosampler tray and initiate the analytical sequence. Set the autosampler to inject 3-µl of each standard and sample onto the instrument.

An example analytical sequence that includes initial calibration (ICAL) and subsequent sample analysis is provided below.

Injection Number	Lab Description
1-3	Instrument Blank
4	Level 1 Tin Standard
5	Level 2 Tin Standard
6	Level 3 Tin Standard
7	Level 4 Tin Standard
8	Level 5 Tin Standard
9	Instrument Blank
10	ICV
11 - 20	10 injections

21	CCV (250ppb Tin Standard)
	Repeat steps 9 -19

Cleaning blanks (IBLK) consisting of hexane may be analyzed after high-level samples at the discretion of the analyst.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

The data processing system identifies the target analytes by comparing the retention times of the peaks to the established retention time windows (refer to section 10.2).

Review and accept or reject the qualitative identifications made by the data processing software using the following guidelines:

Compare the retention times of the peaks to the established RT windows (refer to section 10.2), taking into account the shift of the surrogate peak. If the surrogate peak has shifted, open the retention time window in the direction of the shift. The processing software identifies the peak in the retention time window that is closest to the expected retention time set in the Chrom method, so the peak may need to be re-identified if a shift has occurred.

Look for shoulders on large peaks that may be the peaks of interest. The processing software does not always automatically integrate the shoulder off of the larger peak, so manual integration (split) of the shoulder may be necessary.

Each target analyte must be qualitatively detected on each column for identification to be confirmed.

11.2 Quantitative Identification

The data system calculates the corrected concentration for each target analyte from the calibration curve using the equations given in Appendix C. If sample interference is suspected, the laboratory may choose to report the value from the result that is not affected by interference. The lower value between the two columns is reported unless otherwise specified for the project.

11.3 Calculations

See Appendix C.

11.4 Data Review

11.4.1 Primary Review

Review project documents to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Confirm qualitative and quantitative identification criteria using the criteria provided in Sections 11.1 and 11.2. If the data system does not properly integrate the peaks perform and document manual integration in accordance with laboratory SOP BR-QA-006.

Upload the data files from the data processing system to the laboratory information management system (TALS). Complete the batch information for standards and reagents and verify ICAL and QC sample associations. Review the results and set results to primary, secondary, acceptable or rejected as appropriate. Dilute and reanalyze samples whose results exceed the calibration range. The dilution analysis should result in a determination within the calibration range, preferably in the upper half of the calibration range. A more concentrated analysis is not necessary unless the project requires it. Dilution analyses may be performed to minimize matrix interference.

If a sample was analyzed immediately following a high concentration sample, review the results of the sample for any sign of carryover. If carryover is suspected, reanalyze the sample.

Create an NCM for any calibration, QC and sample data that is reported outside established acceptance criteria and/or schedule necessary corrective action. Set batch to 1st level review and complete the data review checklist.

Monobutyltin has been identified as a poor performing analyte in some matrices based on statistical data. Consequently corrective action will not be taken when LCS or MS/MSD recovery is not within established limits for this analyte. Initiate an NCM to document the exceedance and indicate poor performing analyte as the justification for not taking corrective action.

Monobutyltin has poor extraction efficiency exhibiting a mean recovery of typically less than 5%. The low mean recovery is typical of routine implementation of this method. Although the laboratory has reported control limits of 10-48% for this analyte these control limits are not based on historical performance and do not indicate expected performance of this analyte by this method. The laboratory does not use the recovery or performance of this compound as a basis for acceptance of the analytical batch. All analytical results, both positive and non-detects are considered qualitative values.

11.4.2 Secondary Data Review

Spot-check quantitative and qualitative identifications using the criteria provided in Section 11.1 and Section 11.2.

If manual integrations were performed:

- Review each manual integration to verify that the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006. If a problem is found, immediately consult with the primary analyst or notify the Technical Director or QA Manager.

  Reintegration (by secondary data reviewers) should not be performed except in limited circumstances such as when the primary analyst who performed the initial integration is not available to correct any errors found during secondary review. If reintegration is performed, each integration performed by the secondary reviewer must be reviewed by a peer analyst or the department supervisor to verify the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006.

- Check to ensure an appropriate technical reason code is provided for each manual integration. Acceptable technical reason codes are provided in laboratory SOP BR-QA-006.

Verify that the performance criteria for the QC items listed in Table 1 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. Verify an NCM was initiated for any QC that does not meet established criteria and verify data is qualified accordingly. Set samples to 2nd level review.

Run the QC Checker, investigate and correct any problems found. Run and review the deliverable. Fix any problems found then set the method chain to lab complete.

11.5 Data Reporting

Data reporting and creation of the data deliverable is performed by the LIMS using the formatters set by the project manager during project initiation.

Analytical results above the reporting limit (RL) are reported as the value found. Analytical results less than the RL are reported as non-detect to the adjusted RL. The RL is adjusted for sample dilution/concentration. The unadjusted RL for each target analyte is provided in Section 1. If estimated values are requested by the project, results between the DL and the RL are reported and flagged as estimated.

Electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

Perform a method detection limit (MDL) study at initial method set-up following the procedures specified in laboratory SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP for employee training.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Vials containing sample extracts: Satellite container: 15 gallon bucket connected to a fume hood.

- Solvent Waste: Satellite container: 1 L glass bottle located in fume hood.

15.0 References / Cross-References

- NOAA Status and Trends Program Document: Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Vol. IV, NOAA Technical Memorandum, NOS ORCA 71.
- Corporate Environmental Health and Safety Manual (CW-E-M-001)
- Laboratory SOP BR-QA-011
- Laboratory SOP BR-EH-001
- Laboratory SOP BR-QA-014
- Laboratory SOP BR-QA-006
- Laboratory SOP BR-QA-005

16.0 Method Modifications

Not applicable

17.0 Attachments

- Table 1: Target Compound List and Reporting Limit
- Table 1A: Accuracy and Precision Limits
- Table 2: Primary Materials Used
- Table 3: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

Revision History

BR-GC-008, Rev. 11

- Title Page: Updated approval signatures and copyright date
- Section 6.1: Added value limiting inserts and removed Hydrogen generator
- Section 6.2: Updated GC/FPD hardware and autosampler. Updated software to ChemStation and Chrom.
- Section 10.1: Corrected Injector Temperature to 190℃.
- Section 10.3.1: Changed the number of blanks to at least 1, added internal standards and changed standard names to Chrom ID numbers.
- Section 10.6: Replaced ppb information with ICAL standard level references in the table.
- Appendix B: Updated tables.
- Updated MSDS to SDS

BR-GC-008, Rev. 10

- Incorporated CIPA: BR-GC-008, Rev. 9 into Rev. 10
- In section 10.1 revised time/temperature and flow rate for Instrument Operating Conditions
- In section 11.4.1 updated use of TALS and added statement indicating Monobutyltin as a poor performer.

BR-GC-008, Rev. 9

- SOP updated to the new TestAmerica format.
- Standard concentration tables were added to Appendix B.
- Formulas in Appendix C were revised to use Response Factors instead of Calibration Factors.
- Language was added to section 10.2 to allow for updating RT windows on CCVs.
- Language was added to section 11.4.1 to allow for dilution to minimize matrix interference.
- Added statement after table 1A indicating Monobutyltin as a poor performer.

Table 1: Routine Target Analyte List & Reporting Limit (RL)

ANALYTE	Routine Reporting Limit (RL)[1,2]	
	Water (ug/L)	Solid (ug/Kg)
Tetrabutyltin	0.050	1.7
Tributyltin	0.045	1.5
Dibutyltin	0.039	1.3
Monobutyltin[1]	0.62	20.7
Tripentyltin (Surrogate)	N/A	N/A

[1]*The routine RL is the unadjusted value that can be achieved in a blank matrix.*
[2]*The RL for tissue matrix is project defined.*

Table 1A: Routine Accuracy and Precision Limits[1]

Analyte	In-House Limits[2] (%R)		Precision (RPD) (≤)
	Water	Solid	
Tetrabutyltin	30-150	30-160	30
Tributyltin	30-150	30-160	30
Dibutyltin	30-150	30-160	30
Monobutyltin[1]	10-48	10-48	30
Tripentyltin (Surrogate)	15-150	30-120	N/A

[1] *The control limits for Monobutyltin are advisory because this analyte is a poor performer.*

Table 2: Primary Materials Used

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.

[1] *Always add acid to water to prevent violent reactions.*
[2] *Exposure limit refers to the OSHA regulatory exposure limit.*

Table 3: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action[1]
ICAL	Before sample analysis, when CCVs indicate calibration is no longer valid; after major instrument maintenance	Option 1: RSD for each analyte ≤ 20% Option 2: Linear Regression: r ≥ 0.995	Correct problem, reanalyze, and repeat calibration.
ICV	After each initial calibration	(% R) ± 25% from expected value	Correct problem and verify second source standard. If that fails, repeat initial calibration.
CCV	Daily before sample analysis, every 10 samples and at the end of the analytical sequence	% Difference or Drift ±25%	Re-analyze once, if still outside criteria perform corrective action, sequence can be re-started if two successive CCVs pass, otherwise repeat ICAL and all associated samples since last successful CCV, unless CCV is high and bracketed samples are non-detects.
MB	One per extraction batch of 20 or fewer samples	Target Analyte < RL	Examine project DQO's and take appropriate corrective action, which may include re-analysis of MB, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. If there are no detects in samples, or if all detects are > 10 X MB level, re-prep and reanalysis may not be required.
LCS	One per extraction batch of 20 or fewer samples	See Table 1A	Examine project DQO's and take appropriate corrective action, which may include re-analysis of LCS, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. Flag all reported values outside of control limits.
MS/MSD SD	MS/MSD: Per extraction batch SD: Per client request	See Table 1A	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze and/or re-extract. Flag all reported values outside of control limits.
Surrogate	All field and QC samples	See Table 1A	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze or re-extract. If matrix effect, review project DQOs to determine if a matrix effect must be confirmed by re-analysis. Flag all reported values outside of control limits.

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Internal Standard: a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are only produced in this range and qualified with the proper data reporting flag when a project requires this type of data reporting.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to them.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in hexane using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

Internal standard (tetra-n-propyltin) is added to each calibration, ICV, CCV, and sample aliquot before analysis. 10 uL of internal standard is added to 100 uL of standard or sample aliquot for analysis.

Internal Standard Solution (5 mg/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Tetra-n-propyltin	Retek #31474	2000	0.100	40	5.0

All working calibration standards, ICVs and CCVs for this method are prepared and derivitized by the organic prep department following the procedures given in the extraction SOP.

Final Concentration of Prepared Calibration Standards (as alkyltin chloride compounds)

Component	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)	ICV (ug/L)
Tripentyltin Chloride	50	100	250	500	1000	250
Tetrabutyltin	50	100	250	500	1000	250
Tributyltin chloride	50	100	250	500	1000	250
Dibutyltin dichloride	50	100	250	500	1000	250
Monobutyltin trichloride	100	200	500	1000	2000	500

Final Concentration of Prepared Calibration Standards (as un-substituted alkyltin compounds)

Component	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)	ICV (ug/L)
Tripentyltin	45.0	90.0	225	450	900	225
Tetrabutyltin	50.0	100	250	500	1000	250
Tributyltin	44.5	89.0	222.5	445	890	222.5
Dibutyltin	38.5	77.0	192.5	385	770	192.5
Monobutyltin	62.0	124.0	310	620	1240	310

The alkyltin chloride compounds are reported as un-substituted alkyltin compounds. The factors used to convert from the alkyl tin chloride to the alkyl tin are listed below.

Analyte	Conversion Factor	Report as
Tetrabutyltin	---	Tetrabutyltin

Analyte	Conversion Factor	Report as
Tributyltin chloride	0.89	Tributyltin
Dibutyltin dichloride	0.77	Dibutyltin
Monobutyltin trichloride	0.62	Monobutyltin
Tripentyltin chloride (SS)	0.90	Tripentyltin
Tetrapropyltin (ISTD)	--	Tetrapropyltin

Conversion Factors are determined from the following formula:

$$Conversion\ Factor = \frac{MWT - MWC}{MWT}$$

MWT= Total molecular weight of the analyte

MWC= Number of chlorides * molecular weight of chloride (molecular weight of chloride = 35.5)

Appendix C: Equations

Response Factor (RFx) = $\frac{\text{Peak area or height (x) x Concentration (is)}}{\text{Peak area or height (is) x Concentration (x)}}$

Where: x=compound, is = Internal Standard

Mean Response Factor ($\overline{RF}$) = $\frac{\sum_{i=1}^{n} RF_i}{n}$

where: n = number of calibration levels

Standard Deviation of the Response Factor (SD) = $\sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)2}{n-1}}$

where: n = number of calibration levels

Percent Relative Standard Deviation (RSD) of the Response Factor = $7\frac{SD}{\overline{RF}} \times 100\%$

Percent Difference (%D) = $\frac{RF_v - \overline{RF}}{\overline{RF}} \times 100\%$

where: RF_v = Response Factor from the Continuing Calibration Verification (CCV)

Percent Drift = $\frac{\text{Calculated Concentration – Theoretical Concentration}}{\text{Theoretical Concentration}}$ x 100%

Percent Recovery (%R) = $\frac{C_s}{C_n} \times 100\%$

where: C_s = Measured concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD = $\frac{C_s - C_u}{C_n} \times 100\%$

where: C_s = Measured concentration of the Spiked Sample
C_u = Measured concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (RPD) = $\frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100\%$

where: C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Sample Concentration

Extract

$$C_{extract}\,(ug/L) = \frac{\text{Peak response (x)}}{\text{Peak response (is)}} \times \frac{\text{Concentration (is)}}{\text{Average RF (x)}}$$

Where: x=compound, is = Internal Standard

Water

$$C_{sample}\,(ug/L) = C_{extract}\,(ug/L) \times \frac{\text{extract volume (L)}}{\text{sample volume (L)}} \times DF$$

Solid

$$C_{sample}\,(ug/Kg) = C_{extract}\,(ug/L) \times \frac{\text{extract volume (L)}}{\text{sample weight (Kg)}} \times \frac{100}{\%\,\text{solids}} \times DF$$

No. L-8

Semivolatile Organics

SW-846 Method 8270D

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following RCRA analytes have been determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	39638-32-9	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS	ND	ND	ND	X
Captan	133-06-2	HS	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Chrysene	218-01-9	X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (*cis* or *trans*)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC, OE	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW, OS	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dimethoate	60-51-5	HE, HS	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP, HS	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW, CP	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE, OS	ND	ND	ND	LR
4,4'-Methylenebis(*N*,*N*-dimethyl-aniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE, HS	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DC	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-*o*-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-*n*-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-*n*-propylamine	621-64-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS	ND	ND	ND	X
Phosmet	732-11-6	HS	ND	ND	ND	X
Phosphamidon	13171-21-6	HE	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP, HE	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Resorcinol	108-46-3	DC, OE	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW, OS	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-*p*-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,*O*,*O*-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient.
HE = Hydrolysis during extraction accelerated by acidic or basic conditions.
HS = Hydrolysis during storage potential.
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions.
OS = Oxidation during storage potential.
X = Historically, adequate recovery can be obtained by this technique. However, actual recoveries may vary depending on the extraction efficiency, the number of constituents being analyzed concurrently, and the analytical instrumentation.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3535 describes a solid-phase extraction procedure that may be applied to the extraction of semivolatiles from TCLP leachates (see Tables 16 and 17 of this method for performance data). Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (see Table 11 of this method for surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (see Table 12 of this method for performance data), Method 3561 describes a supercritical fluid device for the extraction of PAHs from solids (see Tables 13, 14, and 15 of this method for performance data), and Method 3546 provides an extraction procedure employing commercially available microwave equipment to extract semivolatiles while using less solvent and taking less time than procedures such as a Soxhlet extraction (see Tables 19 through 23 of this method for the applicable performance data). (The tabulated data are provided for guidance purposes only.)

1.3 This method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride (or other suitable solvents provided that the desired performance data can be generated) and are capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic

nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 may be appropriate for confirmation of the identification of these analytes when concentration in the extract permits. Refer to Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected to be present.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. For this reason, it is acceptable to report the combined result for n-nitrosodiphenylamine and diphenylamine for either of these compounds as a combined concentration.

1.4.6 1,2-Diphenylhydrazine is unstable even at room temperature and readily converts to azobenzene. Given the stability problems, it would be acceptable to calibrate for 1,2-diphenylhydrazine using azobenzene. Under these poor compound separation circumstances the results for either of these compounds should be reported as a combined concentration.

1.4.7 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.8 Pyridine may perform poorly at the GC injection port temperatures listed in this method. Lowering the injection port temperature may reduce the amount of degradation. However, the analyst must use caution in modifying the injection port temperature, as the performance of other analytes may be adversely affected. Therefore, if pyridine is to be determined in addition to other target analytes, it may be necessary to perform separate analyses. In addition, pyridine may be lost during the evaporative concentration of the sample extract. As a result, many of the extraction methods listed above may yield low recoveries unless great care is exercised during the concentration steps. For this reason, analysts may wish to consider the use of extraction techniques such as pressurized fluid extraction (Method 3545), microwave extraction (Method 3546),

or supercritical fluid extraction, which involve smaller extract volumes, thereby reducing or eliminating the need for evaporative concentration techniques for many applications.

1.4.9 Toluene diisocyanate rapidly hydrolyzes in water (half-life of less than 30 min). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.10 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The lower limits of quantitation for this method when determining an individual compound are approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). Lower limits of quantitation will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector. The lower limits of quantitation listed in Table 2 are provided for guidance and may not always be achievable.

1.6 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.7 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) equipped with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is

accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

2.4 This method includes specific calibration and quality control steps that supersede the general recommendations provided in Method 8000.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to Method 8000 for a discussion of interferences.

4.2 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph/mass spectrometer system

6.1.1 Gas chromatograph -- An analytical system equipped with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.1.2 Column -- 30-m x 0.25-mm ID (or 0.32-mm ID) 0.25, 0.5, or 1-µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent). The columns listed in this section were the columns used in developing the method. The listing of these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use these columns or other capillary columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.1.3 Mass spectrometer

6.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria as outlined in Sec. 11.3.1.

6.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria as outlined in Sec. 11.3.1

6.1.4 GC/MS interface -- Any GC-to-MS interface may be used that gives acceptable calibration points for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

6.1.5 Data system -- A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

6.1.6 Guard column (optional) -- (J&W deactivated fused-silica, 0.25-mm ID x 6-m, or equivalent) between the injection port and the analytical column joined with column connectors (Agilent Catalog No. 5062-3556, or equivalent).

6.2 Syringe -- 10-µL.

6.3 Volumetric flasks, Class A -- Appropriate sizes equipped with ground-glass stoppers.

6.4 Balance -- Analytical, capable of weighing 0.0001 g.

6.5 Bottles -- Glass equipped with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water.

7.3 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.4 Stock standard solutions (1000 mg/L) -- Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.4.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.2 Transfer the stock standard solutions into bottles equipped with PTFE-lined screw-caps. Store, protected from light, at #6 EC or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.4.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.4.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

7.4.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

7.5 Internal standard solutions -- The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the criteria in Sec. 11.3.2 are met.

7.5.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1-mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store away from any light source at #6 EC when not in use (-10 EC is recommended). When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.5.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

7.6 GC/MS tuning standard -- A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Alternate concentrations may be used to compensate for different injection volumes if the total amount injected is 50 ng or less. Store away from any light source at #6 EC when not in use (-10 EC is recommended). If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.7 Calibration standards -- A minimum of five calibration standards should be prepared at different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard and/or series of calibration standards prepared at a given concentration should contain all the desired project-specific target analytes for which quantitation and quantitative results are to be reported by this method.

7.7.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

7.7.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored away from any light source at #6 EC when not in use (-10 EC is recommended), and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration

verification standard should be prepared, as necessary, and stored at #6 EC. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.8 Surrogate standards -- The recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

NOTE: In the presence of samples containing residual chlorine, phenol-d_6 has been known to react to form chlorinated phenolic compounds that are not detected as the original spiked surrogate. Sample preservation precautions outlined in Chapter Four should be used when residual chlorine is known to be present in order to minimize degradation of deuterated phenols or any other susceptible target analyte.

7.8.1 Surrogate standard check -- Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

7.8.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute surrogate solution may be necessary.

7.9 Matrix spike and laboratory control standards -- See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS) and the spiking solution should be the same source as used for the initial calibration standards to restrict the influence of standard accuracy on the determination of recovery through preparation and analysis.

7.9.1 Matrix spike check -- Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

7.9.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute matrix and LCS spiking solution may be necessary.

7.9.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

7.10 Solvents -- Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents. All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Store the sample extracts at #6 EC, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 or 5000 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 5000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, discussions regarding the instrument QC requirements listed below can be found in the referenced sections of this method:

- The GC/MS must be tuned to meet the recommended DFTPP criteria prior to the initial calibration and for each 12-hr period during which analyses are performed. See Secs. 11.3.1 and 11.4.1 for further details.

- There must be an initial calibration of the GC/MS system as described in Sec. 11.3. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards). The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

- The GC/MS system must meet the calibration verification acceptance criteria in Sec. 11.4, each 12 hrs.

- The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 11.6.1.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, a method blank must be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the lab should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for

evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. When any changes are made to the system (e.g., the column is changed, a septum is changed), see the guidance in Method 8000 regarding whether recalibration of the system must take place.

9.9 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec 11.3 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample preparation

11.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air (particulates and sorbent resin)	3542
Water (including TCLP leachates)	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3546, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3546, 3550, 3560, 3561, 3580

11.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The quantitation limit is very high (approximately 10,000 µg/L). Therefore, it is only appropriate where concentrations in excess of 10,000 µg/L are expected.

11.2 Extract cleanup -- Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of Interest	Methods
Aniline and aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides	3610, 3620, 3630, 3640, 3660
PCBs	3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique and a GC/ECD analysis, if interferences are encountered on GC/FID.

11.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	#1 sec/scan
Initial temperature:	40 EC, hold for 4 min
Temperature program:	40-320 EC at 10 EC/min
Final temperature:	320 EC, hold until 2 min after benzo[g,h,i]perylene elutes
Injector temperature:	250-300 EC
Transfer line temperature:	250-300 EC
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

11.3.1 The GC/MS system must be hardware-tuned such that injecting 50 ng or less of DFTPP meets the manufacturer's specified acceptance criteria or as listed in Table 3. The tuning criteria as outlined in Table 3 were developed using quadrupole mass spectrometer instrumentation and it is recognized that other tuning criteria may be more effective depending on the type of instrumentation, e.g., Time-of-Flight, Ion Trap, etc. In

these cases it would be appropriate to follow the manufacturer's tuning instructions or some other consistent tuning criteria. However, no matter which tuning criteria is selected, the system calibration must not begin until the tuning acceptance criteria are met with the sample analyses performed under the same conditions as the calibration standards.

11.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach should be used: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or any other discrete peak that does not coelute with DFTPP.

11.3.1.2 Use the DFTPP mass intensity criteria in the manufacturer's instructions as primary tuning acceptance criteria or those in Table 3 as default tuning acceptance criteria if the primary tuning criteria are not available. Alternatively, other documented tuning criteria may be used (e.g. CLP, or Method 625), provided that method performance is not adversely affected. The analyst is always free to choose criteria that are tighter than those included in this method or to use other documented criteria provided they are used consistently throughout the initial calibration, calibration verification, and sample analyses.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

11.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. (See Method 8081 for the percent breakdown calculation.) Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2 given by the following equation:

$$\text{TailingFactor} = \frac{BC}{AB}$$

Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and B is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. (See Figure 1 for an example tailing factor calculation.)

11.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6 to12 in. of the capillary column. The use of a guard column (Sec. 6.1.6) between the injection port and the analytical column may help prolong analytical column performance life.

11.3.2 The internal standards selected in Sec. 7.5 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (e.g., for 1,4-dichlorobenzene-d_4, use m/z 150 for quantitation).

11.3.3 Analyze 1-2 µL of each calibration standard (containing the compounds for quantitation and the appropriate surrogates and internal standards) and tabulate the area of the primary ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 7.7 and Method 8000). Alternate injection volumes may be used if the applicable quality control requirements for using this method are met. The injection volume must be the same for all standards and sample extracts. Figure 2 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

11.3.4 Initial calibration calculations

Calculate response factors (RFs) for each target analyte relative to one of the internal standards (see Table 5) as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

11.3.4.1 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte using the following equations. The RSD should be less than or equal to 20% for each target analyte. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 4, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criteria. For these occasions, it is acknowledged that the failing compounds may not be critical to the specific project and therefore they may be used as qualified data or estimated values for screening purposes. The analyst should also strive to place more emphasis on meeting the calibration criteria for those compounds that are critical project compounds, rather than meeting the criteria for those less important compounds.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
RF = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

11.3.4.2 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 11.3.

11.3.5 Evaluation of retention times -- The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.6 Linearity of target analytes -- If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 11.7.2).

11.3.6.1 If the RSD of any target analyte is greater than 20%, refer to Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed. The average RF should not be used for compounds that have an RSD greater than 20% unless the concentration is reported as estimated.

11.3.6.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

11.3.6.3 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet either the 20% RSD, minimum correlation coefficient criteria (0.99), or the acceptance criteria for alternative calibration procedures in Method 8000. Any calibration method described in Method 8000 may be used, but it should be used consistently. It is considered inappropriate once the calibration analyses are completed to select an alternative calibration procedure in order to pass the recommended criteria on a case-by-case basis. If compounds fail to meet these criteria, the associated concentrations may still be determined but they must be reported as estimated. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit.

11.4 GC/MS calibration verification -- Calibration verification consists of three steps that are performed at the beginning of each 12-hr analytical shift.

11.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng or less of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria as outlined in Sec. 11.3.1 before sample analysis begins. These criteria must be demonstrated each 12-hr shift during which samples are analyzed.

11.4.2 The initial calibration function for each target analyte should be checked immediately after the first occurrence in the region of the middle of the calibration range with a standard from a source different from that used for the initial calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

11.4.3 The initial calibration (Sec. 11.3) for each compound of interest should be verified once every 12 hrs prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard (containing all the compounds for quantitation) at a concentration either near the midpoint concentration for the calibrating range of the GC/MS or near the action level for the project. The results must be compared against the most recent initial calibration curve and should meet the verification acceptance criteria provided in Secs. 11.4.5 through 11.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.4.4 A method blank should be analyzed prior to sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Method 8000 for information regarding method blank performance criteria.

11.4.5 Calibration verification standard criteria

11.4.5.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 4. This criteria is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

11.4.5.2 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.4.5.3 All target compounds of interest must be evaluated using a 20% criterion. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Method 8000 for guidance on calculating percent difference and drift.

11.4.5.4 If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

11.4.5.5 Problems similar to those listed under initial calibration could affect the ability to pass the calibration verification standard analysis. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

11.4.5.6 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000 for additional details). It is not necessary to re-analyze a low concentration standard, rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives and for those situations the minimum quantitation check criteria should be outlined in a laboratory standard operating procedure, or a project-specific Quality Assurance Project Plan. Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered "out of control" and corrective action such as redefining the lower limit of quantitation

and/or reporting those "out of control" target analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

11.4.6 Internal standard retention time -- The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.4.7 Internal standard response -- If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.5 GC/MS analysis of samples

11.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

11.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1 mL of concentrated sample extract obtained from sample preparation.

11.5.3 Inject an aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 11.3). The volume to be injected should include an appropriate concentration that is within the calibration range of base/neutral and acid surrogates using the surrogate solution as noted in Sec. 7.8. The injection volume must be the same volume that was used for the calibration standards.

11.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard solution must be added to the diluted extract to maintain the same concentration as in the calibration standards (usually 40 ng/µL, or other concentrations as appropriate, if a more sensitive GC/MS system is being used). Secondary ion quantitation should be used only when there are sample interferences with the primary ion.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times in all samples, spikes, blanks, and standards to effectively check drifting, method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance. Internal standard responses (area counts) must be monitored in all samples, spikes, blanks for similar reasons. If the EICP area for any of the internal standards in samples, spikes and blanks changes by a factor of two (-50% to +100%) from the areas determined in the continuing calibration analyzed that day, corrective action must be taken. The samples, spikes or blanks should be reanalyzed or the data should be qualified.

11.5.4.1 When ions from a compound in the sample saturate the detector, this analysis should be followed by the analysis of an instrument blank consisting of clean solvent. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences. Contamination from one sample to the next on the instrument usually takes place in the syringe. If adequate syringe washes are employed, then carryover from high concentration samples can usually be avoided.

11.5.4.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

11.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electron impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Using the primary ion for quantitation and the secondary ions for confirmation set up the collection groups based on their retention times. The selected ions are nominal ions and most compounds have small mass defect, usually less than 0.2 amu, in their spectra. These mass defects should be used in the acquisition table. The dwell time may be automatically calculated by the laboratory's GC/MS software or manually calculated using the following formula. The total scan time should be less than 1,000 msec and produce at least 5 to 10 scans per chromatographic peak. The start and stop times for the SIM groups are determined from the full scan analysis using the formula below:

$$\text{Dwell Time for the Group} = \frac{\text{Scan Time (msec)}}{\text{Total Ions in the Group}}$$

Additional guidance for performing SIM analyses, in particular for PAHs and phenol target analyte compounds, can be found in the most recent CLP semivolatile organic methods statement of work (SOW). See the SIM sections from the following CLP SOW for further details: EPA CLP Organics SOW. (Reference 14)

11.6 Analyte identification

11.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

11.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the

target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

11.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.) Use professional judgement in interpretation where interferences are observed.

11.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

11.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

11.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.7 Quantitation

11.7.1 Once a target compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

11.7.1.1 It is highly recommended to use the integration produced by the software if the integration is correct because the software should produce more consistent integrations. However, manual integrations may be necessary when the software does not produce proper integrations because baseline selection is improper; the correct peak is missed; a coelution is integrated; the peak is partially integrated; etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

11.7.1.2 Manual integrations should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates, integration parameter files, etc). The analyst should seek to minimize manual integration by properly maintaining the instrument, updating retention times, and configuring peak integration parameters.

11.7.2 If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 11.3.4). See Method 8000 for the equations describing internal standard calibration and either linear or non-linear calibrations.

11.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 11.6.2) should be estimated. The same formula as in Sec. 11.3.4 should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

11.7.4 The resulting concentration should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

11.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, for example by using Methods 8081 or 8082. However, this method (8270) may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

11.7.6 Quantitation of multicomponent parameters such as diesel range organics (DROs) and total petroleum hydrocarbons (TPH) using the Method 8270 recommended internal standard quantitation technique is beyond the scope of this method. Typically,

analyses for these parameters are performed using GC/FID or GC with a MS detector capability that is available with Method 8015.

11.7.7 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.7 and Method 8000 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Single laboratory initial demonstration of capability data were generated from five replicate measurements using a modified continuous liquid-liquid extractor (Method 3520) with hydrophobic membrane. In this case only a single acid pH extraction was performed using the CLP calibration criteria and the applicable CLP target analytes. These data are presented in Table 6. Laboratories should generate their own acceptance criteria depending on the extraction and instrument conditions. (See Method 8000.)

13.3 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 7. These data are provided for guidance purposes only.

13.4 Method performance data using Method 3541 (automated Soxhlet extraction) are presented in Tables 8 and 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three extractions were performed and each extract was analyzed by gas chromatography/mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data as listed were taken from Reference 7 and are provided for guidance purposes only.

13.5 Surrogate precision and accuracy data are presented in Table 10 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by this method (8270). These data are provided for guidance purposes only.

13.6 Single laboratory precision and bias data using Method 3545 (pressurized fluid extraction) for semivolatile organic compounds are presented in Table 11. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by the Perstorp Environmental Soxtec™ (automated Soxhlet). The data in Table 11 represent seven replicate extractions and analyses for each individual sample and were taken from Reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low - 101.2%, mid - 97.2% and high - 99.2%. These data are provided for guidance purposes only.

13.7 Single laboratory precision and bias data using Method 3561 (SFE extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (EC-1, a lake sediment from Environment Canada and HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 12 and 13 and were taken from Reference 10. These data are provided for guidance purposes only.

13.8 Single laboratory precision and accuracy data using Method 3561 (SFE extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. The instrument conditions that were utilized to extract a 3.4 g sample were as follows: Pressure -- 300 atm; time -- 60 min.; extraction fluid -- CO_2; modifier -- 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature -- 80 EC; Restrictor temperature -- 120 EC; and, trapping fluid -- chloroform (methylene chloride has also been used). The data are found in Table 14 and were taken from Reference 11. These data are provided for guidance purposes only.

13.9 Tables 15 and 16 contain single-laboratory precision and accuracy data for solid-phase extraction of TCLP buffer solutions spiked at two levels and extracted using Method 3535. These data are provided for guidance purposes only.

13.10 Table 17 contains multiple-laboratory data for solid-phase extraction of spiked TCLP soil leachates extracted using Method 3535. These data are provided for guidance purposes only.

13.11 Tables 18 through 22 contain single-laboratory PAH recovery data for microwave extraction of contaminated soils and standard reference materials using Method 3546. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS IN APPROXIMATE RETENTION TIME ORDER [a]

Compound	Primary Ion	Secondary Ion(s)
2-Picoline	93	66,92
Aniline	93	66,65
Phenol	94	65,66
Bis(2-chloroethyl) ether	93	63,95
2-Chlorophenol	128	64,130
1,3-Dichlorobenzene	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	152	150,115
1,4-Dichlorobenzene	146	148,111
Benzyl alcohol	108	79,77
1,2-Dichlorobenzene	146	148,111
N-Nitrosomethylethylamine	88	42,43,56
Bis(2-chloroisopropyl) ether	45	77,121
Ethyl carbamate	62	44,45,74
Thiophenol (Benzenethiol)	110	66,109,84
Methyl methanesulfonate	80	79,65,95
N-Nitrosodi-n-propylamine	70	42,101,130
Hexachloroethane	117	201,199
Maleic anhydride	54	98,53,44
Nitrobenzene	77	123,65
Isophorone	82	95,138
N-Nitrosodiethylamine	102	42,57,44,56
2-Nitrophenol	139	109,65
2,4-Dimethylphenol	122	107,121
p-Benzoquinone	108	54,82,80
Bis(2-chloroethoxy)methane	93	95,123
Benzoic acid	122	105,77
2,4-Dichlorophenol	162	164,98
Trimethyl phosphate	110	79,95,109,140
Ethyl methanesulfonate	79	109,97,45,65
1,2,4-Trichlorobenzene	180	182,145
Naphthalene-d_8 (IS)	136	68
Naphthalene	128	129,127
Hexachlorobutadiene	225	223,227
Tetraethyl pyrophosphate	99	155,127,81,109
Diethyl sulfate	139	45,59,99,111,125
4-Chloro-3-methylphenol	107	144,142
2-Methylnaphthalene	142	141
2-Methylphenol	107	108,77,79,90
Hexachloropropene	213	211,215,117,106,141
Hexachlorocyclopentadiene	237	235,272
N-Nitrosopyrrolidine	100	41,42,68,69
Acetophenone	105	71,51,120
3/4-Methylphenol[b]	107	108,77,79,90

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
2,4,6-Trichlorophenol	196	198,200
o-Toluidine	106	107,77,51,79
2-Chloronaphthalene	162	127,164
N-Nitrosopiperidine	114	42,55,56,41
1,4-Phenylenediamine	108	80,53,54,52
1-Chloronaphthalene	162	127,164
2-Nitroaniline	65	92,138
5-Chloro-2-methylaniline	106	141,140,77,89
Dimethyl phthalate	163	194,164
Acenaphthylene	152	151,153
2,6-Dinitrotoluene	165	63,89
Phthalic anhydride	104	76,50,148
o-Anisidine	108	80,123,52
3-Nitroaniline	138	108,92
Acenaphthene-d_{10} (IS)	164	162,160
Acenaphthene	154	153,152
2,4-Dinitrophenol	184	63,154
2,6-Dinitrophenol	162	164,126,98,63
4-Chloroaniline	127	129,65,92
Isosafrole	162	131,104,77,51
Dibenzofuran	168	139
2,4-Diaminotoluene	121	122,94,77,104
2,4-Dinitrotoluene	165	63,89
4-Nitrophenol	139	109,65
2-Naphthylamine	143	115,116
1,4-Naphthoquinone	158	104,102,76,50,130
p-Cresidine	122	94,137,77,93
Dichlorovos	109	185,79,145
Diethyl phthalate	149	177,150
Fluorene	166	165,167
2,4,5-Trimethylaniline	120	135,134,91,77
N-Nitrosodi-n-butylamine	84	57,41,116,158
4-Chlorophenyl phenyl ether	204	206,141
Hydroquinone	110	81,53,55
4,6-Dinitro-2-methylphenol	198	51,105
Resorcinol	110	81,82,53,69
N-Nitrosodiphenylamine	169	168,167
Safrole	162	104,77,103,135
Hexamethyl phosphoramide	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	92	127,129,65,39
Diphenylamine	169	168,167
1,2,4,5-Tetrachlorobenzene	216	214,179,108,143,218
1-Naphthylamine	143	115,89,63
1-Acetyl-2-thiourea	118	43,42,76
4-Bromophenyl phenyl ether	248	250,141

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
Toluene diisocyanate	174	145,173,146,132,91
2,4,5-Trichlorophenol	196	198,97,132,99
Hexachlorobenzene	284	142,249
Nicotine	84	133,161,162
Pentachlorophenol	266	264,268
5-Nitro-o-toluidine	152	77,79,106,94
Thionazine	107	96,97,143,79,68
4-Nitroaniline	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	188	94,80
Phenanthrene	178	179,176
Anthracene	178	176,179
1,4-Dinitrobenzene	168	75,50,76,92,122
Mevinphos	127	192,109,67,164
Naled	109	145,147,301,79,189
1,3-Dinitrobenzene	168	76,50,75,92,122
Diallate (cis or trans)	86	234,43,70
1,2-Dinitrobenzene	168	50,63,74
Diallate (trans or cis)	86	234,43,70
Pentachlorobenzene	250	252,108,248,215,254
5-Nitro-o-anisidine	168	79,52,138,153,77
Pentachloronitrobenzene	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	174	101,128,75,116
Di-n-butyl phthalate	149	150,104
2,3,4,6-Tetrachlorophenol	232	131,230,166,234,168
Dihydrosaffrole	135	64,77
Demeton-O	88	89,60,61,115,171
Fluoranthene	202	101,203
1,3,5-Trinitrobenzene	75	74,213,120,91,63
Dicrotophos	127	67,72,109,193,237
Benzidine	184	92,185
Trifluralin	306	43,264,41,290
Bromoxynil	277	279,88,275,168
Pyrene	202	200,203
Monocrotophos	127	192,67,97,109
Phorate	75	121,97,93,260
Sulfallate	188	88,72,60,44
Demeton-S	88	60,81,89,114,115
Phenacetin	108	180,179,109,137,80
Dimethoate	87	93,125,143,229
Phenobarbital	204	117,232,146,161
Carbofuran	164	149,131,122
Octamethyl pyrophosphoramide	135	44,199,286,153,243
4-Aminobiphenyl	169	168,170,115
Dioxathion	97	125,270,153
Terbufos	231	57,97,153,103

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
α,α-Dimethylphenylamine	58	91,65,134,42
Pronamide	173	175,145,109,147
Aminoazobenzene	197	92,120,65,77
Dichlone	191	163,226,228,135,193
Dinoseb	211	163,147,117,240
Disulfoton	88	97,89,142,186
Fluchloralin	306	63,326,328,264,65
Mexacarbate	165	150,134,164,222
4,4'-Oxydianiline	200	108,171,80,65
Butyl benzyl phthalate	149	91,206
4-Nitrobiphenyl	199	152,141,169,151
Phosphamidon	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	231	185,41,193,266
Methyl parathion	109	125,263,79,93
Carbaryl	144	115,116,201
Dimethylaminoazobenzene	225	120,77,105,148,42
Propylthiouracil	170	142,114,83
Benz(a)anthracene	228	229,226
Chrysene-d_{12} (IS)	240	120,236
3,3'-Dichlorobenzidine	252	254,126
Chrysene	228	226,229
Malathion	173	125,127,93,158
Kepone	272	274,237,178,143,270
Fenthion	278	125,109,169,153
Parathion	109	97,291,139,155
Anilazine	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	149	167,279
3,3'-Dimethylbenzidine	212	106,196,180
Carbophenothion	157	97,121,342,159,199
5-Nitroacenaphthene	199	152,169,141,115
Methapyrilene	97	50,191,71
Isodrin	193	66,195,263,265,147
Captan	79	149,77,119,117
Chlorfenvinphos	267	269,323,325,295
Crotoxyphos	127	105,193,166
Phosmet	160	77,93,317,76
EPN	157	169,185,141,323
Tetrachlorvinphos	329	109,331,79,333
Di-n-octyl phthalate	149	167,43
2-Aminoanthraquinone	223	167,195
Barban	222	51,87,224,257,153
Aramite	185	191,319,334,197,321
Benzo(b)fluoranthene	252	253,125
Nitrofen	283	285,202,139,253
Benzo(k)fluoranthene	252	253,125

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
Chlorobenzilate	251	139,253,111,141
Fensulfothion	293	97,308,125,292
Ethion	231	97,153,125,121
Diethylstilbestrol	268	145,107,239,121,159
Famphur	218	125,93,109,217
Tri-p-tolyl phosphate[c]	368	367,107,165,198
Benzo(a)pyrene	252	253,125
Perylene-d_{12} (IS)	264	260,265
7,12-Dimethylbenz(a)anthracene	256	241,239,120
5,5-Diphenylhydantoin	180	104,252,223,209
Captafol	79	77,80,107
Dinocap	69	41,39
Methoxychlor	227	228,152,114,274,212
2-Acetylaminofluorene	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	231	266,268,140,195
3,3'-Dimethoxybenzidine	244	201,229
3-Methylcholanthrene	268	252,253,126,134,113
Phosalone	182	184,367,121,379
Azinphos-methyl	160	132,93,104,105
Leptophos	171	377,375,77,155,379
Mirex	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	201	137,119,217,219,199
Dibenz(a,j)acridine	279	280,277,250
Mestranol	277	310,174,147,242
Coumaphos	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	276	138,277
Dibenz(a,h)anthracene	278	139,279
Benzo(g,h,i)perylene	276	138,277
1,2:4,5-Dibenzopyrene	302	151,150,300
Strychnine	334	334,335,333
Piperonyl sulfoxide	162	135,105,77
Hexachlorophene	196	198,209,211,406,408
Aldrin	66	263,220
Aroclor 1016	222	260,292
Aroclor 1221	190	224,260
Aroclor 1232	190	224,260
Aroclor 1242	222	256,292
Aroclor 1248	292	362,326
Aroclor 1254	292	362,326
Aroclor 1260	360	362,394
α-BHC	183	181,109
β-BHC	181	183,109
δ-BHC	183	181,109
γ-BHC (Lindane)	183	181,109
4,4'-DDD	235	237,165

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
4,4'-DDE	246	248,176
4,4'-DDT	235	237,165
Dieldrin	79	263,279
1,2-Diphenylhydrazine	77	105,182
Endosulfan I	195	339,341
Endosulfan II	337	339,341
Endosulfan sulfate	272	387,422
Endrin	263	82,81
Endrin aldehyde	67	345,250
Endrin ketone	317	67,319
2-Fluorobiphenyl (surr)	172	171
2-Fluorophenol (surr)	112	64
Heptachlor	100	272,274
Heptachlor epoxide	353	355,351
Nitrobenzene-d_5 (surr)	82	128,54
N-Nitrosodimethylamine	42	74,44
Phenol-d_6 (surr)	99	42,71
Terphenyl-d_{14} (surr)	244	122,212
2,4,6-Tribromophenol (surr)	330	332,141
Toxaphene	159	231,233

IS = internal standard
surr = surrogate
[a] The data presented are representative of DB-5 type analytical columns
[b] Compounds cannot be separated for quantitation
[c] Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

EXAMPLE LOWER LIMITS OF QUANTITATION FOR SEMIVOLATILE ORGANICS

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-Methylcholanthrene	10	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND

TABLE 2
(continued)

[a] Sample lower limits of quantitation are highly matrix-dependent and those listed here are provided for guidance and may not always be achievable.

[b] Lower limits of quantitation listed for soil/sediment are based on wet weight. When data are reported on a dry weight basis, the lower limits will be higher based on the % dry weight of each sample. These lower limits are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined

NA = Not Applicable

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c]Lower limit of quantitation = (Lower limit of quantitation for low soil/sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	10-80% of Base Peak
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of Base Peak
197	< 2% of mass 198
198	Base peak, or > 50% of Mass 442
199	5-9% of mass 198
275	10-60% of Base Peak
365	> 1% of mass 198
441	present but < 24% of mass 442
442	Base Peak, or > 50% of mass 198
443	15-24% of mass 442

[a] The majority of the data are taken from Reference 13 (Method 525.2).

[b] The criteria in this table are intended to be used as default criteria for quadrupole instrumentation if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected. See Sec. 11.3.1

TABLE 4

RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION USING THE SUGGESTED IONS FROM TABLE 1

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-	Dimethyl phthalate
Ethyl methanesulfonate	phenethylamine	2,4-Dinitrophenol
2-Fluorophenol (surr)	2,4-Dimethylphenol	2,4-Dinitrotoluene
Hexachloroethane	Hexachlorobutadiene	2,6-Dinitrotoluene
Methyl methanesulfonate	Isophorone	Fluorene
2-Methylphenol	2-Methylnaphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Naphthalene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene	1-Naphthylamine
N-Nitroso-di-n-propylamine	Nitrobenzene-d_8 (surr)	2-Naphthylamine
Phenol	2-Nitrophenol	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosodi-n-butylamine	3-Nitroaniline
2-Picoline	N-Nitrosopiperidine	4-Nitroaniline
	1,2,4-Trichlorobenzene	4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
Fluoranthene	p-Dimethyl aminoazobenzene	7,12-Dimethylbenz(a) anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	Indeno(1,2,3-cd) pyrene
Pentachlorophenol		3-Methylcholanthrene
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr) = surrogate

TABLE 6

EXAMPLE SINGLE LABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	x of 5 replicates (µg/L)	% Recovery of Avg.
Acenaphthene	50	46.7	93.4
Acenaphthylene	50	46.1	92.2
Aniline	50	8.3	16.7
Anthracene	50	48.4	96.8
Benzoic acid	50	43.7	87.4
Benz(a)anthracene	50	49.6	99.2
Benzo(b)fluoranthene	50	49.8	99.6
Benzo(k)fluoranthene	50	50.6	101
Benzo(a)pyrene	50	47.7	95.5
Benzo(g,h,i)perylene	50	52.6	105
Benzyl alcohol	50	44.4	88.8
Bis(2-chloroethyl) ether	50	44.2	88.4
Bis(2-chloroethoxy)methane	50	46.6	93.1
Bis(2-chloroisopropyl) ether	50	43.4	86.8
Bis(2-ethylhexyl) phthalate	50	50.2	100
4-Bromophenyl phenyl ether	50	48.6	97.2
Butyl benzyl phthalate	50	49.6	99.3
Carbazole	50	52.1	104
2-Chloroaniline	50	38.9	77.7
4-Chloro-3-methylphenol	50	47.3	94.6
2-Chloronaphthalene	50	45.3	90.8
2-Chlorophenol	50	43.1	86.2
4-Chlorophenyl phenyl ether	50	47.3	94.6
Chrysene	50	50.3	101
Dibenzofuran	50	47.4	94.7
Dibenz(a,h)anthracene	50	51.6	103
Di-n-butyl phthalate	50	50.5	101
1,2-Dichlorobenzene	50	35.8	71.6
1,3-Dichlorobenzene	50	33.3	66.7
1,4-Dichlorobenzene	50	34.4	68.7
3,3'-Dichlorobenzidine	50	32.0	64.0
2,4-Dichlorophenol	50	47.4	94.8
Diethyl phthalate	50	50.0	99.9
Dimethyl phthalate	50	48.5	97.0
2,4-Dimethylphenol	50	31.2	62.3
4,6-Dinitro-2-methylphenol	50	57.6	115
2,4-Dinitrophenol	50	58.7	117
2,4-Dinitrotoluene	50	51.3	103

TABLE 6
(continued)

Compound	Test conc. (µg/L)	x of 5 replicates (µg/L)	% Recovery of Avg.
2,6-Dinitrotoluene	50	50.2	100
Di-n-octyl phthalate	50	51.1	102
Fluoranthene	50	51.0	102
Fluorene	50	48.5	97.0
Hexachlorobenzene	50	49.0	97.9
Hexachlorobutadiene	50	34.7	69.5
Hexachlorocyclopentadiene	50	1.9	3.8
Hexachloroethane	50	29.9	58.8
Indeno(1,2,3-cd)pyrene	50	51.7	103
Isophorone	50	47.1	94.3
2-Methylnaphthalene	50	44.7	89.4
2-Methylphenol	50	41.7	83.4
4-Methylphenol	50	42.6	85.2
Naphthalene	50	43.4	86.8
2-Nitroaniline	50	48.4	96.7
3-Nitroaniline	50	46.8	93.6
4-Nitroaniline	50	56.1	112
Nitrobenzene	50	47.1	94.1
2-Nitrophenol	50	47.3	94.6
4-Nitrophenol	50	55.4	111
N-Nitrosodiphenylamine	50	46.7	93.4
N-Nitroso-di-propylamine	50	44.6	89.3
Pentachlorophenol	50	56.9	114
Phenanthrene	50	49.7	99.4
Phenol	50	40.9	81.8
Pyrene	50	49.2	98.4
1,2,4-Trichlorobenzene	50	39.1	78.2
2,4,5-Trichlorophenol	50	47.7	95.4
2,4,6-Trichlorophenol	50	49.2	98.4

x = Average recovery for five initial demonstration of capability measurements, in µg/L

[a] Extraction using acidic pH only with a modified continuous liquid-liquid extractor with hydrophobic membrane according to Method 3520. These values are for guidance only. Appropriate derivation of acceptance criteria for similar extraction conditions may result in much different recovery ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

	Percent Recovery, Day 0		Percent Recovery, Day 7	
Compound	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 8

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANIC FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

	Clay Soil		Topsoil	
Compound	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 9

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8

Compound	Mean Recovery	RSD
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenz(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 10

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	% RSD
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 10 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 11

PRESSURIZED FLUID EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

	Clay			Loam			Sand			Mean
Compound	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	102.0
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	101.9
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	101.6
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	120.6
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	119.2
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	112.5
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	104.7
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	100.2
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	110.3
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	98.1
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	118.6
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	100.2
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	101.7
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	109.8
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	96.3
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	97.2
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	98.6
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	104.2
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	106.1
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	108.1
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	104.7
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	99.7
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	102.1
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	75.8
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	95.9
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	94.1
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	96.2
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	92.6
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	90.3
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	101.7
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	92.9
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	98.4
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	75.6
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	90.7

TABLE 11
(continued)

Compound	Clay			Loam			Sand			Mean
	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	98.8
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	94.4
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	95.4
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	99.1
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	96.8
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	95.8
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	93.7
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	81.2
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	100.6
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	101.2
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	99.1
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	102.7
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	105.2
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	116.5
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	101.5
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	102.9
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	99.0
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	103.1
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	99.9
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	102.7
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	98.6
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	66.4
Mean	95.1	94.3	101.0	95.5	96.5	104.1	113.0	100.9	92.5	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 12

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4 ± 8.2	29.55	91	10.5
2-Methylnaphthalene	62.1 ± 11.5	76.13	122	2.0
Acenaphthene	632 ± 105	577.28	91	2.9
Dibenzofuran	307 ± 49	302.25	98	4.1
Fluorene	492 ± 78	427.15	87	3.0
Phenanthrene	1618 ± 340	1278.03	79	3.4
Anthracene	422 ± 49	400.80	95	2.6
Fluoranthene	1280 ± 220	1019.13	80	4.5
Pyrene	1033 ± 285	911.82	88	3.1
Benz(a)anthracene	252 ± 8	225.50	89	4.8
Chrysene	297 ± 26	283.00	95	3.8
Benzo(a)pyrene	97.2 ± 17.1	58.28	60	6.5
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153 ± 22	130.88	86	10.7

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

TABLE 15

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS LOW SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	3,750	63	10	63	9
Hexachloroethane	1,500	55	6	77	4
Nitrobenzene	1,000	82	10	100	5
Hexachlorobutadiene	250	65	3	56	4
2,4-Dinitrotoluene	65	89	4	101	5
Hexachlorobenzene	65	98	5	95	6
o-Cresol	100,000	83	10	85	5
m-Cresol*	100,000	86	8	85	3
p-Cresol*	100,000	*	*	*	*
2,4,6-Trichlorophenol	1,000	84	12	95	12
2,4,5-Trichlorophenol	200,000	83	11	88	3
Pentachlorophenol	50,000	82	9	78	9

Results from seven replicate spiked buffer samples.

* In this study, m-cresol and p-cresol co-eluted and were quantitated as a mixture of both isomers.

Data from Reference 12.

TABLE 16

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS HIGH SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	15,000	63	10	63	9
Hexachloroethane	6,000	54	7	46	7
Nitrobenzene	4,000	81	4	81	13
Hexachlorobutadiene	1,000	81	5	70	11
2,4-Dinitrotoluene	260	99	8	98	3
Hexachlorobenzene	260	89	8	91	9
o-Cresol*	400,000	92	15	90	4
m-Cresol*	400,000	95	8	82	6
p-Cresol*	400,000	82	14	84	7
2,4,6-Trichlorophenol	4,000	93	12	104	12
2,4,5-Trichlorophenol	800,000	93	14	97	23
Pentachlorophenol	200,000	84	9	73	8

Results from seven replicate spiked buffer samples.

* In this study, recoveries of these compounds were determined from triplicate spikes of the individual compounds into separate buffer solutions.

Data from Reference 12.

TABLE 17

RECOVERY DATA FROM THREE LABORATORIES FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP LEACHATES FROM SOIL SAMPLES

Buffer 1 pH = 2.886		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,000	86	8	7	35.3	0.7	3	7.6	6	3
m-Cresol**	--	77	8	7	--	--	--	--	--	--
p-Cresol**	--	--	--	--	--	--	--	7.7	11	3
2,4,6-Trichlorophenol	2,000	106	6	7	96.3	3.9	3	44.8	5	3
2,4,5-Trichlorophenol	400,000	93	3	7	80.5	4.5	3	63.3	11	3
Pentachlorophenol	100,000	79	2	7	33.8	12.2	3	29.2	13	3
1,4-Dichlorobenzene	7,500	51	5	7	81.3	5.3	3	19.2	7	3
Hexachloroethane	3,000	50	5	7	66.2	2.1	3	12.6	11	3
Nitrobenzene	2,000	80	8	7	76.3	5.3	3	63.9	12	3
Hexachlorobutadiene	500	53	8	7	63.3	4.8	3	9.6	9	3
2,4-Dinitrotoluene	130	89	8	7	35.7	2.6	3	58.2	17	3
Hexachlorobenzene	130	84	21	7	92.3	1.6	3	71.7	9	3

(continued)

TABLE 17
(continued)

Buffer 2 pH = 4.937		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,00	97	13	7	37.8	4.5	3	6.1	24	3
m-Cresol**	--	83	4	7	--	--	--	6.0	25	3
p-Cresol**	--	--	--	--	--	--	--	--	--	--
2,4,6-Trichlorophenol	2,000	104	4	7	91.7	8.0	3	37.7	25	3
2,4,5-Trichlorophenol	400,000	94	4	7	85.2	0.4	3	64.4	10	3
Pentachlorophenol	100,000	109	11	7	41.9	28.2	3	36.6	32	3
1,4-Dichlorobenzene	7,500	50	5	7	79.7	1.0	3	26.5	68	3
Hexachloroethane	3,000	51	3	7	64.9	2.0	3	20.3	90	3
Nitrobenzene	2,000	80	4	7	79.0	2.3	3	59.4	6	3
Hexachlorobutadiene	500	57	5	7	60	3.3	3	16.6	107	3
2,4-Dinitrotoluene	130	86	6	7	38.5	5.2	3	62.2	6	3
Hexachlorobenzene	130	86	7	7	91.3	0.9	3	75.5	5	3

* 250-mL aliquots of leachate were spiked. Lab 1 spiked at one-half these levels.

** m-Cresol and p-Cresol coelute. Lab 1 and Lab 3 reported o-Cresol and the sum of — and p-Cresol. Lab 2 reported the sum of all three isomers of Cresol.

Data from Reference 12.

TABLE 18

SINGLE-LABORATORY PAH ANALYSIS DATA FROM A REAL SOIL CONTAMINATED WITH CREOSOTE, USING METHOD 3546
(MICROWAVE EXTRACTION)

Compound	Concentration (µg/kg)	RSD (%)	REAC values (µg/kg)
Naphthalene	2,170	12.4	710,000
2-Methylnaphthalene	28,710	3.1	N/R
1-Methylnaphthalene	33,180	2.4	N/R
Biphenyl	13,440	6.0	N/R
2,6-Dimethylnaphthalene	52,990	3.8	N/R
Acenaphthylene	16,320	3.1	21,000
Acenaphthene	801,210	6.0	1,700,000
Fluorene	789,980	3.4	990,000
Phenanthrene	1,627,480	0.7	3,300,000
Anthracene	346,010	4.0	360,000
Benzo(a)anthracene	300,380	2.7	310,000
Fluoranthene	1,331,690	1.6	1,600,000
Pyrene	1,037,710	3.0	1,100,000
Chrysene	293,200	3.4	320,000
Benzo(b)fluoranthene	152,000	3.8	140,000
Benzo(k)fluoranthene	127,740	3.6	130,000
Benzo(e)pyrene	87,610	3.9	N/R
Benzo(a)pyrene	128,330	3.9	110,000
Perylene	35,260	4.3	N/R
Indeno(123-cd)pyrene	63,900	5.0	25,000
Dibenz(a,h)anthracene	17,290	6.9	N/R
Benzo(ghi)perylene	42,720	6.9	20,000

*n = 4

Soil samples obtained from US EPA Emergency Response Center archive bank through their contract laboratory REAC (Edison, NJ). The standard Soxhlet extraction procedures were performed by REAC three years earlier; this long storage period is believed to account for the low naphthalene recovery data in the present study

REAC data labeled N/R = not reported

TABLE 19

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-5 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	250	180 - 320	76
Acenaphthylene	150	*	107
Acenaphthene	230	130 - 330	61
Fluorene	400	300 - 500	63
Phenanthrene	5,200	4,200 - 6,200	72
Anthracene	380	230 - 530	84
Fluoranthene	8,400	5,800 - 10,000	81
Pyrene	5,800	4,000 - 7,600	69
Benzo(a)anthracene	2,900	1,700 - 4,100	53
Chrysene	2,800	1,900 - 3,700	76
Benzo(b)fluoranthene	2,000	1,000 - 3,000	84
Benzo(k)fluoranthene	1,000	600 - 1,400	137
Benzo(a)pyrene	1,700	900 - 2,500	52
Indeno(123-cd) pyrene	1,300	600 - 2,000	63
Dibenz(a,h)anthracene	200	100 - 300	125
Benzo(ghi)perylene	1,300	1000 - 1600	64

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 20

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-4 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	150	*	54
Acenaphthylene	150	*	82
Acenaphthene	150	*	63
Fluorene	150	*	81
Phenanthrene	680	600 - 760	81
Anthracene	140	70 - 210	108
Fluoranthene	1250	1,150 - 1,350	84
Pyrene	940	820 - 1,060	85
Benzo(a)anthracene	530	470 - 580	78
Chrysene	650	570 - 730	84
Benzo(b)fluoranthene	700	550 - 850	84
Benzo(k)fluoranthene	360	310 - 410	156
Benzo(a)pyrene	650	570 - 730	73
Indeno(123-cd) pyrene	510	360 - 660	88
Dibenz(a,h)anthracene	120	70 - 170	117
Benzo(ghi)perylene	580	360 - 800	91

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 21

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-3 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	9,000	8300 - 9,700	61
Acenaphthylene	300	200 - 400	199
Acenaphthene	4,500	3,000 - 6,000	80
Fluorene	13,300	10,200 -16,400	58
Phenanthrene	85,000	65000 -105,000	87
Anthracene	13,400	12,900 -13,900	48
Fluoranthene	60,000	51,000-69,000	91
Pyrene	39,000	30,000-48,000	86
Benzo(a)anthracene	14,600	12,600-16,600	78
Chrysene	14,100	12,100-16,100	91
Benzo(b)fluoranthene	7,700	6,500-8,900	101
Benzo(k)fluoranthene	2,800	800-4,800	275
Benzo(a)pyrene	7,400	3,000-7,000	74
Indeno(123-cd)pyrene	5,400	4,100-6,700	100
Dibenz(a,h)anthracene	1,300	800-1,800	118
Benzo(ghi)perylene	5,000	3,000-7,000	99

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 22

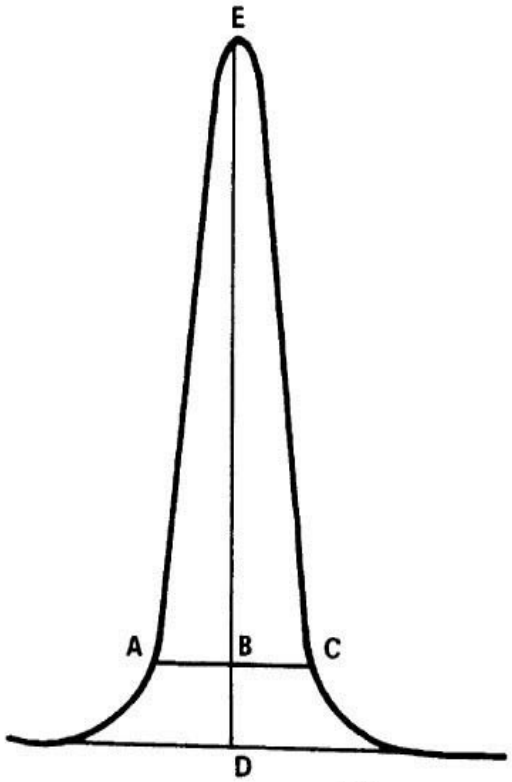
SINGLE-LABORATORY PAH RECOVERY DATA FROM SRM 1941 MARINE SEDIMENT, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Recovery (%)
Naphthalene	1010	97.4
Fluorene	100	100.0
Phenanthrene	490	102.0
Fluoranthene	980	116.7
Pyrene	810	97.3
Benz(a)anthracene	430	89.8
Chrysene	380	130.3
Benzo(b)fluoranthene	740	95.8
Benzo(k)fluoranthene	360	130.2
Benz(e)pyrene	550	81.0
Benzo(a)pyrene	630	76.0
Perylene	450	72.4
Indeno(123-cd)pyrene	500	126.0
Dibenz(a,h)anthracene	110	78.7
Benz(ghi)perylene	530	85.2

n = 3

All RSDs < 10%

FIGURE 1
TAILING FACTOR CALCULATION

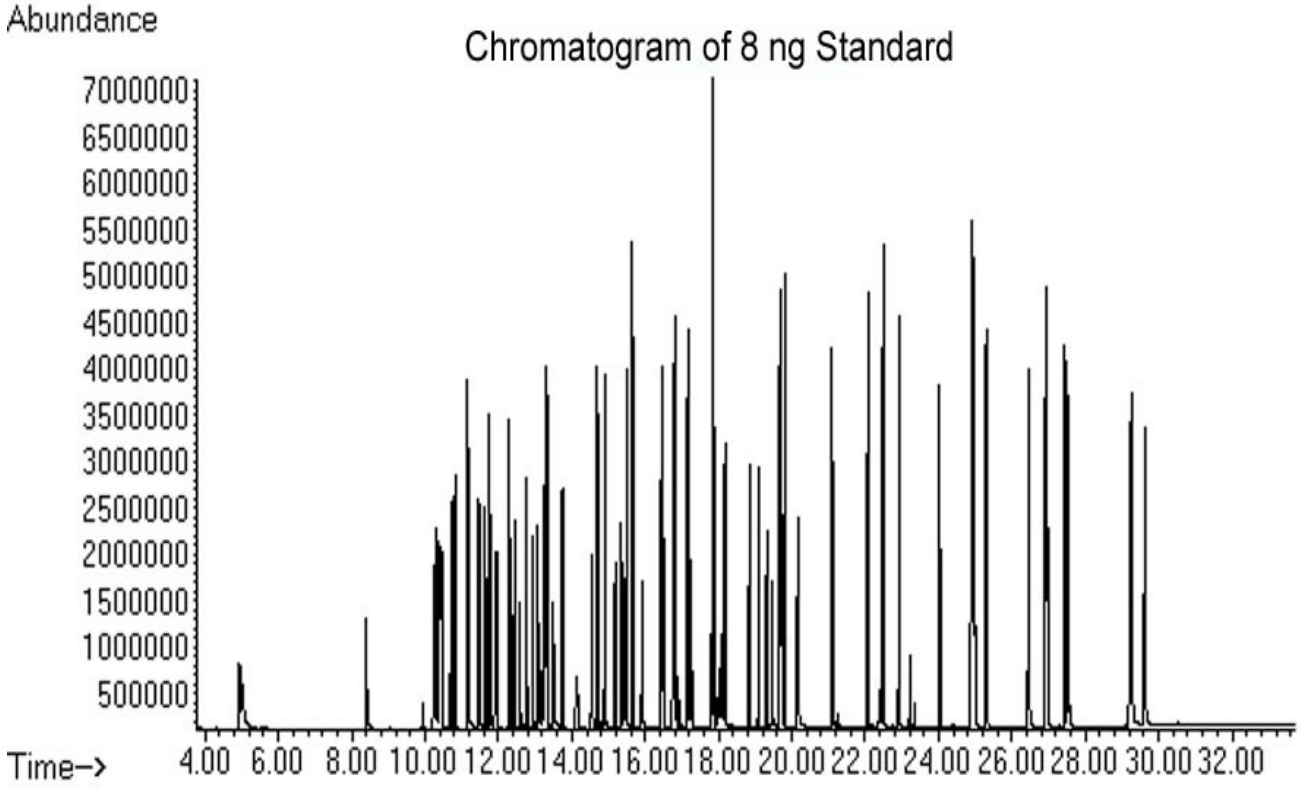


$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

FIGURE 2
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



No. L-9

Semivolatile Organics SIM

SW-846 Method 8270D

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following RCRA analytes have been determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	39638-32-9	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS	ND	ND	ND	X
Captan	133-06-2	HS	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Chrysene	218-01-9	X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (*cis* or *trans*)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC, OE	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW, OS	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dimethoate	60-51-5	HE, HS	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP, HS	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW, CP	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE, OS	ND	ND	ND	LR
4,4'-Methylenebis(*N*,*N*-dimethyl-aniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE, HS	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DC	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-*o*-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-*n*-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-*n*-propylamine	621-64-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS	ND	ND	ND	X
Phosmet	732-11-6	HS	ND	ND	ND	X
Phosphamidon	13171-21-6	HE	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP, HE	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Resorcinol	108-46-3	DC, OE	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW, OS	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-*p*-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,*O*,*O*-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient.
HE = Hydrolysis during extraction accelerated by acidic or basic conditions.
HS = Hydrolysis during storage potential.
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions.
OS = Oxidation during storage potential.
X = Historically, adequate recovery can be obtained by this technique. However, actual recoveries may vary depending on the extraction efficiency, the number of constituents being analyzed concurrently, and the analytical instrumentation.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3535 describes a solid-phase extraction procedure that may be applied to the extraction of semivolatiles from TCLP leachates (see Tables 16 and 17 of this method for performance data). Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (see Table 11 of this method for surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (see Table 12 of this method for performance data), Method 3561 describes a supercritical fluid device for the extraction of PAHs from solids (see Tables 13, 14, and 15 of this method for performance data), and Method 3546 provides an extraction procedure employing commercially available microwave equipment to extract semivolatiles while using less solvent and taking less time than procedures such as a Soxhlet extraction (see Tables 19 through 23 of this method for the applicable performance data). (The tabulated data are provided for guidance purposes only.)

1.3 This method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride (or other suitable solvents provided that the desired performance data can be generated) and are capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic

nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 may be appropriate for confirmation of the identification of these analytes when concentration in the extract permits. Refer to Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected to be present.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. For this reason, it is acceptable to report the combined result for n-nitrosodiphenylamine and diphenylamine for either of these compounds as a combined concentration.

1.4.6 1,2-Diphenylhydrazine is unstable even at room temperature and readily converts to azobenzene. Given the stability problems, it would be acceptable to calibrate for 1,2-diphenylhydrazine using azobenzene. Under these poor compound separation circumstances the results for either of these compounds should be reported as a combined concentration.

1.4.7 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.8 Pyridine may perform poorly at the GC injection port temperatures listed in this method. Lowering the injection port temperature may reduce the amount of degradation. However, the analyst must use caution in modifying the injection port temperature, as the performance of other analytes may be adversely affected. Therefore, if pyridine is to be determined in addition to other target analytes, it may be necessary to perform separate analyses. In addition, pyridine may be lost during the evaporative concentration of the sample extract. As a result, many of the extraction methods listed above may yield low recoveries unless great care is exercised during the concentration steps. For this reason, analysts may wish to consider the use of extraction techniques such as pressurized fluid extraction (Method 3545), microwave extraction (Method 3546),

or supercritical fluid extraction, which involve smaller extract volumes, thereby reducing or eliminating the need for evaporative concentration techniques for many applications.

1.4.9 Toluene diisocyanate rapidly hydrolyzes in water (half-life of less than 30 min). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.10 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The lower limits of quantitation for this method when determining an individual compound are approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). Lower limits of quantitation will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector. The lower limits of quantitation listed in Table 2 are provided for guidance and may not always be achievable.

1.6 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.7 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) equipped with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is

accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

2.4 This method includes specific calibration and quality control steps that supersede the general recommendations provided in Method 8000.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to Method 8000 for a discussion of interferences.

4.2 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph/mass spectrometer system

6.1.1 Gas chromatograph -- An analytical system equipped with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.1.2 Column -- 30-m x 0.25-mm ID (or 0.32-mm ID) 0.25, 0.5, or 1-µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent). The columns listed in this section were the columns used in developing the method. The listing of these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use these columns or other capillary columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.1.3 Mass spectrometer

6.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria as outlined in Sec. 11.3.1.

6.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria as outlined in Sec. 11.3.1

6.1.4 GC/MS interface -- Any GC-to-MS interface may be used that gives acceptable calibration points for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

6.1.5 Data system -- A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

6.1.6 Guard column (optional) -- (J&W deactivated fused-silica, 0.25-mm ID x 6-m, or equivalent) between the injection port and the analytical column joined with column connectors (Agilent Catalog No. 5062-3556, or equivalent).

6.2 Syringe -- 10-µL.

6.3 Volumetric flasks, Class A -- Appropriate sizes equipped with ground-glass stoppers.

6.4 Balance -- Analytical, capable of weighing 0.0001 g.

6.5 Bottles -- Glass equipped with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water.

7.3 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.4 Stock standard solutions (1000 mg/L) -- Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.4.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.2 Transfer the stock standard solutions into bottles equipped with PTFE-lined screw-caps. Store, protected from light, at #6 EC or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.4.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.4.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

7.4.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

7.5 Internal standard solutions -- The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the criteria in Sec. 11.3.2 are met.

7.5.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1-mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store away from any light source at #6 EC when not in use (-10 EC is recommended). When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.5.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

7.6 GC/MS tuning standard -- A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Alternate concentrations may be used to compensate for different injection volumes if the total amount injected is 50 ng or less. Store away from any light source at #6 EC when not in use (-10 EC is recommended). If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.7 Calibration standards -- A minimum of five calibration standards should be prepared at different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard and/or series of calibration standards prepared at a given concentration should contain all the desired project-specific target analytes for which quantitation and quantitative results are to be reported by this method.

7.7.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

7.7.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored away from any light source at #6 EC when not in use (-10 EC is recommended), and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration

verification standard should be prepared, as necessary, and stored at #6 EC. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.8 Surrogate standards -- The recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

NOTE: In the presence of samples containing residual chlorine, phenol-d_6 has been known to react to form chlorinated phenolic compounds that are not detected as the original spiked surrogate. Sample preservation precautions outlined in Chapter Four should be used when residual chlorine is known to be present in order to minimize degradation of deuterated phenols or any other susceptible target analyte.

7.8.1 Surrogate standard check -- Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

7.8.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute surrogate solution may be necessary.

7.9 Matrix spike and laboratory control standards -- See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS) and the spiking solution should be the same source as used for the initial calibration standards to restrict the influence of standard accuracy on the determination of recovery through preparation and analysis.

7.9.1 Matrix spike check -- Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

7.9.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute matrix and LCS spiking solution may be necessary.

7.9.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

7.10 Solvents -- Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents. All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Store the sample extracts at #6 EC, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 or 5000 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 5000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, discussions regarding the instrument QC requirements listed below can be found in the referenced sections of this method:

- The GC/MS must be tuned to meet the recommended DFTPP criteria prior to the initial calibration and for each 12-hr period during which analyses are performed. See Secs. 11.3.1 and 11.4.1 for further details.

- There must be an initial calibration of the GC/MS system as described in Sec. 11.3. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards). The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

- The GC/MS system must meet the calibration verification acceptance criteria in Sec. 11.4, each 12 hrs.

- The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 11.6.1.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, a method blank must be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the lab should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for

evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. When any changes are made to the system (e.g., the column is changed, a septum is changed), see the guidance in Method 8000 regarding whether recalibration of the system must take place.

9.9 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec 11.3 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample preparation

11.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air (particulates and sorbent resin)	3542
Water (including TCLP leachates)	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3546, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3546, 3550, 3560, 3561, 3580

11.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The quantitation limit is very high (approximately 10,000 µg/L). Therefore, it is only appropriate where concentrations in excess of 10,000 µg/L are expected.

11.2 Extract cleanup -- Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of Interest	Methods
Aniline and aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides	3610, 3620, 3630, 3640, 3660
PCBs	3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique and a GC/ECD analysis, if interferences are encountered on GC/FID.

11.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	#1 sec/scan
Initial temperature:	40 EC, hold for 4 min
Temperature program:	40-320 EC at 10 EC/min
Final temperature:	320 EC, hold until 2 min after benzo[g,h,i]perylene elutes
Injector temperature:	250-300 EC
Transfer line temperature:	250-300 EC
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

11.3.1 The GC/MS system must be hardware-tuned such that injecting 50 ng or less of DFTPP meets the manufacturer's specified acceptance criteria or as listed in Table 3. The tuning criteria as outlined in Table 3 were developed using quadrupole mass spectrometer instrumentation and it is recognized that other tuning criteria may be more effective depending on the type of instrumentation, e.g., Time-of-Flight, Ion Trap, etc. In

these cases it would be appropriate to follow the manufacturer's tuning instructions or some other consistent tuning criteria. However, no matter which tuning criteria is selected, the system calibration must not begin until the tuning acceptance criteria are met with the sample analyses performed under the same conditions as the calibration standards.

11.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach should be used: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or any other discrete peak that does not coelute with DFTPP.

11.3.1.2 Use the DFTPP mass intensity criteria in the manufacturer's instructions as primary tuning acceptance criteria or those in Table 3 as default tuning acceptance criteria if the primary tuning criteria are not available. Alternatively, other documented tuning criteria may be used (e.g. CLP, or Method 625), provided that method performance is not adversely affected. The analyst is always free to choose criteria that are tighter than those included in this method or to use other documented criteria provided they are used consistently throughout the initial calibration, calibration verification, and sample analyses.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

11.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. (See Method 8081 for the percent breakdown calculation.) Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2 given by the following equation:

$$\text{TailingFactor} = \frac{BC}{AB}$$

Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and B is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. (See Figure 1 for an example tailing factor calculation.)

11.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6 to12 in. of the capillary column. The use of a guard column (Sec. 6.1.6) between the injection port and the analytical column may help prolong analytical column performance life.

11.3.2 The internal standards selected in Sec. 7.5 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (e.g., for 1,4-dichlorobenzene-d_4, use m/z 150 for quantitation).

11.3.3 Analyze 1-2 µL of each calibration standard (containing the compounds for quantitation and the appropriate surrogates and internal standards) and tabulate the area of the primary ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 7.7 and Method 8000). Alternate injection volumes may be used if the applicable quality control requirements for using this method are met. The injection volume must be the same for all standards and sample extracts. Figure 2 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

11.3.4 Initial calibration calculations

Calculate response factors (RFs) for each target analyte relative to one of the internal standards (see Table 5) as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

11.3.4.1 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte using the following equations. The RSD should be less than or equal to 20% for each target analyte. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 4, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criteria. For these occasions, it is acknowledged that the failing compounds may not be critical to the specific project and therefore they may be used as qualified data or estimated values for screening purposes. The analyst should also strive to place more emphasis on meeting the calibration criteria for those compounds that are critical project compounds, rather than meeting the criteria for those less important compounds.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
RF = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

11.3.4.2 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 11.3.

11.3.5 Evaluation of retention times -- The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.6 Linearity of target analytes -- If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 11.7.2).

11.3.6.1 If the RSD of any target analyte is greater than 20%, refer to Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed. The average RF should not be used for compounds that have an RSD greater than 20% unless the concentration is reported as estimated.

11.3.6.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

11.3.6.3 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet either the 20% RSD, minimum correlation coefficient criteria (0.99), or the acceptance criteria for alternative calibration procedures in Method 8000. Any calibration method described in Method 8000 may be used, but it should be used consistently. It is considered inappropriate once the calibration analyses are completed to select an alternative calibration procedure in order to pass the recommended criteria on a case-by-case basis. If compounds fail to meet these criteria, the associated concentrations may still be determined but they must be reported as estimated. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit.

11.4 GC/MS calibration verification -- Calibration verification consists of three steps that are performed at the beginning of each 12-hr analytical shift.

11.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng or less of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria as outlined in Sec. 11.3.1 before sample analysis begins. These criteria must be demonstrated each 12-hr shift during which samples are analyzed.

11.4.2 The initial calibration function for each target analyte should be checked immediately after the first occurrence in the region of the middle of the calibration range with a standard from a source different from that used for the initial calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

11.4.3 The initial calibration (Sec. 11.3) for each compound of interest should be verified once every 12 hrs prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard (containing all the compounds for quantitation) at a concentration either near the midpoint concentration for the calibrating range of the GC/MS or near the action level for the project. The results must be compared against the most recent initial calibration curve and should meet the verification acceptance criteria provided in Secs. 11.4.5 through 11.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.4.4 A method blank should be analyzed prior to sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Method 8000 for information regarding method blank performance criteria.

11.4.5 Calibration verification standard criteria

11.4.5.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 4. This criteria is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

11.4.5.2 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.4.5.3 All target compounds of interest must be evaluated using a 20% criterion. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Method 8000 for guidance on calculating percent difference and drift.

11.4.5.4 If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

11.4.5.5 Problems similar to those listed under initial calibration could affect the ability to pass the calibration verification standard analysis. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

11.4.5.6 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000 for additional details). It is not necessary to re-analyze a low concentration standard, rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives and for those situations the minimum quantitation check criteria should be outlined in a laboratory standard operating procedure, or a project-specific Quality Assurance Project Plan. Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered "out of control" and corrective action such as redefining the lower limit of quantitation

and/or reporting those "out of control" target analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

11.4.6 Internal standard retention time -- The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.4.7 Internal standard response -- If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.5 GC/MS analysis of samples

11.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

11.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1 mL of concentrated sample extract obtained from sample preparation.

11.5.3 Inject an aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 11.3). The volume to be injected should include an appropriate concentration that is within the calibration range of base/neutral and acid surrogates using the surrogate solution as noted in Sec. 7.8. The injection volume must be the same volume that was used for the calibration standards.

11.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard solution must be added to the diluted extract to maintain the same concentration as in the calibration standards (usually 40 ng/µL, or other concentrations as appropriate, if a more sensitive GC/MS system is being used). Secondary ion quantitation should be used only when there are sample interferences with the primary ion.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times in all samples, spikes, blanks, and standards to effectively check drifting, method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance. Internal standard responses (area counts) must be monitored in all samples, spikes, blanks for similar reasons. If the EICP area for any of the internal standards in samples, spikes and blanks changes by a factor of two (-50% to +100%) from the areas determined in the continuing calibration analyzed that day, corrective action must be taken. The samples, spikes or blanks should be reanalyzed or the data should be qualified.

11.5.4.1 When ions from a compound in the sample saturate the detector, this analysis should be followed by the analysis of an instrument blank consisting of clean solvent. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences. Contamination from one sample to the next on the instrument usually takes place in the syringe. If adequate syringe washes are employed, then carryover from high concentration samples can usually be avoided.

11.5.4.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

11.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electron impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Using the primary ion for quantitation and the secondary ions for confirmation set up the collection groups based on their retention times. The selected ions are nominal ions and most compounds have small mass defect, usually less than 0.2 amu, in their spectra. These mass defects should be used in the acquisition table. The dwell time may be automatically calculated by the laboratory's GC/MS software or manually calculated using the following formula. The total scan time should be less than 1,000 msec and produce at least 5 to 10 scans per chromatographic peak. The start and stop times for the SIM groups are determined from the full scan analysis using the formula below:

$$\text{Dwell Time for the Group} = \frac{\text{Scan Time (msec)}}{\text{Total Ions in the Group}}$$

Additional guidance for performing SIM analyses, in particular for PAHs and phenol target analyte compounds, can be found in the most recent CLP semivolatile organic methods statement of work (SOW). See the SIM sections from the following CLP SOW for further details: EPA CLP Organics SOW. (Reference 14)

11.6 Analyte identification

11.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

11.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the

target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

11.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.) Use professional judgement in interpretation where interferences are observed.

11.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

11.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

11.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.7 Quantitation

11.7.1 Once a target compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

11.7.1.1 It is highly recommended to use the integration produced by the software if the integration is correct because the software should produce more consistent integrations. However, manual integrations may be necessary when the software does not produce proper integrations because baseline selection is improper; the correct peak is missed; a coelution is integrated; the peak is partially integrated; etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

11.7.1.2 Manual integrations should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates, integration parameter files, etc). The analyst should seek to minimize manual integration by properly maintaining the instrument, updating retention times, and configuring peak integration parameters.

11.7.2 If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 11.3.4). See Method 8000 for the equations describing internal standard calibration and either linear or non-linear calibrations.

11.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 11.6.2) should be estimated. The same formula as in Sec. 11.3.4 should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

11.7.4 The resulting concentration should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

11.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, for example by using Methods 8081 or 8082. However, this method (8270) may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

11.7.6 Quantitation of multicomponent parameters such as diesel range organics (DROs) and total petroleum hydrocarbons (TPH) using the Method 8270 recommended internal standard quantitation technique is beyond the scope of this method. Typically,

analyses for these parameters are performed using GC/FID or GC with a MS detector capability that is available with Method 8015.

11.7.7 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.7 and Method 8000 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Single laboratory initial demonstration of capability data were generated from five replicate measurements using a modified continuous liquid-liquid extractor (Method 3520) with hydrophobic membrane. In this case only a single acid pH extraction was performed using the CLP calibration criteria and the applicable CLP target analytes. These data are presented in Table 6. Laboratories should generate their own acceptance criteria depending on the extraction and instrument conditions. (See Method 8000.)

13.3 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 7. These data are provided for guidance purposes only.

13.4 Method performance data using Method 3541 (automated Soxhlet extraction) are presented in Tables 8 and 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three extractions were performed and each extract was analyzed by gas chromatography/mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data as listed were taken from Reference 7 and are provided for guidance purposes only.

13.5 Surrogate precision and accuracy data are presented in Table 10 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by this method (8270). These data are provided for guidance purposes only.

13.6 Single laboratory precision and bias data using Method 3545 (pressurized fluid extraction) for semivolatile organic compounds are presented in Table 11. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by the Perstorp Environmental Soxtec™ (automated Soxhlet). The data in Table 11 represent seven replicate extractions and analyses for each individual sample and were taken from Reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low - 101.2%, mid - 97.2% and high - 99.2%. These data are provided for guidance purposes only.

13.7 Single laboratory precision and bias data using Method 3561 (SFE extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (EC-1, a lake sediment from Environment Canada and HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 12 and 13 and were taken from Reference 10. These data are provided for guidance purposes only.

13.8 Single laboratory precision and accuracy data using Method 3561 (SFE extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. The instrument conditions that were utilized to extract a 3.4 g sample were as follows: Pressure -- 300 atm; time -- 60 min.; extraction fluid -- CO_2; modifier -- 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature -- 80 EC; Restrictor temperature -- 120 EC; and, trapping fluid -- chloroform (methylene chloride has also been used). The data are found in Table 14 and were taken from Reference 11. These data are provided for guidance purposes only.

13.9 Tables 15 and 16 contain single-laboratory precision and accuracy data for solid-phase extraction of TCLP buffer solutions spiked at two levels and extracted using Method 3535. These data are provided for guidance purposes only.

13.10 Table 17 contains multiple-laboratory data for solid-phase extraction of spiked TCLP soil leachates extracted using Method 3535. These data are provided for guidance purposes only.

13.11 Tables 18 through 22 contain single-laboratory PAH recovery data for microwave extraction of contaminated soils and standard reference materials using Method 3546. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS IN APPROXIMATE RETENTION TIME ORDER [a]

Compound	Primary Ion	Secondary Ion(s)
2-Picoline	93	66,92
Aniline	93	66,65
Phenol	94	65,66
Bis(2-chloroethyl) ether	93	63,95
2-Chlorophenol	128	64,130
1,3-Dichlorobenzene	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	152	150,115
1,4-Dichlorobenzene	146	148,111
Benzyl alcohol	108	79,77
1,2-Dichlorobenzene	146	148,111
N-Nitrosomethylethylamine	88	42,43,56
Bis(2-chloroisopropyl) ether	45	77,121
Ethyl carbamate	62	44,45,74
Thiophenol (Benzenethiol)	110	66,109,84
Methyl methanesulfonate	80	79,65,95
N-Nitrosodi-n-propylamine	70	42,101,130
Hexachloroethane	117	201,199
Maleic anhydride	54	98,53,44
Nitrobenzene	77	123,65
Isophorone	82	95,138
N-Nitrosodiethylamine	102	42,57,44,56
2-Nitrophenol	139	109,65
2,4-Dimethylphenol	122	107,121
p-Benzoquinone	108	54,82,80
Bis(2-chloroethoxy)methane	93	95,123
Benzoic acid	122	105,77
2,4-Dichlorophenol	162	164,98
Trimethyl phosphate	110	79,95,109,140
Ethyl methanesulfonate	79	109,97,45,65
1,2,4-Trichlorobenzene	180	182,145
Naphthalene-d_8 (IS)	136	68
Naphthalene	128	129,127
Hexachlorobutadiene	225	223,227
Tetraethyl pyrophosphate	99	155,127,81,109
Diethyl sulfate	139	45,59,99,111,125
4-Chloro-3-methylphenol	107	144,142
2-Methylnaphthalene	142	141
2-Methylphenol	107	108,77,79,90
Hexachloropropene	213	211,215,117,106,141
Hexachlorocyclopentadiene	237	235,272
N-Nitrosopyrrolidine	100	41,42,68,69
Acetophenone	105	71,51,120
3/4-Methylphenol[b]	107	108,77,79,90

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
2,4,6-Trichlorophenol	196	198,200
o-Toluidine	106	107,77,51,79
2-Chloronaphthalene	162	127,164
N-Nitrosopiperidine	114	42,55,56,41
1,4-Phenylenediamine	108	80,53,54,52
1-Chloronaphthalene	162	127,164
2-Nitroaniline	65	92,138
5-Chloro-2-methylaniline	106	141,140,77,89
Dimethyl phthalate	163	194,164
Acenaphthylene	152	151,153
2,6-Dinitrotoluene	165	63,89
Phthalic anhydride	104	76,50,148
o-Anisidine	108	80,123,52
3-Nitroaniline	138	108,92
Acenaphthene-d_{10} (IS)	164	162,160
Acenaphthene	154	153,152
2,4-Dinitrophenol	184	63,154
2,6-Dinitrophenol	162	164,126,98,63
4-Chloroaniline	127	129,65,92
Isosafrole	162	131,104,77,51
Dibenzofuran	168	139
2,4-Diaminotoluene	121	122,94,77,104
2,4-Dinitrotoluene	165	63,89
4-Nitrophenol	139	109,65
2-Naphthylamine	143	115,116
1,4-Naphthoquinone	158	104,102,76,50,130
p-Cresidine	122	94,137,77,93
Dichlorovos	109	185,79,145
Diethyl phthalate	149	177,150
Fluorene	166	165,167
2,4,5-Trimethylaniline	120	135,134,91,77
N-Nitrosodi-n-butylamine	84	57,41,116,158
4-Chlorophenyl phenyl ether	204	206,141
Hydroquinone	110	81,53,55
4,6-Dinitro-2-methylphenol	198	51,105
Resorcinol	110	81,82,53,69
N-Nitrosodiphenylamine	169	168,167
Safrole	162	104,77,103,135
Hexamethyl phosphoramide	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	92	127,129,65,39
Diphenylamine	169	168,167
1,2,4,5-Tetrachlorobenzene	216	214,179,108,143,218
1-Naphthylamine	143	115,89,63
1-Acetyl-2-thiourea	118	43,42,76
4-Bromophenyl phenyl ether	248	250,141

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
Toluene diisocyanate	174	145,173,146,132,91
2,4,5-Trichlorophenol	196	198,97,132,99
Hexachlorobenzene	284	142,249
Nicotine	84	133,161,162
Pentachlorophenol	266	264,268
5-Nitro-o-toluidine	152	77,79,106,94
Thionazine	107	96,97,143,79,68
4-Nitroaniline	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	188	94,80
Phenanthrene	178	179,176
Anthracene	178	176,179
1,4-Dinitrobenzene	168	75,50,76,92,122
Mevinphos	127	192,109,67,164
Naled	109	145,147,301,79,189
1,3-Dinitrobenzene	168	76,50,75,92,122
Diallate (cis or trans)	86	234,43,70
1,2-Dinitrobenzene	168	50,63,74
Diallate (trans or cis)	86	234,43,70
Pentachlorobenzene	250	252,108,248,215,254
5-Nitro-o-anisidine	168	79,52,138,153,77
Pentachloronitrobenzene	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	174	101,128,75,116
Di-n-butyl phthalate	149	150,104
2,3,4,6-Tetrachlorophenol	232	131,230,166,234,168
Dihydrosaffrole	135	64,77
Demeton-O	88	89,60,61,115,171
Fluoranthene	202	101,203
1,3,5-Trinitrobenzene	75	74,213,120,91,63
Dicrotophos	127	67,72,109,193,237
Benzidine	184	92,185
Trifluralin	306	43,264,41,290
Bromoxynil	277	279,88,275,168
Pyrene	202	200,203
Monocrotophos	127	192,67,97,109
Phorate	75	121,97,93,260
Sulfallate	188	88,72,60,44
Demeton-S	88	60,81,89,114,115
Phenacetin	108	180,179,109,137,80
Dimethoate	87	93,125,143,229
Phenobarbital	204	117,232,146,161
Carbofuran	164	149,131,122
Octamethyl pyrophosphoramide	135	44,199,286,153,243
4-Aminobiphenyl	169	168,170,115
Dioxathion	97	125,270,153
Terbufos	231	57,97,153,103

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
α,α-Dimethylphenylamine	58	91,65,134,42
Pronamide	173	175,145,109,147
Aminoazobenzene	197	92,120,65,77
Dichlone	191	163,226,228,135,193
Dinoseb	211	163,147,117,240
Disulfoton	88	97,89,142,186
Fluchloralin	306	63,326,328,264,65
Mexacarbate	165	150,134,164,222
4,4'-Oxydianiline	200	108,171,80,65
Butyl benzyl phthalate	149	91,206
4-Nitrobiphenyl	199	152,141,169,151
Phosphamidon	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	231	185,41,193,266
Methyl parathion	109	125,263,79,93
Carbaryl	144	115,116,201
Dimethylaminoazobenzene	225	120,77,105,148,42
Propylthiouracil	170	142,114,83
Benz(a)anthracene	228	229,226
Chrysene-d_{12} (IS)	240	120,236
3,3'-Dichlorobenzidine	252	254,126
Chrysene	228	226,229
Malathion	173	125,127,93,158
Kepone	272	274,237,178,143,270
Fenthion	278	125,109,169,153
Parathion	109	97,291,139,155
Anilazine	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	149	167,279
3,3'-Dimethylbenzidine	212	106,196,180
Carbophenothion	157	97,121,342,159,199
5-Nitroacenaphthene	199	152,169,141,115
Methapyrilene	97	50,191,71
Isodrin	193	66,195,263,265,147
Captan	79	149,77,119,117
Chlorfenvinphos	267	269,323,325,295
Crotoxyphos	127	105,193,166
Phosmet	160	77,93,317,76
EPN	157	169,185,141,323
Tetrachlorvinphos	329	109,331,79,333
Di-n-octyl phthalate	149	167,43
2-Aminoanthraquinone	223	167,195
Barban	222	51,87,224,257,153
Aramite	185	191,319,334,197,321
Benzo(b)fluoranthene	252	253,125
Nitrofen	283	285,202,139,253
Benzo(k)fluoranthene	252	253,125

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
Chlorobenzilate	251	139,253,111,141
Fensulfothion	293	97,308,125,292
Ethion	231	97,153,125,121
Diethylstilbestrol	268	145,107,239,121,159
Famphur	218	125,93,109,217
Tri-p-tolyl phosphate[c]	368	367,107,165,198
Benzo(a)pyrene	252	253,125
Perylene-d_{12} (IS)	264	260,265
7,12-Dimethylbenz(a)anthracene	256	241,239,120
5,5-Diphenylhydantoin	180	104,252,223,209
Captafol	79	77,80,107
Dinocap	69	41,39
Methoxychlor	227	228,152,114,274,212
2-Acetylaminofluorene	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	231	266,268,140,195
3,3'-Dimethoxybenzidine	244	201,229
3-Methylcholanthrene	268	252,253,126,134,113
Phosalone	182	184,367,121,379
Azinphos-methyl	160	132,93,104,105
Leptophos	171	377,375,77,155,379
Mirex	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	201	137,119,217,219,199
Dibenz(a,j)acridine	279	280,277,250
Mestranol	277	310,174,147,242
Coumaphos	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	276	138,277
Dibenz(a,h)anthracene	278	139,279
Benzo(g,h,i)perylene	276	138,277
1,2:4,5-Dibenzopyrene	302	151,150,300
Strychnine	334	334,335,333
Piperonyl sulfoxide	162	135,105,77
Hexachlorophene	196	198,209,211,406,408
Aldrin	66	263,220
Aroclor 1016	222	260,292
Aroclor 1221	190	224,260
Aroclor 1232	190	224,260
Aroclor 1242	222	256,292
Aroclor 1248	292	362,326
Aroclor 1254	292	362,326
Aroclor 1260	360	362,394
α-BHC	183	181,109
β-BHC	181	183,109
δ-BHC	183	181,109
γ-BHC (Lindane)	183	181,109
4,4'-DDD	235	237,165

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
4,4'-DDE	246	248,176
4,4'-DDT	235	237,165
Dieldrin	79	263,279
1,2-Diphenylhydrazine	77	105,182
Endosulfan I	195	339,341
Endosulfan II	337	339,341
Endosulfan sulfate	272	387,422
Endrin	263	82,81
Endrin aldehyde	67	345,250
Endrin ketone	317	67,319
2-Fluorobiphenyl (surr)	172	171
2-Fluorophenol (surr)	112	64
Heptachlor	100	272,274
Heptachlor epoxide	353	355,351
Nitrobenzene-d_5 (surr)	82	128,54
N-Nitrosodimethylamine	42	74,44
Phenol-d_6 (surr)	99	42,71
Terphenyl-d_{14} (surr)	244	122,212
2,4,6-Tribromophenol (surr)	330	332,141
Toxaphene	159	231,233

IS = internal standard
surr = surrogate
[a] The data presented are representative of DB-5 type analytical columns
[b] Compounds cannot be separated for quantitation
[c] Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

EXAMPLE LOWER LIMITS OF QUANTITATION FOR SEMIVOLATILE ORGANICS

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-Methylcholanthrene	10	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND

TABLE 2
(continued)

[a] Sample lower limits of quantitation are highly matrix-dependent and those listed here are provided for guidance and may not always be achievable.

[b] Lower limits of quantitation listed for soil/sediment are based on wet weight. When data are reported on a dry weight basis, the lower limits will be higher based on the % dry weight of each sample. These lower limits are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined

NA = Not Applicable

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c]Lower limit of quantitation = (Lower limit of quantitation for low soil/sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	10-80% of Base Peak
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of Base Peak
197	< 2% of mass 198
198	Base peak, or > 50% of Mass 442
199	5-9% of mass 198
275	10-60% of Base Peak
365	> 1% of mass 198
441	present but < 24% of mass 442
442	Base Peak, or > 50% of mass 198
443	15-24% of mass 442

[a] The majority of the data are taken from Reference 13 (Method 525.2).

[b] The criteria in this table are intended to be used as default criteria for quadrupole instrumentation if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected. See Sec. 11.3.1

TABLE 4

RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION USING THE SUGGESTED IONS FROM TABLE 1

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-	Dimethyl phthalate
Ethyl methanesulfonate	phenethylamine	2,4-Dinitrophenol
2-Fluorophenol (surr)	2,4-Dimethylphenol	2,4-Dinitrotoluene
Hexachloroethane	Hexachlorobutadiene	2,6-Dinitrotoluene
Methyl methanesulfonate	Isophorone	Fluorene
2-Methylphenol	2-Methylnaphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Naphthalene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene	1-Naphthylamine
N-Nitroso-di-n-propylamine	Nitrobenzene-d_8 (surr)	2-Naphthylamine
Phenol	2-Nitrophenol	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosodi-n-butylamine	3-Nitroaniline
2-Picoline	N-Nitrosopiperidine	4-Nitroaniline
	1,2,4-Trichlorobenzene	4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
Fluoranthene	p-Dimethyl aminoazobenzene	7,12-Dimethylbenz(a) anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	Indeno(1,2,3-cd) pyrene
Pentachlorophenol		3-Methylcholanthrene
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr) = surrogate

TABLE 6

EXAMPLE SINGLE LABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	x of 5 replicates (µg/L)	% Recovery of Avg.
Acenaphthene	50	46.7	93.4
Acenaphthylene	50	46.1	92.2
Aniline	50	8.3	16.7
Anthracene	50	48.4	96.8
Benzoic acid	50	43.7	87.4
Benz(a)anthracene	50	49.6	99.2
Benzo(b)fluoranthene	50	49.8	99.6
Benzo(k)fluoranthene	50	50.6	101
Benzo(a)pyrene	50	47.7	95.5
Benzo(g,h,i)perylene	50	52.6	105
Benzyl alcohol	50	44.4	88.8
Bis(2-chloroethyl) ether	50	44.2	88.4
Bis(2-chloroethoxy)methane	50	46.6	93.1
Bis(2-chloroisopropyl) ether	50	43.4	86.8
Bis(2-ethylhexyl) phthalate	50	50.2	100
4-Bromophenyl phenyl ether	50	48.6	97.2
Butyl benzyl phthalate	50	49.6	99.3
Carbazole	50	52.1	104
2-Chloroaniline	50	38.9	77.7
4-Chloro-3-methylphenol	50	47.3	94.6
2-Chloronaphthalene	50	45.3	90.8
2-Chlorophenol	50	43.1	86.2
4-Chlorophenyl phenyl ether	50	47.3	94.6
Chrysene	50	50.3	101
Dibenzofuran	50	47.4	94.7
Dibenz(a,h)anthracene	50	51.6	103
Di-n-butyl phthalate	50	50.5	101
1,2-Dichlorobenzene	50	35.8	71.6
1,3-Dichlorobenzene	50	33.3	66.7
1,4-Dichlorobenzene	50	34.4	68.7
3,3'-Dichlorobenzidine	50	32.0	64.0
2,4-Dichlorophenol	50	47.4	94.8
Diethyl phthalate	50	50.0	99.9
Dimethyl phthalate	50	48.5	97.0
2,4-Dimethylphenol	50	31.2	62.3
4,6-Dinitro-2-methylphenol	50	57.6	115
2,4-Dinitrophenol	50	58.7	117
2,4-Dinitrotoluene	50	51.3	103

TABLE 6
(continued)

Compound	Test conc. (µg/L)	x of 5 replicates (µg/L)	% Recovery of Avg.
2,6-Dinitrotoluene	50	50.2	100
Di-n-octyl phthalate	50	51.1	102
Fluoranthene	50	51.0	102
Fluorene	50	48.5	97.0
Hexachlorobenzene	50	49.0	97.9
Hexachlorobutadiene	50	34.7	69.5
Hexachlorocyclopentadiene	50	1.9	3.8
Hexachloroethane	50	29.9	58.8
Indeno(1,2,3-cd)pyrene	50	51.7	103
Isophorone	50	47.1	94.3
2-Methylnaphthalene	50	44.7	89.4
2-Methylphenol	50	41.7	83.4
4-Methylphenol	50	42.6	85.2
Naphthalene	50	43.4	86.8
2-Nitroaniline	50	48.4	96.7
3-Nitroaniline	50	46.8	93.6
4-Nitroaniline	50	56.1	112
Nitrobenzene	50	47.1	94.1
2-Nitrophenol	50	47.3	94.6
4-Nitrophenol	50	55.4	111
N-Nitrosodiphenylamine	50	46.7	93.4
N-Nitroso-di-propylamine	50	44.6	89.3
Pentachlorophenol	50	56.9	114
Phenanthrene	50	49.7	99.4
Phenol	50	40.9	81.8
Pyrene	50	49.2	98.4
1,2,4-Trichlorobenzene	50	39.1	78.2
2,4,5-Trichlorophenol	50	47.7	95.4
2,4,6-Trichlorophenol	50	49.2	98.4

x = Average recovery for five initial demonstration of capability measurements, in µg/L

[a] Extraction using acidic pH only with a modified continuous liquid-liquid extractor with hydrophobic membrane according to Method 3520. These values are for guidance only. Appropriate derivation of acceptance criteria for similar extraction conditions may result in much different recovery ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

	Percent Recovery, Day 0		Percent Recovery, Day 7	
Compound	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 8

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANIC FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

	Clay Soil		Topsoil	
Compound	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 9

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8

Compound	Mean Recovery	RSD
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenz(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 10

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	% RSD
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 10 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 11

PRESSURIZED FLUID EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

	Clay			Loam			Sand			Mean
Compound	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	102.0
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	101.9
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	101.6
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	120.6
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	119.2
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	112.5
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	104.7
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	100.2
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	110.3
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	98.1
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	118.6
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	100.2
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	101.7
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	109.8
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	96.3
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	97.2
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	98.6
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	104.2
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	106.1
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	108.1
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	104.7
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	99.7
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	102.1
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	75.8
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	95.9
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	94.1
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	96.2
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	92.6
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	90.3
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	101.7
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	92.9
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	98.4
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	75.6
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	90.7

TABLE 11
(continued)

Compound	Clay			Loam			Sand			Mean
	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	98.8
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	94.4
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	95.4
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	99.1
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	96.8
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	95.8
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	93.7
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	81.2
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	100.6
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	101.2
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	99.1
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	102.7
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	105.2
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	116.5
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	101.5
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	102.9
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	99.0
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	103.1
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	99.9
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	102.7
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	98.6
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	66.4
Mean	95.1	94.3	101.0	95.5	96.5	104.1	113.0	100.9	92.5	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 12

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4 ± 8.2	29.55	91	10.5
2-Methylnaphthalene	62.1 ± 11.5	76.13	122	2.0
Acenaphthene	632 ± 105	577.28	91	2.9
Dibenzofuran	307 ± 49	302.25	98	4.1
Fluorene	492 ± 78	427.15	87	3.0
Phenanthrene	1618 ± 340	1278.03	79	3.4
Anthracene	422 ± 49	400.80	95	2.6
Fluoranthene	1280 ± 220	1019.13	80	4.5
Pyrene	1033 ± 285	911.82	88	3.1
Benz(a)anthracene	252 ± 8	225.50	89	4.8
Chrysene	297 ± 26	283.00	95	3.8
Benzo(a)pyrene	97.2 ± 17.1	58.28	60	6.5
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153 ± 22	130.88	86	10.7

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

TABLE 15

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS LOW SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	3,750	63	10	63	9
Hexachloroethane	1,500	55	6	77	4
Nitrobenzene	1,000	82	10	100	5
Hexachlorobutadiene	250	65	3	56	4
2,4-Dinitrotoluene	65	89	4	101	5
Hexachlorobenzene	65	98	5	95	6
o-Cresol	100,000	83	10	85	5
m-Cresol*	100,000	86	8	85	3
p-Cresol*	100,000	*	*	*	*
2,4,6-Trichlorophenol	1,000	84	12	95	12
2,4,5-Trichlorophenol	200,000	83	11	88	3
Pentachlorophenol	50,000	82	9	78	9

Results from seven replicate spiked buffer samples.

* In this study, m-cresol and p-cresol co-eluted and were quantitated as a mixture of both isomers.

Data from Reference 12.

TABLE 16

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS HIGH SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	15,000	63	10	63	9
Hexachloroethane	6,000	54	7	46	7
Nitrobenzene	4,000	81	4	81	13
Hexachlorobutadiene	1,000	81	5	70	11
2,4-Dinitrotoluene	260	99	8	98	3
Hexachlorobenzene	260	89	8	91	9
o-Cresol*	400,000	92	15	90	4
m-Cresol*	400,000	95	8	82	6
p-Cresol*	400,000	82	14	84	7
2,4,6-Trichlorophenol	4,000	93	12	104	12
2,4,5-Trichlorophenol	800,000	93	14	97	23
Pentachlorophenol	200,000	84	9	73	8

Results from seven replicate spiked buffer samples.

* In this study, recoveries of these compounds were determined from triplicate spikes of the individual compounds into separate buffer solutions.

Data from Reference 12.

TABLE 17

RECOVERY DATA FROM THREE LABORATORIES FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP LEACHATES FROM SOIL SAMPLES

Buffer 1 pH = 2.886		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,000	86	8	7	35.3	0.7	3	7.6	6	3
m-Cresol**	--	77	8	7	--	--	--	--	--	--
p-Cresol**	--	--	--	--	--	--	--	7.7	11	3
2,4,6-Trichlorophenol	2,000	106	6	7	96.3	3.9	3	44.8	5	3
2,4,5-Trichlorophenol	400,000	93	3	7	80.5	4.5	3	63.3	11	3
Pentachlorophenol	100,000	79	2	7	33.8	12.2	3	29.2	13	3
1,4-Dichlorobenzene	7,500	51	5	7	81.3	5.3	3	19.2	7	3
Hexachloroethane	3,000	50	5	7	66.2	2.1	3	12.6	11	3
Nitrobenzene	2,000	80	8	7	76.3	5.3	3	63.9	12	3
Hexachlorobutadiene	500	53	8	7	63.3	4.8	3	9.6	9	3
2,4-Dinitrotoluene	130	89	8	7	35.7	2.6	3	58.2	17	3
Hexachlorobenzene	130	84	21	7	92.3	1.6	3	71.7	9	3

(continued)

TABLE 17
(continued)

Buffer 2 pH = 4.937		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,00	97	13	7	37.8	4.5	3	6.1	24	3
m-Cresol**	--	83	4	7	--	--	--	6.0	25	3
p-Cresol**	--	--	--	--	--	--	--	--	--	--
2,4,6-Trichlorophenol	2,000	104	4	7	91.7	8.0	3	37.7	25	3
2,4,5-Trichlorophenol	400,000	94	4	7	85.2	0.4	3	64.4	10	3
Pentachlorophenol	100,000	109	11	7	41.9	28.2	3	36.6	32	3
1,4-Dichlorobenzene	7,500	50	5	7	79.7	1.0	3	26.5	68	3
Hexachloroethane	3,000	51	3	7	64.9	2.0	3	20.3	90	3
Nitrobenzene	2,000	80	4	7	79.0	2.3	3	59.4	6	3
Hexachlorobutadiene	500	57	5	7	60	3.3	3	16.6	107	3
2,4-Dinitrotoluene	130	86	6	7	38.5	5.2	3	62.2	6	3
Hexachlorobenzene	130	86	7	7	91.3	0.9	3	75.5	5	3

* 250-mL aliquots of leachate were spiked. Lab 1 spiked at one-half these levels.

** m-Cresol and p-Cresol coelute. Lab 1 and Lab 3 reported o-Cresol and the sum of — and p-Cresol. Lab 2 reported the sum of all three isomers of Cresol.

Data from Reference 12.

TABLE 18

SINGLE-LABORATORY PAH ANALYSIS DATA FROM A REAL SOIL CONTAMINATED WITH CREOSOTE, USING METHOD 3546
(MICROWAVE EXTRACTION)

Compound	Concentration (µg/kg)	RSD (%)	REAC values (µg/kg)
Naphthalene	2,170	12.4	710,000
2-Methylnaphthalene	28,710	3.1	N/R
1-Methylnaphthalene	33,180	2.4	N/R
Biphenyl	13,440	6.0	N/R
2,6-Dimethylnaphthalene	52,990	3.8	N/R
Acenaphthylene	16,320	3.1	21,000
Acenaphthene	801,210	6.0	1,700,000
Fluorene	789,980	3.4	990,000
Phenanthrene	1,627,480	0.7	3,300,000
Anthracene	346,010	4.0	360,000
Benzo(a)anthracene	300,380	2.7	310,000
Fluoranthene	1,331,690	1.6	1,600,000
Pyrene	1,037,710	3.0	1,100,000
Chrysene	293,200	3.4	320,000
Benzo(b)fluoranthene	152,000	3.8	140,000
Benzo(k)fluoranthene	127,740	3.6	130,000
Benzo(e)pyrene	87,610	3.9	N/R
Benzo(a)pyrene	128,330	3.9	110,000
Perylene	35,260	4.3	N/R
Indeno(123-cd)pyrene	63,900	5.0	25,000
Dibenz(a,h)anthracene	17,290	6.9	N/R
Benzo(ghi)perylene	42,720	6.9	20,000

*n = 4

Soil samples obtained from US EPA Emergency Response Center archive bank through their contract laboratory REAC (Edison, NJ). The standard Soxhlet extraction procedures were performed by REAC three years earlier; this long storage period is believed to account for the low naphthalene recovery data in the present study

REAC data labeled N/R = not reported

TABLE 19

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-5 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	250	180 - 320	76
Acenaphthylene	150	*	107
Acenaphthene	230	130 - 330	61
Fluorene	400	300 - 500	63
Phenanthrene	5,200	4,200 - 6,200	72
Anthracene	380	230 - 530	84
Fluoranthene	8,400	5,800 - 10,000	81
Pyrene	5,800	4,000 - 7,600	69
Benzo(a)anthracene	2,900	1,700 - 4,100	53
Chrysene	2,800	1,900 - 3,700	76
Benzo(b)fluoranthene	2,000	1,000 - 3,000	84
Benzo(k)fluoranthene	1,000	600 - 1,400	137
Benzo(a)pyrene	1,700	900 - 2,500	52
Indeno(123-cd) pyrene	1,300	600 - 2,000	63
Dibenz(a,h)anthracene	200	100 - 300	125
Benzo(ghi)perylene	1,300	1000 - 1600	64

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 20

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-4 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	150	*	54
Acenaphthylene	150	*	82
Acenaphthene	150	*	63
Fluorene	150	*	81
Phenanthrene	680	600 - 760	81
Anthracene	140	70 - 210	108
Fluoranthene	1250	1,150 - 1,350	84
Pyrene	940	820 - 1,060	85
Benzo(a)anthracene	530	470 - 580	78
Chrysene	650	570 - 730	84
Benzo(b)fluoranthene	700	550 - 850	84
Benzo(k)fluoranthene	360	310 - 410	156
Benzo(a)pyrene	650	570 - 730	73
Indeno(123-cd) pyrene	510	360 - 660	88
Dibenz(a,h)anthracene	120	70 - 170	117
Benzo(ghi)perylene	580	360 - 800	91

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 21

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-3 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	9,000	8300 - 9,700	61
Acenaphthylene	300	200 - 400	199
Acenaphthene	4,500	3,000 - 6,000	80
Fluorene	13,300	10,200 -16,400	58
Phenanthrene	85,000	65000 -105,000	87
Anthracene	13,400	12,900 -13,900	48
Fluoranthene	60,000	51,000-69,000	91
Pyrene	39,000	30,000-48,000	86
Benzo(a)anthracene	14,600	12,600-16,600	78
Chrysene	14,100	12,100-16,100	91
Benzo(b)fluoranthene	7,700	6,500-8,900	101
Benzo(k)fluoranthene	2,800	800-4,800	275
Benzo(a)pyrene	7,400	3,000-7,000	74
Indeno(123-cd)pyrene	5,400	4,100-6,700	100
Dibenz(a,h)anthracene	1,300	800-1,800	118
Benzo(ghi)perylene	5,000	3,000-7,000	99

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 22

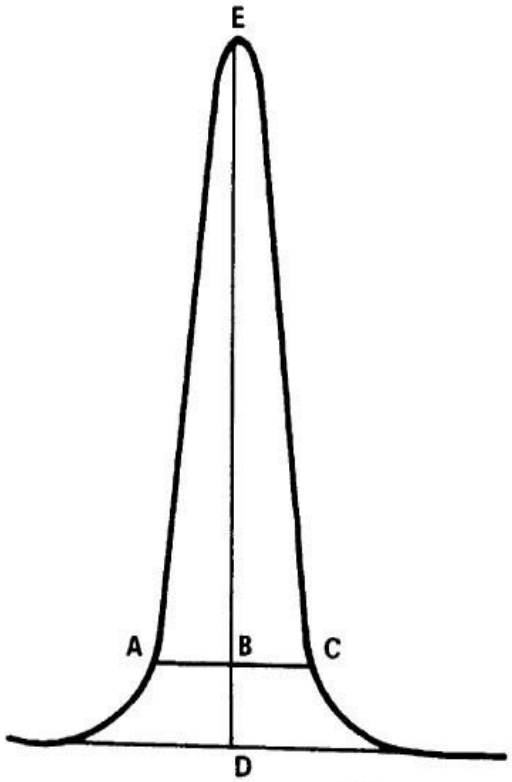
SINGLE-LABORATORY PAH RECOVERY DATA FROM SRM 1941 MARINE SEDIMENT, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Recovery (%)
Naphthalene	1010	97.4
Fluorene	100	100.0
Phenanthrene	490	102.0
Fluoranthene	980	116.7
Pyrene	810	97.3
Benz(a)anthracene	430	89.8
Chrysene	380	130.3
Benzo(b)fluoranthene	740	95.8
Benzo(k)fluoranthene	360	130.2
Benz(e)pyrene	550	81.0
Benzo(a)pyrene	630	76.0
Perylene	450	72.4
Indeno(123-cd)pyrene	500	126.0
Dibenz(a,h)anthracene	110	78.7
Benz(ghi)perylene	530	85.2

n = 3

All RSDs < 10%

FIGURE 1
TAILING FACTOR CALCULATION

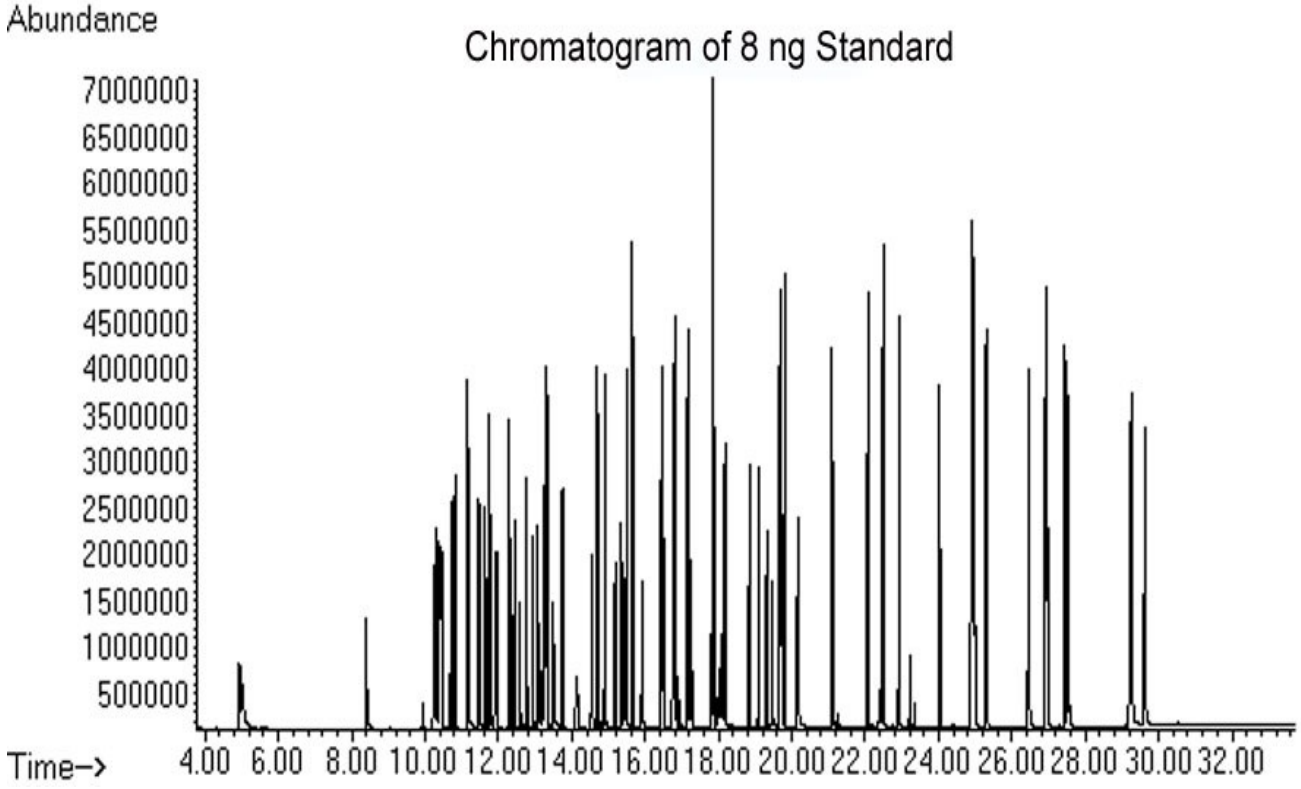


$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

FIGURE 2
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



No. L-10

Aroclor PCBs

SW-846 Method 8082

METHOD 8082

POLYCHLORINATED BIPHENYLS (PCBs)
BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). When compared to packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The target compounds listed below may be determined by either a single- or dual-column analysis system. The PCB congeners listed below have been tested by this method, and the method may be appropriate for additional congeners.

Compound	CAS Registry No.	IUPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-
Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobiphenyl	16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

1.3 Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment. Therefore, this method provides procedures for the determination of selected individual PCB congeners. The 19 PCB congeners listed above have been tested by this method.

1.4 The PCB congener approach potentially affords greater quantitative accuracy when PCBs are known to be present. As a result, this method may be used to determine Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs. The congener method is of particular value in determining weathered Aroclors. However, analysts should use caution when using the congener method when regulatory requirements are based on Aroclor concentrations.

1.5 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique when sensitivity permits (Sec. 8.0).

1.6 This method also describes a dual-column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis. Analysts are cautioned that the dual-column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when highly contaminated samples are analyzed.

1.7 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.8 The MDLs for Aroclors vary in the range of 0.054 to 0.90 µg/L in water and 57 to 70 µg/kg in soils. Estimated quantitation limits may be determined using the data in Table 1.

1.9 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), or other appropriate technique.

2.4 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081.

2.5 After cleanup, the extract is analyzed by injecting a 2-µL aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

2.6 The chromatographic data may be used to determine the seven Aroclors in Sec. 1.1, individual PCB congeners, or total PCBs.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a discussion of interferences.

3.2 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix to which the detector will respond.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

3.3.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

3.3.2 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.3.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

3.4 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free

reagent water. Drain the glassware, and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

NOTE: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

3.5 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.

4.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 8.4 describes how GC/MS confirmation techniques may be employed). The single-column approach may employ either narrow-bore (≤ 0.32 mm ID) columns or wide-bore (0.53 mm ID) columns. The dual-column approach involves a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach employs only wide-bore (0.53 mm ID) columns. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use other capillary columns provided that they document method performance (e.g., chromatographic resolution, analyte breakdown, and MDLs) that equals or exceeds the performance specified in this method.

4.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.2.1.1 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

4.2.1.2 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1 µm film thickness.

4.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.2.2.1 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

4.2.2.2 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

4.2.2.3 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

4.2.3 Wide-bore columns for dual-column analysis (choose one of the two pairs of columns listed below).

4.2.3.1 Column pair 1

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

4.2.3.2 Column pair 2

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14**%** cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 2 is mounted in an 8 in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

4.3 Column rinsing kit - Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

4.4 Volumetric flasks - 10-mL and 25-mL, for preparation of standards.

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4°C in polytetrafluoroethylene (PTFE)-sealed containers

in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC (Sec. 8.0) indicates a problem. All other standard solutions must be replaced after six months or sooner if routine QC (Sec. 8.0) indicates a problem.

5.2 Sample extracts prepared by Methods 3510, 3520, 3540, 3541, 3545, or 3550 need to undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots should be pesticide quality or equivalent and should be determined to be phthalate-free.

5.2.1 n-Hexane, C_6H_{14}

5.2.2 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

5.3 The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide quality or equivalent and should be determined to be phthalate-free.

5.3.1 Acetone, $(CH_3)_2CO$

5.3.2 Toluene, $C_6H_5CH_3$

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.5 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.5.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solution.

5.5.2 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6 Calibration standards for Aroclors

5.6.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.6.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Sec. 5.6.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor. Prepare a standard for each of the other Aroclors. The concentrations should correspond to the mid-point of the linear range of the detector.

5.7 Calibration standards for PCB congeners

5.7.1 If results are to be determined for individual PCB congeners, then standards for the pure congeners must be prepared. The table in Sec. 1.1 lists 19 PCB congeners that have been tested by this method along with the IUPAC numbers designating these congeners. This procedure may be appropriate for other congeners as well.

5.7.2 Stock standards may be prepared in a fashion similar to that described for the Aroclor standards, or may be purchased as commercially-prepared solutions. Stock standards should be used to prepare a minimum of five concentrations by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.8 Internal standard

5.8.1 When PCB congeners are to be determined, the use of an internal standard is highly recommended. Decachlorobiphenyl may be used as an internal standard, added to each sample extract prior to analysis, and included in each of the initial calibration standards.

5.8.2 When PCBs are to be determined as Aroclors, an internal standard is not used, and decachlorobiphenyl is employed as a surrogate (see Sec. 5.8).

5.9 Surrogate standards

5.9.1 When PCBs are to be determined as Aroclors, decachlorobiphenyl is used as a surrogate, and is added to each sample prior to extraction. Prepare a solution of decachlorobiphenyl at a concentration of 5 mg/L in acetone.

5.9.2 When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as an internal standard, and therefore, cannot also be used as a surrogate. Therefore, tetrachloro-meta-xylene may be used as a surrogate for PCB congener analysis. Prepare a solution of tetrachloro-meta-xylene at a concentration of 5 mg/L in acetone.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Four, Organic Analytes for sample collection and preservation instructions.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Sample extraction

7.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520) or other appropriate procedure. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541) procedures, ultrasonic extraction (Method 3550), or other appropriate procedure.

NOTE: Use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

7.1.2 Reference materials, field-contaminated samples, or spiked samples should be used to verify the applicability of the selected extraction technique to each new sample type. Such samples should contain or be spiked with the compounds of interest in order to determine the percent recovery and the limit of detection for that sample type (see Chapter One). When other materials are not available and spiked samples are used, they should be spiked with the analytes of interest, either specific Aroclors or PCB congeners. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be an appropriate choice for spiking. See Methods 3500 and 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 Extract cleanup

Refer to Methods 3660 and 3665 for information on extract cleanup.

7.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. Either wide- or narrow-bore columns may be used. See Sec. 7.7 for information on techniques for making positive identifications of multi-component analytes.

7.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow-bore) or 0.53 mm ID capillary columns (wide-bore). The use of narrow-bore (0.25-0.32 mm ID) columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm ID) are suitable for more complex environmental and waste matrices.

7.3.2 Dual-column analysis

The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors.

7.3.3 GC temperature programs and flow rates

7.3.3.1 Table 2 lists GC operating conditions for the analysis of PCBs as Aroclors for single-column analysis, using either narrow-bore or wide-bore capillary columns. Table 3 lists GC operating conditions for the dual-column analysis. Use the conditions in these tables as guidance and establish the GC temperature program and flow rate necessary to separate the analytes of interest.

7.3.3.2 When determining PCBs as congeners, difficulties may be encountered with coelution of congener 153 and other sample components. When determining PCBs as Aroclors, chromatographic conditions should be adjusted to give adequate separation of the characteristic peaks in each Aroclor (see Sec. 7.4.6).

7.3.3.3 Tables 4 and 5 summarize the retention times of up to 73 Aroclor peaks determined during dual-column analysis using the operating conditions listed in Table 2. These retention times are provided as guidance as to what may be achieved using the GC columns, temperature programs, and flow rates described in this method. Note that the peak numbers used in these tables are *not* the IUPAC congener numbers, but represent the elution order of the peaks on these GC columns.

7.3.3.4 Once established, the same operating conditions must be used for the analysis of samples and standards.

7.4 Calibration

7.4.1 Prepare calibration standards as described in Sec. 5.0. Refer to Method 8000 (Sec. 7.0) for proper calibration techniques for both initial calibration and calibration verification. When PCBs are to be determined as congeners, the use of internal standard calibration is highly recommended. Therefore, the calibration standards must contain the internal standard (see Sec. 5.7) at the same concentration as the sample extracts. When PCBs are to be determined as Aroclors, external standard calibration should be used.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.2 When PCBs are to be quantitatively determined as congeners, an initial five-point calibration must be performed that includes standards for all the target analytes (congeners).

7.4.3 When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below.

7.4.3.1 As noted in Sec. 5.6.1, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260 described in Sec. 5.6.1.

7.4.3.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Sec. 7.3.4.1 has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards in Sec. 7.3.4.1.

7.4.3.3 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a five-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern) and not use the 1016/1260 mixture described in Sec. 7.4.3.1 or the pattern recognition standards described in 7.4.3.2.

7.4.4 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 7.3). Optimize the instrumental conditions for resolution of the target compounds and sensitivity. A final temperature of 240-270°C may be required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.4.5 A 2-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

7.4.6 Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.

7.4.6.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

7.4.6.2 Late-eluting Aroclor peaks are generally the most stable in the environment. Table 6 lists diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for single-column analysis. Table 7 lists 13 specific PCB congeners found in Aroclor mixtures. Table 8 lists PCB congeners with corresponding retention times on a DB-5 wide-bore GC column. Use these tables as guidance in choosing the appropriate peaks.

7.4.7 When determining PCB congeners by the internal standard procedure, calculate the response factor (RF) for each congener in the calibration standards relative to the internal standard, decachlorobiphenyl, using the equation that follows.

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.4.8 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards (from either Sec. 7.4.3.1 or 7.4.3.2) using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. The single standard for each of the other Aroclors (see Sec. 7.4.3.1) will generate at least three calibration factors, one for each selected peak.

7.4.9 The response factors or calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each congener or Aroclor peak. See Method 8000 for the specifics of the evaluation of the linearity of the calibration and guidance on performing non-linear calibrations. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model (see Method 8000) chosen for this mixture must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors (see Sec. 7.4.3.3), use the calibration factors from those standards to evaluate linearity.

7.5 Retention time windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. When PCBs are determined as congeners by an internal standard technique, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard). Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows.

7.6 Gas chromatographic analysis of sample extracts

7.6.1 The same GC operating conditions used for the initial calibration must be employed for samples analyses.

7.6.2 Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process

does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

7.6.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

7.6.2.2 When internal standard calibration is used for PCB congeners, the response factor calculated from the calibration verification standard (RF_v) must not exceed a ± 15 percent difference when compared to the mean response factor from the initial calibration

$$\% \text{ Difference} = \frac{\overline{RF} - RF_v}{\overline{RF}} \times 100$$

7.6.2.3 If this criterion is exceeded for any calibration factor or response factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

7.6.2.4 If routine maintenance does not return the instrument performance to meet the QC requirements (Sec. 8.2) based on the last initial calibration, then a new initial calibration must be performed.

7.6.3 Inject a 2-µL aliquot of the concentrated sample extract. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area (or peak height) units.

7.6.4 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Sec. 7.7.

7.6.5 Quantitative results are determined for each identified analyte (Aroclors or congeners), using the procedures described in Secs. 7.8 and 7.9 for either the internal or the external calibration procedure (Method 8000). If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

7.6.6 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

Multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

7.6.7 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

7.6.8 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.6.9 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.6.10 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.7 Qualitative identification

The identification of PCBs as either Aroclors or congeners using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. See Method 8000 for information on the establishment of retention time windows.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS (see Sec. 7.10).

7.7.1 When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 7.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.7.2 The results of a single column/single injection analysis may be confirmed on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. That standard may be either the individual congeners, individual Aroclor or the Aroclor 1016/1260 mixture.

7.7.3 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

- The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.
- The absence of major peaks representing any other Aroclor.
- The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

This information should either be provided to the data user or maintained by the laboratory.

7.7.4 See Sec. 7.10 for information on GC/MS confirmation.

7.8 Quantitation of PCBs as congeners

7.8.1 The quantitation of PCB congeners is accomplished by the comparison of the sample chromatogram to those of the PCB congener standards, using the internal standard technique (see Method 8000). Calculate the concentration of each congener.

7.8.2 Depending on project requirements, the PCB congener results may be reported as congeners, or may be summed and reported as total PCBs. The analyst should use caution when using the congener method for quantitation when regulatory requirements are based on Aroclor concentrations. See Sec. 9.3.

7.9 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.9.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.9.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Sec. 7.4.6.1. and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.9.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor

concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method. If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

7.10 GC/MS confirmation may be used in conjunction with either single-or dual-column analysis if the concentration is sufficient for detection by GC/MS.

7.10.1 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while ion trap or SIM may only require a concentration of 1 ng/µL.

7.10.2 The GC/MS must be calibrated for the specific target analytes. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

7.10.3 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

7.10.4 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

7.10.5 A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those PCBs identified by GC/ECD can be confirmed by GC/MS.

7.11 Chromatographic System Maintenance as Corrective Action

When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

7.11.1 Splitter connections

For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.11.2 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the

injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.11.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

7.11.2.2 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

7.11.3 Column rinsing

The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation techniques can be found in Method 3500. If an extract cleanup procedure was performed, refer to Method 3600 for the appropriate quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.3.1 The QC Reference Sample concentrate (Method 3500) should contain PCBs as Aroclors at 10-50 mg/L for water samples, or PCBs as congeners at the same concentrations. A 1-mL volume of this concentrate spiked into 1 L of organic-free reagent water will result in a sample concentration of 10-50 µg/L. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the QC reference sample.

8.3.1.1 The frequency of analysis of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples.

8.3.1.2 If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.3.2 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.3.3 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs for Aroclors vary in the range of 0.054 to 0.90 µg/L in water and 57 to 70 µg/kg in soils, with the higher MDLs for the more heavily chlorinated Aroclors. Estimated quantitation limits may be determined using the data in Table 1.

9.2 Estimated quantitation limits for PCBs as congeners vary by congener, in the range of 5 - 25 ng/L in water and 160 - 800 ng/kg in soils, with the higher values for the more heavily chlorinated congeners.

9.3 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used. Table 9 provides single laboratory recovery data for Aroclors spiked into clay and soil and extracted with automated Soxhlet. Table 10 provides multiple laboratory data on the precision and accuracy for Aroclors spiked into soil and extracted by automated Soxhlet.

9.4 During method performance studies, the concentrations determined as Aroclors were larger than those obtained using the congener method. In certain soils, interference prevented the measurement of congener 66. Recoveries of congeners from soils spiked with Aroclor 1254 and Aroclor 1260 were between 80% and 90%. Recoveries of congeners from environmental reference materials ranged from 51 - 66% of the certified Aroclor values.

10.0 REFERENCES

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TABLE 1

FACTORS FOR DETERMINATION OF ESTIMATED QUANTITATION LIMITS[a] (EQLs)
FOR VARIOUS MATRICES

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]EQL = [MDL for water (see Sec. 1.8)] times [Factor in this table]

For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. EQLs determined using these factors are provided as guidance and may not always be achievable.

TABLE 2

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE COLUMN ANALYSIS

Narrow-bore columns

Narrow-bore Column 1 - 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Narrow-bore Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent) 25 µm coating thickness, 1 µm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

Wide-bore columns

Wide-bore Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Wide-bore Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Carrier gas (He)	5-7 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

(continued)

TABLE 2 (cont.)

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE COLUMN ANALYSIS

Wide-bore Columns (continued)

Wide-bore Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas (He)	6 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 3

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1 - DB-1701 or equivalent, 30 m x 0.53 mm ID, 1.0 µm film thickness.

Column 2 - DB-5 or equivalent, 30 m x 0.53 mm ID, 1.5 µm film thickness.

Carrier gas (He) flow rate	6 mL/min
Makeup gas (N_2) flow rate	20 mL/min
Temperature program	0.5 min hold 150°C to 190°C, at 12°C/min, 2 min hold 190°C to 275°C, at 4°C/min, 10 min hold
Injector temperature	250°C
Detector temperature	320°C
Injection volume	2 µL
Solvent	Hexane
Type of injector	Flash vaporization
Detector type Dual ECD	
Range	10
Attenuation 64 (DB-1701)/64 (DB-5)	
Type of splitter	J&W Scientific press-fit Y-shaped inlet splitter

TABLE 4

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		5.85	5.85				
2		7.63	7.64	7.57			
3	8.41	8.43	8.43	8.37			
4	8.77	8.77	8.78	8.73			
5	8.98	8.99	9.00	8.94	8.95		
6	9.71			9.66			
7	10.49	10.50	10.50	10.44	10.45		
8	10.58	10.59	10.59	10.53			
9	10.90		10.91	10.86	10.85		
10	11.23	11.24	11.24	11.18	11.18		
11	11.88		11.90	11.84	11.85		
12	11.99		12.00	11.95			
13	12.27	12.29	12.29	12.24	12.24		
14	12.66	12.68	12.69	12.64	12.64		
15	12.98	12.99	13.00	12.95	12.95		
16	13.18		13.19	13.14	13.15		
17	13.61		13.63	13.58	13.58	13.59	13.59
18	13.80		13.82	13.77	13.77	13.78	
19	13.96		13.97	13.93	13.93	13.90	
20	14.48		14.50	14.46	14.45	14.46	
21	14.63		14.64	14.60	14.60		
22	14.99		15.02	14.98	14.97	14.98	
23	15.35		15.36	15.32	15.31	15.32	
24	16.01			15.96			
25			16.14	16.08	16.08	16.10	
26	16.27		16.29	16.26	16.24	16.25	16.26
27						16.53	
28			17.04		16.99	16.96	16.97
29			17.22	17.19	17.19	17.19	17.21
30			17.46	17.43	17.43	17.44	
31					17.69	17.69	
32				17.92	17.91	17.91	
33				18.16	18.14	18.14	
34			18.41	18.37	18.36	18.36	18.37
35			18.58	18.56	18.55	18.55	
36							18.68

(continued)

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 4 (cont.)

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			18.83	18.80	18.78	18.78	18.79
38			19.33	19.30	19.29	19.29	19.29
39						19.48	19.48
40						19.81	19.80
41			20.03	19.97	19.92	19.92	
42						20.28	20.28
43					20.46	20.45	
44						20.57	20.57
45				20.85	20.83	20.83	20.83
46			21.18	21.14	21.12	20.98	
47					21.36	21.38	21.38
48						21.78	21.78
49				22.08	22.05	22.04	22.03
50						22.38	22.37
51						22.74	22.73
52						22.96	22.95
53						23.23	23.23
54							23.42
55						23.75	23.73
56						23.99	23.97
57							24.16
58						24.27	
59							24.45
60						24.61	24.62
61						24.93	24.91
62							25.44
63						26.22	26.19
64							26.52
65							26.75
66							27.41
67							28.07
68							28.35
69							29.00

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		4.45	4.45				
2		5.38					
3		5.78					
4		5.86	5.86				
5	6.33	6.34	6.34	6.28			
6	6.78	6.78	6.79	6.72			
7	6.96	6.96	6.96	6.90	6.91		
8	7.64			7.59			
9	8.23	8.23	8.23	8.15	8.16		
10	8.62	8.63	8.63	8.57			
11	8.88		8.89	8.83	8.83		
12	9.05	9.06	9.06	8.99	8.99		
13	9.46		9.47	9.40	9.41		
14	9.77	9.79	9.78	9.71	9.71		
15	10.27	10.29	10.29	10.21	10.21		
16	10.64	10.65	10.66	10.59	10.59		
17				10.96	10.95	10.95	
18	11.01		11.02	11.02	11.03		
19	11.09		11.10				
20	11.98		11.99	11.94	11.93	11.93	
21	12.39		12.39	12.33	12.33	12.33	
22			12.77	12.71	12.69		
23	12.92			12.94	12.93		
24	12.99		13.00	13.09	13.09	13.10	
25	13.14		13.16				
26						13.24	
27	13.49		13.49	13.44	13.44		
28	13.58		13.61	13.54	13.54	13.51	13.52
29				13.67		13.68	
30			14.08	14.03	14.03	14.03	14.02
31			14.30	14.26	14.24	14.24	14.25
32					14.39	14.36	
33			14.49	14.46	14.46		
34						14.56	14.56
35					15.10	15.10	
36			15.38	15.33	15.32	15.32	

(continued)

[a]GC operating conditions are given in Table 3. All retention times in minutes.
[b]The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5 (cont.)

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			15.65	15.62	15.62	15.61	16.61
38			15.78	15.74	15.74	15.74	15.79
39			16.13	16.10	16.10	16.08	
40							16.19
41						16.34	16.34
42						16.44	16.45
43						16.55	
44			16.77	16.73	16.74	16.77	16.77
45			17.13	17.09	17.07	17.07	17.08
46						17.29	17.31
47				17.46	17.44	17.43	17.43
48				17.69	17.69	17.68	17.68
49					18.19	18.17	18.18
50				18.48	18.49	18.42	18.40
51						18.59	
52						18.86	18.86
53				19.13	19.13	19.10	19.09
54						19.42	19.43
55						19.55	19.59
56						20.20	20.21
57						20.34	
58							20.43
59					20.57	20.55	
60						20.62	20.66
61						20.88	20.87
62							21.03
63						21.53	21.53
64						21.83	21.81
65						23.31	23.27
66							23.85
67							24.11
68							24.46
69							24.59
70							24.87
71							25.85
72							27.05
73							27.72

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 6

PEAKS DIAGNOSTIC OF PCBs OBSERVED ON 0.53 mm ID COLUMN
DURING SINGLE COLUMN ANALYSIS

Peak No.[a]	RT on DB-608[b]	RT on DB-1701[b]	Aroclor[c]
I	4.90	4.66	1221
II	7.15	6.96	1221, 1232, 1248
III	7.89	7.65	1061, 1221, 1232, 1242,
IV	9.38	9.00	1016, 1232, 1242, 1248,
V	10.69	10.54	1016, 1232, 1242,
VI	14.24	14.12	1248, 1254
VII	14.81	14.77	1254
VIII	16.71	16.38	1254
IX	19.27	18.95	1254, 1260
X	21.22	21.23	1260
XI	22.89	22.46	1260

[a] Peaks are sequentially numbered in elution order and are not isomer numbers

[b] Temperature program: T_i = 150°C, hold 30 seconds; 5°C/minute to 275°C.

[c] Underline indicates largest peak in the pattern for that Aroclor

TABLE 7

SPECIFIC PCB CONGENERS IN AROCLORS

Congener	IUPAC number	Aroclor 1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
23-DCB	5	X	X	X	X	X		
34-DCB	12	X		X	X	X		
244'-TCB	28*	X		X	X	X	X	
22'35'-TCB	44			X	X	X	X	X
23'44'-TCB	66*					X	X	X
233'4'6-PCB	110						X	
23'44'5-PCB	118*						X	X
22'44'55'-HCB	153							X
22'344'5'-HCB	138							X
22'344'55'-HpCB	180							X
22'33'44'5-HpCB	170							X

*Apparent co-elution of:

28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

TABLE 8

RETENTION TIMES OF PCB CONGENERS
ON THE DB-5 WIDE-BORE COLUMN

IUPAC #	Retention Time (min)	
1	6.52	
5	10.07	
18	11.62	
31	13.43	
52	14.75	
44	15.51	
66	17.20	
101	18.08	
87	19.11	
110	19.45	
151	19.87	
153	21.30	
138	21.79	
141	22.34	
187	22.89	
183	23.09	
180	24.87	
170	25.93	
206	30.70	
209	32.63	(internal standard)

TABLE 9

SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF
PCBs FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	1254	5	1	87.0
			2	92.7
			3	93.8
			4	98.6
			5	79.4
			6	28.3
Clay	1254	50	1	65.3
			2	72.6
			3	97.2
			4	79.6
			5	49.8
			6	59.1
Clay	1260	5	1	87.3
			2	74.6
			3	60.8
			4	93.8
			5	96.9
			6	113.1
Clay	1260	50	1	73.5
			2	70.1
			3	92.4
			4	88.9
			5	90.2
			6	67.3

(continued)

[a] The operating conditions for the automated Soxhlet

Immersion time: 60 min
Reflux time: 60 min

[b] Multiple results from two different extractors.

Data from Reference 9.

TABLE 9 (cont.)

SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF
PCBs FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	1254	5	1	69.7
			2	89.1
			3	91.8
			4	83.2
			5	62.5
Soil	1254	50	1	84.0
			2	77.5
			3	91.8
			4	66.5
			5	82.3
			6	61.6
Soil	1260	5	1	83.9
			2	82.8
			3	81.6
			4	96.2
			5	93.7
			6	93.8
			7	97.5
Soil	1260	50	1	76.9
			2	69.4
			3	92.6
			4	81.6
			5	83.1
			6	76.0

[a] The operating conditions for the automated Soxhlet

Immersion time: 60 min
Reflux time: 60 min

[b] Multiple results from two different extractors.

Data from Reference 9.

TABLE 10

MULTIPLE LABORATORY PRECISION AND ACCURACY DATA
FOR THE EXTRACTION OF PCBs FROM SPIKED SOIL
BY METHOD 3541 (AUTOMATED SOXHLET)

		Percent Recovery						
		Aroclor 1254			Aroclor 1260			
		Spike Conc. (µg/kg)			Spike Conc. (µg/kg)			
		5	50	500	5	50	500	All Levels
Laboratory 1	N	3	3		3	3		12
	Mean	101.2	74.0		83.9	78.5		84.4
	S. D.	34.9	41.8		7.4	7.4		26.0
Laboratory 2	N		6	6		6	6	24
	Mean		56.5	66.9		70.1	74.5	67.0
	S. D.		7.0	15.4		14.5	10.3	13.3
Laboratory 3	N	3	3		3	3		12
	Mean	72.8	63.3		70.6	57.2		66.0
	S. D.	10.8	8.3		2.5	5.6		9.1
Laboratory 4	N	6	6		6	6		24
	Mean	112.6	144.3		100.3	84.8		110.5
	S. D.	18.2	30.4		13.3	3.8		28.5
Laboratory 5	N		3	3		3	3	12
	Mean		97.1	80.1		79.5	77.0	83.5
	S. D.		8.7	5.1		3.1	9.4	10.3
Laboratory 6	N	2	3		3	4		12
	Mean	140.9	127.7		138.7	105.9		125.4
	S. D.	4.3	15.5		15.5	7.9		18.4
Laboratory 7	N	3	3		3	3		12
	Mean	100.1	123.4		82.1	94.1		99.9
	S. D.	17.9	14.6		7.9	5.2		19.0
Laboratory 8	N	3	3		3	3		12
	Mean	65.0	38.3		92.8	51.9		62.0
	S. D.	16.0	21.9		36.5	12.8		29.1
All Laboratories	N	20	30	9	21	31	9	120
	Mean	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	S. D.	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Data from Reference 7.

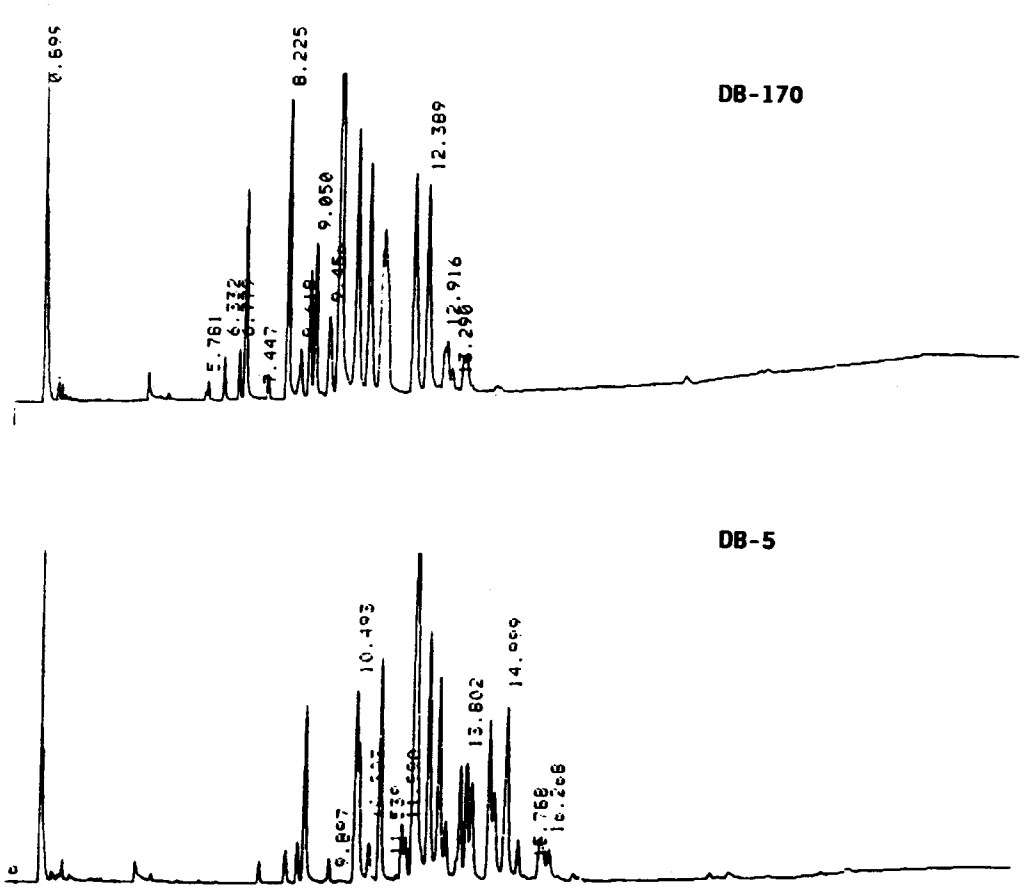


FIGURE 1. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

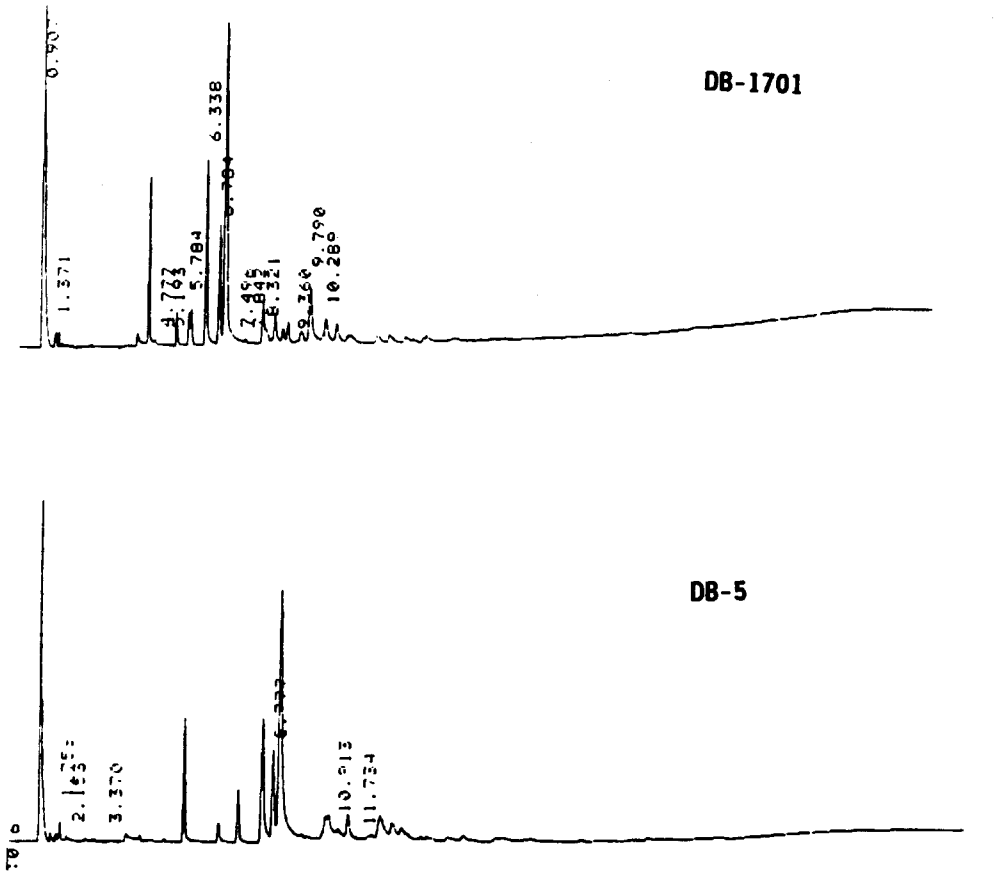


FIGURE 2. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

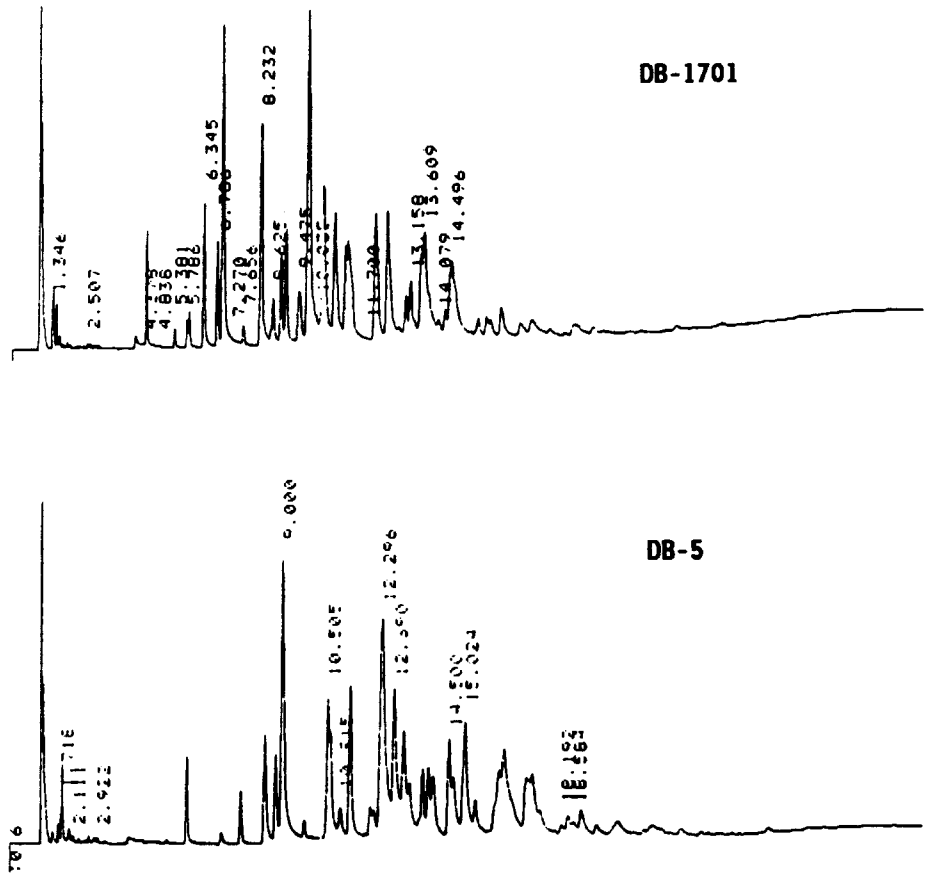


FIGURE 3. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

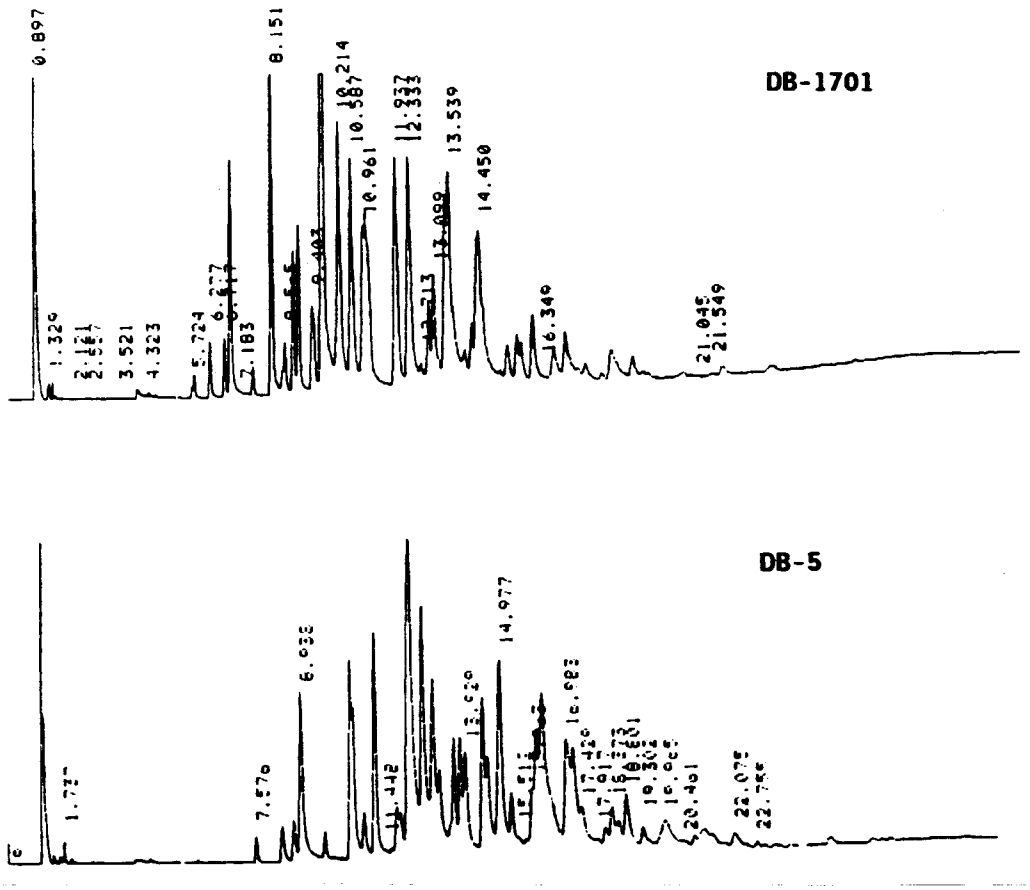


FIGURE 4. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

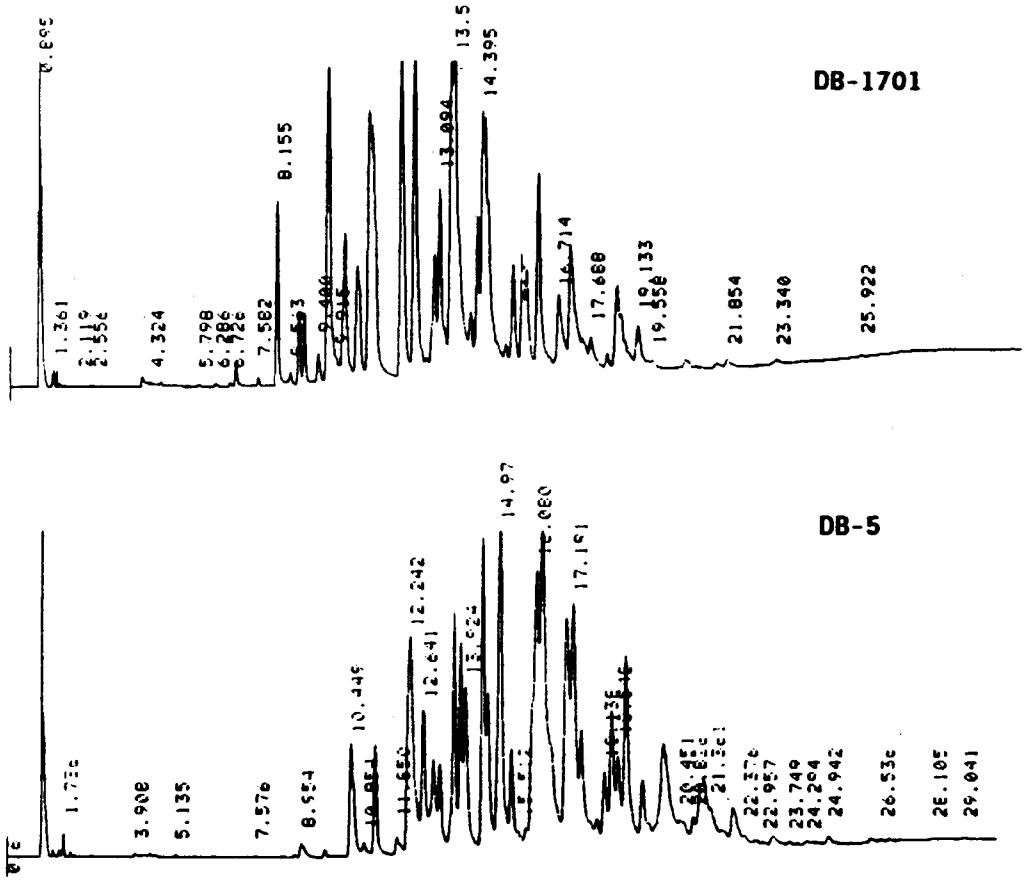


FIGURE 5. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

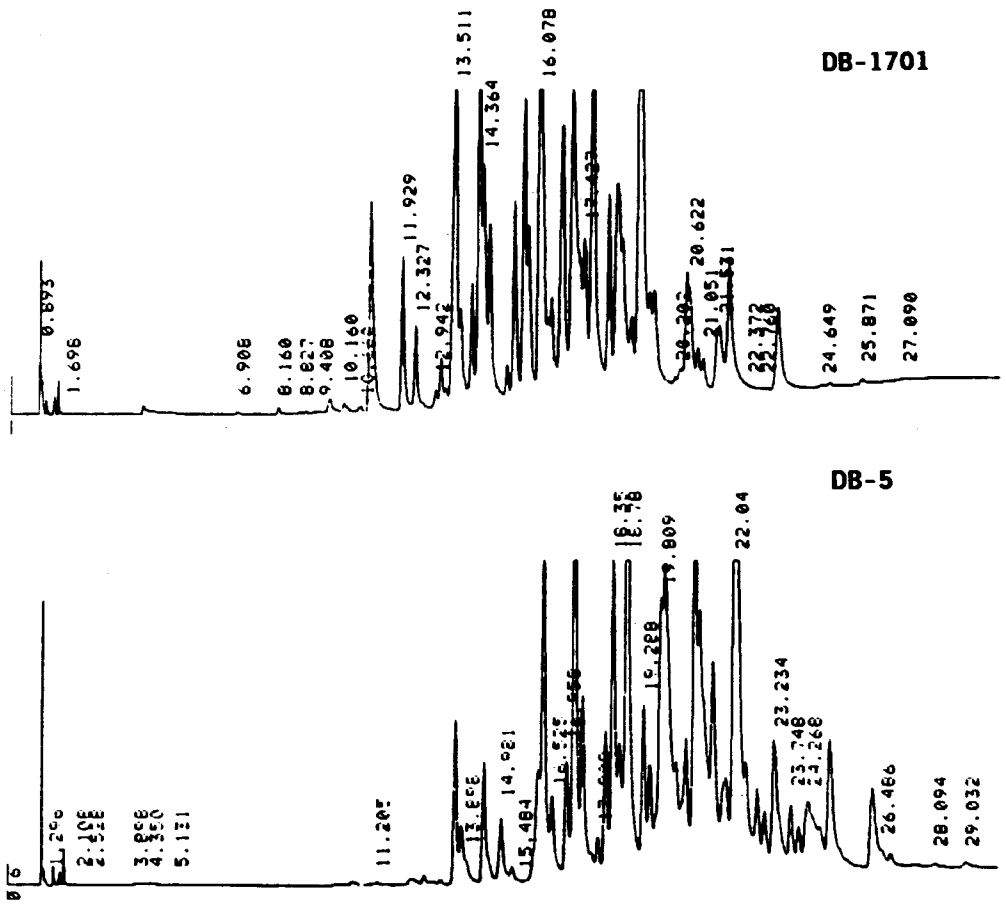


FIGURE 6. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

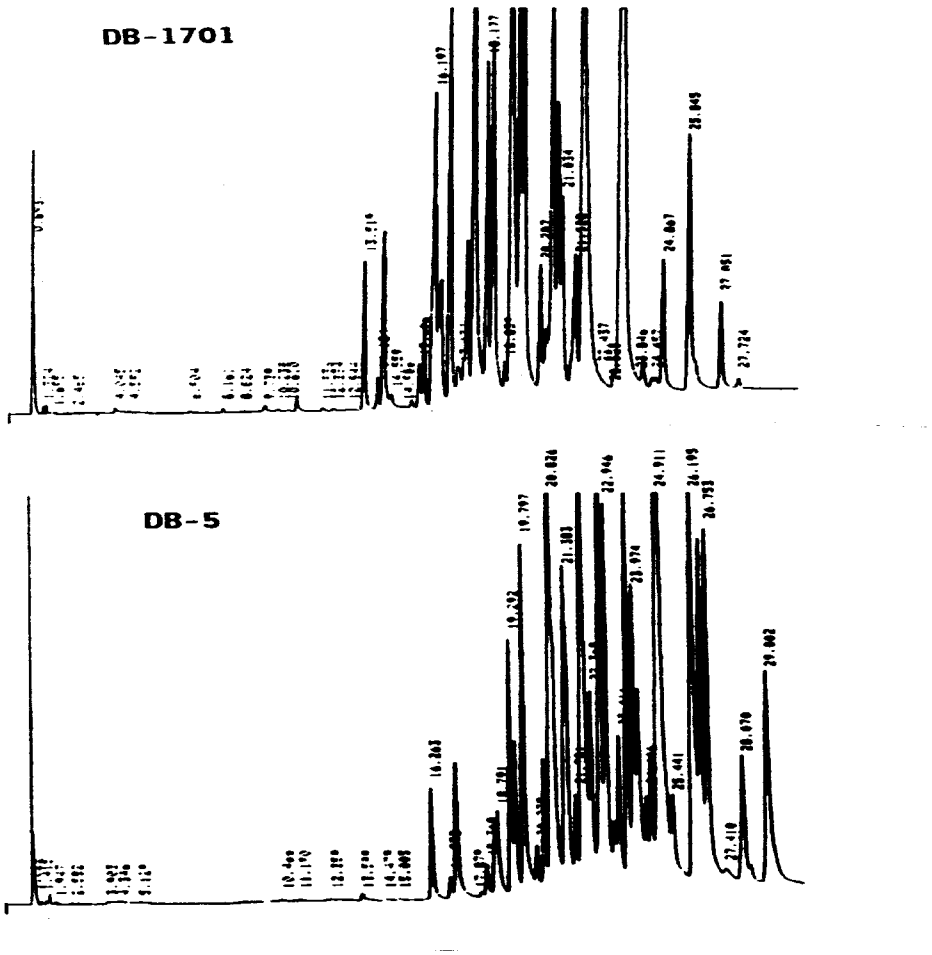
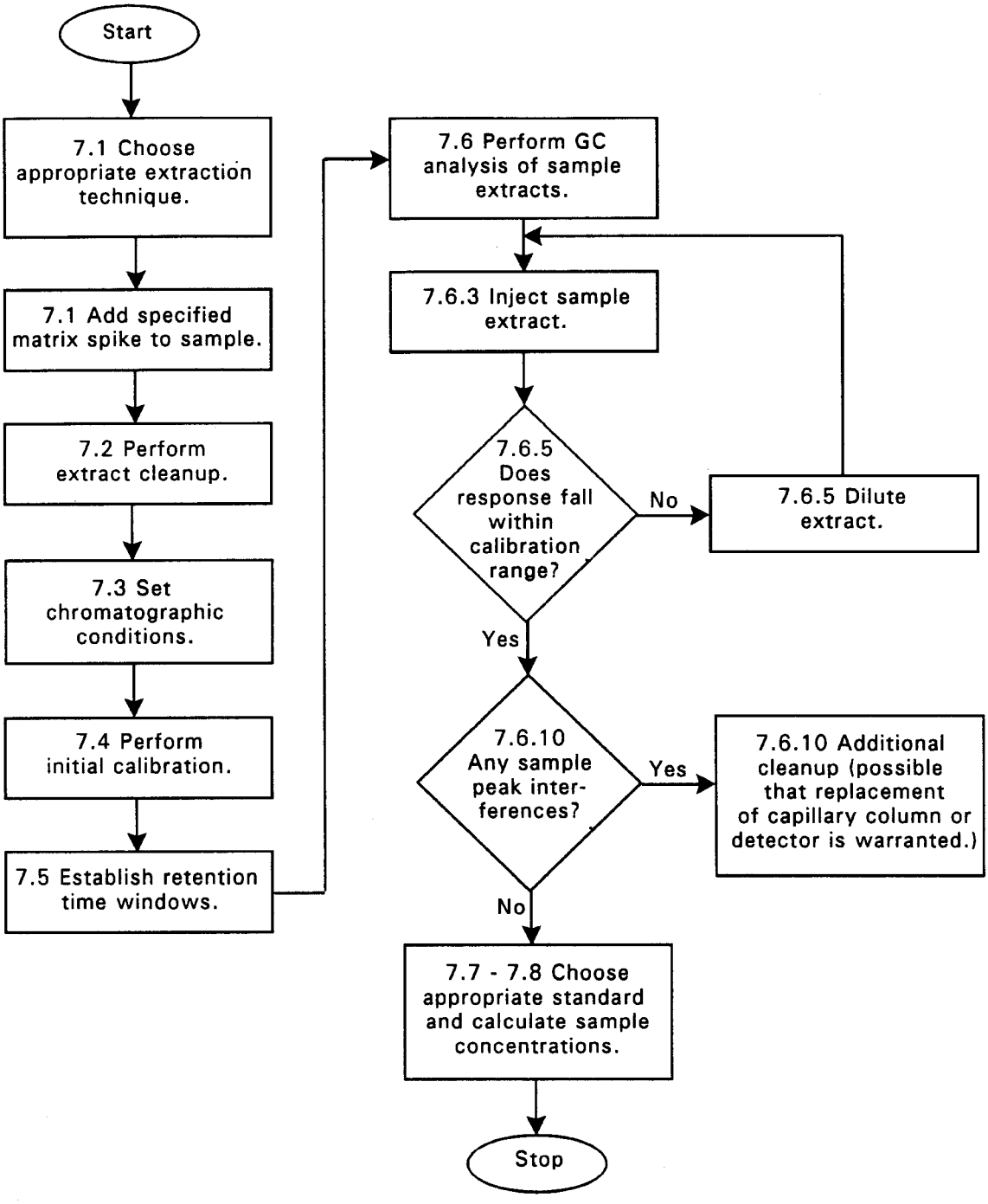


FIGURE 7. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.


Start
7.1 Choose appropriate extraction technique.
7.1 Add specified matrix spike to sample.
7.2 Perform extract cleanup.
7.3 Set chromatographic conditions.
7.4 Perform initial calibration.
7.5 Establish retention time windows.
7.6 Perform GC analysis of sample extracts.
7.6.3 Inject sample extract.
7.6.5 Does response fall within calibration range?
No
7.6.5 Dilute extract.
Yes
7.6.10 Any sample peak interferences?
Yes
7.6.10 Additional cleanup (possible that replacement of capillary column or detector is warranted.)
No
7.7 - 7.8 Choose appropriate standard and calculate sample concentrations.
Stop

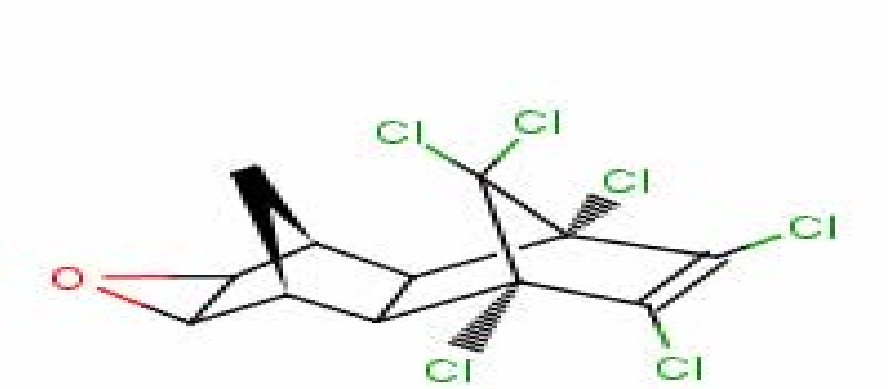
No. L-11

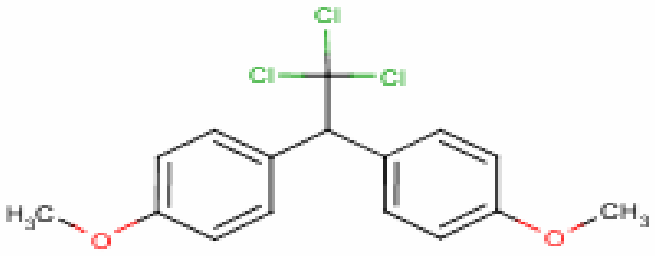
Pesticides

USEPA Method 1699

Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS

December 2007





U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division (4303T)
1200 Pennsylvania Avenue, NW
Washington, DC 20460

EPA-821-R-08-001
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Introduction

EPA Method 1699 determines organochlorine, organophosphorus, triazine, and pyrethroid pesticides in environmental samples by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using isotope dilution and internal standard quantitation techniques. This method has been developed for use with aqueous, solid, tissue and biosolids matrices.

Disclaimer

This method has been reviewed by the Engineering and Analytical Support Branch of the Engineering and Analysis Division (EAD) in OST. The method is available for general use, but has not been published in 40 CFR Part 136. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Contacts

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Table of Contents

Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS

1.0 Scope and Application

1.1 Method 1699 is for determination of selected organochlorine, organo-phosphorus, triazine, and pyrethroid pesticides in multi-media environmental samples by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

1.2 This Method was developed for use in EPA's Clean Water Act (CWA) programs; other applications are possible. It is based on existing EPA methods (Reference 1) and procedures developed at Axys Analytical Services (Reference 2).

1.3 The analytes that may be measured by this method and their corresponding Chemical Abstracts Service Registry Numbers (CASRNs) and ambient water quality criteria are listed in Table 1.

1.4 The detection limits and quantitation levels in this Method are usually dependent on the level of interferences rather than instrumental limitations. The method detection limits (MDLs; 40 CFR 136, appendix B) and minimum levels of quantitation (MLs; 68 FR 11790) in Table 1 are the levels at which pesticides can be determined in the absence of interferences.

1.5 This Method is restricted for use by analysts experienced in HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.6 This method is performance-based which means that you may modify the method to improve performance (e.g., to overcome interferences or improve the accuracy or precision of the results) provided that you meet all performance requirements in this method. These requirements for establishing equivalency of a modification are in Section 9.1.2. For Clean Water Act (CWA) uses, additional flexibility is described at 40 CFR 136.6. Modifications not in the scope of Part 136.6 or in Section 9 of this method may require prior review and approval.

2.0 Summary of Method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

2.1 Extraction (Section 12)

2.1.1 Aqueous samples (samples containing less than one percent solids) – Stable isotopically labeled analogs of the pesticides are spiked into a 1-L sample. The sample is extracted at neutral pH with methylene chloride using separatory funnel extraction (SFE) or continuous liquid/liquid extraction (CLLE).

2.1.2 Solid, semi-solid, and multi-phase samples (excluding municipal sludge and tissue) – The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted with methylene chloride, methylene chloride:hexane (1:1) or acetone:hexane (1:1) in a Soxhlet extractor or with toluene in a Soxhlet/Dean-Stark (SDS) extractor (Reference 3).

2.1.3 Municipal sludges are homogenized, spiked with labeled compounds, and Soxhlet extracted with dichloromethane.

2.1.4 Fish and other tissue – A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is mixed with anhydrous sodium sulfate, allowed to dry for 30 minutes minimum, and extracted for 18 - 24 hours using methylene chloride in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.2 Concentration (Section 12)

2.2.1 Extracts are macro-concentrated using rotary evaporation, a heating mantle, or a Kuderna-Danish evaporator.

2.2.2 Extracts to be injected into the HRGC/HRMS are concentrated to a final volume of 20 μL using nitrogen evaporation (blowdown).

2.3 Cleanup (Section 13)

2.3.1 Extracts of aqueous, solid or mixed phase samples are cleaned up using an aminopropyl SPE column followed by a microsilica column.

2.3.2 Extracts may be further cleaned up using gel permeation chromatography (GPC) or solid-phase cartridge techniques.

2.3.3 Extracts in which the organo-chlorine pesticides only are to be determined may be further cleaned up using silica gel, Florisil, or alumina chromatography.

2.4 Determination by GC/HRMS – Immediately prior to injection, a labeled injection internal standard is added to each extract and an aliquot of the extract is injected into the gas chromatograph (GC). The analytes are separated by the GC and detected by a high-resolution (≥8,000) mass spectrometer. Two exact m/z's for each pesticide are monitored throughout a pre-determined retention time window.

2.5 An individual pesticide is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's.

2.6 Quantitative analysis is performed in one of two ways using selected ion current profile (SICP) areas:

2.6.1 For pesticides for which a labeled analog is available, the GC/HRMS is multi-point calibrated and the concentration is determined using the isotope dilution technique.

2.6.2 Pesticides for which a labeled analog is not available are determined using the internal standard technique. The labeled compounds are used as internal standards, affording recovery correction for all pesticides.

2.7 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3.0 Definitions and units of measure

Definitions and units of measure are given in the glossary at the end of this Method.

4.0 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts, elevated baselines, and/or lock-mass suppression causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent

solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.

4.2.3 Baking of glassware in a kiln or other high temperature furnace (300 - 500°C) may be warranted after particularly dirty samples are encountered. The kiln or furnace should be vented to prevent laboratory contamination by pesticide vapors. Baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb pesticides. Volumetric ware should not be baked at high temperature.

4.2.4 After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.2.5 Immediately prior to use, the Soxhlet apparatus should be pre-extracted for approximately 3 hours and the extraction apparatus should be rinsed with the extraction solvent.

4.3 All materials used in the analysis must be demonstrated to be free from interferences by running reference matrix method blanks (Section 9.5) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the pesticides in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed.

4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.

4.4 Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the pesticides. The most frequently encountered interferences are chlorinated biphenyls, chlorinated and brominated dibenzodioxins and dibenzofurans, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, brominated diphenyl ethers, polynuclear aromatics, and polychlorinated naphthalenes. Because very low levels of pesticides are measured by this Method, elimination of interferences is essential. The cleanup steps given in Section 13

can be used to reduce or eliminate these interferences and thereby permit reliable determination of the pesticides at the levels shown in Table 1.

4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Organic acids and other substances make it difficult to extract and clean up biosolids (sewage sludge) samples. The exact procedures to be used are dependent on the analytes to be determined. If all analytes in this Method are to be determined, gel permeation chromatography (GPC), the amino-propyl SPE column, and the layered alumina/Florisil column have been found effective. For the organo-chlorine pesticides, sequential extraction with acetonitrile and methylene chloride followed by back extraction with sodium sulfate-saturated water has been found effective. An anthropogenic isolation column (Section 13.6; see Section 7.5.2 for column details), GPC (Section 13.2), high performance liquid chromatography (HPLC; Section 13.5), Florisil (Section 13.7), and alumina (Section 13.8) are additional steps that may be employed to minimize interferences in the sludge matrix.

4.7 The natural lipid content of tissue can interfere in the analysis of tissue samples for measurement of pesticides. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for sample extracts. Lipids must be removed by the anthropogenic isolation column procedure in Section 13.6, followed by GPC (Section 13.2).

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 Some pesticides, most notably 4,4'-DDT and 4,4'-DDD, have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standards of the pesticides should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this Method. However, if primary solutions are prepared, they must be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator must be worn when high concentrations are handled.

5.2 This Method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this Method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this Method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 4-7. The references and bibliography at the end of Reference 6 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 The pure pesticides and samples suspected to contain high concentrations of these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a strict safety program for handling these compounds. The practices in Reference 8 for handling chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDDs/CDFs) are also recommended for handling pesticides.

5.3.1 Facility – When finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

5.3.2 Protective equipment – Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the pesticides, an additional set of gloves can also be worn beneath the latex gloves.

5.3.3 Training – Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene – Hands and forearms should be washed thoroughly after each operation involving high concentrations of the pesticides, and before breaks (coffee, lunch, and shift).

5.3.5 Confinement – Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors – The effluent of the sample splitter from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols to condense pesticide vapors.

5.3.7 Waste handling – Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel should be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel – Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces – Chlorothene NU Solvent is a less toxic solvent that should be effective in removing pesticides. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. If glassware is first rinsed with solvent, the wash water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.

5.3.9 Laundry – Clothing known to be contaminated should be collected in plastic bags. Persons that convey the bags and launder clothing should be advised of the hazard and trained in proper handling. Clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests – A useful method of determining cleanliness of work surfaces and tools is to perform a wipe test of the surface suspected of being contaminated.

5.3.10.1 Using a piece of filter paper moistened with Chlorothene or other solvent, wipe an area approximately 10 x 10 cm.

5.3.10.2 Extract and analyze the wipe by GC with an electron capture detector (ECD) or by this Method.

5.3.10.3 Using the area wiped (e.g., 10 x 10 cm = 0.01 m^2), calculate the concentration in µg/m^2. A concentration less than 1 µg/m^2 indicates acceptable cleanliness; anything higher warrants further cleaning. More than 100 µg/m^2 constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

5.4 Biosolids samples may contain high concentrations of biohazards, and must be handled with gloves and opened in a hood or biological safety cabinet to prevent exposure. Laboratory staff should know and observe the safety procedures required in a microbiology laboratory that handles pathogenic organisms when handling biosolids samples.

6.0 Apparatus and materials

Note: *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this Method is the responsibility of the laboratory.*

6.1 Sampling equipment for discrete or composite sampling

6.1.1 Sample bottles and caps

6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5 percent solids or less) – Sample bottle, amber glass, 1.1-L minimum, with screw cap.

6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5 percent solids) – Sample bottle, wide mouth, amber glass, 500-mL minimum.

6.1.1.3 If amber bottles are not available, samples must be protected from light.

6.1.1.4 Bottle caps – Threaded to fit sample bottles. Caps must be lined with fluoropolymer.

6.1.1.5 Cleaning

6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.

6.1.1.5.2 Liners are detergent water washed and rinsed with reagent water (Section 7.6.1).

6.1.2 Compositing equipment – Automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing must be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing must be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

6.2 Equipment for glassware cleaning

Note: *If blanks from bottles or other glassware or with fewer cleaning steps than required in this Method show no detectable pesticide contamination, unnecessary cleaning steps and equipment may be eliminated.*

6.2.1 Laboratory sink with overhead fume hood

6.2.2 Kiln – Capable of reaching 450°C within 2 hours and maintaining 450 - 500°C within ∀10°C, with temperature controller and safety switch (Cress Manufacturing Co, Santa Fe Springs, CA, B31H, X31TS, or equivalent). See the precautions in Section 4.2.3.

6.2.3 Aluminum foil – solvent rinsed or baked in a kiln. If baked in a kiln, heavy-duty aluminum foil is required, as thinner foil will become brittle and unusable.

6.3 Equipment for sample preparation

6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.3.2 Glove box (optional)

6.3.3 Tissue homogenizer – VirTis Model 45 Macro homogenizer (American Scientific Products H-3515, or equivalent) with stainless steel Macro-shaft and Turbo-shear blade.

6.3.4 Meat grinder – Hobart, or equivalent, with 3- to 5-mm holes in inner plate.

6.3.5 Equipment for determining percent moisture

6.3.5.1 Oven – Capable of maintaining a temperature of 110 ∀5°C

6.3.5.2 Desiccator

6.3.6 Balances

6.3.6.1 Analytical – Capable of weighing 0.1 mg

6.3.6.2 Top loading – Capable of weighing 10 mg

6.4 Extraction apparatus

6.4.1 Water and solid samples

6.4.1.1 pH meter, with combination glass electrode

6.4.1.2 pH paper, wide range (Hydrion Papers, or equivalent)

6.4.1.3 Graduated cylinder, glass, 1-L capacity and Erlenmeyer Flask, glass, 1-L capacity

6.4.1.4 Liquid/liquid extraction – Separatory funnels, 250-, 500-, and 2000-mL, with fluoropolymer stopcocks

6.4.1.5 Solid-phase extraction

6.4.1.5.1 1-L filtration apparatus, including glass funnel, frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.

6.4.1.5.2 Vacuum source – Capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge

6.4.1.5.3 Glass-fiber filter – Whatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1

6.4.1.5.4 Solid-phase extraction disk containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix – Fisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1

6.4.1.6 Continuous liquid/liquid extraction (CLLE) – Fluoropolymer or glass connecting joints and stopcocks without lubrication, 1.5-2 L capacity (Hershberg-Wolf Extractor, Cal-Glass, Costa Mesa, California, 1000 mL or 2000 mL, or equivalent)

6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5 and Reference 3) for filters and solid/sludge samples

6.4.2.1 Soxhlet – 50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask)

6.4.2.2 Thimble – 43 H 123 to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent)

6.4.2.3 Moisture trap – Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet

6.4.2.4 Heating mantle – Hemispherical, to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent)

6.4.2.5 Variable transformer – Powerstat (or equivalent), 110-volt, 10-amp

6.4.3 Beakers – 400- to 500-mL

6.4.4 Spatulas – Stainless steel

6.5 Filtration apparatus

6.5.1 Pyrex glass wool – Solvent-extracted using a Soxhlet or SDS extractor for 3 hours minimum

6.5.2 Glass funnel – 125- to 250-mL

6.5.3 Glass-fiber filter paper – Whatman GF/D (or equivalent), to fit glass funnel in Section 6.5.2.

6.5.4 Drying column – 15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug

6.5.5 Buchner funnel – 15-cm

6.5.6 Glass-fiber filter paper for Buchner funnel above

6.5.7 Filtration flasks – glass, 1.5- to 2.0-L, with side arm

6.5.8 Pressure filtration apparatus – Millipore YT30 142 HW, or equivalent

6.6 Centrifuge apparatus

6.6.1 Centrifuge – Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum

6.6.2 Centrifuge bottles – 500-mL, with screw-caps, to fit centrifuge

6.6.3 Centrifuge tubes – 12- to 15-mL, with screw-caps, to fit centrifuge

6.7 Cleanup apparatus

6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent)

6.7.1.1 Column – 600-700 mm long H 25 mm ID glass, packed with 70 g of 200-400 mesh SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent)

6.7.1.2 Syringe – 10-mL, with Luer fitting

6.7.1.3 Syringe filter holder – stainless steel, and glass-fiber or fluoropolymer filters (Gelman 4310, or equivalent)

6.7.1.4 UV detectors – 254-nm, preparative or semi-preparative flow cell (Isco, Inc., Type 6; Schmadzu, 5-mm path length; Beckman-Altex 152W, 8-µL micro-prep flow cell, 2-mm path; Pharmacia UV-1, 3-mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent)

6.7.2 Reverse-phase high-performance liquid chromatograph (Reference 9)

6.7.2.1 Pump – Perkin-Elmer Series 410, or equivalent

6.7.2.2 Injector – Perkin-Elmer ISS-100 Autosampler, or equivalent

6.7.2.3 6-Port switching valve – Valco N60, or equivalent

6.7.2.4 Column – Hypercarb, 100 x 4.6 mm, 5 Φm particle size, Keystone Scientific, or equivalent

6.7.2.5 Detector – Altex 110A (or equivalent) operated at 0.02 AUFS at 235 nm

6.7.2.6 Fraction collector – Isco Foxy II, or equivalent

6.7.3 Pipets, precleaned

6.7.3.1 Disposable, Pasteur, 150-mm long x 5-mm ID (Fisher Scientific 13-678-6A, or equivalent)

6.7.3.2 Disposable, serological, 50-mL (8- to 10- mm ID)

6.7.4 Glass chromatographic columns

6.7.4.1 150-mm long x 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir

6.7.4.2 200-mm long x 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir

6.7.4.3 300-mm long x 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock

6.7.5 Oven – For baking and storage of adsorbents, capable of maintaining a constant temperature (∀ 5°C) in the range of 105-250°C

6.7.6 System for solid-phase extraction

6.7.6.1 Vac-Elute Manifold (Analytichem International, or equivalent)

6.7.6.2 Vacuum trap: Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing

6.7.6.3 Rack for holding 50-mL volumetric flasks in the manifold

6.8 Concentration apparatus

6.8.1 Rotary evaporator – Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath

6.8.1.1 Vacuum source for rotary evaporator equipped with vacuum gauge and with shutoff valve at the evaporator

6.8.1.2 A recirculating water pump and chiller are recommended. Use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.8.1.3 Round-bottom flask – 100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator

6.8.2 Kuderna-Danish (K-D) concentrator

6.8.2.1 Concentrator tube – 10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.8.2.2 Evaporation flask – 500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent)

6.8.2.3 Snyder column – Three-ball macro (Kontes K-503000-0232, or equivalent)

6.8.2.4 Boiling chips

6.8.2.4.1 Glass or silicon carbide – Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for one hour minimum

6.8.2.4.2 Fluoropolymer (optional) – Extracted with methylene chloride

6.8.2.5 Water bath – Heated, with concentric ring cover, capable of maintaining a temperature within ∀ 2°C, installed in a fume hood

6.8.3 Nitrogen evaporation apparatus – Equipped with water bath controlled in the range of 30 - 60°C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood

6.8.4 Sample vials

6.8.4.1 Amber glass, 2- to 5-mL with fluoropolymer-lined screw-cap

6.8.4.2 Glass, 0.3-mL, conical, with fluoropolymer-lined screw or crimp cap

6.9 Gas chromatograph – Must have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and must meet all of the performance specifications in Section 10.

6.9.1 GC column – 60 ∀ 5-m long x 0.25 ∀ 0.02-mm ID; 0.10-µm film DB-17, or equivalent

6.9.1.1 The column must meet the following minimum retention time and resolution criteria, and must be adjusted or replaced when these criteria are not met:

6.9.1.1.1 The retention time for methoxychlor must be greater than 39 minutes.

6.9.1.1.2 trans-chlordane and trans-nonachlor (or the labeled analogs) must be uniquely resolved to a valley height less than 10 percent of the shorter of the two peaks.

6.9.1.2 Endrin and DDT breakdown – The column must meet the endrin/DDT breakdown criteria in Section 10.6.2.3. Some GC injectors may be unable to meet requirements for endrin and DDT breakdown. This problem can be minimized by operating the injector at 200 - 205 °C, using a Pyrex (not quartz) methyl silicone deactivated injector liner, and deactivating the injector with dichlorodimethylsilane. A temperature

programmed injector has also been shown to minimize decomposition of labile substances such as endrin and DDT (Reference 10).

6.10 Mass spectrometer – 28- to 40-eV electron impact ionization, must be capable of selectively monitoring a minimum of 22 exact m/z's minimum at high resolution (greater than 8,000) during a period less than 1.5 seconds, and must meet all of the performance specifications in Section 10.

6.11 GC/MS interface – The mass spectrometer (MS) must be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.12 Data system – Capable of collecting, recording, storing, and processing MS data

6.12.1 Data acquisition – The signal at each exact m/z must be collected repetitively throughout the monitoring period and stored on a mass storage device.

6.12.2 Response factors and multipoint calibrations – The data system must record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibrations. Computations of relative standard deviation (RSD) are be used to test calibration linearity. Statistics on initial (Section 9.4) and ongoing (Section 15.6.4) performance should be computed and maintained, either on the instrument data system, or on a separate computer system.

7.0 Reagents and standards

7.1 pH adjustment and back-extraction

7.1.1 Potassium hydroxide (KOH) – Dissolve 20 g reagent grade KOH in 100 mL reagent water.

7.1.2 Sulfuric acid (H_2SO_4) – Reagent grade (specific gravity 1.84)

7.1.3 Hydrochloric acid – Reagent grade, 6N

7.1.4 Sodium chloride solution – Prepare at 5% (w/v) solution in reagent water

7.1.4 Sodium sulfate solution – Prepare at 2% (w/v) in reagent water; pH adjust to 8.5 - 9.0 with KOH or H_2SO_4

7.2 Solution and tissue drying, municipal sludge extract back-extraction, and solvent evaporation (blowdown)

7.2.1 Solution drying – Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium

sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Tissue drying – Sodium sulfate, reagent grade, powdered, treated and stored as in Section 7.2.1

7.2.3 Solution for back-extraction of municipal sludge extracts – Sodium sulfate solution: 2% (w/v) in reagent water, pH adjusted to pH 8.5 to 9.0 with KOH or H_2SO_4

7.2.4 Prepurified nitrogen

7.3 Extraction

7.3.1 Solvents – Acetone, toluene, cyclohexane, hexane, methanol, methylene chloride, isooctane, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences

7.3.2 White quartz sand, 60/70 mesh – For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450 – 500°C for 4 hours minimum.

7.4 GPC calibration solution – Prepare a solution containing 2.5 mg/mL corn oil, 0.05 mg/mL bis(2-ethylhexyl) phthalate (BEHP), 0.01 mg/mL methoxychlor, 0.002 mg/mL perylene, and 0.008 mg/mL sulfur, or at concentrations appropriate to the response of the detector.

7.5 Adsorbents for sample cleanup

7.5.1 Silica gel

7.5.1.1 Activated silica gel – 100-200 mesh, Supelco 1-3651 (or equivalent), mesh, rinsed with methylene chloride, baked at 180±5 °C for a minimum of 1 hour, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.5.1.1.1 10% deactivated silica – Place 100 g of activated silica gel (Section 7.5.1.1) in a clean glass bottle or jar and add 10 g (or mL) of reagent water. Cap the bottle tightly to prevent moisture from entering or escaping.

7.5.1.1.2 Tumble the bottle for 5 - 10 hours to thoroughly mix the water and silica. Keep bottle tightly sealed when silica is not being removed for use.

7.5.1.2 Acid silica gel (30% w/w) – Thoroughly mix 44 g of concentrated sulfuric acid with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.5.1.3 Basic silica gel – Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.5.1.4 Potassium silicate

7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750- to 1000-mL flat-bottom flask.

7.5.1.4.2 Add 100 g of activated silica gel (Section 7.5.1.1) and a stirring bar, and stir on an explosion-proof hot plate at 60-70°C for 1-2 hours.

7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100-mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.

7.5.1.4.4 Spread the potassium silicate on solvent-rinsed aluminum foil and dry for 2-4 hours in a hood. Observe the precaution in Section 5.3.2.

7.5.1.4.5 Activate overnight at 200-250°C prior to use.

7.5.2 Anthropogenic isolation column – Pack the column in Section 6.7.4.3 from bottom to top with the following:

7.5.2.1 2 g silica gel (Section 7.5.1.1)

7.5.2.2 2 g potassium silicate (Section 7.5.1.4)

7.5.2.3 2 g granular anhydrous sodium sulfate (Section 7.2.1)

7.5.2.4 10 g acid silica gel (Section 7.5.1.2)

7.5.2.5 2 g granular anhydrous sodium sulfate

7.5.3 Aminopropyl solid-phase extraction (SPE) column – 1 g aminopropyl-bonded silica (Varian NH2, or equivalent).

Note: *Other SPE columns (e.g., C_{18} octadecyl, cyanopropyl) may be used provided the laboratory establishes the elution conditions and meets the requirements in Section 9.2 with the SPE column as an integral part of the analysis.*

7.5.4 Florisil column

7.5.4.1 Florisil – PR grade, 60-100 mesh (U.S. Silica Corp, Berkeley Springs, WV, or equivalent). Alternatively, prepacked Florisil columns may be used. Use the following procedure for Florisil activation and column packing.

7.5.4.2 Fill a clean 1- to 2-L bottle 1/2 to 2/3 full with Florisil and place in an oven at 130-150°C for a minimum of three days to activate the Florisil.

7.5.4.3 Immediately prior to use, dry pack a 300-mm x 22-mm ID glass column (Section 6.7.4.3) bottom to top with 0.5-1.0 cm of warm to hot anhydrous sodium sulfate (Section 7.2.1), 10-10.5 cm of warm to hot activated Florisil (Section 7.5.4.2), and 1-2 cm of warm to hot anhydrous sodium sulfate. Allow the column to cool and pre-elute immediately with 100 mL of n-hexane. Keep column wet with hexane to prevent water from entering.

7.5.4.4 Using the procedure in Section 13.7.3, establish the elution pattern for each carton of Florisil or each lot of Florisil columns received.

7.5.5 Alumina column

7.5.5.1 Alumina – Neutral, Brockman Activity I, 80-200 mesh (Fisher Scientific Certified, or equivalent). Heat for 16 hours at 400 to 450°C. Seal and cool to room temperature. Add 7% (W/W) reagent water and tumble for 1 to 2 hours. Keep bottle tightly sealed.

7.5.5.2 Immediately prior to use, partially fill a 150-mm x 8-mm ID glass column (Section 6.7.4.1) with n-hexane. Pack the column bottom to top with 0.5 - 1 cm of warm to hot anhydrous sodium sulfate (Section 7.2.1), 10 - 10.5 cm alumina (Section 7.5.5.1) and 1 - 1.5 cm of warm to hot anhydrous sodium sulfate. Allow the column to cool and pre-elute immediately with 100 mL of hexane. Keep column wet with hexane to prevent moisture from entering.

7.6 Reference matrices – Matrices in which the pesticides and interfering compounds are not detected by this Method

7.6.1 Reagent water – Bottled water purchased locally, or prepared by passage through activated carbon

7.6.2 High-solids reference matrix – Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450°C for a minimum of 4 hours.

7.6.3 Paper reference matrix – Glass-fiber filter, Gelman type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.

7.6.4 Tissue reference matrix – Corn or other vegetable oil.

7.6.5 Other matrices – This Method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the pesticides, but in no case must the background level of the pesticides in the reference matrix exceed the minimum levels in Table 1. If low background levels of the pesticides are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio of approximately 5 (Reference 11).

7.7 Standard solutions – Prepare from materials of known purity and composition or purchase as solutions or mixtures with certification to their purity, concentration, and authenticity. If the chemical purity is 98 % or greater, the weight may be used without correction to calculate the concentration of the standard. Observe the safety precautions in Section 5 and the recommendation in Section 5.1.2.

7.7.1 For preparation of stock solutions from neat materials, dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 10 to 20 mg of lindane to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the compound is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.

7.7.2 When not being used, store standard solutions in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps. Place a mark on the vial at the level of the solution so that solvent loss by evaporation can be detected. Replace the solution if solvent loss has occurred.

7.8 Native (unlabeled) stock solutions

7.8.1 Native stock solution – Prepare to contain the pesticides at the concentrations shown in Table 3, or purchase prepared solutions. If additional pesticides are to be determined, include the additional native compounds in this stock solution.

7.8.2 Stock solutions should be checked for signs of degradation (e.g., discoloration, precipitation) prior to preparing calibration or performance test standards. Reference standards that can be used to determine the accuracy of standard solutions are available from several vendors.

7.9 Labeled compound stock solutions (Table 3)

7.9.1 Labeled pesticide stock solution – Prepare the labeled pesticides in isooctane or nonane at the concentrations in Table 3 or purchase prepared standards. If additional pesticides are to be determined by isotope dilution, include the additional labeled compounds in this stock solution.

7.9.2 Labeled injection internal standard stock solution – Prepare labeled PCB 52 in nonane or isooctane at the concentration shown in Table 3, or purchase a prepared standard.

7.10 Calibration standards – Combine and dilute the solutions in Sections 7.8 and 7.9 to produce the calibration solutions in Table 4 or purchase prepared standards for the CS-1 to CS-6 set of calibration solutions. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS-4 standard is used for calibration verification (VER).

7.11 Native IPR/OPR standard spiking solution – Used for determining initial precision and recovery (IPR; Section 9.2) and ongoing precision and recovery (OPR; Section 15.6). Dilute the Native stock solution (Section 7.8.1) with acetone to produce the concentrations of the pesticides as shown in Table 3. When 1 mL of this solution is spiked into the IPR (Section 9.2.1) or OPR (Section 15.6) and concentrated to a final volume of 20 µL, the concentration of the pesticides in the final volume will be either 8 or 20 ng/mL (pg/ΦL), as shown in Table 3. Prepare only the amount necessary for each reference matrix with each sample batch.

7.12 Labeled standard spiking solution – This solution is spiked into each sample (Section 9.3) and into the IPR (Section 9.2.1), OPR (Section 15.6), and blank (Section 9.5) to measure recovery. Dilute the Labeled pesticide stock solution (Section 7.9.1) with acetone to produce the concentrations of the labeled compounds shown in Table 3. When 1 mL of this solution is spiked into an IPR, OPR, blank, or sample and concentrated to a final extract volume of 20 µL, the concentration in the final volume will be as shown in Table 3. Prepare only the amount necessary for each reference matrix with each sample batch.

7.13 Endrin/4,4'-DDT breakdown solution – Prepare a solution to contain 100 ng/mL (pg/µL) of DDT and 50 ng/mL (pg/µL) of endrin in isooctane or nonane. This solution is to determine endrin/4,4'-DDT breakdown in Sections 10.6 and 15.5.

7.14 Labeled injection internal standard spiking solution – This solution is added to each concentrated extract prior to injection into the HRGC/HRMS. Dilute the Labeled injection internal standard stock solution (Section 7.9.2) in nonane to produce a concentration of the injection internal standards at 800 ng/mL, as shown in Table 3. When 2 µL of this solution is spiked into a 20 µL extract, the concentration of each injection internal standard will be nominally 80 ng/mL (pg/µL), as shown in Table 3.

Note: *The addition of 2 µL of the Labeled injection internal standard spiking solution to a 20 µL final extract has the effect of diluting the concentration of the components in the extract by 10%.*

Provided all calibration solutions and all extracts undergo this dilution as a result of adding the Labeled injection internal standard spiking solution, the effect of the 10% solution is compensated, and correction for this dilution should not be made.

7.15 QC Check Sample – A QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified Standard Reference Material (SRM) containing the pesticides in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has SRMs, and the Institute for National Measurement Standards of the National Research Council of Canada in Ottawa has certified reference materials (CRMs), for pesticides in various matrices.

7.16 Stability of solutions – Standard solutions used for quantitative purposes (Sections 7.8 - 7.14) should be assayed periodically (e.g., every 6 months) against SRMs from NIST (if available), or certified reference materials from a source that will attest to the authenticity and concentration, to assure that the composition and concentrations have not changed.

8.0 Sample collection, preservation, storage, and holding times

8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 12); collect field and trip blanks as necessary to validate the sampling.

8.2 Aqueous samples

8.2.1 Samples that flow freely are collected as grab samples or in refrigerated bottles using automatic sampling equipment. Collect 1-L. If high concentrations of the pesticides are expected, collect a smaller volume (e.g., 100 mL) in addition to the 1-L sample. Do not rinse the bottle with sample before collection.

8.2.2 If residual chlorine is present, add 80 mg sodium thiosulfate per liter of water. Any method suitable for field use may be employed to test for residual chlorine (Reference 9).

8.2.3 Maintain aqueous samples in the dark at <6°C from the time of collection until receipt at the laboratory (see 40 CFR 136.6(e), Table II). If the sample will be frozen, allow room for expansion.

8.2.4 If the sample will not be analyzed within 72 hours, adjust the pH to a range of 5.0 to 9.0 with sodium hydroxide or sulfuric acid solution. Record the volume of acid or base used.

8.3 Solid, mixed-phase, semi-solid, and oily samples, excluding tissue.

8.3.1 Collect samples as grab samples using wide-mouth jars. Collect a sufficient amount of wet material to produce a minimum of 20 g of solids.

8.3.2 Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <6°C from the time of collection until receipt at the laboratory. Store solid, semi-solid, oily, and mixed-phase samples in the dark at less than -10°C.

8.4 Fish and other tissue samples

8.4.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.4.2 Collect fish, wrap in aluminum foil, and maintain at <6°C from the time of collection until receipt at the laboratory, to a maximum time of 24 hours. If a longer transport time is necessary, freeze the sample. Ideally, fish should be frozen upon collection and shipped to the laboratory under dry ice.

8.4.3 Freeze tissue samples upon receipt at the laboratory and maintain in the dark at less than -10°C until prepared. Maintain unused sample in the dark at less than -10°C.

8.4.4 Store sample extracts in the dark at less than -10°C until analyzed.

8.5 Holding times – See 40 CFR 136.3(e) Table II

8.5.1 Aqueous samples – Extract within 7 days of collection, and analyze within 40 days of extraction.

8.5.2 Solid, mixed-phase, semi-solid, tissue, and oily samples – Extract and analyze within 1 year of collection. If a sample is to be stored for more than 14 days, and results are to be reported in solids units, either hermetically seal the sample container or determine the moisture content upon receipt and immediately prior to analysis. Adjust the final concentration based on the original moisture content.

9.0 Quality assurance/quality control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 14). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the Method.

If the Method is to be applied to a sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate reference matrix (Sections 7.6.2 - 7.6.5 and 7.15) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.

9.1.1 The laboratory must make an initial demonstration of the ability to generate acceptable precision and recovery with this Method. This demonstration is given in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, and cleanup procedures, and changes in columns and detectors (see also 40 CFR 136.6). Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade Method performance, are not allowed. If an analytical technique other than the techniques specified in this Method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this Method for the analytes of interest.

9.1.2.1 Each time a modification is made to this Method, the laboratory is required to repeat the procedure in Section 9.2. If the detection limit of the Method will be affected by the change, the laboratory is required to demonstrate that the MDLs (40 CFR Part 136, Appendix B) are lower than one-third the regulatory compliance level or the MDLs in this Method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per Section 10. Once the modification is demonstrated to produce results equivalent or superior to results produced by this Method as written, that modification may be used routinely thereafter, so long as the other requirements in this Method are met (e.g., labeled compound recovery).

9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this Method, including:

a) Calibration (Section 10)
b) Calibration verification (Section 15.3)
c) Initial precision and recovery (Section 9.2)
d) Labeled compound recovery (Section 9.3)

e) Analysis of blanks (Section 9.5)
f) Accuracy assessment (Section 9.4)

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers
b) Extraction dates
c) Analysis dates and times
d) Analysis sequence/run chronology
e) Sample weight or volume (Section 11)
f) Extract volume prior to each cleanup step (Section 13)
g) Extract volume after each cleanup step (Section 13)
h) Final extract volume prior to injection (Section 14)
i) Injection volume (Sections 10.3 and 14.3)
j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5)
k) Instrument and operating conditions
l) Column (dimensions, liquid phase, solid support, film thickness, etc)
m) Operating conditions (temperatures, temperature program, flow rates)
n) Detector (type, operating conditions, etc)
o) Chromatograms, printer tapes, and other recordings of raw data
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported

9.1.2.3 Alternate HRGC columns and column systems – If a column or column system alternate to those specified in this Method is used, that column or column system must meet the requirements in Section 6.9.1.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are given in Sections 9.5 and 15.7.

9.1.4 The laboratory must spike all samples with labeled compounds to monitor Method performance. This test is described in Section 9.3. When results of these spikes indicate atypical Method performance for samples, the samples are diluted to bring Method performance within acceptable limits. Procedures for dilution are given in Section 17.5.

9.1.5 The laboratory must, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery standard (OPR) and

blanks that the analytical system is in control. These procedures are given in Sections 15.1 through 15.7.

9.1.6 The laboratory should maintain records to define the quality of data generated. Development of accuracy statements is described in Sections 9.4 and 15.6.4.

9.2 Initial precision and recovery (IPR) – To establish the ability to generate acceptable precision and recovery, the laboratory must perform the following operations:

9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with 1 mL each of the Native spiking solution (Section 7.11) and the Labeled spiking solution (Section 7.12), according to the procedures in Sections 11 through 18. For an alternate sample matrix, four aliquots of the alternate reference matrix (Sections 7.6.1 - 7.6.5) are used. All sample processing steps that are to be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), must be included in this test.

9.2.2 Using results of the set of four analyses, compute the average percent recovery (X) of the extracts and the relative standard deviation (RSD) of the concentration for each compound, by isotope dilution for pesticides with a labeled analog, and by internal standard for pesticides without a labeled analog and for the labeled compounds.

9.2.3 For each pesticide and labeled compound, compare RSD and X with the corresponding limits for initial precision and recovery in Table 5. If RSD and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual RSD exceeds the precision limit or any individual X falls outside the range for recovery, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).

9.3 To assess Method performance on the sample matrix, the laboratory must spike all samples with the Labeled spiking solution (Section 7.12).

9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.

9.3.2 Compute the percent recovery of the labeled pesticides using the internal standard method (Section 17.2).

9.3.3 The recovery of each labeled compound must be within the limits in Table 5. If the recovery of any compound falls outside of these limits, Method performance is unacceptable for that compound in that sample. Additional cleanup procedures must then be employed to attempt to bring the recovery within the normal range. If the recovery cannot be brought within the normal range after all cleanup procedures have been employed, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are analyzed per Section 18.

9.4 It is suggested but not required that recovery of labeled compounds from samples be assessed and records maintained.

9.4.1 After the analysis of 30 samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (S_R) for the labeled compounds only. Express the assessment as a percent recovery interval from R ! $2S_R$ to R + $2S_R$ for each matrix. For example, if R = 90% and S_R = 10% for five analyses of pulp, the recovery interval is expressed as 70 to 110%.

9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each five to ten new measurements).

9.5 Method blanks – A reference matrix Method blank is analyzed with each sample batch (Section 4.3) to demonstrate freedom from contamination. The matrix for the Method blank must be similar to the sample matrix for the batch, e.g., a 1-L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3); tissue blank (Section 7.6.4), or alternate reference matrix blank (Section 7.6.5).

9.5.1 Spike 1.0 mL each of the Labeled spiking solution (Section 7.12) into the Method blank, according to the procedures in Sections 11 through 18. Prepare, extract, clean up, and concentrate the Method blank. Analyze the blank immediately after analysis of the OPR (Section 15.6) to demonstrate freedom from contamination.

9.5.2 If any pesticide (Table 1) is found in the blank at greater than the minimum level (Table 1) or one-third the regulatory compliance limit, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each pesticide in Table 1 (assuming a response factor of 1 relative to the quantitation reference in Table 2 for a potentially interfering compound; i.e., a compound not listed in this Method), analysis of samples must be halted until the sample batch is re-extracted and the extracts re-analyzed, and the blank associated with the sample batch shows no evidence of contamination at these levels. All samples must be associated with an uncontaminated Method blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes.

9.6 QC Check Sample – Analyze the QC Check Sample (Section 7.15) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.

9.7 The specifications contained in this Method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.6) precision and recovery should be identical, so that the most precise results will be obtained. A GC/HRMS instrument will provide the most reproducible

results if dedicated to the settings and conditions required for determination of pesticides by this Method.

9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

10.0 Calibration

10.1 Establish the operating conditions necessary to meet the retention times (RTs) and relative retention times (RRTs) for the pesticides in Table 2.

10.1.1 Suggested operating conditions:

GC conditions	
Injector	Split/splitless, 2 min
Carrier gas	Helium @ 200 kPa
Injector temperature	180 - 220°C or temperature programmed
Maximum column temperature	300°C
GC Temperature program	
Initial temperature and hold	50°C for 1 minute
Initial ramp	50 - 180°C @ 10°C per minute
Second hold	180°C for 0 minute
Second ramp	180 - 200°C @ 1.5°C per minute
Third hold	200°C for 2 minutes
Third ramp	200 - 295°C @ 6°C per minute
Final hold	295°C for 1 minutes or until methoxychlor elutes
Interface temperature	290°C
Mass spectrometer conditions	
Source temperature	250°C
Electron energy	35 eV
Trap current	500 - 900 ΦA
Mass resolution	8000
Detector potential	340 - 400 V

10.1.1.1 All portions of the column that connect the GC to the ion source should remain at or above the interface temperature during analysis to preclude condensation of less volatile compounds.

10.1.1.2 The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR standards, and samples.

10.1.2 Retention time calibration for the native and labeled pesticides

10.1.2.1 Inject the CS-4 calibration standard (Section 7.10 and Table 4). Establish the beginning and ending retention times for the scan descriptors in Table 6. Scan descriptors other than those listed in Table 6 may be used provided the MLs in Table 1 are met. Store the retention time (RT) and relative retention time (RRT) for each compound in the data system.

10.1.2.2 The absolute retention time of methoxychlor must exceed 39 minutes on the DB-17 column; otherwise, the GC temperature program must be adjusted and this test repeated until the minimum retention time criterion is met. If a GC column or column system alternate to the DB-17 column is used, a similar minimum retention time specification must be established for the alternate column or column systems so that interferences that may be encountered in environmental samples will be resolved from the analytes of interest. This specification is deemed to be met if the retention time of methoxychlor is greater than 39 minutes on such alternate column.

10.2 Mass spectrometer (MS) resolution

10.2.1 Using PFK (or other reference substance) and a molecular leak, tune the instrument to meet the minimum required resolving power of 8,000 (10% valley) at m/z 280.9825 or other significant PFK fragment in the range of 250 - 300. For each descriptor (Table 6), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The level of PFK (or other reference substance) metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Note: *Different lots and types of PFK can contain varying levels of contamination, and excessive PFK (or other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.*

10.2.2 The analysis time for the pesticides may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, mass-drift correction is mandatory and a lock-mass m/z from perfluorokerosene (PFK) or other reference substance is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 6. The deviation between each monitored exact m/z and the theoretical m/z (Table 6) must be less than 5 ppm.

10.2.3 Obtain a selected ion current profile (SICP) at the two exact m/z's specified in Table 6 and at ∃8,000 resolving power for each native and labeled pesticide. Because of the extensive mass range covered in each function, it may not be possible to maintain 8,000 resolution throughout the mass range during the function. Therefore, resolution must be ∃6,000 throughout the mass range and must be ∃8,000 in the center of the mass range for each function.

10.2.4 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below the minimum (Section 10.2.1 and 10.2.3) to save re-analysis time.

10.3 Ion abundance ratios, minimum levels, and signal-to-noise ratios during calibration. Choose an injection volume of either 1 or 2 µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 or 2 µL aliquot of the CS-1 calibration solution (Table 4) using the GC conditions in Section 10.1.1.

10.3.1 Measure the SICP areas for each pesticide, and compute the ion abundance ratios at the exact m/z's specified in Table 6. Compare the computed ratio to the theoretical ratio given in Table 6.

10.3.1.1 The exact m/z's to be monitored in each descriptor are shown in Table 6. Each group or descriptor must be monitored in succession as a function of GC retention time to ensure that the pesticides are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the descriptors listed in Table 6, provided that the laboratory is able to monitor the m/z's of all pesticides that may elute from the GC in a given RT window.

10.3.1.2 The mass spectrometer must be operated in a mass-drift correction mode, using PFK (or other reference substance) to provide lock m/z's. The lock mass for each group of m/z's is shown in Table 6. Each lock mass must be monitored and must not vary by more than ∀ 20% throughout its respective retention time window. Variations of lock mass by more than 20% indicate the presence of co-eluting interferences that raise the source pressure and may significantly reduce the sensitivity of the mass spectrometer. Re-injection of another aliquot of the sample extract may not resolve the problem and additional cleanup of the extract may be

required to remove the interference. A lock mass interference or suppression in a retention time region in which pesticides and labeled compounds do not elute may be ignored.

10.3.2 All pesticides and labeled compounds in the CS-1 standard must be within the QC limits in Table 6 for their respective ion abundance ratios; otherwise, the mass spectrometer must be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.2.1) prior to repeat of the test.

10.3.3 Verify that the HRGC/HRMS instrument meets the minimum levels (MLs) in Table 1. The peaks representing the pesticides and labeled compounds in the CS-1 calibration standard must have signal-to-noise ratios (S/N) $\exists$ 3; otherwise, the mass spectrometer must be adjusted and this test repeated until the minimum levels in Table 1 are met.

10.4 Calibration by isotope dilution – Isotope dilution is used for calibration of the native pesticides for which a labeled analog is available. The reference compound for each native compound is its labeled analog, as listed in Table 2. A 6-point calibration encompassing the concentration range is prepared for each native compound.

10.4.1 For the pesticides determined by isotope dilution, the relative response (RR) (labeled to native) vs. concentration in the calibration solutions (Table 4) is computed over the calibration range according to the procedures described below. Five calibration points are employed for less-sensitive HRMS instruments (e.g., VG 70); five or six points may be employed for more-sensitive instruments (e.g., Micromass Autospec Ultima).

10.4.2 Determine the response of each pesticide relative to its labeled analog using the area responses of both the primary and secondary exact m/z's specified in Table 6, for each calibration standard. Use the labeled compounds listed in Table 2 as the quantitation reference and the two exact m/z's listed in Table 6 for quantitation. The areas at the two exact m/z's for the compound is summed and divided by the summed area of the two exact m/z's for the quantitation reference.

Note: *Both exact m/z's are used as reference to reduce the effect of an interference at a single m/z. Other quantitation references and procedures may be used provided that the results produced are as accurate as results produced by the quantitation references and procedures described in this Section.*

10.4.3 Calibrate the native compounds with a labeled analog using the following equation:

$$RR = \frac{(A1_n + A2_n)\, C_l}{(A1_l + A2_l)\, C_n}$$

Where:

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the pesticide

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_l = The concentration of the labeled compound in the calibration standard (Table 4).

C_n = The concentration of the native compound in the calibration standard (Table 4).

10.4.4 To calibrate the analytical system by isotope dilution, inject calibration standards CS-2 through CS-6 (Section 7.10 and Table 4) for a less sensitive instrument (e.g. VG 70) or CS-1 through CS-6 for a more sensitive instrument (e.g., Micromass Autospec Ultima). Use a volume identical to the volume chosen in Section 10.3, the procedure in Section 14, and the conditions in Section 10.1.1. Compute and store the relative response (RR) for each pesticide at each concentration. Compute the average (mean) RR and the RSD of the 6 RRs.

10.4.5 Linearity – If the RRs for any pesticide are constant (less than 20% RSD), the average RR may be used for that pesticide; otherwise, the complete calibration curve for that pesticide must be used over the calibration range.

10.5 Calibration by internal standard – Internal standard calibration is applied to determination of the native pesticides for which a labeled compound is not available, and to determination of the labeled compounds for performance tests and intra-laboratory statistics (Sections 9.4 and 15.6.4). The reference compound for each compound is listed in Table 2. For the labeled compounds, calibration is performed at a single concentration using data from the 6 points in the calibration (Section 10.4).

10.5.1 Response factors – Internal standard calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_s + A2_s)\, C_{is}}{(A1_{is} + A2_{is})\, C_s}$$

Where:

$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the pesticide.

$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard.

C_{is} = The concentration of the internal standard (Table 4).

C_s = The concentration of the compound in the calibration standard (Table 4).

10.5.2 To calibrate the analytical system for pesticides that do not have a labeled analog, and for the labeled compounds, use the data from the 6-point calibration (Section 10.4.4 and Table 4).

10.5.3 Compute and store the response factor (RF) for all native pesticides that do not have a labeled analog and for the labeled compounds. Use the labeled compounds

listed in Table 2 as the quantitation reference and the two exact m/z's listed in Table 6 for quantitation. For example, the areas at the two exact m/z's for the compound is summed and divided by the summed area of the two exact m/z's for the quantitation reference.

10.5.4 Compute and store the response factor (RF) for the labeled compounds using the Labeled injection internal standard as the quantitation reference, as given in Table 2.

10.5.5 Linearity – If the RFs for any pesticide are constant (less than 35% RSD), the average RF may be used for that pesticide; otherwise, the complete calibration curve for that pesticide must be used over the calibration range.

10.6 Endrin/4,4'-DDT breakdown – This test is run after calibration (Section 10.4 and 10.5) or calibration verification (Section 15.3) to assure that the labile pesticides do not decompose in the GC.

10.6.1 Inject the endrin/4,4'-DDT breakdown solution (Section 7.13) using the same volume chosen in Section 10.3.

10.6.2 Measure and sum the peak areas for both exact m/z's separately for 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, endrin, endrin aldehyde, and endrin ketone using the calibration data from Section 10.4.

10.6.2.1 Add the summed peak areas for endrin aldehyde and endrin ketone and separately add the peak areas for 4,4'-DDD and 4,4'-DDE.

10.6.2.2 Calculate the endrin and 4,4'-DDT breakdown as follows:

$$\textit{Endrin breakdown (percent)} = \frac{\textit{(areas for endrin aldehyde + endrin ketone)}}{\textit{areas for endrin}} \times \textit{100}$$

$$\textit{4,4'-DDT breakdown (percent)} = \frac{\textit{(areas for 4,4'-DDD + 4,4'-DDE)}}{\textit{areas for 4,4'-DDT}} \times \textit{100}$$

10.6.2.3 If the breakdown of endrin or 4,4'-DDT exceeds 20 percent, endrin or 4,4'-DDT is decomposing. If decomposition greater than 20 percent of either endrin or 4,4'-DDT occurs, clean and recondition the injector, break off a short section of the inlet end of the column, or alter the GC conditions to reduce the decomposition to where the 20 percent criterion is met (see Section 6.9.1.2).

11.0 Sample preparation

11.1 Sample preparation involves modifying the physical form of the sample so that the pesticides can be extracted efficiently. In general, the samples must be in a liquid form or

in the form of finely divided solids in order for efficient extraction to take place. Table 7 lists the phases and suggested quantities for extraction of various sample matrices.

For samples known or expected to contain high levels of the pesticides, the smallest sample size representative of the entire sample should be used (see Section 18). For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.

11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.

11.1.2 Aqueous samples – Because the pesticides may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.

11.1.2.1 Aqueous samples containing one percent solids or less are prepared per Section 11.4 and extracted directly using one of the extraction techniques in Section 12.2.

11.1.2.2 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.

11.1.3 Solid Samples - Solid samples are prepared using the procedure described in Section 11.5 followed by extraction using the SDS procedure in Section 12.3.

11.1.4 Multi-phase samples – The phase(s) containing the pesticides is separated from the non-pesticide phase using pressure filtration and centrifugation, as described in Section 11.6. The pesticides will be in the organic phase in a multi-phase sample in which an organic phase exists.

11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.

11.1.6 Tissue samples – Preparation procedures for fish and other tissues are given in Section 11.8.

11.2 Determination of percent suspended solids

Note: *This aliquot is used for determining the solids content of the sample, not for pesticide determination.*

11.2.1 Aqueous liquids and multi-phase samples consisting of mainly an aqueous phase.

11.2.1.1 Desiccate and weigh a GF/D filter (Section 6.5.3) to three significant figures.

11.2.1.2 Filter 10.0 ∀0.02 mL of well-mixed sample through the filter.

11.2.1.3 Dry the filter a minimum of 12 hours at 110 ± 5°C and cool in a desiccator.

11.2.1.4 Calculate percent solids as follows:

$$\% \text{ Solids} = \frac{\text{Weight of sample aliquot after drying (g)} - \text{weight of filter (g)}}{10 \text{ g}} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous; but not tissues.

11.2.2.1 Weigh 5 to 10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at 110 ∀5°C, and cool in a desiccator.

11.2.2.3 Calculate percent solids as follows:

$$\% \text{ Solids} = \frac{\text{Weight of sample aliquot after drying}}{\text{Weight of sample aliquot before drying}} \times 100$$

11.3 Estimation of particle size

11.3.1 Spread the dried sample from Section 11.2.1.3 or 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of aqueous samples containing one percent suspended solids or less.

11.4.1 Aqueous samples containing one percent suspended solids or less are prepared using the procedure below and extracted using the one of the extraction techniques in Section 12.2.

11.4.2 Preparation of sample and QC aliquots

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to ∀ 1 g.

11.4.2.2 Spike 1.0 mL of the Labeled pesticide spiking solution (Section 7.12) into the sample bottle. Cap the bottle and mix the sample by shaking. Allow the sample to equilibrate for 1 to 2 hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0-L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the Labeled pesticide spiking solution (Section 7.12) into both reagent water aliquots. One of these aliquots will serve as the Method blank.

11.4.2.5 Spike 1.0 mL of the Native pesticide spiking solution (Section 7.11) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.6).

11.4.2.6 For extraction using SPE, add 5 mL of methanol to the sample and QC aliquots. Cap and shake the sample and QC aliquots to mix thoroughly, and proceed to Section 12.2 for extraction.

11.5 Preparation of samples containing greater than one percent solids.

11.5.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar, to a maximum of 1 L of sample.

11.5.2 Spike 1.0 mL of the Labeled pesticide spiking solution (Section 7.12) into the sample.

11.5.3 Prepare the blank and OPR aliquots per Sections 11.4.2.3 - 11.4.2.5.

11.5.4 Stir or tumble and equilibrate the aliquots for 1 to 2 hours.

11.5.5 Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

11.5.6 If particles >1 mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).

11.5.7 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.1.

11.6 Multi-phase samples, including high solids municipal sludge samples

11.6.1 Using the percent solids determined in Section 11.2.1.4 or 11.2.2.3, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.

11.6.2 Spike 1.0 mL of the Labeled pesticide spiking solution (Section 7.12) into the amount of sample determined in Section 11.6.1, and into the OPR and blank.

11.6.3 Prepare the blank and OPR aliquots per Sections 11.4.2.3 - 11.4.2.5.

11.6.4 Pressure filter the sample, blank, and OPR through Whatman GF/D glass-fiber filter paper (Section 6.5.3). If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration. Discard any aqueous phase (if present). Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample (Section 11.5.5) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.1.5).

11.6.5 If particles >1 mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. Observe the precaution in Section 5.3.1.

11.6.6 After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced-size particles using the SDS procedure in Section 12.3. If particles >1 mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

11.7 Sample grinding, homogenization, or blending – Samples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.

11.7.1 Each size-reducing preparation procedure on each matrix must be verified by running the tests in Section 9.2 before the procedure is employed routinely.

11.7.2 The grinding, homogenization, or blending procedures must be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.7.3 Grinding – Certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Sections 11.5.7 or 11.6.6 in a clean grinder. Do not allow the sample temperature to exceed 50°C. Grind the blank and reference matrix aliquots using a clean grinder.

11.7.4 Homogenization or blending – Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the particles or filter from Sections 11.5.7 or 11.6.6 for the sample, blank, and OPR aliquots.

11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.1.

11.8 Fish and other tissues – Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish-skin on, whole fish-skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.

11.8.1 Tissue homogenization

11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.

11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extraction of a second aliquot of the same homogenized sample, if re-analysis is required. When whole fish analysis is necessary, the entire fish is homogenized.

11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.

11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400- to 500-mL beaker.

11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-lined lid. Seal the jar and store the tissue at less than -10°C. Return any tissue that was not homogenized to its original container and store at less than -10°C.

11.8.2 Tissue QC aliquots

11.8.2.1 Prepare a Method blank by adding approximately 1-2 g of the oily liquid reference matrix (Section 7.6.4) to a 400- to 500-mL beaker. Record the weight to the nearest 10 mg.

11.8.2.2 Prepare an ongoing precision and recovery aliquot by adding 1-2 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400- to 500-mL beaker. Record the weight to the nearest 10 mg.

11.8.3 Spiking

11.8.3.1 Spike 1.0 mL of the Labeled pesticide spiking solution (Section 7.12) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the Native spiking solution (Section 7.11) into the OPR aliquot.

11.8.4 Extract the aliquots using the Soxhlet procedure in Section 12.4.

12.0 Extraction and concentration

12.1 Extraction procedures include: solid phase (Section 12.2.1), separatory funnel (Section 12.2.2), or continuous liquid/liquid (Section 12.2.3) for aqueous liquids; Soxhlet/Dean-Stark (Section 12.3.1) for sludge, solids and filters; and Soxhlet extraction (Section 12.4) for tissues.

Macro-concentration procedures include: rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish (K-D) evaporation (Section 12.6.3). Micro-concentration uses nitrogen evaporation (Section 12.7).

12.2 Extraction of aqueous liquids – separatory or continuous liquid/liquid extraction.

12.2.1 Solid-phase extraction of samples containing less than one percent solids

12.2.1.1 Disk preparation

12.2.1.1.1 Remove the test tube from the suction flask (Figure 4). Place an SPE disk on the base of the filter holder and wet with methylene chloride. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with methylene chloride and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1-L glass reservoir and the vacuum filtration flask.

12.2.1.1.2 Rinse the sides of the reservoir with approx 15 mL of methylene chloride using a squeeze bottle or pipet. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the methylene chloride through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

12.2.1.2 Sample extraction

12.2.1.2.1 Pre-wet the disk by adding approx 20 mL of methanol to the reservoir. Pull most of the methanol through the filter/disk, retaining a layer of methanol approx 2 mm

thick on the filter. Do not allow the filter/disk to go dry from this point until the extraction is completed.

12.2.1.2.2 Add approx 20 mL of reagent water to the reservoir and pull most through, leaving a layer approx 2 mm thick on the filter/disk.

12.2.1.2.3 Allow the sample (Section 11.4.2.6) to stand for 1-2 hours, if necessary, to settle the suspended particles. Decant the clear layer of the sample, the blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into its respective reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10 minutes. For samples containing a high concentration of particles (suspended solids), the extraction time may be an hour or longer.

12.2.1.2.4 Before all of the sample has been pulled through the filter/disk, add approx 50 mL of reagent water to the sample bottle, swirl to suspend the solids (if present), and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all solids are removed.

12.2.1.2.5 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.

12.2.1.2.6 Partially dry the filter/disk under vacuum for approx 3 minutes.

12.2.1.3 Elution of the filter/disk

12.2.1.3.1 Release the vacuum, remove the entire filter/disk/reservoir assembly from the vacuum flask, and empty the flask. Insert a test tube for eluant collection into the flask. The test tube should have sufficient capacity to contain the total volume of the elution solvent (approx 50 mL) and should fit around the drip tip. The drip tip should protrude into the test tube to preclude loss of sample from spattering when vacuum is applied (see Figure 4). Re-assemble the filter/disk/reservoir assembly on the vacuum flask.

12.2.1.3.2 Wet the filter/disk with 4-5 mL of acetone. Allow the acetone to spread evenly across the disk and soak for 15-20 seconds. Pull the acetone through the disk, releasing the vacuum when approx 1 mm thickness remains on the filter.

12.2.1.3.3 Rinse the sample bottle with approx 20 mL of methylene chloride and transfer to the reservoir. Pull approx half of the solvent through the filter/disk and release the vacuum. Allow the filter/disk to soak for approx 1 minute. Pull all of the solvent through the disk. Repeat the bottle rinsing and elution step with another 20 mL of methylene chloride. Pull all of the solvent through the disk.

12.2.1.3.4 Release the vacuum, remove the filter/disk/reservoir assembly, and remove the test tube containing the sample solution. Quantitatively transfer the solution to a 250-mL separatory funnel and proceed to Section 12.5 for back-extraction.

12.2.2 Separatory funnel extraction

12.2.2.1 Pour the spiked sample (Section 11.4.2.2) into a 2-L separatory funnel. Rinse the bottle or flask twice with 5 mL of reagent water and add these rinses to the separatory funnel.

12.2.2.2 Add 100 mL methylene chloride to the empty sample bottle. Cap the bottle and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms and is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation

(see note below). Drain the methylene chloride extract through a solvent-rinsed glass funnel and dry over anhydrous sodium sulfate (Section 7.2.1) into an Erlenmeyer flask (1 L).

Note: *If an emulsion forms, the laboratory must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase (Section 12.2.1), CLLE (Section 12.2.3), or other extraction techniques may be used to prevent emulsion formation. Any alternative technique is acceptable so long as the requirements in Section 9.2 are met.*

12.2.2.3 Extract the water sample two more times with 100-mL portions of methylene chloride. Dry each portion over anhydrous sodium sulfate . After the third extraction, rinse the separatory funnel with at least 20 mL of methylene chloride, and add to the three 100-mL portions of methylene chloride. Repeat this rinse at least twice. Allow the methylene chloride extract to dry for 30 min. Transfer to a solvent-rinsed concentration device (Section 12.6).

12.2.2.4 Add 1 mL of a toluene "keeper" to the extract and concentrate using one of the macro-concentration procedures in Section 12.6, then proceed to back extraction in Section 12.5.

12.2.3 Continuous liquid/liquid extraction

12.2.3.1 Place 100-150 mL methylene chloride in each continuous extractor and 200-300 mL in each distilling flask.

12.2.3.2 Pour the sample(s), blank, and QC aliquots into the extractors. Rinse the sample containers with 50-100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

12.2.3.3 Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1-2 drops of methylene chloride per second will fall from the condenser tip into the water. Extract for 16-24 hours.

12.2.3.4 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate into the concentration flask. Rinse the distilling flask with 30-50 mL of methylene chloride and pour through the drying column.

12.2.3.5 Add 1 mL of a toluene "keeper" to the extract and concentrate using one of the macro-concentration procedures in Section 12.6, then proceed to back extraction in Section 12.5.

12.3 Extraction of solids – Solid or sludge samples are extracted using a Soxhlet/Dean-Stark extractor (Section 12.3.1).

12.3.1 Soxhlet/Dean-Stark extraction

12.3.1.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2). Do not disturb the silica layer throughout the extraction process.

12.3.1.2 Place the thimble in a clean extractor. Place 30 to 40 mL of toluene in the receiver and 200 to 250 mL of toluene in the flask.

12.3.1.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1 to 2 drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of 3 hours.

12.3.1.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

12.3.1.5 Load the wet sample and/or filter from Sections 11.5.7, 11.6.6, or 11.7.5 and any non-aqueous liquid from Section 11.6.4 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.

12.3.1.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of 300 mL 80:20 toluene:acetone to the receiver and reflux flask. Apply power to the heating mantle to begin re-fluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first 2 hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides. Soxhlet extract for 12-24 hours.

12.3.1.7 Drain the water from the receiver at 1-2 hours and 8-9 hours, or sooner if the receiver fills with water. After 12-24 hours cool and disassemble the apparatus. Record the total volume of water collected.

12.3.1.8 Remove the distilling flask. Drain the water from the receiver and add any toluene in the receiver to the extract in the flask.

12.3.1.9 Concentrate the extracts from particles to approximately 10 mL using the rotary evaporator (Section 12.6.1) or heating mantle (Section 12.6.2), transfer to a 250-mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.4 Soxhlet extraction of tissue

Note: *This procedure includes determination of the lipid content of the sample (Section 12.4.9), using the same sample extract that is analyzed by GC/HRMS. Alternatively, a separate sample aliquot may be used for the lipid determination. If a separate aliquot is used for GC/HRMS determination, use nitrogen to evaporate the main portion of the sample extract only to the extent necessary to effect the solvent exchange to n-hexane, so that loss of low molecular weight pesticides is avoided, i.e., it is not necessary to dry the main portion of the sample to constant weight (Section 12.4.8).*

12.4.1 Add 30 to 40 g of powdered anhydrous sodium sulfate (Section 7.2.2) to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with aluminum foil and dry until the mixture becomes a free-flowing powder (30 minutes minimum). Remix prior to extraction to prevent clumping.

12.4.2 Assemble and pre-extract the Soxhlet apparatus per Sections 12.3.1-12.3.1.4, except use methylene chloride for the pre-extraction and rinsing and omit the quartz sand.

12.4.3 Re-assemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride to the reflux flask.

12.4.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.

12.4.5 Rinse the beaker with several portions of solvent and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18-24 hours.

12.4.6 After extraction, cool and disassemble the apparatus.

12.4.7 Quantitatively transfer the extract to a macro-concentration device (Section 12.6) and concentrate to near dryness. Set aside the concentration apparatus for re-use.

12.4.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.9 Percent lipid determination

12.4.9.1 Re-dissolve the residue in the receiver in hexane.

12.4.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.6); retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all

material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$\textit{Percent lipid} = \frac{\textit{Weight of residue (g)}}{\textit{Weight of tissue (g)}} \times 100$$

12.4.9.4 The laboratory should determine the lipid content of the blank, IPR, and OPR to assure that the extraction system is working effectively.

12.5 Back-extraction with base and acid

Note: *Some pesticides may be decomposed by acid or base. If acid or base back-extraction is employed, the laboratory must evaluate the strengths of the acid and base solutions, and the exposure times, to preclude decomposition.*

12.5.1 Back-extraction may not be necessary for some samples, and back-extraction with strong acid and/or base with long contact times may destroy some pesticides. For some samples, the presence of color in the extract may indicate that back-extraction is necessary. If back-extraction is not necessary, concentrate the extract for cleanup or analysis (Section 12.6 and/or 12.7). If back-extraction is necessary, back-extract the extracts from Section 12.2.3.5 or 12.3.1.9 as follows:

12.5.2 Back-extract each extract three times sequentially with 500 mL of the aqueous sodium sulfate solution (Section 7.1.5), returning the bottom (organic) layer to the separatory funnel the first two times while discarding the top (aqueous) layer. On the final back-extraction, filter each pesticide extract through a prerinsed drying column containing 7 to 10 cm anhydrous sodium sulfate into a 500- to 1000-mL graduated cylinder. Record the final extract volume. Re-concentrate the sample and QC aliquots per Sections 12.6-12.7, and clean up the samples and QC aliquots per Section 13.

12.6 Macro-concentration – Extracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danish apparatus.

Note: *In the concentration procedures below, the extract must not be allowed to concentrate to dryness because low molecular weight pesticides may be totally or partially lost. It may be advantageous to add 1 mL of toluene as a "keeper" to prevent loss of the low molecular weight pesticides.*

12.6.1 Rotary evaporation – Concentrate the extracts in separate round-bottom flasks.

12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, pre-

clean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2- to 3- mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.

12.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

Note: *If the rate of concentration is too fast, analyte loss may occur.*

12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

12.6.1.5 Proceed to Section 12.5 for back-extraction or Section 12.7 for micro-concentration and solvent exchange.

12.6.2 Heating mantle – Concentrate the extracts in separate round-bottom flasks.

12.6.2.1 Add one or two clean boiling chips to the round-bottom flask, and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottom flask in a heating mantle, and apply heat as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottom flask from the heating mantle and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.

12.6.2.3 Proceed to Section 12.6 for preparation for back-extraction or Section 12.7 for micro-concentration and solvent exchange.

12.6.3 Kuderna-Danish (K-D) – Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-D technique unless a water bath fed by a steam generator is used.

12.6.3.1 Add 1 to 2 clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of solvent. A 5-mL syringe is recommended for this operation.

12.6.3.4 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

12.6.3.7 Proceed to 12.6 for preparation for back-extraction or Section 12.7 for micro-concentration and solvent exchange.

12.7 Micro-concentration and solvent exchange

12.7.1 Extracts to be subjected to GPC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, Florisil, the SPE cartridge, and/or HPLC are exchanged into hexane.

12.7.2 Transfer the vial containing the sample extract to a nitrogen evaporation device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

Note: *A large vortex in the solvent may cause analyte loss.*

12.7.3 Lower the vial into a 30°C water bath and continue concentrating.

12.7.3.1 If the extract or an aliquot of the extract is to be concentrated to dryness for weight determination (Sections 12.4.8 and 13.6.4), blow dry until a constant weight is obtained.

12.7.3.2 If the extract is to be concentrated for injection into the GC/HRMS or the solvent is to be exchanged for extract cleanup, proceed as follows:

12.7.4 When the volume of the liquid is approximately 100 µL, add 2 to 3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other cleanups) and continue concentration to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, concentrate the extract to 1.0 mL. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.5, respectively).

12.7.6 If the extract is to be cleaned up by column chromatography or the SPE cartridge, bring the final volume to 1.0 mL with hexane. Proceed with column cleanup (Sections 13.3, 13.4, 13.7, or 13.8).

12.7.7 If the extract is to be concentrated for injection into the GC/HRMS (Section 14), quantitatively transfer the extract to a 0.3-mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100 µL. Add 20 µL of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC/HRMS analysis. If GC/HRMS analysis will not be performed on the same day, store the vial at less than -10°C.

13.0 Extract cleanup

13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure. The following table suggests cleanups that may be used for the various analyte groups.

Analyte group	Suggested cleanups
All	GPC (13.2); SPE (13.3); Micro-silica (13.4)

Organo-chlorine	GPC, SPE, Micro-silica plus Florisil (13.7) or alumina (13.8)
Specific compounds	GPC, SPE, Micro-silica plus HPLC (13.5)

13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts. It may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids). It should also be used for tissue extracts after initial cleanup on the anthropogenic isolation column (Section 13.6).

13.1.2 Micro-silica (Section 13.4), the SPE cartridge (Section 13.3), Florisil (Section 13.7), and alumina (Section 13.8) may be used to remove non-polar and polar interferences.

13.1.3 HPLC (Section 13.5) is used to provide specificity for certain pesticides.

13.1.4 The anthropogenic isolation column (Section 13.6) is used for removal of lipids from tissue samples.

13.2 Gel permeation chromatography (GPC)

13.2.1 Column packing

13.2.1.1 Place 70 to 75 g of SX-3 Bio-beads (Section 6.7.1.1) in a 400- to 500-mL beaker.

13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).

13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5 to 5.5 mL/minute prior to connecting the column to the detector.

13.2.1.4 After purging the column with solvent for 1 to 2 hours, adjust the column head pressure to 7 to 10 psig and purge for 4 to 5 hours to remove air. Maintain a head pressure of 7 to 10 psig. Connect the column to the detector (Section 6.7.1.4).

13.2.2 Column calibration

13.2.2.1 Load 5 mL of the GPC calibration solution (Section 7.4) into the sample loop.

13.2.2.2 Inject the GPC calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethylhexyl) phthalate (BEHP), methoxychlor, perylene, and sulfur.

13.2.2.3 Set the "dump time" to allow >85% removal of BEHP and >85% collection of methoxychlor.

13.2.2.4 Set the "collect time" to the time of the sulfur peak maximum.

13.2.2.5 Verify calibration with the GPC calibration solution after every 20 extracts. Calibration is verified if the recovery of methoxychlor is greater than 85%. If calibration is not verified, the system must be recalibrated using the GPC calibration solution, and the previous sample batch must be re-extracted and cleaned up using a calibrated GPC system.

13.2.3 Extract cleanup – GPC requires that the column not be overloaded. The column specified in this Method is designed to handle a maximum of 0.5 g of material from an aqueous, soil, or mixed-phase sample in a 5-mL extract, and has been shown to handle 1.5 g of lipid from a tissue sample in a 5-mL extract. If the extract is known or expected to contain more than these amounts, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50-µL aliquot.

13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove particles. Load the 5.0-mL extract onto the column.

13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400- to 500-mL beaker. Allow the system to rinse for additional 10 minutes before injecting the next sample.

13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

13.2.3.4 If an extract is encountered that could overload the GPC column to the extent that carry-over could occur, a 5.0-mL methylene chloride blank must be run through the system to check for carry-over.

13.2.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the GC/MS.

13.3 Solid-phase extraction (SPE) cartridge

13.3.1 Setup

13.3.1.1 Attach the Vac-elute manifold (6.7.6.1) to a water aspirator or vacuum pump with the trap and gauge installed between the manifold and vacuum source.

13.3.1.2 Place the SPE cartridge(s) in the manifold, turn on the vacuum source, and adjust the vacuum to 5 to 10 psig.

Note: *Do not allow the SPE cartridge to go dry during the following steps.*

13.3.2 Cartridge washing – Pre-elute the cartridge sequentially with two 6-mL volumes of 1:2:1 ethyl acetate:acetonitrile:toluene.

13.3.3 Using a pipette or a 1-mL syringe, transfer 1.0 mL of the extract in 1:2:1 ethyl acetate:acetonitrile:toluene (Section 12.2.3.5, 12.3.1.9, 12.4.8 or 12.5.2) onto the SPE cartridge followed by a rinse of 1 mL 1:2:1 ethyl acetate:acetonitrile:toluene.

13.3.4 As soon as the sample is loaded, begin to collect the eluate in a round bottom flask or centrifuge tube (if using a manifold). Elute the SPE cartridge with 11 mL of 1:2:1 ethyl acetate:acetonitrile: toluene.

13.3.5 Concentrate the eluted extract per Sections 12.6 and 12.7 and proceed to other cleanups or determination by HRGC/HRMS.

13.4 Micro-silica column

13.4.1 Place a small glass-wool plug in a clean Pasteur pipette. Rinse the pipette and glass wool twice with small (e.g., 2 - 5 mL) volumes of toluene, followed by two rinsings with small volumes of hexane. Allow the pipette to drain. Dry pack the column bottom to top with 0.75 gram of 10% deactivated silica (Section 7.5.1.1). Tap the column to settle the silica.

13.4.2 Rinse the column with hexane until the column is completely wetted (typically 5-10 mL). Allow the hexane to drain to the top of the silica.

13.4.3 Adjust the extract volume to 1.0 mL and apply to the column. Allow the extract to drain to the top of the silica. Rinse the extract onto the column with 500 µL of hexane.

13.4.4 Rinse the centrifuge tube that contained the extract with 300-µL of 10% methanol in dichloromethane and apply to the column. Collect the eluate in a round-bottom flask. Repeat this rinse and collect the eluate in the flask.

13.4.5 Elute the column with 5 mL of 10% methanol in dichloromethane. Collect the eluate in the round bottom flask.

13.4.6 Add 5 mL of acetone and 1 mL of iso-octane to the round bottom flask and concentrate the eluate per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.4.7 For extracts of samples known to contain large quantities of other organic compounds, it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strength of the acid silica and including basic silica gel. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 40% w/w (6.7 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used. Larger columns may also be used if needed.

Note: *The use of stronger acid and basic silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of the pesticides. Increasing the strengths of the acid and basic silica gel may also require different volumes of eluants than those specified above to elute the analytes from the column. The performance of the Method after such modifications must be verified by the procedure in Section 9.2.*

13.5 HPLC (Reference 9)

13.5.1 Column calibration

13.5.1.1 Prepare a calibration standard containing the pesticides at the concentrations of the stock solution in Table 3, or at a concentration appropriate to the response of the detector.

13.5.1.2 Inject the calibration standard into the HPLC and record the signal from the detector. Collect the eluant for reuse.

13.5.1.3 Establish the collection time for the pesticides of interest. Following calibration, flush the injection system with solvent to ensure that residual pesticides are removed from the system.

13.5.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pesticides is 75 to 125% compared to the calibration (Section 13.5.1.1). If calibration is not verified, the system must be recalibrated using the calibration solution, and the batch of samples run on the uncalibrated system must be re-extracted and cleaned up using a calibrated system.

13.5.2 Extract cleanup – HPLC requires that the column not be overloaded. The column specified in this Method is designed to handle a maximum of 50 Φg of a given pesticide, depending on the particular compound. If the amount of material in the extract will overload the column, split the extract into fractions and combine the fractions after elution from the column.

13.5.2.1 Rinse the sides of the vial containing the sample and adjust to the volume required for the sample loop for injection.

13.5.2.2 Inject the sample extract into the HPLC.

13.5.2.3 Elute the extract using the calibration data determined in Section 13.5.1. Collect the fraction(s) in clean 20-mL concentrator tubes.

13.5.2.4 If an extract containing greater than 500 µg of total material is encountered, a blank must be run through the system to check for carry-over.

13.5.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/HRMS.

13.6 Anthropogenic isolation column (Reference 15) – Used for removal of lipids from tissue extracts

13.6.1 Prepare the column as given in Section 7.5.2.

13.6.2 Pre-elute the column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

13.6.3 Load the sample and rinses (Section 12.4.9.2) onto the column by draining each portion to the top of the bed. Elute the pesticides from the column into the apparatus used for concentration (Section 12.4.7) using 200 mL of hexane.

13.6.4 Remove a small portion (e.g., 50 µL) of the extract for determination of residue content. Estimate the percent of the total that this portion represents. Concentrate the small portion to constant weight per Section 12.7.3.1. Calculate the total amount of residue in the extract. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.

13.6.5 If necessary, exchange the extract to a solvent suitable for the additional cleanups to be used (Section 13.2 - 13.8).

13.6.6 Clean up the extract using the procedures in Sections 13.2 - 13.8. GPC (Section 13.2) and Florisil (Section 13.7) are recommended as minimum additional cleanup steps.

13.6.7 Following cleanup, concentrate the extract to 20 ΦL per Section 12.7 and proceed with the analysis in Section 14.

13.7 Florisil

13.7.1 Begin to drain the n-hexane from the column (Section 7.5.4.3). Adjust the flow rate of eluant to 4.5 - 5.0 mL/min.

13.7.2 When the n-hexane is within 1 mm of the sodium sulfate, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1-mL portions of hexane and apply to the column, allowing the hexane to drain to the top of the sodium sulfate layer.

13.7.3 Elute Fraction 1 with 200 mL of 6% ethyl ether in n-hexane and collect the eluate. Elute Fraction 2 with 200 mL of 15% ethyl ether in hexane and collect the eluate. Elute Fraction 3 with 50% ethyl ether in hexane and collect the eluate. The exact volumes of solvents will need to be determined for each batch of Florisil. If the pesticides are not to be collected in separate fractions, elute all pesticides with 50% ethyl ether in hexane.

13.7.4 Concentrate the eluate(s) per Sections 12.6 - 12.7 for further cleanup or for injection into the HPLC or GC/HRMS.

13.8 Alumina

13.8.1 Begin to drain the hexane from the column (Section 7.5.5.2). Adjust the flow rate of eluant to 4.5 - 5.0 mL/min.

13.8.2 When the n-hexane is within 1 mm of the sodium sulfate, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1-mL portions of hexane and apply to the column, allowing the hexane to drain to the top of the sodium sulfate layer.

13.8.3 Elute the pesticides with 150 mL of n-hexane. If all pesticides are not eluted, elute the remaining pesticides with 50 mL of 15% methylene chloride in n-hexane.

13.8.4 Concentrate the eluate(s) per Sections 12.6 - 12.7 for further cleanup or for injection into the HPLC or GC/HRMS.

14.0 HRGC/HRMS analysis

14.1 Establish the operating conditions given in Section 10.1.

14.2 Add 2 µL of the labeled injection internal standard spiking solution (Section 7.14) to the 20 µL sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more labeled injection internal standard spiking solution. Rather, bring the extract back to its previous volume (e.g., 19 µL) with pure nonane (18 µL if 2 µL injections are used).

14.3 Inject 1.0 or 2.0 µL of the concentrated extract containing the Labeled injection internal standards using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10.3).

14.3.1 Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes.

14.3.2 Monitor the exact m/z's for each pesticide throughout its retention time window. Where warranted, monitor m/z's associated with pesticides at higher levels of chlorination to assure that fragments are not interfering with the m/z's for pesticides at lower levels of chlorination. Also where warranted, monitor m/z's associated with interferents expected to be present.

14.3.3 Stop data collection after permethrin and cypermethrin have eluted. Return the column to the initial temperature for analysis of the next sample extract or standard.

15.0 System and laboratory performance

15.1 At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all the pesticides and labeled compounds. For these tests, analysis of the CS-4 calibration verification (VER) standard (Section 7.10 and Table 4) must be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) must be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.

15.2 MS resolution – Static resolving power checks must be performed at the beginning and at the end of each shift per Sections 10.2.1. If analyses are performed on successive shifts, only the beginning of shift static resolving power check is required. If the requirement in Section 10.2.1 cannot be met, the problem must be corrected before analyses can proceed. If any of the samples in the previous shift may be affected by poor resolution, those samples must be re-analyzed.

15.3 Calibration verification

15.3.1 Inject the VER (CS-4) calibration standard using the procedure in Section 14.

15.3.2 The m/z abundance ratios for all pesticides must be within the limits in Table 6; otherwise, the mass spectrometer must be adjusted until the m/z abundance ratios fall within the limits specified when the verification test is be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.2.1) prior to repeat of the verification test.

15.3.3 The GC peak representing each native pesticide and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer must be adjusted and the verification test repeated.

15.3.4 Compute the concentration of the pesticides that have labeled analogs by isotope dilution and the concentration of the pesticides that do not have labeled analogs by the internal standard technique. These concentrations are computed based on the calibration data in Section 10.

15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 5. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly. In this event, prepare a fresh calibration standard or correct the problem and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10).

15.4 Retention times and GC resolution

15.4.1 Retention times.

15.4.1.1 Absolute – The absolute retention times of the Labeled compounds in the verification test (Section 15.3) must be within ∀ 15 seconds of the respective retention times in the calibration (Section 10.1)

15.4.1.2 Relative – The relative retention times of native pesticides and the labeled compounds in the verification test (Section 15.3) must be within their respective RRT limits in Table 2 or, if an alternate column or column system is employed, within their respective RRT limits for the alternate column or column system (Sections 9.1.2.3 and 6.9.1).

15.4.1.3 If the absolute or relative retention time of any compound is not within the limits specified, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.

15.4.2 GC resolution and minimum analysis time

15.4.2.1 The resolution and minimum analysis time specifications in Sections 6.9.1.1.2 and 6.9.1.1.1, respectively, must be met for the DB-17 column or, if an alternate column or column system is employed, must be met as specified for the alternate column or column system (Sections 9.1.2.3 and 6.9.1). If these specifications are not met, the GC analysis conditions must be adjusted until the specifications are met, or the column must be replaced and the calibration verification tests repeated Sections 15.3 - 15.4), or the system must be recalibrated (Section 10).

15.4.2.2 After the resolution and minimum analysis time specifications are met, update the retention times and relative retention times, but not the relative responses and response factors. For the relative responses and response factors, the multi-point calibration data (Sections 10.4 and 10.5) must be used.

15.5 Endrin/4,4'-DDT breakdown – Perform the endrin/4,4'-DDT breakdown test (Section 10.6). The breakdown specification (Section 10.6.2.3) must be met before an OPR, sample, or blank may be analyzed.

15.6 Ongoing precision and recovery

15.6.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.3, 11.6.3, or 11.8.3.2) prior to analysis of samples from the same batch.

15.6.2 Compute the percent recovery of the pesticides with labeled analogs by isotope dilution (Section 10.4). Compute the percent recovery of each labeled compound by the internal standard method (Section 10.5).

15.6.3 For the pesticides and labeled compounds, compare the recovery to the OPR limits given in Table 5. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.6).

15.6.4 If desired, add results that pass the specifications in Section 15.6.3 to initial (Section 9.4) and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each pesticide in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (S_R). Express the accuracy as a recovery interval from R ! $2S_R$ to R + $2S_R$. For example, if R = 95% and S_R = 5%, the accuracy is 85 to 105%.

15.7 Blank – Analyze the Method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. If pesticides will be carried from the OPR into the Method blank, analyze one or more aliquots of solvent between the OPR and the Method blank. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

16.0 Qualitative determination

A pesticide or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

16.1 The signals for the two exact m/z's in Table 6 must be present and must maximize within the same two scans.

16.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each pesticide detected in a sample extract, and greater than or equal to 10 for all pesticides in the calibration and verification standards (Sections 10.3.3 and 15.6.3).

16.3 The ratio of the integrated areas of the two exact m/z's specified in Table 6 must be within the limit in Table 6, or within ∀ 15 percent of the ratio in the midpoint (CS-4) calibration or calibration verification (VER), whichever is most recent.

16.4 The relative retention time of the peak for a pesticide must be within the RRT QC limits specified in Table 2 or within similar limits developed from calibration data (Section 10.1.2). If an alternate column (Section 9.1.2.3) is employed, the RRT for the pesticide must be within its respective RRT QC limits for the alternate column or column system (Section 6.9.1).

Note: *For native pesticides determined by internal standard quantitation, a pesticide with the same exact m/z's as other pesticides may fall within more than one RT window and be mis-identified unless the RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other pesticides and the labeled compounds may be required for rigorous pesticide identification. Retention time regression may aid in this identification.*

16.5 Because of pesticide RT overlap and the potential for interfering substances, it is possible that all of the identification criteria (Sections 16.1 - 16.4) may not be met. It is also possible that loss of one or more chlorines from a highly chlorinated pesticide or interferent may inflate or produce a false concentration for a less-chlorinated pesticide that elutes at the same retention time (see Section 18). If identification is ambiguous, an experienced spectrometrist (Section 1.5) must determine the presence or absence of the pesticide.

16.6 If the criteria for identification in Sections 16.1 - 16.5 are not met, the pesticide has not been identified and the result for that pesticide may not be reported or used for permitting or regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

17.0 Quantitative determination

17.1 Isotope dilution quantitation

17.1.1 By adding a known amount of the labeled pesticides to every sample prior to extraction, correction for recovery of each pesticide can be made because the native

compound and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative responses (RRs) are used in conjunction with the calibration data in Section 10.4 to determine concentrations in the final extract, so long as labeled compound spiking levels are constant.

17.1.2 Compute the concentrations of the pesticides in the extract using the RRs from the calibration data (Section 10.4) and following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

Where:

C_{ex} = The concentration of the pesticide in the extract, and the other terms are as defined in Section 10.4.3

17.2 Internal standard quantitation and labeled compound recovery

17.2.1 Compute the concentrations in the extract of the native compounds that do not have labeled analogs using the response factors determined from the calibration data (Section 10.5) and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ RF}$$

Where:

C_{ex} = The concentration of the labeled compound in the extract, and the other terms are as defined in Section 10.5.1

17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the labeled pesticides other labeled cleanup standard using the following equation:

$$Recovery\ (\%) = \frac{Concentration\ found\ (ng/mL)}{Concentration\ spiked\ (ng/mL)} \times 100$$

17.3 The concentration of a native compound in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.2.2.3), as follows:

$$Concentration\ in\ solid\ (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

Where:

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
W_s = The sample weight (dry weight) in kg.

17.4 The concentration of a native pesticide in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4), as follows:

$$\textit{Concentration in aqueous phase (pg/L)} = 1000 \times \frac{(C_{ex} \times V_{ex})}{V_s}$$

Where:

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
V_s = The sample volume in liters.

17.5 If the SICP area at either quantitation m/z for any pesticide exceeds the calibration range of the system, dilute the sample extract by the factor necessary to bring the concentration within the calibration range, adjust the concentration of the Labeled injection internal standard to 100 pg/µL in the extract, and analyze an aliquot of this diluted extract. If the pesticides cannot be measured reliably by isotope dilution, dilute and analyze an aqueous sample or analyze a smaller portion of a soil, tissue, or mixed-phase sample. Adjust the pesticide concentrations, detection limits, and minimum levels to account for the dilution.

17.6 Reporting of results

17.6.1 Reporting units and levels

17.6.1.1 Aqueous samples – Report results in pg/L (parts-per-quadrillion).

17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost) – Report results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be converted to aqueous units.

17.6.1.3 Tissues – Report results in ng/kg of wet tissue, not on the basis of the lipid content of the tissue. Report the percent lipid content, so that the data user can calculate the concentration on a lipid basis if desired.

17.6.2 Reporting level

17.6.2.1 Report the result for each pesticide in each sample, blank, or standard (VER, IPR, OPR) at or above the minimum level of quantitation (ML; Table 1) to 3 significant figures. Report the result below the ML in each sample as <ML (where ML is the concentration at the ML) or as required by the regulatory authority or permit.

17.6.2.2 Blanks – Report the result for each pesticide below the ML but above the MDL to 2 significant figures. Report results below the MDL as <MDL (where MDL is the concentration at the MDL) or as required by the regulatory authority or permit. In addition to reporting results for

the samples and blank(s) separately, the concentration of each pesticide in a method blank or field blank associated with the sample may be subtracted from the results for that sample, or must be subtracted if requested or required by a regulatory authority or in a permit.

17.6.2.3 Results for a pesticide in a sample that has been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5).

17.6.2.4 For a pesticide having a labeled analog, report results at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the Method (Section 9.3 and Table 5).

17.6.2.5 Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results.

18.0 Analysis of complex samples

18.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts may not concentrate to 20 µL (Section 12.7); others may overload the GC column and/or mass spectrometer. A fragment ion from a pesticide at a higher level of chlorination may interfere with determination of a pesticide at a lower level of chlorination.

18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to 20 ΦL after all cleanup procedures have been exhausted. If a smaller aliquot of soils or mixed-phase samples is analyzed, attempt to assure that the sample is representative.

18.3 Perform integration of peak areas and calculate concentrations manually when interferences preclude computerized calculations.

18.4 Recovery of labeled compounds – In most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).

18.4.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 5), a diluted sample must be analyzed (Section 17.5).

18.4.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.10 and Table 5) must be analyzed and calibration verified (Section 15.3).

18.4.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.

18.4.4 If calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the Method does not apply to the sample being analyzed and the result may not be reported or used for permitting or regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this Method or an alternate GC column must be employed to resolve the interference. If all cleanup procedures in this Method and an alternate GC column have been employed and labeled compound recovery remains outside of the normal range, extraction and/or cleanup procedures that are beyond this scope of this Method will be required to analyze the sample.

19.0 Pollution prevention

19.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

19.2 The pesticides in this Method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

19.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477 (http://membership.acs.org/c/ccs/pubs/less_is_better.pdf).

20.0 Waste management

20.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

20.2 Samples containing HCl or H_2SO_4 to pH <2, or KOH or NaOH to pH >12 must be handled as hazardous waste, or must be neutralized before being poured down a drain.

20.3 The pesticides decompose above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross

quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

20.4 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better-Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

21.0 Method performance

Method 1699 was validated and preliminary data were collected in a single laboratory (Reference 2). Single laboratory performance data are included in Table 8.

22.0 References

1 EPA Methods 608, 1656, 1613, and 1668A.

2 "Analytical Method for the Analysis of Multi-residue Pesticides in Aqueous and XAD Column Samples by HRGC/HRMS," Axys Analytical Services (proprietary).

3 Lamparski, L.L., and Nestrick, T.J., "Novel Extraction Device for the Determination of Chlorinated Dibenzo-*p*-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Matrices Containing Water," *Chemosphere*, 19:27-31, 1989.

4 "Working with Carcinogens," Department of Health, Education, & Welfare, Public Health Service, Centers for Disease Control, NIOSH, Publication 77-206, August 1977, NTIS PB-277256.

5 "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 *CFR* 1910.

6 "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety, 1979.

7 "Standard Methods for the Examination of Water and Wastewater," 18th edition and later revisions, American Public Health Association, 1015 15th St, N.W., Washington, DC 20005, 1-35: Section 1090 (Safety), 1992.

8 "Method 613 – 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin," 40 *CFR* 136 (49 *FR* 43234), December 26, 1984, Section 4.1.

9 Echols, Kathy, Robert Gale, Donald E. Tillitt, Ted Schwartz, and Jerome O'Laughlin, *Environmental Toxicology and Chemistry* 16:8 1590-1597 (1997)

10 U.S. EPA Office of Superfund Remediation and Technology Innovation, Contract Laboratory Program *Summary of Requirements; Reporting and Deliverables Requirements; Target Compound List and Contract Required Quantitation Limits; and Analytical Methods* (http://www.epa.gov/superfund/programs/clp/olm4.htm).

11 Provost, L.P., and Elder, R.S., "Interpretation of Percent Recovery Data," *American Laboratory*, 15: 56-83, 1983.

12 "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.

13 e.g., "Standard Methods for the Examination of Water and Wastewater," 18th edition and later revisions, American Public Health Association, 1015 15th St, N.W., Washington, DC 20005, Methods 4500-Cl adapted for field use.

14 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA EMSL, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

15 "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth MN 55804, EPA/600/3-90/022, March 1990.

23.0 Tables and Figures

Table 1. Names, CAS Registry numbers, and ambient water quality criteria for pesticides determined by isotope dilution and internal standard HRGC/HRMS.

Pesticide	CAS Number	Labeled analog	Lowest Ambient Criterion (pg/L) (1)	MDLs and MLs, matrix and concentration (2)				
				Water (pg/L)		Solid (ng/kg)		Extract (pg/µL)
Organochlorine				**MDL**	**ML**	**MDL**	**ML**	**ML**
Aldrin	309-00-2	$^{13}C_{12}$-Aldrin	49	6	90	0.6	10	3
BHC, alpha	319-84-6	$^{13}C_{6}$-BHC, alpha	2600	7	60	1.3	10	3
BHC, beta	319-85-7	$^{13}C_{6}$-BHC, beta	9100	6	60	0.6	10	3
BHC, delta	319-86-8	$^{13}C_{6}$-BHC, delta		5	60	2.0	10	3
BHC, gamma (lindane)	58-89-9	$^{13}C_{6}$-BHC, gamma	160000	9	60	0.7	10	3
Captan	133-06-2			182	500	35	100	25
Chlordane, alpha (cis)	5103-71-9		800	7	30	0.6	5	1.5
Chlordane, gamma (trans)	5103-74-2	$^{13}C_{10}$-Chlordane, gamma	800	6	50	0.8	5	2
Chlorothalonil	1897-45-6			35	100	1.9	10	5
Dacthal	1861-32-1			4	20	0.9	2	1
DDD, o,p-	53-19-0			3	30	0.8	5	1.5
DDD, p,p-	72-54-8		11	5	30	1.5	5	1.5
DDE, o,p-	3424-82-6			3	30	0.5	5	1.5
DDE, p,p-	72-55-9	$^{13}C_{12}$-p,p-DDE	11	6	30	0.7	5	1.5
DDT, o,p-	789-02-6	$^{13}C_{12}$-o,p-DDT		2	30	0.3	5	1.5
DDT, p,p-	50-29-3	$^{13}C_{12}$-p,p-DDT	11	1	30	0.3	5	1.5
Dieldrin	60-57-1	$^{13}C_{12}$-Dieldrin	52	5	30	0.5	5	1.5
Endosulfan-alpha	959-98-8	$^{13}C_{9}$-alpha-Endosulfan	8700	24	100	--	--	5
Endosulfan-beta	33213-65-9	$^{13}C_{9}$-beta-Endosulfan	8700	30	100	--	--	5
Endosulfan-sulfate	1031-07-8		62000000	13	40	11	50	2
Endrin	72-20-8	13C_{12}-Endrin	2300	3	30	0.4	5	1.5
Endrin-ketone	53494-70-5			12	40	1.6	5	2
Heptachlor	76-44-8	$^{13}C_{4}$-Heptachlor	79	7	30	--	--	1.5
Heptachlor-epoxide	1024-57-3	$^{13}C_{10}$-Heptachlor-epoxide	40	12	40	0.3	5	2
Hexachlorobenzene	118-74-1	$^{13}C_{6}$-Hexachlorobenzene		4	40	1.9	5	2
Methoxychlor	72-43-5	$^{13}C_{12}$-Methoxychlor	30000	7	30	0.3	5	1.5
Mirex	2385-85-5	$^{13}C_{8}$-Mirex	1000	35	100	--	--	5
Nonachlor, cis-	5103-73-1	$^{13}C_{10}$-Nonachlor, cis-		4	30	0.5	5	1.5
Nonachlor, trans-	39765-80-5	$^{13}C_{10}$-Nonachlor, trans-		11	40	0.8	5	2
Octachlorostyrene	29082-74-4			12	40	1.1	5	2
Oxychlordane	27304-13-8	$^{13}C_{10}$-Oxychlordane		7	60	0.5	10	3
Perthane	72-56-0			36	100	--	--	5
Quintozene	82-68-8			18	80	4.7	20	4
Tecnazene	117-18-0			22	80	3.2	10	4

Organophosphate								
Azinphos-methyl	86-50-0	Azinphos-methyl-d_6		57	200	1.4	20	10
Chlorpyriphos	2921-88-2			20	80	2.0	10	4
Chlorpyriphos-methyl	5598-13-0			19	100	3.0	10	5
Chlorpyriphos-oxon	5598-15-2			24	80	3.5	10	4
Diazinon	333-41-5	Diazinon-d_{10}	170000	27	80	24	100	4
Diazinon-oxon	962-58-3			22	80	--	--	4
Disulfoton	298-04-4			64	400	7.1	100	20
Disulfoton sulfone	2497 05 06			9	30	1.6	5	1.5
Fenitrothion	122-14-5			24	80	4.6	20	4
Fonofos	944-22-9	$^{13}C_6$-Fonofos		11	80	0.8	8	4
Malathion	121-75-5		100000	296	1000	41	200	50
Methamidophos	10265-92-6			269	1000	--	--	50
Parathion-ethyl	56-38-2		13000	15	80	3.5	10	4
Parathion-methyl	298-00-0			39	200	6.1	20	10
Phorate	298-02-2			49	200	3.5	20	10
Phosmet	732-11-6			63	200	12	50	10
Pirimiphos-methyl	29232-93-7			14	80	7.3	20	4
Triazine								
Ametryn	834-12-8			11	80	13	50	4
Atrazine	1912-24-9	$^{13}C_3$-Atrazine		14	80	--	--	4
Cyanazine	21725-46-2			38	80	--	--	4
Desethyl atrazine	6190-65-4			5	40	1.3	5	2
Hexazinone	51235-04-2			20	100	1.0	10	5
Metribuzin	21087-64-9			14	60	--	--	3
Simazine	122-34-9			12	80	1.4	10	4
Pyrethroid								
Cypermethrin	52315-07-8			66	200	2.4	20	10
Permethrins-peak 1	52645-53-1	$^{13}C_6$-cis/trans-Permethrin[3]		59	200	230	1000	10
Permethrins-peak 2	52645-53-1	$^{13}C_6$-cis/trans-Permethrin[3]		44	100	340	1000	5

1. *National Recommended Water Quality Criteria*, 2004, http://epa.gov/waterscience/criteria/wqcriteria.html, and Great Lakes Criteria (40 CFR 132.6), whichever is lower. A blank cell means there is no ambient criterion.
2. Method detection limits (MDLs) and minimum levels of quantitation (MLs) with no interferences present.
3. Elution order of cis/trans permethrin unknown

Table 2. Retention times (RTs); relative retention times (RRTs); and retention time and quantitation references for the pesticides

Pesticide	RT (1)	RRT (2)	RRT Limits (3)	Retention time and quantitation reference (4)	Quant Ref RT
Methamidophos	09:01	0.413	0.397 - 0.428	$^{13}C_{12}$-PCB-52	21:51
Tecnazene	14:44	0.927	0.906 - 0.948	13C_6-HCB	15:54
$^{13}C_6$-Hexachlorobenzene	15:54	0.728	0.712 - 0.743	$^{13}C_{12}$-PCB-52	21:51
Hexachlorobenzene	15:55	1.001	0.991 - 1.012	$^{13}C_6$-HCB	15:54
Phorate	16:11	0.741	0.725 - 0.756	$^{13}C_{12}$-PCB-52	21:51
BHC-alpha	16:35	0.909	0.890 - 0.927	$^{13}C_6$-gamma-BHC	18:15
Desethylatrazine	16:50	0.935	0.917 - 0.954	$^{13}C_3$-Atrazine	18:00
Diazinon-d10	17:32	0.802	0.787 - 0.818	$^{13}C_{12}$-PCB-52	21:51
Quintozene	17:39	1.110	1.089 - 1.131	$^{13}C_6$-HCB	15:54
Diazinon	17:44	1.011	1.002 - 1.021	Diazinon-d10	17:32
Diazinon-oxon	17:55	1.022	1.003 - 1.041	Diazinon-d10	17:32
$^{13}C_3$-Atrazine	18:00	0.824	0.809 - 0.839	$^{13}C_{12}$-PCB-52	21:51
Atrazine	18:01	1.001	0.992 - 1.010	$^{13}C_3$-Atrazine	18:00
$^{13}C_6$-gamma-BHC	18:15	0.835	0.820 - 0.850	$^{13}C_{12}$-PCB-52	21:51
gamma-BHC	18:16	1.001	0.992 - 1.010	$^{13}C_6$-gamma-BHC	18:15
Simazine	18:21	1.019	1.001 - 1.038	$^{13}C_3$-Atrazine	18:00
Fonofos	18:25	1.000	0.991 - 1.009	$^{13}C_6$-Fonofos	18:25
$^{13}C_6$-Fonofos	18:25	0.843	0.828 - 0.858	$^{13}C_{12}$-PCB-52	21:51
Disulfoton	18:34	0.850	0.834 - 0.865	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_6$-beta-BHC	19:26	0.889	0.874 - 0.905	$^{13}C_{12}$-PCB-52	21:51
beta-BHC	19:27	1.001	0.992 - 1.009	$^{13}C_6$-beta-BHC	19:26
$^{13}C_4$-Heptachlor	19:36	0.897	0.882 - 0.912	$^{13}C_{12}$-PCB-52	21:51
Heptachlor	19:37	1.001	0.992 - 1.009	$^{13}C_4$-Heptachlor	19:36
$^{13}C_6$-delta-BHC	21:00	0.961	0.946 - 0.976	$^{13}C_{12}$-PCB-52	21:51
delta-BCH	21:01	1.001	0.993 - 1.009	$^{13}C_6$-delta-BHC	21:00
Chlorothalonil.	21:08	0.967	0.952 - 0.982	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{12}$-Aldrin	21:15	0.973	0.957 - 0.988	$^{13}C_{12}$-PCB-52	21:51
Aldrin	21:17	1.002	0.994 - 1.009	$^{13}C_{12}$-Aldrin	21:15
Chlorpyriphos-methyl	21:26	0.981	0.966 - 0.996	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{12}$-PCB-52	21:51	N/A	N/A	N/A	N/A
Parathion-methyl	22:28	1.028	1.013 - 1.043	$^{13}C_{12}$-PCB-52	21:51
Ametryn	22:41	1.038	1.023 - 1.053	$^{13}C_{12}$-PCB-52	21:51
Pirimiphos-methyl	22:42	1.039	1.024 - 1.054	$^{13}C_{12}$-PCB-52	21:51
Metribuzin	23:04	1.056	1.040 - 1.071	$^{13}C_{12}$-PCB-52	21:51
Octachlorostyrene	23:18	1.096	1.081 - 1.112	$^{13}C_{12}$-Aldrin	21:15
Dacthal	23:18	1.066	1.051 - 1.082	$^{13}C_{12}$-PCB-52	21:51
Chlorpyriphos	23:33	1.078	1.063 - 1.093	$^{13}C_{12}$-PCB-52	21:51
Fenitrothion	24:07	1.104	1.088 - 1.119	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{10}$-Oxychlordane	24:09	1.105	1.090 - 1.121	$^{13}C_{12}$-PCB-52	21:51
Oxychlordane	24:11	1.001	0.994 - 1.008	$^{13}C_{10}$-Oxychlordane	24:09
Malathion	24:12	1.108	1.092 - 1.123	$^{13}C_{12}$-PCB-52	21:51
Heptachlor-epoxide	25:14	0.962	0.956 - 0.969	$^{13}C_{12}$-Heptachlor-epoxide	25:11
^{13}C-Permethrins-Peak_2	42:21	1.114	1.099 - 1.130	$^{13}C_{12}$-PCB-52	21:51
Parathion-ethyl	24:26	1.118	1.103 - 1.133	$^{13}C_{12}$-PCB-52	21:51
Chlorpyriphos-oxon	24:30	1.121	1.106 - 1.137	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_6$-Permethrins-Peak_1	42:04	1.124	1.108 - 1.139	$^{13}C_{12}$-PCB-52	21:51
Azinphos-ethyl-d6	24:33	1.124	1.108 - 1.139	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{12}$-Heptachlor-epoxide	25:11	1.153	1.137 - 1.168	$^{13}C_{12}$-PCB-52	21:51

$^{13}C_{10}$-t-Chlordane	26:39	1.220	1.204 - 1.235	$^{13}C_{12}$-PCB-52	21:51
t-Chlordane	26:41	1.001	0.995 - 1.008	$^{13}C_{10}$-t-Chlordane	26:39
$^{13}C_{10}$-t-Nonachlor	26:48	1.227	1.211 - 1.242	$^{13}C_{12}$-PCB-52	21:51
t-Nonachlor	26:50	1.001	0.995 - 1.007	$^{13}C_{10}$-t-Nonachlor	26:48
c-Chlordane	27:44	1.041	1.028 - 1.053	$^{13}C_{10}$-t-Chlordane	26:39
$^{13}C_{9}$-alpha-Endosulfan	27:51	1.275	1.259 - 1.290	$^{13}C_{12}$-PCB-52	21:51
Alpha-Endosulfan	27:53	1.001	0.995 - 1.007	$^{13}C_{9}$-alpha-Endosulfan	27:51
o,p-DDE	28:07	0.862	0.852 - 0.873	$^{13}C_{12}$-p,p-DDE	30:36
Cyanazine	28:13	1.291	1.276 - 1.307	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{12}$-Dieldrin	30:31	1.397	1.381 - 1.412	$^{13}C_{12}$-PCB-52	21:51
Dieldrin	30:34	1.002	0.996 - 1.007	$^{13}C_{12}$-Dieldrin	30:31
p,p-DDE	30:38	0.940	0.935 - 0.945	$^{13}C_{12}$-p,p-DDE	30:36
Captan	31:26	1.439	1.423 - 1.454	$^{13}C_{12}$-PCB-52	21:51
o,p-DDD	32:21	0.952	0.943 - 0.962	$^{13}C_{12}$-o,p-DDT	33:58
$^{13}C_{12}$-p,p-DDE	30:36	1.492	1.477 - 1.507	$^{13}C_{12}$-PCB-52	21:51
Disulfoton-Sulfone.	32:49	1.502	1.487 - 1.517	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{12}$-Endrin	32:53	1.505	1.490 - 1.520	$^{13}C_{12}$-PCB-52	21:51
Endrin	32:56	1.002	0.996 - 1.007	$^{13}C_{12}$-Endrin	32:53
Perthane	32:58	1.509	1.494 - 1.524	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{10}$-c-Nonachlor	33:17	1.523	1.508 - 1.539	$^{13}C_{12}$-PCB-52	21:51
c-Nonachlor	33:19	1.001	0.996 - 1.006	$^{13}C_{10}$-c-Nonachlor	33:17
$^{13}C_{12}$-o,p-DDT	33:58	1.555	1.539 - 1.570	$^{13}C_{12}$-PCB-52	21:51
o,p-DDT	33:59	1.000	0.996 - 1.005	^{13}C-o,p-DDT	33:58
^{13}C9-beta-Endosulfan	34:30	1.579	1.564 - 1.594	$^{13}C_{12}$-PCB-52	21:51
p,p-DDD	34:31	0.865	0.857 - 0.874	$^{13}C_{12}$-p,p-DDT	35:53
beta-Endosulfan	34:32	1.001	0.996 - 1.006	$^{13}C_{9}$-beta-Endosulfan	34:30
p,p-DDT	35:54	0.900	0.896 - 0.904	$^{13}C_{12}$-p,p-DDT	35:53
Endosulfan-sulfate	36:54	1.070	1.060 - 1.079	$^{13}C_{9}$-beta-Endosulfan	34:30
$^{13}C_{8}$-Mirex	39:29	1.807	1.792 - 1.822	$^{13}C_{12}$-PCB-52	21:51
Mirex	39:30	1.000	0.996 - 1.005	$^{13}C_{8}$-Mirex	39:29
Hexazinone	39:38	1.814	1.799 - 1.829	$^{13}C_{12}$-PCB-52	21:51
$^{13}C_{12}$-Methoxychlor	39:43	1.818	1.802 - 1.833	$^{13}C_{12}$-PCB-52	21:51
Methoxychlor	39:44	1.000	0.996 - 1.005	$^{13}C_{12}$-Methoxychlor	39:43
Endrin-Ketone	39:47	1.210	1.200 - 1.220	$^{13}C_{12}$-Endrin	32:53
$^{13}C_{12}$-p,p-DDT	35:53	1.825	1.810 - 1.841	$^{13}C_{12}$-PCB-52	21:51
Phosmet	40:55	1.873	1.857 - 1.888	$^{13}C_{12}$-PCB-52	21:51
Permethrins-Peak_1	42:04	1.714	1.707 - 1.72	$^{13}C_{6}$-Permethrins-Peak_1	42:04
Permethrins-Peak_2	42:21	1.739	1.732 - 1.746	$^{13}C_{6}$-Permethrins-Peak_2	42:21
Azinphos-methyl	42:39	1.737	1.730 - 1.744	Azinphos-methyl-d6	42:33
Cypermethrins-Peak_1	43:52	N/A	N/A	$^{13}C_{6}$-Permethrins-Peak_1+2	
Cypermethrins-Peak_2	44:03	N/A	N/A	$^{13}C_{6}$-Permethrins-Peak_1+2	
Cypermethrins-Peak_3	44:11	N/A	N/A	$^{13}C_{6}$-Permethrins-Peak_1+2	

1. Retention time of pesticide or labeled compound.
2. Relative retention time (RRT) between the target and reference compounds.
3. RRT limits based on estimated RRT variability.
4. Labeled compounds that form both the retention time and quantitation reference.
5. Method detection limits (MDLs) and minimum levels of quantitation (MLs) with no interferences present.

Table 3. Concentrations of native and labeled pesticides in stock solutions, spiking solutions, and final extracts

Pesticide	Stock (ng/mL)	Spiking solution (pg/mL)	In 20 µL extract (ng/mL; pg/µL)
Tecnazene	800	800	40
Hexachlorobenzene	800	800	40
Quintozene	1600	1600	80
Heptachlor	600	600	30
Alpha-BHC	1200	1200	60
gamma-BHC (Lindane)	1200	1200	60
beta-BHC	1200	1200	60
delta-BHC	1200	1200	60
Aldrin	1200	1200	60
Dacthal	400	400	20
Octachlorostyrene	600	600	30
Oxychlordane	1200	1200	60
Heptachlor epoxide B	600	600	30
Trans-Chlordane	600	600	30
cis-Chlordane	600	600	30
Trans-Nonachlor	800	800	40
cis-Nonachlor	600	600	30
Endosulfan I (alpha)	600	600	30
Endosulfan II (beta)	600	600	30
Dieldrin	600	600	30
2,4'-DDD	600	600	30
4,4'-DDD	600	600	30
2,4'-DDE	600	600	30
4,4'-DDE	600	600	30
2,4'-DDT	600	600	30
4,4'-DDT	600	600	30
Perthane	600	600	30
Endrin	600	600	30
Endosulfan sulfate	600	600	30
Mirex	600	600	30
Methoxychlor	600	600	30
Endrin ketone	600	600	30
Desethylatrazine	800	800	40
Simazine	1600	1600	80
Atrazine	1600	1600	80
Ametryn	1600	1600	80
Metribuzin	400	400	20
Cyanazine	1600	1600	80
Hexazinone	2000	2000	100

Permethrin	800	800	40
Cypermethrin	4000	4000	200
Chlorothalonil	800	800	40
Diazinon	1600	1600	80
Disulfoton	8000	8000	400
Phorate	1600	1600	80
Methamidophos	1600	1600	80
Diazinon-oxon	1600	1600	80
Fonofos	1600	1600	80
Chlorpyriphos-methyl	2000	2000	100
Parathion-methyl	4000	4000	200
Pirimphos-methyl	1600	1600	80
Chlorpyriphos	1600	1600	80
Fenitrothion	1600	1600	80
Malathion	20000	20000	1000
Parathion-ethyl	1600	1600	80
Chlorpyriphos-oxon	1600	1600	80
Disulfoton sulfone	400	400	20
Azinphos-methyl	2000	2000	100
Captan	4000	4000	200
Phosmet (Imidan)	4000	4000	200
13C6-HCB	1800	1800	90
13C6-gamma-BHC	2600	2600	130
13C4-Heptachlor	1400	1400	70
13C6-beta-BHC	1600	1600	80
13C6-delta-BHC	1600	1600	80
13C12-Aldrin	1600	1600	80
13C10-Oxychlordane	1600	1600	80
13C10-Heptachlor-epoxide	1600	1600	80
13C9-alpha-Endosulfan	1600	1600	80
13C12-Dieldrin	1600	1600	80
13C10-t-Chlordane	1600	1600	80
13C10-t-Nonachlor	1600	1600	80
13C12-p,p-DDE	1600	1600	80
13C12-Endrin	1600	1600	80
13C9-beta-Endosulfan	1600	1600	80
13C10-c-Nonachlor	1600	1600	80
13C12-o,p-DDT	1600	1600	80
13C12-p,p-DDT	1600	1600	80
13C8-Mirex	1600	1600	80
13C12-Methoxychlor	1600	1600	80
Azinphos-methyl-d6	1600	1600	80
Diazinon-d10	1600	1600	80
13C6-Fonofos	1600	1600	80

13C3-Atrazine	1600	1600	80
13C6-Permethrins	1600	1600	80
13C12 PCB 52	1600	1600	80

Table 4. Concentration of pesticides in calibration and calibration verification standards (ng/mL)

Solution concentration (ng/mL)						
Pesticide	**CS-1 (Hi sens) (1)**	**CS-2**	**CS-3**	**CS-4 (VER)**	**CS-5**	**CS-6**
Tecnazene	2.0	8.0	16.0	40.0	100.0	200.0
Hexachlorobenzene	2.0	8.0	16.0	40.0	100.0	200.0
Quintozene	4.0	16.0	32.0	80.0	200.0	400.0
Heptachlor	1.5	6.0	12.0	30.0	75.0	150.0
alpha-BHC	3.0	12.0	24.0	60.0	150.0	300.0
gamma-BHC (Lindane)	3.0	12.0	24.0	60.0	150.0	300.0
beta-BHC	3.0	12.0	24.0	60.0	150.0	300.0
delta-BHC	3.0	12.0	24.0	60.0	150.0	300.0
Aldrin	3.0	12.0	24.0	60.0	150.0	300.0
Dacthal	1.0	4.0	8.0	20.0	50.0	100.0
Octachlorostyrene	1.5	6.0	12.0	30.0	75.0	150.0
Oxychlordane	3.0	12.0	24.0	60.0	150.0	300.0
Heptachlor epoxide	1.5	6.0	12.0	30.0	75.0	150.0
trans-Chlordane	1.5	6.0	12.0	30.0	75.0	150.0
cis-Chlordane	1.5	6.0	12.0	30.0	75.0	150.0
trans-Nonachlor	2.0	8.0	16.0	40.0	100.0	200.0
cis-Nonachlor	1.5	6.0	12.0	30.0	75.0	150.0
Endosulfan I (alpha)	1.5	6.0	12.0	30.0	75.0	150.0
Endosulfan II (beta)	1.5	6.0	12.0	30.0	75.0	150.0
Dieldrin	1.5	6.0	12.0	30.0	75.0	150.0
2,4'-DDD	1.5	6.0	12.0	30.0	75.0	150.0
4,4'-DDD	1.5	6.0	12.0	30.0	75.0	150.0
2,4'-DDE	1.5	6.0	12.0	30.0	75.0	150.0
4,4'-DDE	1.5	6.0	12.0	30.0	75.0	150.0
2,4'-DDT	1.5	6.0	12.0	30.0	75.0	150.0
4,4'-DDT	1.5	6.0	12.0	30.0	75.0	150.0
Perthane	1.5	6.0	12.0	30.0	75.0	150.0
Endrin	1.5	6.0	12.0	30.0	75.0	150.0
Endosulfan sulfate	1.5	6.0	12.0	30.0	75.0	150.0
Mirex	1.5	6.0	12.0	30.0	75.0	150.0
Methoxychlor	1.5	6.0	12.0	30.0	75.0	150.0
Endrin ketone	1.5	6.0	12.0	30.0	75.0	150.0
Desethylatrazine	2.0	8.0	16.0	40.0	100.0	200.0
Simazine	4.0	16.0	32.0	80.0	200.0	400.0
Atrazine	4.0	16.0	32.0	80.0	200.0	400.0
Ametryn	4.0	16.0	32.0	80.0	200.0	400.0
Metribuzin	1.0	4.0	8.0	20.0	50.0	100.0
Cyanazine	4.0	16.0	32.0	80.0	200.0	400.0
Hexazinone	5.0	20.0	40.0	100.0	250.0	500.0
Permethrin	2.0	8.0	16.0	40.0	100.0	200.0

Cypermethrin	10.0	40.0	80.0	200.0	500.0	1000.0
Chlorothalonil	2.0	8.0	16.0	40.0	100.0	200.0
Diazinon	4.0	16.0	32.0	80.0	200.0	400.0
Disulfoton	20.0	80.0	160.0	400.0	1000.0	2000.0
Phorate	4.0	16.0	32.0	80.0	200.0	400.0
Methamidophos (Monitor)	4.0	16.0	32.0	80.0	200.0	400.0
Diazinon-oxon	4.0	16.0	32.0	80.0	200.0	400.0
Fonofos (Dyfonate)	4.0	16.0	32.0	80.0	200.0	400.0
Chlorpyriphos-methyl	5.0	20.0	40.0	100.0	250.0	500.0
Parathion-methyl	10.0	40.0	80.0	200.0	500.0	1000.0
Pirimphos-methyl	4.0	16.0	32.0	80.0	200.0	400.0
Chlorpyriphos (Dursban)	4.0	16.0	32.0	80.0	200.0	400.0
Fenitrothion	4.0	16.0	32.0	80.0	200.0	400.0
Malathion	50.0	200.0	400.0	1000.0	2500.0	5000.0
Parathion-ethyl (Parathion)	4.0	16.0	32.0	80.0	200.0	400.0
Chlorpyriphos-oxon	4.0	16.0	32.0	80.0	200.0	400.0
Disulfoton sulfone	1.0	4.0	8.0	20.0	50.0	100.0
Azinphos-methyl	5.0	20.0	40.0	100.0	250.0	500.0
Captan	10.0	40.0	80.0	200.0	500.0	1000.0
Phosmet (Imidan)	10.0	40.0	80.0	200.0	500.0	1000.0
13C6-HCB	90.0	90.0	90.0	90.0	90.0	100.0
13C6-gamma-BHC	130.0	130.0	130.0	130.0	130.0	150.0
13C4-Heptachlor	70.0	70.0	70.0	70.0	70.0	100.0
13C6-beta-BHC	80.0	80.0	80.0	80.0	80.0	80.0
13C6-delta-BHC	80.0	80.0	80.0	80.0	80.0	80.0
13C12-Aldrin	80.0	80.0	80.0	80.0	80.0	80.0
13C10-Oxychlordane	80.0	80.0	80.0	80.0	80.0	80.0
13C10-Heptachlor-epoxide	80.0	80.0	80.0	80.0	80.0	80.0
13C9-alpha-Endosulfan	80.0	80.0	80.0	80.0	80.0	80.0
13C12-Dieldrin	80.0	80.0	80.0	80.0	80.0	80.0
13C10-t-Chlordane	80.0	80.0	80.0	80.0	80.0	80.0
13C10-t-Nonachlor	80.0	80.0	80.0	80.0	80.0	80.0
13C12-p,p-DDE	80.0	80.0	80.0	80.0	80.0	80.0
13C12-Endrin	80.0	80.0	80.0	80.0	80.0	80.0
13C9-beta-Endosulfan	80.0	80.0	80.0	80.0	80.0	80.0
13C10-c-Nonachlor	80.0	80.0	80.0	80.0	80.0	80.0
13C12-o,p-DDT	80.0	80.0	80.0	80.0	80.0	80.0
13C12-p,p-DDT	80.0	80.0	80.0	80.0	80.0	80.0
13C8-Mirex	80.0	80.0	80.0	80.0	80.0	80.0
13C12-Methoxychlor	80.0	80.0	80.0	80.0	80.0	80.0
Azinphos-methyl-d6	80.0	80.0	80.0	80.0	80.0	80.0
Diazinon-d10	80.0	80.0	80.0	80.0	80.0	80.0
13C6-Fonofos	80.0	80.0	80.0	80.0	80.0	80.0
13C3-Atrazine	80.0	80.0	80.0	80.0	80.0	80.0

13C6-Permethrins	80.0	80.0	80.0	80.0	80.0	80.0
13C12 PCB 52	80.0	80.0	80.0	80.0	80.0	80.0

1. Additional concentration used for calibration of high sensitivity HRGC/HRMS systems

Table 5. QC acceptance criteria for pesticides in VER, IPR, OPR, and samples[1]

Pesticide (1) (2)	VER (%) (3)	IPR Rec. Limits % (4)	IPR RSD Max	OPR Rec. limits (%) (5)	Recovery in samples (%) (6)
13C12-Aldrin	70-130	6 - 113	75	5 - 126	5 - 120
13C3-Atrazine	70-130	20 - 133	45	18 - 147	36 - 132
13C6-beta-BHC	70-130	19 - 127	46	17 - 141	32 - 130
13C10-c-Nonachlor	70-130	18 - 139	47	17 - 154	36 - 139
13C6-delta-BHC	70-130	18 - 135	47	16 - 150	36 - 137
13C12-Dieldrin	70-130	21 - 145	46	19 - 161	40 - 151
13C6-Fonofos	70-130	6 - 108	63	5 - 120	5 - 132
13C6-gamma-BHC	70-130	6 - 112	62	5 - 124	11 - 120
13C6-Hexachlorobenzene	70-130	6 - 108	70	5 - 120	5 - 120
13C4-Heptachlor	70-130	6 - 115	67	5 - 128	5 - 120
13C10-Heptachlor-epoxide	70-130	9 - 131	52	8 - 146	27 - 137
13C8-Mirex	70-130	6 - 125	56	5 - 138	5 - 120
13C12-o,p-DDT	70-130	16 - 180	51	14 - 200	5 - 199
13C10-Oxychlordane	70-130	6 - 129	54	5 - 144	23 - 135
13C12-p,p-DDE	70-130	29 - 152	43	26 - 169	47 - 160
13C12-p,p-DDT	70-130	15 - 180	52	13 - 200	5 - 120
13C6-Permethrin-Peak_1	70-130	35 - 180	43	32 - 200	35 - 189
13C6-Permethrin-Peak_2	70-130	35 - 180	43	31 - 200	31 - 192
13C10-T-Chlordane	70-130	17 - 130	47	15 - 144	21 - 132
13C10-T-Nonachlor	70-130	15 - 134	49	13 - 149	14 - 136
13C12-Endrin	70-130	22 - 141	45	20 - 157	35 - 155
13C12-Methoxychlor	70-130	8 - 180	54	8 - 200	5 - 120
13C9-alpha-Endosulfan	70-130	6 - 130	63	5 - 144	15 - 148
13C9-beta-Endosulfan	70-130	6 - 108	59	5 - 120	5 - 122
Diazinon-d10	75 -125	6 - 130	54	5 - 145	21 - 141
Azinphos-methyl-d6	70 -130	6 - 180	57	5 - 200	20 - 179
o,p'-DDD	75 - 125	55 - 108	30	50 - 120	
o,p'-DDE	75 - 125	26 - 111	30	24 - 123	
o,p'-DDT	75 - 125	55 - 108	30	50 - 120	
p,p'-DDD	75 - 125	47 - 108	30	42 - 120	
p,p'-DDE	75 - 125	55 - 108	30	50 - 120	
p,p'-DDT	75 - 125	55 - 108	30	50 - 120	
Aldrin	75 - 125	55 - 108	30	50 - 120	
Alpha-Endosulfan	75 - 125	55 - 108	30	50 - 120	
beta-Endosulfan	75 - 125	5-200	50	5-200	
Disulfoton	75 - 125	5-200	50	5-200	
alpha-BHC	75 - 125	55 - 108	30	50 - 120	
Ametryn	75 - 125	6 - 160	52	5 - 178	
Atrazine	75 - 125	55 - 108	30	50 - 120	
Azinphos-methyl	75 - 125	55 - 108	30	50 - 120	

beta-BHC	75 - 125	55 - 108	30	50 - 120	
c-Chlordane	75 - 125	55 - 108	30	50 - 120	
c-Nonachlor	75 - 125	55 - 108	30	50 - 120	
Captan	75 - 125	6 - 108	39	5 - 120	
Chlorothalonil	75 - 125	6 - 108	47	5 - 120	
Chlorpyrifos	75 - 125	21 - 147	46	19 - 163	
Chlorpyrifos-methyl	75 - 125	10 - 130	51	9 - 145	
Chlorpyrifos-oxon	75 - 125	6 - 143	43	5 - 158	
Octachlorostyrene	70 -130	55 - 158	30	50 - 175	
Cyanazine	75 - 125	10 - 176	53	9 - 195	
Dacthal	75 - 125	18 - 129	46	16 - 143	
delta-BHC	75 - 125	55 - 108	30	50 - 120	
Desethylatrazine	75 - 125	55 - 108	30	50 - 120	
Diazinon	75 - 125	55 - 108	30	50 - 120	
Diazinon-oxon	75 - 125	55 - 144	30	50 - 160	
Dieldrin	75 - 125	55 - 108	30	50 - 120	
Disulfoton sulfone	75 - 125	6 - 180	79	5 - 200	
Endosulfan-sulfate	75 - 125	55 - 180	30	50 - 200	
Endrin	75 - 125	55 - 108	30	50 - 120	
Endrin-ketone	75 - 125	55 - 120	30	50 - 134	
Fenitrothion	75 - 125	15 - 168	50	14 - 186	
Fonofos	75 - 125	55 - 108	30	50 - 120	
Gamma-BHC	75 - 125	55 - 108	30	50 - 120	
Hexachlorobenzene	75 - 125	55 - 108	30	50 - 120	
Heptachlor	75 - 125	55 - 108	30	50 - 120	
Heptachlor-epoxide	75 - 125	55 - 108	30	50 - 120	
Hexazinone	75 - 125	6 - 154	74	5 - 171	
Malathion	75 - 125	15 - 136	48	14 - 151	
Methamidophos	75 - 125	6 - 108	68	5 - 120	
Methoxychlor	75 - 125	55 - 108	30	50 - 120	
Metribuzin	75 - 125	6 - 134	58	5 - 149	
Mirex	75 - 125	55 - 108	30	50 - 120	
Oxychlordane	75 - 125	55 - 108	30	50 - 120	
Parathion-ethyl	75 - 125	13 - 147	50	12 - 164	
Parathion-methyl	75 - 125	7 - 136	53	7 - 151	
Perthane	75 - 125	26 - 180	46	24 - 200	
Phorate	75 - 125	6 - 108	291	5 - 120	
Phosmet	75 - 125	14 - 138	49	13 - 153	
Pirimiphos-methyl	75 - 125	6 - 151	64	5 - 168	
Quintozene	75 - 125	55 - 180	30	50 - 200	
Simazine	75 - 125	55 - 108	30	50 - 120	
t-Chlordane	75 - 125	55 - 108	30	50 - 120	
t-Nonachlor	75 - 125	55 - 108	30	50 - 120	
Technazene	75 - 125	55 - 154	30	50 - 171	

Total-Cypermethrins	75 - 125	55 - 108	30	50 - 120	
Total-Permethrins	75 - 125	55 - 180	30	50 - 200	

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
2. For concentrations see Table 3 spike solutions.
3. Section 15.3.
4. Section 9.2.
5. Section 15.6.
6. Section 9.3: Recovery of labeled compounds from samples.

Table 6. Scan functions; exact m/z's (m1 and m2), ratios and tolerances; retention times (RTs); and quantitation references.

Func -tion	Pesticide	m1 (1)	m2 (1)	m1/m2		RT (min)	Quantified against labeled standard
				Ratio	Tolerance (+/-)		
1	Methamidophos	93.9642	94.9721		0.35	09:01	13C12-PCB-52
2	HCB	283.8102	285.8072	1.25	0.25	15:55	13C6-HCB
2	Tecnazene	258.8761	260.8732	0.78	0.35	14:44	13C6-HCB
2	13C6-HCB	289.8303	291.8273	1.25	0.25	15:54	13C12-PCB-52
2	Phorate	260.0128	262.0086	6.92	0.35	16:11	13C12-PCB-52
3	Desethylatrazine	172.0390	174.0360	3.11	0.35	16:50	13C3-Atrazine
3	Alpha-HCH	218.9116	220.9086	2.08	0.25	16:35	13C6-gamma-BHC
4	Atrazine	215.0938	217.0908	3.08	0.35	18:01	13C3-Atrazine
4	Simazine	201.0781	203.0752	3.1	0.35	18:21	13C3-Atrazine
4	Fonofos	246.0302	247.0336		0.35	18:25	13C6-Fonofos
4	gamma-HCH	218.9116	220.9086	2.08	0.25	18:16	13C6-gamma-BHC
4	Quintozene	236.8413	238.8384	1.56	0.35	17:39	13C6-HCB
4	13C3-Atrazine	218.1038	220.1009	3.08	0.35	18:00	13C12-PCB-52
4	13C6-Fonofos	252.0503	253.0537	1000	0.35	18:25	13C12-PCB-52
4	13C6-gamma-BHC	222.9346	224.9317	0.77	0.25	18:15	13C12-PCB-52
4	Diazinon-d10	282.1074	314.1638	1000	0.35	17:32	13C12-PCB-52
4	Disulfoton	274.0285	275.0318		0.35	18:34	13C12-PCB-52
4	Diazinon	276.0698	304.1011		0.35	17:44	Diazinon-d10
4	Diazinon-oxon	273.1004	288.1239		0.35	17:55	Diazinon-d10
5	Aldrin	262.8569	264.854	1.56	0.25	21:17	13C12-Aldrin
5	Beta-BHC	218.9116	220.9086	2.08	0.25	19:27	13C6-beta-BHC
5	Delta-BHC	218.9116	220.9086	2.08	0.25	21:01	13C6-delta-BHC
5	Heptachlor	271.8102	273.8072	1.25	0.25	19:37	13C4-Heptachlor
5	13C12-Aldrin	269.8804	271.8775	1.56	0.25	21:15	13C12-PCB-52
5	13C6-beta-BHC	222.9346	224.9317	0.77	0.25	19:26	13C12-PCB-52
5	13C6-delta-BHC	222.9346	224.9317	0.77	0.25	21:00	13C12-PCB-52
5	13C4-Heptachlor	276.8269	278.824	1.24	0.25	19:36	13C12-PCB-52
5	Chlorothalonil.	263.8816	265.8786	0.78	0.35	21:08	13C12-PCB-52
5	Chlorpyriphos-methyl	285.9261	287.9232	1.44	0.35	21:26	13C12-PCB-52
5	13C12-PCB-52	301.9626	303.9597	0.78	0.25	21:51	
6	Octachlorostyrene	270.8443	272.8413	0.63	0.25	23:18	13C12-Aldrin
6	Ametryn	227.1205	228.1238		0.35	22:41	13C12-PCB-52
6	Dacthal	298.8836	300.8807	0.78	0.35	23:18	13C12-PCB-52
6	Metribuzin	198.0701	199.0735		0.35	23:04	13C12-PCB-52
6	Parathion-methyl	263.0017	264.0051		0.35	22:28	13C12-PCB-52
6	Pirimiphos-methyl	276.0572	290.0728		0.35	22:42	13C12-PCB-52
7	Oxychlordane	262.8569	264.8540	1.56	0.25	24:11	13C10-Oxychlordane
7	13C10-Oxychlordane	269.8804	271.8775	1.56	0.25	24:09	13C12-PCB-52
7	Chlorpyriphos	313.9574	315.9545	1.44	0.35	23:33	13C12-PCB-52
7	Chlorpyriphos-oxon	269.9490	271.9462	1.54	0.35	24:30	13C12-PCB-52

7	Fenitrothion	260.0146	277.0174		0.35	24:07	13C12-PCB-52
7	Malathion	283.9942	285.0020		0.35	24:12	13C12-PCB-52
7	Parathion-ethyl	291.0330	292.0364		0.35	24:26	13C12-PCB-52
8	Heptachlor-epoxide	262.8569	264.8540	1.56	0.25	24:14	13C12-Heptachlor-epoxide
8	alpha-Endosulfan	262.8569	264.8540	1.56	0.25	27:53	13C9-alpha-Endosulfan
8	Dieldrin	262.8569	264.8540	1.56	0.25	30:34	13C12-Dieldrin
8	o,p-DDE	246.0003	247.9974	1.56	0.25	28:07	13C12-p,p-DDE
8	p,p-DDE	246.0003	247.9974	1.56	0.25	30:38	13C12-p,p-DDE
8	13C12-Heptachlor-epoxide	269.8804	271.8775	1.56	0.25	25:11	13C12-PCB-52
8	13C9-alpha-Endosulfan	269.8804	271.8775	1.56	0.25	27:51	13C12-PCB-52
8	13C12-Dieldrin	269.8804	271.8775	1.56	0.25	30:31	13C12-PCB-52
8	13C12-p,p-DDE	258.0406	260.0376	1.56	0.25	32:36	13C12-PCB-52
8	13C10-t-Chlordane	269.8804	271.8775	1.56	0.25	26:39	13C12-PCB-52
8	13C10-t-Nonachlor	269.8804	271.8775	1.56	0.25	26:48	13C12-PCB-52
8	Cyanazine	240.0890	242.0861	3.06	0.35	28:13	13C12-PCB-52
8	c-Chlordane	262.8569	264.854	1.56	0.25	27:44	13C10-t-Chlordane
8	t-Chlordane	262.8569	264.854	1.56	0.25	26:41	13C10-t-Chlordane
8	t-Nonachlor	262.8569	264.854	1.56	0.25	26:50	13C10-t-Nonachlor
9	Endrin	262.8569	264.854	1.56	0.25	32:56	13C12-Endrin
9	c-Nonachlor	262.8569	264.854	1.56	0.25	33:19	13C10-c-Nonachlor
9	o,p-DDD	235.0081	237.0052	1.56	0.25	32:21	13C12-o,p-DDT
9	13C12-Endrin	269.8804	271.8775	1.56	0.25	32:53	13C12-PCB-52
9	Captan	263.9653	265.9623	1.44	0.35	31:26	13C12-PCB-52
9	Disulfoton-Sulfone.	213.0173	214.0251		0.35	32:49	13C12-PCB-52
9	Perthane	224.1520	223.1487		0.35	32:58	13C12-PCB-52
10	beta-Endosulfan	264.8540	262.8569	0.64	0.25	34:32	13C9-beta-Endosulfan
10	Endosulfan-sulfate	264.8540	262.8569	0.64	0.25	36:54	13C9-beta-Endosulfan
10	o,p-DDT	235.0081	237.0052	1.56	0.25	33:59	13C12-o,p-DDT
10	p,p-DDD	235.0081	237.0052	1.56	0.25	34:31	13C12-p,p-DDT
10	p,p-DDT	235.0081	237.0052	1.56	0.25	35:54	13C12-p,p-DDT
10	13C9-beta-Endosulfan	269.8804	271.8775	1.56	0.25	34:30	13C12-PCB-52
10	13C10-c-Nonachlor	269.8804	271.8775	1.56	0.25	33:17	13C12-PCB-52
10	13C12-o,p-DDT	247.0484	249.0454	1.56	0.25	33:58	13C12-PCB-52
10	13C12-p,p-DDT	247.0484	249.0454	1.56	0.25	39:53	13C12-PCB-52
11	Endrin-ketone	247.8521	249.8491	0.63	0.25	39:47	13C12-Endrin
11	Methoxychlor	227.1072	228.1106		0.35	39:44	13C12-Methoxychlor
11	Mirex	236.8413	238.8384	1.56	0.25	39:30	13C8-Mirex
11	13C12-Methoxychlor	239.1475	240.1508		0.35	39:43	13C12-PCB-52
11	13C8-Mirex	241.8581	243.8551	1.56	0.25	39:29	13C12-PCB-52
11	13C6-Permethrins-Peak_1	189.1011	190.1045		0.35	24:33	13C12-PCB-52
11	13C6-Permethrins-Peak_2	189.1011	190.1045		0.35	24:21	13C12-PCB-52
11	Azinphos-methyl-d6	160.0511	161.0544		0.35	24:33	13C12-PCB-52
11	Hexazinone	171.0882	172.0916		0.35	39:38	13C12-PCB-52
11	Phosmet	160.0399	161.0432		0.35	40:55	13C12-PCB-52

11	Permethrins-Peak_1	183.0081	184.0843		0.35	42:04	13C6-Permethrins-Peak_1
11	Cypermethrins-Peak_1	163.0081	165.0052	1.56	0.35	43:52	13C6-Permethrins-Peak_1+2
11	Cypermethrins-Peak_2	163.0081	165.0052	1.56	0.35	44:03	13C6-Permethrins-Peak_1+2
11	Cypermethrins-Peak_3	163.0081	165.0052	1.56	0.35	44:11	13C6-Permethrins-Peak_1+2
11	Permethrins-Peak_2	183.0081	184.0843		0.35	42:21	13C6-Permethrins-Peak_2
11	Azinphos-methyl	160.0511	161.0544		0.35	42:39	Azinphos-methyl-d6
11	Total-Cypermethrins	163.0081	165.0052	1.56	0.35		
11	Total-Permethrins	183.0081	184.0843		0.35		

1. Isotopic masses used for accurate mass calculation

^{1}H	1.0078
^{12}C	12.0000
^{13}C	13.0034
^{35}Cl	34.9689
^{37}Cl	36.9659
^{19}F	18.9984
^{14}N	14.0031
^{16}O	15.9949

Table 7. Suggested sample quantities to be extracted for various matrices [1]

Sample matrix[2]	Example	Percent solids	Phase	Quantity extracted
Single-phase				
Aqueous	Drinking water	<1	–[3]	1000 mL
	Groundwater			
	Treated wastewater			
Solid	Dry soil	>20	Solid	10 g
	Compost			
	Ash			
Organic	Waste solvent	<1	Organic	10 g
	Waste oil			
	Organic polymer			
Tissue	Fish	–	Organic	10 g
	Human adipose			
Multi-phase				
Liquid/Solid				
Aqueous/Solid	Wet soil	1-30	Solid	10 g
	Untreated effluent			
	Digested municipal sludge			
	Filter cake			
	Paper pulp			
Organic/solid	Industrial sludge	1-100	Both	10 g
	Oily waste			
Liquid/Liquid				
Aqueous/organic	In-process effluent	<1	Organic	10 g
	Untreated effluent			
	Drum waste			
Aqueous/organic/solid	Untreated effluent	>1	Organic & solid	10 g
	Drum waste			

1. The quantity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing one percent solids will contain 10 grams of solids. For aqueous samples containing greater than one percent solids, a lesser volume is used so that 10 grams of solids (dry weight) will be extracted.

2. The sample matrix may be amorphous for some samples. In general, when the pesticides are in contact with a multi-phase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low water solubility.

3. Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

Table 8. Performance data from single laboratory validation.

	Solid-Based			Reagent Water-Based			Biosolids-Based on 8 (native)		
	on 5 samples			on 4 samples			or 6 (label) samples		
	Solids Average Recovery	Solids Standard Deviation	Solids Relative Standard Deviation	Water Average Recovery	Water Standard Deviation	Water Relative Standard Deviation	Biosolids Average Recovery	Biosolids Standard Deviation	Biosolids Relative Standard Deviation
13C12-ENDRIN	90.43	31.77	28.73	86.81	8.60	7.46	104.57	13.16	13.76
13C12-METHOXYCHLOR	128.41	32.12	41.25	100.11	7.61	7.62	20.64	53.78	11.10
13C9-ALPHA-ENDOSULPHAN	78.70	35.89	28.25	58.13	8.21	4.77	99.81	7.05	7.04
13C9-BETA-ENDOSULPHAN	41.74	33.54	14.00	29.95	7.71	2.31	84.12	10.42	8.76
13C-ALDRIN	63.24	40.59	25.67	44.20	23.24	10.27	55.15	13.54	7.47
13C-ATRAZINE	79.29	33.93	26.90	87.33	6.03	5.27	85.34	7.72	6.59
13C-BETA-HCH	82.51	31.58	26.05	74.98	6.06	4.55	84.55	11.92	10.08
13C-C-NONACHLOR	90.04	31.72	28.56	79.79	5.75	4.59	89.72	8.54	7.66
13C-DELTA-HCH	88.30	31.10	27.46	76.82	6.14	4.72	91.15	6.01	5.48
13C-DIELDRIN	93.89	31.51	29.59	85.15	5.83	4.96	103.06	5.37	5.53
13C-FONOFOS	50.73	40.18	20.38	49.40	27.30	13.49	90.65	8.48	7.69
13C-GAMMA-HCH	68.29	32.52	22.21	48.74	23.03	11.22	71.55	17.26	12.35
13C-HCB	52.33	31.93	16.71	29.07	37.79	10.98	54.51	17.21	9.38
13C-HEPTACHLOR	68.85	33.42	23.01	42.58	27.19	11.58	55.32	34.65	19.17
13C-HEPTACHLOR-EPOXIDE	83.80	31.90	26.73	68.38	10.13	6.93	90.61	7.70	6.98
13C-MIREX	79.07	31.94	25.25	59.67	9.65	5.76	46.84	24.47	11.46
13C-O,P-DDT	123.18	30.97	38.16	99.18	7.07	7.02	48.25	43.86	21.16
13C-OXYCHLORDANE	83.09	30.78	25.58	62.67	10.04	6.29	87.54	11.61	10.16
13C-P,P-DDE	99.83	30.31	30.25	94.99	6.26	5.95	111.80	5.68	6.34
13C-P,P-DDT	140.36	30.94	43.42	110.00	4.43	4.87	33.09	50.74	16.79
13C-PERMETHRINS-PEAK_1	116.88	32.00	37.40	128.45	6.05	7.77	97.01	11.02	10.69
13C-PERMETHRINS-PEAK_2	118.48	32.32	38.30	130.18	6.11	7.95	94.06	11.15	10.49
13C-T-CHLORDANE	86.23	29.38	25.34	71.73	7.67	5.50	72.27	21.41	15.47
13C-T-NONACHLOR	87.23	31.29	27.30	74.09	7.72	5.72	66.33	26.20	17.38
2,4'-DDD	81.14	1.09	0.89	102.00	1.33	1.36	270.95	81.98	222.13
2,4'-DDE	84.86	15.50	13.15	58.65	7.59	4.45	101.19	2.88	2.91
2,4'-DDT	97.46	0.50	0.48	98.77	0.77	0.76	98.26	9.75	9.58
4,4'-DDD	45.89	3.04	1.40	46.43	1.70	0.79	430.55	97.71	420.69
4,4'-DDE	99.45	0.67	0.66	92.40	1.23	1.14	102.43	7.38	7.56
4,4'-DDT	95.81	0.94	0.90	97.66	0.66	0.64	97.19	7.90	7.68
ALDRIN	97.30	1.88	1.83	99.82	5.14	5.13	97.94	15.24	14.93
ALPHA-ENDOSULPHAN	94.02	4.50	4.23	91.74	4.03	3.70	90.06	13.49	12.15

ALPHA-HCH	86.44	2.34	2.03	80.00	12.67	10.14	94.43	11.18	10.56
AMETRYN	38.46	57.63	22.17	105.31	6.94	7.31	124.18	15.18	18.85
ATRAZINE	99.47	1.51	1.50	98.95	0.76	0.75	108.25	25.55	27.66
AZINPHOS-METHYL	95.50	1.32	1.27	91.43	2.10	1.92	92.45	12.98	12.00
BETA-ENDOSULPHAN	*	*	*	*	*	*	97.41	12.31	11.99
BETA-HCH	101.26	1.23	1.24	103.95	0.62	0.65	96.72	10.14	9.81
CAPTAN	2.03			39.76	15.77	6.27	*	*	*
C-CHLORDANE	97.89	1.77	1.73	95.29	2.47	2.36	109.10	98.97	107.98
CHLOROTHALONIL	18.32	43.37	7.94	46.46	12.52	5.82	5.43	124.49	6.76
CHLORPYRIPHOS	95.97	30.61	29.38	85.71	9.45	8.10	112.15	9.12	10.23
CHLORPYRIPHOS-METHYL	82.40	31.23	25.73	70.07	17.14	12.01	95.67	16.32	15.61
CHLORPYRIPHOS-OXON	0.64	42.62	0.27	84.10	14.59	12.27	59.89	47.09	28.20
CL8-STYRENE	122.49	16.49	20.20	109.15	12.37	13.50	132.75	7.10	9.42
C-NONACHLOR	99.49	1.65	1.64	99.95	0.99	0.99	99.96	7.50	7.50
CYANAZINE	104.03	38.26	39.80	99.88	5.26	5.25	121.57	31.95	38.84
D10-DIAZINON	77.75	36.37	28.28	71.13	15.58	11.08	88.11	16.37	14.43
D6-AZINPHOS-METHYL	93.60	42.99	40.24	118.19	4.83	5.71	90.12	18.63	16.79
DACTHAL	81.66	31.90	26.05	77.16	12.06	9.31	100.50	25.52	25.65
DELTA-HCH	102.16	1.56	1.59	99.31	3.08	3.06	97.90	9.92	9.71
DESETHYLATRAZINE	99.84	2.63	2.63	86.50	4.41	3.81	111.16	20.68	22.99
DIAZINON	98.58	1.85	1.83	98.08	1.36	1.33	93.14	7.25	6.75
DIAZINON-OXON	*	*	*	131.28	5.15	6.76	82.64	36.03	29.78
DIELDRIN	101.70	0.95	0.97	103.87	0.71	0.74	95.23	16.77	15.97
DIMETHOATE	75.95	38.51	29.25	85.52	10.34	8.84	114.22	20.38	23.28
DISULFOTON	*	*	*	*	*	*	60.23	46.33	27.91
DISULFOTON SULFONE	477.45	41.55	198.40	651.23	39.89	259.79	139.98	57.09	79.91
ENDOSULPHAN-SULPHATE	231.97	1.94	4.50	271.05	3.40	9.22	88.54	20.18	17.87
ENDRIN	101.22	3.00	3.04	103.49	1.60	1.66	98.44	9.29	9.15
ENDRIN-KETONE	104.25	10.11	10.54	95.59	8.87	8.48	71.24	41.83	29.80
ETHION	90.12	61.34	55.28	49.68	4.65	2.31	167.53	32.83	54.99
FENITROTHION	101.29	35.89	36.36	98.41	9.50	9.35	151.55	17.43	26.42
FONOFOS	106.68	2.93	3.13	98.46	2.43	2.40	98.06	7.60	7.45
GAMMA-HCH	95.92	1.44	1.39	94.86	0.82	0.78	95.09	10.82	10.28
HCB	102.21	0.10	0.10	102.89	2.58	2.65	100.09	7.31	7.32
HEPTACHLOR	100.14	1.30	1.30	99.58	3.27	3.26	91.71	9.12	8.37
HEPTACHLOR-EPOXIDE	101.40	1.84	1.87	101.50	2.31	2.35	102.08	7.48	7.64
HEXAZINONE	27.26	90.24	24.60	89.16	19.32	17.23	130.31	21.84	28.45
MALATHION	83.84	34.77	29.15	81.02	7.61	6.17	95.88	37.53	35.98
METHAMIDOPHOS	29.71	37.83	11.24	*	*	*	32.62	40.38	13.17
METHOXYCHLOR	101.14	2.51	2.54	98.17	1.44	1.41	105.54	9.42	9.95
METRIBUZIN	80.54	37.63	30.31	67.41	5.70	3.84	130.08	13.38	17.41
MIREX	103.40	2.45	2.53	94.01	3.69	3.46	103.95	10.84	11.27
OXYCHLORDANE	97.11	0.88	0.86	103.17	2.14	2.21	93.78	12.65	11.86
PARATHION-ETHYL	91.86	34.54	31.72	82.74	7.33	6.06	146.11	22.28	32.55

PARATHION-METHYL	82.54	35.71	29.48	74.72	13.29	9.93	139.95	16.25	22.74
PERTHANE	120.82	31.57	38.14	108.82	6.85	7.45	144.00	23.38	33.67
PHORATE	5.72	167.39	9.57	14.53	137.43	19.96	81.78	21.37	17.48
PHOSMET	80.19	36.61	29.36	86.54	8.34	7.22	86.09	75.25	64.78
PIRIMIPHOS-METHYL	73.75	48.99	36.13	87.90	8.09	7.11	112.14	33.53	37.60
QUINTOZENE	129.60	3.06	3.96	163.36	15.06	24.60	142.76	25.37	36.22
SIMAZINE	106.25	2.05	2.18	104.43	3.02	3.15	110.07	11.58	12.75
T-CHLORDANE	101.65	5.24	5.33	104.93	1.01	1.06	104.36	26.02	27.16
TECNAZENE	120.17	3.76	4.52	107.67	23.63	25.44	132.60	36.97	49.02
TERBUFOS	7.50	167.78	12.58	20.86	127.25	26.54	84.92	26.80	22.75
T-NONACHLOR	100.91	1.81	1.83	102.74	4.02	4.13	94.64	35.56	33.65
TOTAL-CYPERMETHRINS	93.50	3.29	3.07	93.57	4.36	4.08	71.64	7.06	5.06
TOTAL-PERMETHRINS	145.58	16.20	23.58	144.77	2.53	3.66	655.40	124.74	817.53

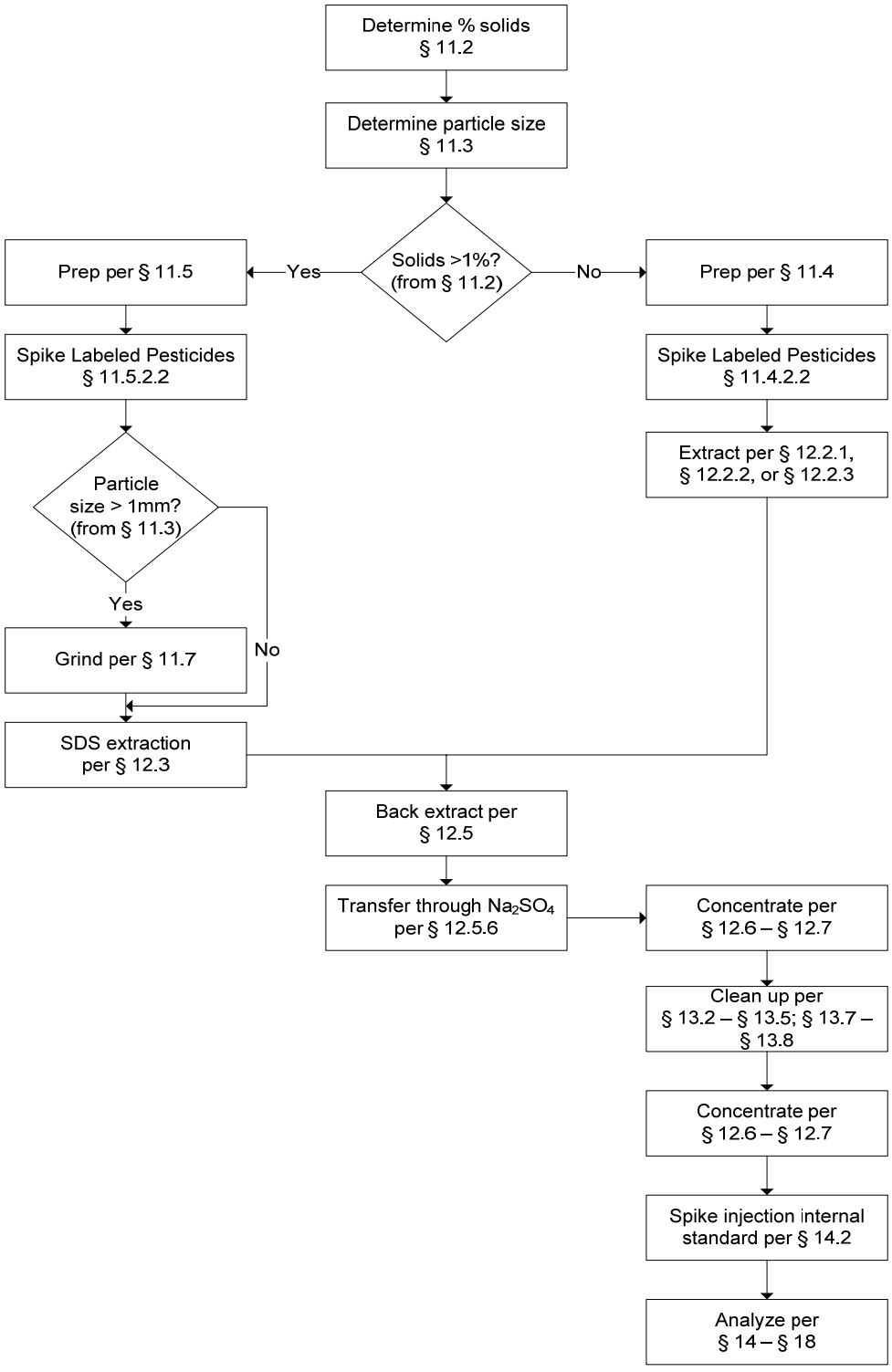

Figure 1 Flow Chart for Analysis of Aqueous and Solid Samples

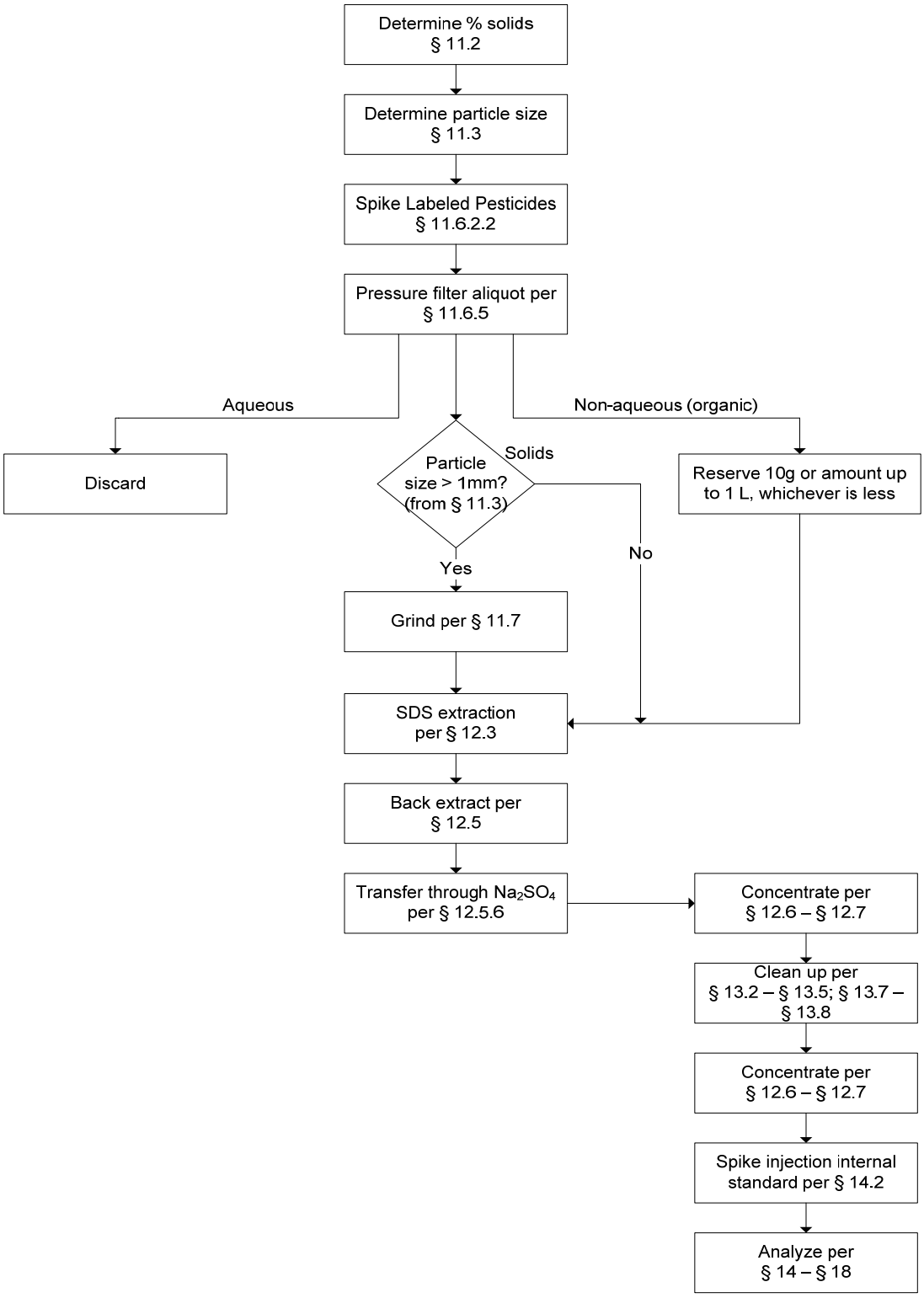

Figure 2 Flow Chart for Analysis of Multi-Phase Samples

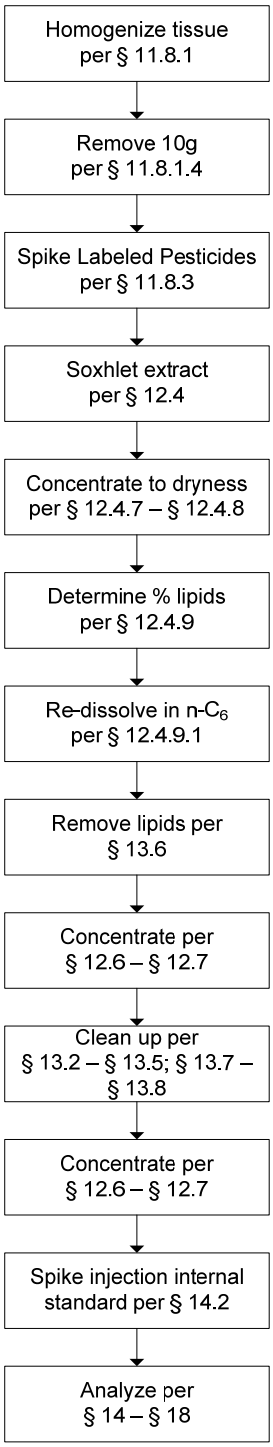

Figure 3 Flow Chart for Analysis of Tissue Samples

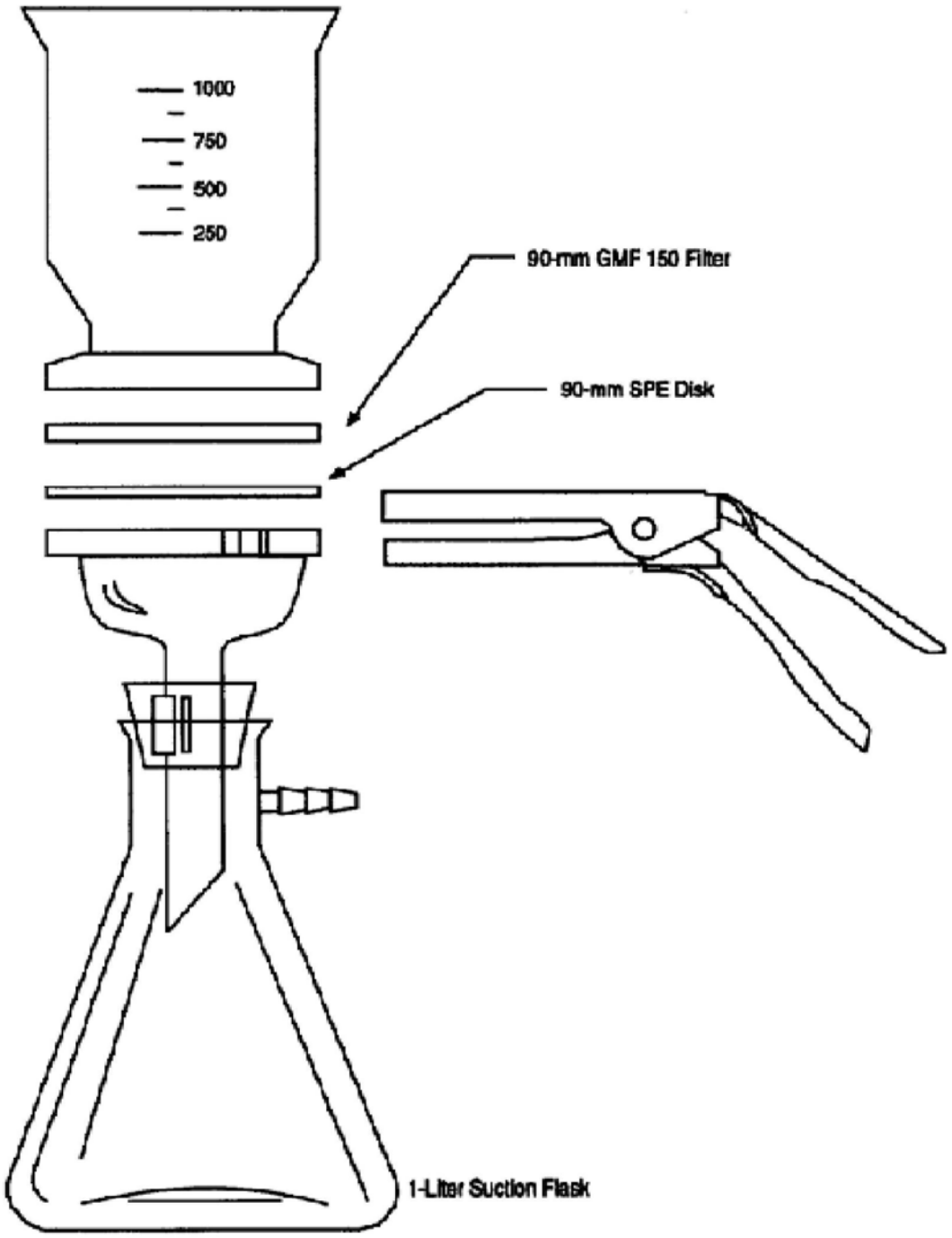

Figure 4 Solid-phase Extraction Apparatus

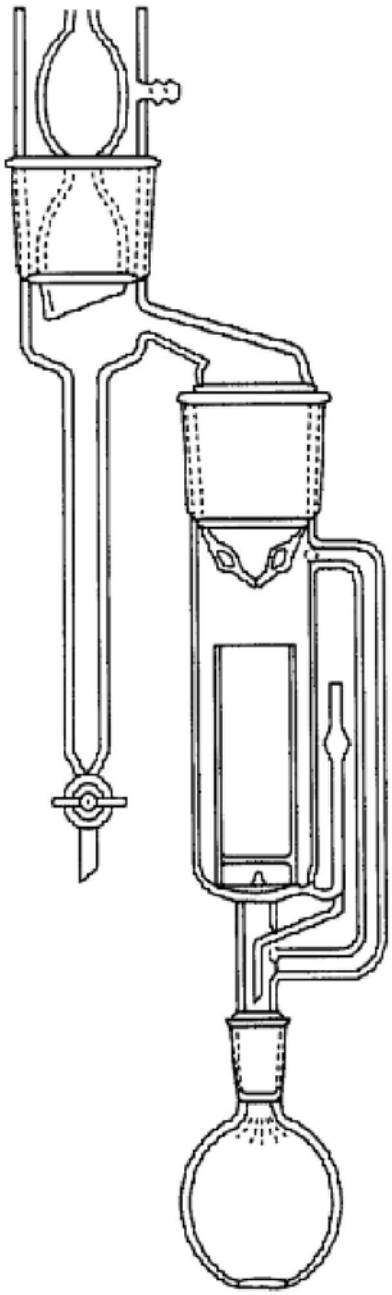

Figure 5 Soxhlet/Dean-Stark Extractor

24.0 Glossary

These definitions and purposes are specific to this Method but have been conformed to common usage to the extent possible.

24.1 Units of weight and measure

24.1.1 Symbols

EC	degrees Celsius
ΦL	microliter
Φm	micrometer
<	less than
>	greater than
%	percent

24.1.2 Alphabetical abbreviations

cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	mass or meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppq	part-per-quadrillion
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

25.0 Definitions and acronyms (in alphabetical order)

Analyte – A pesticide tested for by this Method. The analytes are listed in Table 1.

Calibration standard (CAL) – A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the HRGC/HRMS instrument.

Calibration verification standard (VER) – The mid-point calibration standard (CS-4) that is used to verify calibration. See Table 4.

CS-1, CS-2, CS-3, CS-4, CS-5, CS-6 – See Calibration standards and Table 4.

Field blank – An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC – Gas chromatograph or gas chromatography

GPC – Gel permeation chromatograph or gel permeation chromatography

HPLC – High performance liquid chromatograph or high performance liquid chromatography

HRGC – High resolution GC

HRMS – High resolution MS

Labeled injection internal standard – Labeled PCB52 is spiked into the concentrated extract immediately prior to injection of an aliquot of the extract into the HRGC/HRMS.

Internal standard – a labeled compound used as a reference for quantitation of other labeled compounds and for quantitation of native pesticides other than the pesticide of which it is a labeled analog. See Internal standard quantitation.

Internal standard quantitation – A means of determining the concentration of (1) a naturally occurring (native) compound by reference to a compound other than its labeled analog and (2) a labeled compound by reference to another labeled compound.

IPR – Initial precision and recovery; four aliquots of a reference matrix spiked with the analytes of interest and labeled compounds and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IPR is performed prior to the first time this Method is used and any time the Method or instrumentation is modified.

Isotope dilution quantitation – A means of determining a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched. In this Method, labeled are enriched with carbon-13 to produce ^{13}C-labeled analogs. The ^{13}C-labeled pesticides are spiked into each sample to allow identification and correction of the concentration of the native compounds in the analytical process.

K-D – Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent

Laboratory blank – See Method blank

Laboratory control sample (LCS) – See Ongoing precision and recovery standard (OPR)

Laboratory reagent blank – See Method blank

May – This action, activity, or procedural step is neither required nor prohibited.

May not – This action, activity, or procedural step is prohibited.

Method blank – An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The Method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Method detection limit (MDL) – The lowest concentration at which a pesticide can be detected under routine operating conditions (see 40 CFR 136, appendix B). MDLs are listed in Table 1.

Minimum level (ML) – The greater of a multiple of the MDL or the lowest calibration point (see 68 FR 11790, March 12, 2003.)

MS – Mass spectrometer or mass spectrometry

Must – This action, activity, or procedural step is required.

OPR – Ongoing precision and recovery standard (OPR); a method blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this Method for precision and recovery.

Perfluorokerosene (PFK) – A mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation blank – See Method blank

Quality control check sample (QCS) – A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

Reagent water – water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative standard deviation (RSD) – The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RF – Response factor. See Section 10.5

RR – Relative response. See Section 10.4

RSD – See relative standard deviation

SDS – Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials (Reference 3 and Figure 5).

Signal-to-noise ratio (S/N) – The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

Should – Although this action, activity, or procedural step is suggested and not required, you may be asked why you changed or omitted this action, activity, or procedural step.

SICP – Selected ion current profile; the line described by the signal at an exact m/z.

SPE – Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock solution – A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Unique GC resolution or uniquely resolved – Two adjacent chromatographic peaks in which the height of the valley is less than 10 percent of the height of the shorter peak (see Section 6.9.1.1.2).

VER – See Calibration verification.

No. L-12

Volatile Organics

SW-846 Method 8260B

Content of Soil by the Microwave Oven Method[4]
D 4753 Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing[4]
D 6026 Guide for Using Significant Digits in Calculating and Reporting Geotechnical Test Data[5]
E 145 Specification for Gravity-Convection And Forced-Ventilation Ovens[6]

3. Terminology

3.1 Refer to Terminology D 653 for standard definitions of terms.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *water content (of a material)*—the ratio expressed as a percent of the mass of "pore" or "free" water in a given mass of material to the mass of the solid material. A standard temperature of 110° ± 5°C is used to determine these masses.

4. Summary of Test Method

4.1 A test specimen is dried in an oven at a temperature of 110° ± 5°C to a constant mass. The loss of mass due to drying is considered to be water. The water content is calculated using the mass of water and the mass of the dry specimen.

5. Significance and Use

5.1 For many materials, the water content is one of the most significant index properties used in establishing a correlation between soil behavior and its index properties.

5.2 The water content of a material is used in expressing the phase relationships of air, water, and solids in a given volume of material.

5.3 In fine-grained (cohesive) soils, the consistency of a given soil type depends on its water content. The water content of a soil, along with its liquid and plastic limits as determined by Test Method D 4318, is used to express its relative consistency or liquidity index.

6. Apparatus

6.1 *Drying Oven*, thermostatically-controlled, preferably of the forced-draft type, meeting the requirements of Specification E 145 and capable of maintaining a uniform temperature of 110 ± 5°C throughout the drying chamber.

6.2 *Balances*—All balances must meet the requirements of Specification D 4753 and this section. A Class GP1 balance of 0.01g readability is required for specimens having a mass of up to 200 g (excluding mass of specimen container) and a Class GP2 balance of 0.1g readability is required for specimens having a mass over 200 g. However, the balance used may be controlled by the number of significant digits needed (see 8.2.1 and 12.1.2).

6.3 *Specimen Containers*—Suitable containers made of material resistant to corrosion and change in mass upon repeated heating, cooling, exposure to materials of varying pH, and cleaning. Unless a dessicator is used, containers with close-fitting lids shall be used for testing specimens having a mass of less than about 200 g; while for specimens having a mass greater than about 200 g, containers without lids may be used (see Note 7). One container is needed for each water content determination.

NOTE 2—The purpose of close-fitting lids is to prevent loss of moisture from specimens before initial mass determination and to prevent absorption of moisture from the atmosphere following drying and before final mass determination.

6.4 *Desiccator*—A desiccator cabinet or large desiccator jar of suitable size containing silica gel or anhydrous calcium sulfate. It is preferable to use a desiccant which changes color to indicate it needs reconstitution. See 10.5.

NOTE 3—Anhydrous calcium sulfate is sold under the trade name Drierite.

6.5 *Container Handling Apparatus*, gloves, tongs, or suitable holder for moving and handling hot containers after drying.

6.6 *Miscellaneous*, knives, spatulas, scoops, quartering cloth, sample splitters, etc, as required.

7. Samples

7.1 Samples shall be preserved and transported in accordance with Practice 4220 Groups B, C, or D soils. Keep the samples that are stored prior to testing in noncorrodible airtight containers at a temperature between approximately 3 and 30°C and in an area that prevents direct contact with sunlight. Disturbed samples in jars or other containers shall be stored in such a way as to prevent or minimize moisture condensation on the insides of the containers.

7.2 The water content determination should be done as soon as practicable after sampling, especially if potentially corrodible containers (such as thin-walled steel tubes, paint cans, etc.) or plastic sample bags are used.

8. Test Specimen

8.1 For water contents being determined in conjunction with another ASTM method, the specimen mass requirement stated in that method shall be used if one is provided. If no minimum specimen mass is provided in that method then the values given below shall apply. See Howard[7] for background data for the values listed.

8.2 The minimum mass of moist material selected to be representative of the total sample shall be in accordance with the following:

Maximum particle size (100 % passing)	Standard Sieve Size	Recommended minimum mass of moist test specimen for water content reported to ±0.1 %	Recommended minimum mass of moist test specimen for water content reported to ±1 %
2 mm or less	No. 10	20 g	20 g[A]
4.75 mm	No. 4	100 g	20 g[A]
9.5 mm	⅜-In.	500 g	50 g
19.0 mm	¾-In.	2.5 kg	250 g
37.5 mm	1½ in.	10 kg	1 kg

[5] *Annual Book of ASTM Standards*, Vol 04.09.
[6] *Annual Book of ASTM Standards*, Vol 14.02.
[7] Howard, A. K., "Minimum Test Specimen Mass for Moisture Content Determination", *Geotechnical Testing Journal*, A.S.T.M., Vol. 12, No. 1, March 1989, pp. 39-44.

75.0 mm	3-in.	50 kg	5 kg

[A]To be representative not less than 20 g shall be used.

8.2.1 The minimum mass used may have to be increased to obtain the needed significant digits for the mass of water when reporting water contents to the nearest 0.1 % or as indicated in 12.1.2.

8.3 Using a test specimen smaller than the minimum indicated in 8.2 requires discretion, though it may be adequate for the purposes of the test. Any specimen used not meeting these requirements shall be noted on the test data forms or test data sheets.

8.4 When working with a small (less than 200g) specimen containing a relatively large gravel particle, it is appropriate not to include this particle in the test specimen. However, any discarded material shall be described and noted on the test data forms or test data sheets.

8.5 For those samples consisting entirely of intact rock, the minimum specimen mass shall be 500 g. Representative portions of the sample may be broken into smaller particles, depending on the sample's size, the container and balance being used and to facilitate drying to constant mass, see 10.4. Specimen sizes as small as 200 g may be tested if water contents of only two significant digits are acceptable.

9. Test Specimen Selection

9.1 When the test specimen is a portion of a larger amount of material, the specimen must be selected to be representative of the water condition of the entire amount of material. The manner in which the test specimen is selected depends on the purpose and application of the test, type of material being tested, the water condition, and the type of sample (from another test, bag, block, and the likes.)

9.2 For disturbed samples such as trimmings, bag samples, and the like, obtain the test specimen by one of the following methods (listed in order of preference):

9.2.1 If the material is such that it can be manipulated and handled without significant moisture loss and segregation, the material should be mixed thoroughly and then select a representative portion using a scoop of a size that no more than a few scoopfuls are required to obtain the proper size of specimen defined in 8.2.

9.2.2 If the material is such that it cannot be thoroughly mixed or mixed and sampled by a scoop, form a stockpile of the material, mixing as much as possible. Take at least five portions of material at random locations using a sampling tube, shovel, scoop, trowel, or similar device appropriate to the maximum particle size present in the material. Combine all the portions for the test specimen.

9.2.3 If the material or conditions are such that a stockpile cannot be formed, take as many portions of the material as practical, using random locations that will best represent the moisture condition. Combine all the portions for the test specimen.

9.3 Intact samples such as block, tube, split barrel, and the like, obtain the test specimen by one of the following methods depending on the purpose and potential use of the sample.

9.3.1 Using a knife, wire saw, or other sharp cutting device, trim the outside portion of the sample a sufficient distance to see if the material is layered and to remove material that appears more dry or more wet than the main portion of the sample. If the existence of layering is questionable, slice the sample in half. If the material is layered, see 9.3.3.

9.3.2 If the material is not layered, obtain the specimen meeting the mass requirements in 8.2 by: (1) taking all or one-half of the interval being tested; (2) trimming a representative slice from the interval being tested; or (3) trimming the exposed surface of one-half or from the interval being tested.

NOTE 4—Migration of moisture in some cohesionless soils may require that the full section be sampled.

9.3.3 If a layered material (or more than one material type is encountered), select an average specimen, or individual specimens, or both. Specimens must be properly identified as to location, or what they represent, and appropriate remarks entered on the test data forms or test data sheets.

10. Procedure

10.1 Determine and record the mass of the clean and dry specimen container (and its lid, if used).

10.2 Select representative test specimens in accordance with Section 9.

10.3 Place the moist test specimen in the container and, if used, set the lid securely in position. Determine the mass of the container and moist material using a balance (see 6.2) selected on the basis of the specimen mass. Record this value.

NOTE 5—To prevent mixing of specimens and yielding of incorrect results, all containers, and lids if used, should be numbered and the container numbers shall be recorded on the laboratory data sheets. The lid numbers should match the container numbers to eliminate confusion.

NOTE 6—To assist in the oven-drying of large test specimens, they should be placed in containers having a large surface area (such as pans) and the material broken up into smaller aggregations.

10.4 Remove the lid (if used) and place the container with moist material in the drying oven. Dry the material to a constant mass. Maintain the drying oven at 110 ± 5°C unless otherwise specified (see 1.4). The time required to obtain constant mass will vary depending on the type of material, size of specimen, oven type and capacity, and other factors. The influence of these factors generally can be established by good judgment, and experience with the materials being tested and the apparatus being used.

NOTE 7—In most cases, drying a test specimen overnight (about 12 to 16 h) is sufficient. In cases where there is doubt concerning the adequacy of drying, drying should be continued until the change in mass after two successive periods (greater than 1 h) of drying is an insignificant amount (less than about 0.1 %). Specimens of sand may often be dried to constant mass in a period of about 4 h, when a forced-draft oven is used.

NOTE 8—Since some dry materials may absorb moisture from moist specimens, dried specimens should be removed before placing moist specimens in the same oven. However, this would not be applicable if the previously dried specimens will remain in the drying oven for an additional time period of about 16 h.

10.5 After the material has dried to constant mass remove the container from the oven (and replace the lid if used). Allow the material and container to cool to room temperature or until the container can be handled comfortably with bare hands and the operation of the balance will not be affected by convection currents and/or its being heated. Determine the mass of the container and oven-dried material using the same type/capacity

balance used in 10.3. Record this value. Tight fitting lids shall be used if it appears that the specimen is absorbing moisture from the air prior to determination of its dry mass.

NOTE 9—Cooling in a desiccator is acceptable in place of tight fitting lids since it greatly reduces absorption of moisture from the atmosphere during cooling especially for containers without tight fitting lids.

11. Calculation

11.1 Calculate the water content of the material as follows:

$$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)] \times 100 = \frac{M_w}{M_s} \times 100 \quad (1)$$

where:

w = water content, %,
M_{cws} = mass of container and wet specimen, g,
M_{cs} = mass of container and oven dry specimen, g,
M_c = mass of container, g,
M_w = mass of water ($M_w = M_{cws} - M_{cds}$), g, and
M_s = mass of solid particles ($M_s = M_{cds} - M_c$), g.

12. Report

12.1 Test data forms or test data sheets shall include the following:

12.1.1 Identification of the sample (material) being tested, such as boring number, sample number, test number, container number etc.

12.1.2 Water content of the specimen to the nearest 1 % or 0.1 %, as appropriate based on the minimum sample used. If this method is used in concert with another method, the water content of the specimen should be reported to the value required by the test method for which the water content is being determined. Refer to Guide D 6026 for guidance concerning significant digits, especially if the value obtained from this test method is to be used to calculate other relationships such as unit weight or density. For instance, if it is desired to express dry unit weight to the nearest 0.1 lbf/ft^3(0.02 kN/m^3), it may be necessary to use a balance with a greater readability or use a larger specimen mass to obtain the required significant digits the mass of water so that the water content can be determined to the required significant digits. Also, the significant digits in Guide D 6026 may need to be increased when calculating phase relationships requiring four significant digits.

12.1.3 Indicate if test specimen had a mass less than the minimum indicated in 8.2.

12.1.4 Indicate if test specimen contained more than one material type (layered, etc.).

12.1.5 Indicate the temperature of drying if different from 110 ± 5°C.

12.1.6 Indicate if any material (size and amount) was excluded from the test specimen.

12.2 When reporting water content in tables, figures, etc., any data not meeting the requirements of this test method shall be noted, such as not meeting the mass, balance, or temperature requirements or a portion of the material is excluded from the test specimen.

13. Precision and Bias

13.1 *Statement on Bias*—There is no accepted reference value for this test method; therefore, bias cannot be determined.

13.2 *Statements on Precision*:

13.2.1 *Single-Operator Precision (Repeatability)*—The single-operator coefficient of variation has been found to be 2.7 percent. Therefore, results of two properly conducted tests by the same operator with the same equipment should not be considered suspect unless they differ by more than 7.8 percent of their mean.[8]

13.2.2 *Multilaboratory Precision (Reproducibility)*[9]—The multilaboratory coefficient of variation has been found to be 5.0 percent. Therefore, results of two properly conducted tests by different operators using different equipment should not be considered suspect unless they differ by more than 14.0 percent of their mean.

14. Keywords

14.1 consistency; index property; laboratory; moisture analysis; moisture content; soil aggregate; water content

[8] These numbers represent the (1s) and (d2s) limits as described in Practice C 670.

[9] These numbers represent the (1s %) and (d2s %) limits as described in Practice C 670.

SUMMARY OF CHANGES

Committee D-18 has identified the location of selected changes to this standard since the last issue. (D 2216-92) that may impact the use of this standard.

(*1*) Title was changed to emphasize that mass is the basis for the standard.
(*2*) Section 1.1 was revised to clarify "similar materials".
(*3*) New 1.2 was added to explain a limitation in scope. The other sections were renumbered as appropriate.
(*4*) An information reference was included in 1.5.
(*5*) An information reference was included in 1.6
(*6*) A new ASTM referenced document was included in 2.1.
(*7*) New Footnotes 2, 3, and 5 were added and identified. Other footnotes were renumbered where necessary for sequential identification.
(*8*) Information concerning balances was added in 6.2
(*9*) Section 6.3 was revised to clarify the use of close-fitting lids, and a reference to Note 8 was added.

(*10*) In 6.4, "anhydrous calcium phosphate" was changed to "anyhydrous calcium sulfate" to correct an error and to agree with Note 3.
(*11*) A typo in 8.1 was corrected from "before" to "below" and a footnoted reference was added for information.
(*12*) A portion of 8.2 was deleted for clarity.
(*13*) A new 8.2.1 was added to clarify minimum mass requirements.
(*14*) Sections 8.3, 8.4, 9.3.3, and 12.1 were changed to substitute "test data form/sheet" for "report".
(*15*) Footnote seven was identified.
(*16*) Section 9.2.1 was revised to improve clarity and intent.
(*17*) The word "possible" was changed to "practical" in 9.2.3.
(*18*) Section 9.3.1 and 9.3.2 were revised to improve clarity and for practicality.
(*19*) A reference to Guide D 6026 was added in 12.1.2.
(*20*) Footnotes 8 and 9 were added to 13.2.1 and 13.2.2, respectively. These were inadvertently omitted from the 1992 version. These explanations provide clarity and information to the user.
(*21*) A Summary of Changes was added to reflect D-18's policy.

No. L-21

% Moisture (tissue)

1-P-QM-WI-9015165

Eurofins Document Reference	1-P-QM-WI -9015065	**Revision**	13
Effective Date	Nov 15, 2012	**Status**	Effective
Historical/Local Document Number	Analysis DOD - 0111, 6111, 7611, 11624, 12845		
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Prepared by	Chad Wettig
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Revision Log:

Revision: 13		**Effective Date:** This version
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Throughout Document	Reflect re-identification of documents in EtQ	Replaced all prior Level 1, 2, 3, and 4 document numbers (analyses excluded) with EtQ numbers
Historical/Local Document Number	New Parallax scan number	Added analysis number 12845
Scope 6.	New Parallax scan number	Defined Analysis 12845
Comments 2.f. and 3.d.	New Parallax scan numbers	Defined Analysis 12846 and 12847

Revision: 12		**Effective Date:** 04/26/2012
Section	**Justification**	**Changes**
Revision Log	Formatting requirements per LOM-SOP-LAB-201	Removed revision logs up to the previous version.
Procedure 8.	Reflects current practices	Timeframe changed from 18 to 48 hours.

Reference:

1. Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, Method 2540 G (modified).

2. Method 160.3 (modified), Methods for the Chemical Analysis of Water and Wastes USEPA 600.

3. Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass, ASTM D 2216-98.

4. *Chemical Hygiene Plan*, Eurofins, Lancaster Laboratories, Inc., current version.

Cross Reference:

Document	Document Title
1-P-QM-PRO-9015413	Sample Support Ovens
1-P-QM-PRO-9015414	Maintenance of Desiccators
1-P-QM-PRO-9015519	Outlier Quality Control Data
1-P-QM-PRO-9015520	Instructions for Collecting Data on the LLENS System
1-P-QM-QMA-9017309	Determining Method Detection Limits and Limits of Quantitation
1-P-QM-QMA-9017316	Monitoring Temperatures in Refrigerators, Freezers, Incubators, and Ovens Using the Andover System
1-P-QM-QMA-9017328	Reagents and Standards
1-P-QM-QMA-9017363	Laboratory Balances
1-P-QM-QMA-9017372	Laboratory Notebooks, Logbooks, and Documentation

Scope:

This method is for the determination of moisture in most solid and semisolid samples.

1. SM20 2540-G is the preferred method when performing the moisture procedure and is used as our default method.

2. EPA Method 160.3 is a modified water procedure only used when specifically requested by a client.

3. Analysis 6111 is used for Client Account #11187 only. ASTM D 2216-98 is only used for analysis 6111.

4. Analysis 7611 is used for sieved samples only. All other samples are analyzed by analysis 0111.

5. Analysis 11624 is used for Client Account #13013 only. The procedure follows SM20 2540-G but has client specific QC criteria.

6. Analysis 12845 is used for Client Account #12528 only. The procedure follows EPA 160.3 but has specific QC and LCS requirements.

Basic Principles:

A measured amount of sample is placed in an empty tared pan and dried in an oven at 103° to 105°C. The decrease in weight of the sample, after drying, is calculated as the moisture content of the sample.

Reference Modifications:

The method has been modified by using purchased aluminum foil pans that are not preconditioned, as this step is unnecessary.

EPA Method 160.3 is a water method used to determine percent solids.
The modification is that it is used on solids to determine percent moisture.

Method SM2540 G requires multiple weights to be taken until the change in weight from the previous weight is within 4% or 50 mg (whichever is less). The modification is based on a study that was performed which determined that a constant weight was achieved after the initial drying cycle and therefore multiple weights were not necessary.

Interferences:

The determination of moisture in solid and semisolid materials is subject to error due to loss of ammonium carbonate and volatile organic matter during drying.

Non-representative, nonhomogeneous materials, such as stones, are excluded from the analysis if their inclusion is not desired in the final result.

Safety Precautions and Waste Handling:

All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state and local state laws and regulations.

See Chemical Hygiene Plan for general information regarding employee safety, waste management and pollution prevention.

Personnel Training and Qualifications:

All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and an annual documented Demonstration of Capability (DOC) which is maintained in the analyst's training records.

Initially, each technician performing the analysis must work with an experienced technician for a period of time until they can independently perform the analysis. Proficiency is measured through an Initial Demonstration of Capability (IDOC).

The IDOC and the DOC consists of four laboratory control samples (or alternatively, one blind sample for the DOC) that are carried through all steps of the analysis and meet the defined acceptance criteria for the LCS.

Sample Collection, Preservation, and Handling:

Samples for moisture analysis must be kept in an unpreserved container and refrigerated at 4° + 2°C. Samples must be analyzed within 14 days of collection.

Apparatus and Equipment:

1. Disposable aluminum foil pans, or equivalent

2. Oven maintained at 103° to 105°C. Adjust as needed to stay in this range. Refer to 1-P-QM-PRO-9015413.

3. Analytical balance, or equivalent. Refer to 1-P-QM-QMA-9017363

4. Desiccators, or equivalent. Refer to 1-P-QM-PRO-9015414

5. The LLENS is computer program that integrates a PC with an analytical balance to collect data directly from the balance. It also organizes the data, performs calculations and transmits the final results to the central computer system. The LLENS system must be used for moisture analysis. Refer to 1-P-QM-PRO-9015520.

Reagents and Standards:

Alternate weights are acceptable but final concentrations must remain the same. Refer to 1-P-QM-QMA-9017328 for the proper labeling and documentation of reagent preparations.

Standard solution of 10.5% NaCl: Add 895 ± 0.5g reagent water to 105 ± 0.2g NaCl in a beaker and mix thoroughly. Store at 4° ± 2°C. This solution is used as prepared. Stable 6 months. (Concentration of solution is approximately 89.5% moisture.)

Calibration:

Refer to 1-P-QM-QMA-9017363 for calibration procedures for analytical balances.

Procedure:

1. Verify that the balance has been calibrated each day before use.

2. Set up the batch in LLENS.

3. Number (for identification) the purchased disposable aluminum foil pans before use.

4. Place one aluminum foil pan on a zeroed balance. Record pan tare weight in LLENS.

5. With the aluminum foil pan remaining on the balance, again zero the balance.

6. Place 5 to 10 grams of well-mixed sample into the pan.

7. Record the weight of the sample in LLENS.

8. Record the date and time on the LLENS batch worksheet according to 1-P-QM-QMA-9017372, and then place the pans containing sample into the oven.

    a. Dry at 103° to 105°C for 8 to 48 hours.

    b. Oven temperatures are monitored and logged by the Andover System through the use of a stationary probe. These temperature logs are maintained and eventually archived by the Sample Support staff. Refer to 1-P-QM-QMA-9017316.

9. Record the date and time on the LLENS batch worksheet, and then remove the pans containing dried sample from the oven.

10. Cool in a desiccator for 1 hour.

    NOTE: Check desiccant to verify that the indicator crystals are still blue and not pink.

11. Again, verify that the balance has been calibrated each day before use.

12. Use tongs to place the pan containing dried sample on a zeroed balance. Record weight of pan and dried sample in LLENS.

Calculations:

$$\%moisture = \frac{A - B}{C} \times 100$$

Where:

A = Weight of sample and container before drying (in grams)

B = Weight of sample and container after drying (in grams)

C = Weight of sample before drying (in grams)

Statistical Information/Method Performance:

Refer to 1-P-QM-QMA-9017309

Quality Assurance/Quality Control:

Calibration verification of the balances must be performed each day before use.

An 89.5 % LCS must be run on each batch. Batch size is limited to 20 samples or less.

When sample volume permits, a sample matrix duplicate must be run with each group of not more than ten samples unless a client specifies otherwise.

See LIMS for current quality control (QC) acceptance windows. Follow guidelines in 1-P-QM-PRO-9015519 for outlier QC data.

Comments:

1. The analysis report for 6111 must include a comment stating, “A 5 g aliquot was dried at 103°-105°C and calculated as %moisture.”

2. When a client submits a designated sample for QC, the matrix spike (MS) sample is entered for scan 0118.

a. This allows the LLENS program to upload the moisture value from the client-designated background sample; this moisture value is often needed in the calculations of other analyses.

b. A client-submitted continuation sample is also entered for scan 0118 for the same reason.

c. Scan 6118 is specific to moistures done for Client Account #11187 only.

d. Scan 7618 is specific to moistures done on sieved samples only.

e. Scan 11625 is specific to moistures done for Client Account #13013 only.

f. Scan 12846 is specific to moistures done for Client Account #12528 only.

g. All other accounts use scan 0118.

3. When a client submits a designated sample for QC, the matrix spike duplicate (MSD) sample is entered for scan 0118 and scan 0121. (Scan 0118 provides the result for the MS and scan 0121 for the sample matrix duplicate.)

a. Scan 6121 is specific to moistures done for Client Account #11187 only.

b. Scan 7621 is specific to moistures done on sieved samples only.

c. Scan 11626 is specific to moistures done for Client Account #13013 only.

d. Scan 12847 is specific to moistures done for Client Account #12528 only.

e. All other accounts use scan 0121.

No. L-22

Total Sulfide

SW-846 Method 9030B/9034

Revision Log:

Revision: 10	Effective Date:	This version
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per LOM-SOP-LAB-201	Removed revision logs up to the previous version
Throughout SOP	Formatting requirement	Changed temp to 4° ± 2°C; Changed deionized water to reagent water
Reagents and Standards 1	Reflect current practice	ORP standard expiration date updated to read must be manufactures expiration date.
Procedure 2	Reflect current practice	Clarified taking two readings for LCS/CCV's as well as with samples.

Revision: 09	Effective Date:	08/12/10
Section	**Justification**	**Changes**
Revision Log	Formatting requirements per LOM-SOP-LAB-201	Removed revision logs up to the previous version.
Reference 1	Formatting requirements per LOM-SOP-LAB-201	Updated reference to match parallax
Reagents and Standards 2	No longer used	Removed item – Redox standard solution

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Reference:

1. Annual Book of ASTM Standards, Method D 1498

2. *Test Method for Evaluating Solid Waste*, SW-846, USEPA, Vol. IC, p. 9045C (modified).

3. *Chemical Hygiene Plan*, Eurofins Lancaster Laboratories, current version.

Cross Reference:

Document	Document Title
LOM-SOP-ES-225	Reagents and Standards
SOP-WQ-017	Quality Control Data for Wet Chemistry

Scope:

This method covers the procedure for the electrometric measurement of oxidation-reduction potential in potable waters and wastewaters. This method is also modified to perform Oxidation-Reduction Potential on solid waste and soil samples. The electrodes are reliable in nearly all aqueous solutions and are not subject to interference from color, turbidity, colloidal matter, or suspended matter. Applicable concentration ranges and reporting limits are found in the LIMS.

Basic Principles:

Oxidation-reduction potential is defined as the electromotive force between a noble metal electrode and a reference electrode when immersed in a solution, referred to the standard hydrogen electrode. The oxidation-reduction potential electrodes are inert and measure the ratio of the activities of the oxidized to the reduced species in the process reactions.

Interferences:

Particulate matter present in a sample has the possibility of causing interference to the electrode.

Safety Precautions and Waste Handling:

All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations.

See the *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

Personnel Training and Qualifications:

All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and a documented Demonstration of Capability.

Analysts are considered proficient when they have successfully completed a Demonstration of Capability. This consists of four laboratory control samples that are carried through all steps of the analysis and that meet the defined acceptance criteria. Demonstration of Capability is performed annually and documentation is maintained in each individual's training records.

Sample Collection, Preservation, and Handling:

Samples for this analysis must be in an unpreserved container. Water samples are collected in unpreserved plastic or glass containers. Solid samples are collected in unpreserved glass containers. The samples are stored at 4° ± 2°C. The samples are analyzed as soon as possible after collection. There is no defined holding time for this analysis.

Apparatus and Equipment:

1. pH meter – A pH meter capable of storing and calibrating on a Redox standard solution must be used.

2. Oxidation-reduction combination electrode – Platinum, with appropriate filling solution.

Reagents and Standards:

Alternative weights and volumes are used as long as final concentrations remain unchanged. Refer to LOM-SOP-ES-225 for appropriate labeling and documentation.

1. ORP Standard - Purchased; The expiration date must be the manufacturer's suggested expiration date. See container for storage information.

2. 0.5 N $CaCl_2$ – Using a 2-L volumetric flask, dissolve 111 ± .5 g $CaCl_2$ and dilute to 2 L with reagent water. Solution expires 6 months from the date of preparation. Store at room temperature.

3. Ag/AgCl – Reference Electrode filling solution. Store at room temperature. Re-evaluate yearly.

Calibration:

Not applicable to this procedure

Procedure:

NOTE: Electrode Preparation - Remove traces of foreign matter and oily residues, and change filling solution if necessary.

1. Assemble pH meter and connect oxidation-reduction potential electrode. Set the meter to RmV.

2. Place the oxidation-reduction potential electrode into approximately 50 mL of ORP Standard. Make sure the reading falls within the acceptance range before proceeding.

3. Repeat this procedure until two successive readings of sample differ by no more then 10 mV.

4. For the result, take the average of the two successive trials. Record this reading as the LCS/CCV.

5. When analyzing soils, make a 1:1 slurry by adding equal amount of sample and reagent water to a beaker.

   NOTE: It is possible to make a 1:1 slurry by using equal amounts of 0.5 N CaCl2 and sample to a beaker at the client's request.

6. Use a stirring rod and mix the sample gently.

7. Add magnetic stir bar and stir for five minutes.

8. When the reading is stabilized read the millivolt potential of the solution.

9. Repeat this procedure until two successive readings of sample differ by no more then 10 mV. For the result, take the average of the two successive trials.

10. When analyzing waters, use 50 mL sample.

Calculations:

The oxidation-reduction potential is related to the reference electrode used in the measurement. Calculate the oxidation-reduction potential of the sample, in millivolts, referred to the hydrogen scale:

$$E_{(h)} = E_{(obs)} + E_{(ref)}$$

Where:

$E_{(h)}$ = oxidation-reduction potential referred to the hydrogen scale, mV

$E_{(obs)}$ = observed oxidation-reduction potential of the platinum electrode, mV

$E_{(ref)}$ = oxidation-reduction potential of the reference electrode as related to the hydrogen standards, mV (see Table I)

Statistical Information/Method Performance:

See LIMS for MDL/ QC windows.

Quality Assurance/Quality Control:

ORP standard is analyzed at the beginning of each batch as a laboratory control standard (LCS) and is repeated after every 10 samples as a CCV. The ORP standard is also analyzed at the end of each batch. The acceptance range for this solution is the certified value ± 30 mV or the manufactures suggested range, whichever is less.

Two duplicates must be analyzed for each batch of 20 samples.

See LIMS for current quality control acceptance windows. Refer to SOP-WQ-017 if any of the QC samples do not meet required specifications.

No. L-29

Titanium

USEPA Method 6010C / 1-P-QM-WI-9015160

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) may be used to determine trace elements in solution. With the exception of groundwater samples, all aqueous and solid matrices need acid digestion prior to analysis. Groundwater samples that were prefiltered and acidified will not need acid digestion. Samples which are not digested need either an internal standard or should be matrix-matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards. Refer to Chapter Three, "Inorganic Analytes," for a listing of digestion procedures that may be appropriate. The following analytes have been determined by this method:

Element	Symbol	CAS Number	Element	Symbol	CAS Number
Aluminum	Al	7429-90-5	Mercury	Hg	7439-97-6
Antimony	Sb	7440-36-0	Molybdenum	Mo	7439-98-7
Arsenic	As	7440-38-2	Nickel	Ni	7440-02-0
Barium	Ba	7440-39-3	Phosphorus	P	7723-14-0
Beryllium	Be	7440-41-7	Potassium	K	7440-09-7
Boron	B	7440-42-8	Selenium	Se	7782-49-2
Cadmium	Cd	7440-43-9	Silica	SiO_2	7631-86-9
Calcium	Ca	7440-70-2	Silver	Ag	7440-22-4
Chromium	Cr	7440-47-3	Sodium	Na	7440-23-5
Cobalt	Co	7440-48-4	Strotium	Sr	7440-24-6
Copper	Cu	7440-50-8	Thallium	TI	7440-28-0
Iron	Fe	7439-89-6	Tin	Sn	7440-31-5
Lead	Pb	7439-92-1	Titanium	Ti	7440-32-6
Lithium	Li	7439-93-2	Vanadium	V	7440-62-2

Element	Symbol	CAS Number	Element	Symbol	CAS Number
Magnesium	Mg	7439-95-4	Zinc	Zn	7440-66-6
Manganese	Mn	7439-96-5			

CAS Number: Chemical Abstract Service Registry Number.

1.2 Table 1 lists all of the elements for which this method was validated. The sensitivity and the optimum and linear ranges for each element will vary with the wavelength, spectrometer, matrix, and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits (IDLs) for the elements in clean aqueous matrices with insignificant background interferences. Other elements and matrices may be analyzed by this method if appropriate performance at the concentrations of interest (see Sec. 9.0) is demonstrated.

1.3 Analysts should clearly understand the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Prior to employing this method, analysts are advised to consult the each preparative method that may be employed in the overall analysis (e.g., a 3000 series method) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, spectroscopists appropriately experienced and trained in the correction of spectral, chemical, and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis (refer to Sec. 1.1).

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

2.3 Background correction is required for trace element determination. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences identified in Sec. 4.0 should also be recognized and appropriate corrections made; tests for their presence are described in Secs. 9.6 and 9.7. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

4.2 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.2.1 Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

4.2.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must

be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single-element solutions are sufficient. However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range (refer to Chapter Three).

4.2.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions. Instruments that use equations for interelement correction require that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.2.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al, according to Table 2, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. These data are provided for guidance purposes only. The interference effects must be evaluated for each individual instrument, since the intensities will vary.

4.2.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

4.2.6 The interference effects must be evaluated for each individual instrument, whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected

interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

4.2.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

4.2.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.2.9 When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for five consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.2.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

4.2.10.1 One method to verify the absence of interferences is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

4.2.10.2 Another way to verify the absence of interferences is to analyze an interference check solution which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

4.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, by using a tip washer, by using a high solids nebulizer, or by diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers. The test described in Sec. 9.9 will help determine if a physical interference is present.

4.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element. The analyst is encouraged to review the information in all of Sec. 4.0 to deal with the majority of interferences likely to be encountered when using this method.

4.4.1 The method of standard additions (MSA) can be useful when certain interferences are encountered. Refer to Method 7000 for a more detailed discussion of the MSA.

4.4.2 An alternative to using the method of standard additions is to use the internal standard technique, which involves adding one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium are often used. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

4.5 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. Note the length of time necessary for reducing analyte signals to "equal to" or "less than" the lower limit of quantitation. Until the required rinse time is established, the rinse period should be at least 60 sec between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon the project-specific DQOs.

4.6 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative

values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of a measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

4.7 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.8 The calibration blank (Sec. 7.5.1) may restrict the sensitivity of the quantitation limit or degrade the precision and accuracy of the analysis. Consult Chapter Three for recommended precautions and procedures necessary in reducing the magnitude and variability of the calibration blank.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled argon plasma emission spectrometer

6.1.1 Computer-controlled emission spectrometer with background correction.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Optional mass flow controller for argon nebulizer gas supply.

6.1.4 Optional peristaltic pump.

6.1.5 Optional autosampler.

6.1.6 Argon gas supply -- high purity.

6.2 Volumetric flasks of suitable precision and accuracy.

6.3 Volumetric pipets of suitable precision and accuracy.

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the lower limit of quantitation, then the reagent is acceptable.

7.1.1 Hydrochloric acid (conc), HCl.

7.1.2 Hydrochloric acid HCl (1:1) -- Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L in an appropriately- sized beaker.

7.1.3 Nitric acid (conc), HNO_3.

7.1.4 Nitric acid, HNO_3 (1:1) -- Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 L in an appropriately-sized beaker.

7.2 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

7.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99% pure or greater). With several exceptions specifically noted, all salts must be dried for 1 hr at 105 EC.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

NOTE: This section does not apply when analyzing samples prepared by Method 3040.

NOTE: The weight of the analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4% error for some of the compounds.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

7.3.1 Aluminum solution, stock, 1 mL = 1000 µg of Al

Dissolve 1.000 g of aluminum metal, accurately weighed to at least four significant figures, in an acid mixture of 4.0 mL of HCl (1:1) and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to dissolve the metal. When dissolution is complete, transfer solution quantitatively to a 1000-mL volumetric flask, add an additional 10.0 mL of HCl (1:1) and dilute to volume with reagent water.

7.3.2 Antimony solution, stock, 1 mL = 1000 µg of Sb

Dissolve 2.6673 g of $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), accurately weighed to at least four significant figures, in reagent water, add 10 mL of HCl (1:1), and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.3 Arsenic solution, stock, 1 mL = 1000 µg of As

Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), accurately weighed to at least four significant figures, in 100 mL of reagent water containing 0.4 g of NaOH. Acidify the solution with 2 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.4 Barium solution, stock, 1 mL = 1000 µg of Ba

Dissolve 1.5163 g of $BaCl_2$ (element fraction Ba = 0.6595), dried at 250 EC for 2 hr, accurately weighed to at least four significant figures, in 10 mL of reagent water with 1 mL of HCl (1:1). Add 10.0 mL of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.5 Beryllium solution, stock, 1 mL = 1000 µg of Be

Do not dry. Dissolve 19.6463 g of $BeSO_4 4H_2O$ (element fraction Be = 0.0509), accurately weighed to at least four significant figures, in reagent water, add 10.0 mL of concentrated HNO_3, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.6 Boron solution, stock, 1 mL = 1000 µg of B

Do not dry. Dissolve 5.716 g of anhydrous H_3BO_3 (B fraction = 0.1749), accurately weighed to at least four significant figures, in reagent water and dilute in a 1-L

volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass container. The use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

7.3.7 Cadmium solution, stock, 1 mL = 1000 µg of Cd

Dissolve 1.1423 g of CdO (element fraction Cd = 0.8754), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase the rate of dissolution. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.8 Calcium solution, stock, 1 mL = 1000 µg of Ca

Suspend 2.4969 g of $CaCO_3$ (element Ca fraction = 0.4005), dried at 180 EC for 1 hr before weighing, accurately weighed to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.9 Chromium solution, stock, 1 mL = 1000 µg of Cr

Dissolve 1.9231 g of CrO_3 (element fraction Cr = 0.5200), accurately weighed to at least four significant figures, in reagent water. When dissolution is complete, acidify with 10 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.10 Cobalt solution, stock, 1 mL = 1000 µg of Co

Dissolve 1.000 g of cobalt metal, accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.11 Copper solution, stock, 1 mL = 1000 µg of Cu

Dissolve 1.2564 g of CuO (element fraction Cu = 0.7989), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.12 Iron solution, stock, 1 mL = 1000 µg of Fe

Dissolve 1.4298 g of Fe_2O_3 (element fraction Fe = 0.6994), accurately weighed to at least four significant figures, in a warm mixture of 20 mL HCl (1:1) and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.13 Lead solution, stock, 1 mL = 1000 µg of Pb

Dissolve 1.5985 g of $Pb(NO_3)_2$ (element fraction Pb = 0.6256), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.14 Lithium solution, stock, 1 mL = 1000 µg of Li

Dissolve 5.3248 g of lithium carbonate (element fraction Li = 0.1878), accurately weighed to at least four significant figures, in a minimum amount of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.15 Magnesium solution, stock, 1 mL = 1000 µg of Mg

Dissolve 1.6584 g of MgO (element fraction Mg = 0.6030), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of (1:1) concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.16 Manganese solution, stock, 1 mL = 1000 µg of Mn

Dissolve 1.00 g of manganese metal, accurately weighed to at least four significant figures, in acid mixture (10 mL of concentrated HCl and 1 mL of concentrated HNO_3) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.17 Mercury solution, stock, 1 mL = 1000 µg of Hg

WARNING: Do not dry, **mercury is a highly toxic element**.

Dissolve 1.354 g of $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL of concentrated HNO_3 and dilute to volume in 1000-mL volumetric flask with reagent water.

7.3.18 Molybdenum solution, stock, 1 mL = 1000 µg of Mo

Dissolve 1.7325 g of $(NH_4)_6Mo_7O_{24}·4H_2O$ (element fraction Mo = 0.5772), accurately weighed to at least four significant figures, in reagent water and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.19 Nickel solution, stock, 1 mL = 1000 µg of Ni

Dissolve 1.000 g of nickel metal, accurately weighed to at least four significant figures, in 10.0 mL of hot concentrated HNO_3, cool, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.20 Phosphate solution, stock, 1 mL = 1000 µg of P

Dissolve 4.3937 g of anhydrous KH_2PO_4 (element fraction P = 0.2276), accurately weighed to at least four significant figures, in water. Dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.21 Potassium solution, stock, 1 mL = 1000 µg of K

Dissolve 1.9069 g of KCl (element fraction K = 0.5244) dried at 110 EC, accurately weighed to at least four significant figures, in reagent water, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.22 Selenium solution, stock, 1 mL = 1000 µg of Se

Do not dry. Dissolve 1.6332 g of H_2SeO_3 (element fraction Se = 0.6123), accurately weighed to at least four significant figures, in reagent water and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2

Do not dry. Dissolve 2.964 g of NH_4SiF_6, accurately weighed to at least four significant figures, in 200 mL (1:20) HCl with heating at 85 EC to dissolve the solid. Let solution cool and dilute to volume in a 1000-mL volumetric flask with reagent water. Store in a PTFE container and protect from light.

7.3.24 Silver solution, stock, 1 mL = 1000 µg of Ag

Dissolve 1.5748 g of $AgNO_3$ (element fraction Ag = 0.6350), accurately weighed to at least four significant figures, in water and 10 mL of concentrated HNO_3. Dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.25 Sodium solution, stock, 1 mL = 1000 µg of Na

Dissolve 2.5419 g of NaCl (element fraction Na = 0.3934), accurately weighed to at least four significant figures, in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.26 Strontium solution, stock, 1 mL = 1000 µg of Sr

Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), accurately weighed to at least four significant figures, in a 1000-mL flask containing 10 mL of concentrated HCl and 700 mL of reagent water. Dilute to volume with reagent water.

7.3.27 Thallium solution, stock, 1 mL = 1000 µg of Tl

Dissolve 1.3034 g of $TlNO_3$ (element fraction Tl = 0.7672), accurately weighed to at least four significant figures, in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.28 Tin solution, stock, 1 mL = 1000 µg of Sn

Dissolve 1.000 g of Sn shot, accurately weighed to at least 4 significant figures, in 200 mL of HCl (1:1) with heating to dissolve the metal. Let solution cool and dilute with HCl (1:1) in a 1000-mL volumetric flask.

7.3.29 Vanadium solution, stock, 1 mL = 1000 µg of V

Dissolve 2.2957 g of NH_4VO_3 (element fraction V = 0.4356), accurately weighed to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to dissolve the metal. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.30 Zinc solution, stock, 1 mL = 1000 µg of Zn

Dissolve 1.2447 g of ZnO (element fraction Zn = 0.8034), accurately weighed to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.31 Yttrium solution, stock, 1 mL = 1000 µg of Y

Dissolve 4.3081 g of $Y(NO_3)_3$0$6H_2$0 (element fraction Y = 0.2321), accurately weighed to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.4 Mixed calibration standard solutions

Prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions above in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix-matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Freshly-mixed standards should be prepared, as needed, with the realization that concentration can change with age. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.) Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination initially results in a precipitate, then add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver is stable under these conditions in a water matrix for 30 days, if protected from the light. Higher concentrations of silver require additional HCl.

7.5 Blanks

Two types of blanks are required for the analysis of samples prepared by any method other than Method 3040. The calibration blank is used in establishing the analytical curve and the method blank is used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration.

7.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations.

7.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.5).

7.6 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a

standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.3.3 for use). This standard may also be purchased.

7.7 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.3.4 for use).

7.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to the 3000 series method to be used (e.g., Method 3005, 3010, 3015, 3031, 3040, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.0.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

9.6 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

9.7 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and, if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 -120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.8 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.9 should be conducted.

9.8.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$RPD = \frac{*D_1 - D_2*}{\left(\frac{*D_1 + D_2*}{2}\right)} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.8.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.9 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.9.1 and 9.9.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum, these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.9.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.9.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.9.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

CAUTION: If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

9.10 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with proper operating parameters established as detailed below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

10.1.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the location of the background points being used for correction; the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

10.1.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

10.1.3 The lower limits of quantitation should be established for all wavelengths utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.1.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.1.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

10.1.4 Specific recommended wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions are not provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

For radial viewed plasma, operating conditions for aqueous solutions usually vary from:

- 1100 to 1200 watts forward power,
- 14 to 18 mm viewing height,
- 15 to 19 L/min argon coolant flow,
- 0.6 to 1.5 L/min argon nebulizer flow,
- 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

For an axial viewed plasma, the conditions will usually vary from:

- 1100 to 1500 watts forward power,
- 15 to 19 L/min argon coolant flow,
- 0.6 to 1.5 L/min argon nebulizer flow,
- 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

One recommended way to achieve repeatable interference correction factors is to adjust the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively. This can be performed before daily calibration and after the instrument warm-up period.

10.1.5 Plasma optimization

The plasma operating conditions need to be optimized prior to use of the instrument. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine is not required on a daily basis, it is only required when first setting up a new instrument, or following a change in operating conditions. The following procedure is recommended, or follow the manufacturer's recommendations.

10.1.5.1 Ignite the radial plasma and select an appropriate incident radio frequency (RF) power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

10.1.5.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of a calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

10.1.5.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure is written for vertical optimization in the radial mode, but it also can be used for horizontal optimization.

Aspirate a solution containing 10 µg/L of several selected elements. As, Se, Tl, and Pb are the least sensitive of the elements and most in need of optimization. However, other elements may be used, based on the judgement of the analyst or project-specific protocols. (V, Cr, Cu, Li and Mn also have been used with success.) Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the

best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

10.1.5.4 The instrument operating conditions finally selected as being optimum should provide the most appropriate instrument responses that correlate to the desired target analyte sensitivity while meeting the minimum quality control criteria noted in this method or as specified in the project-specific planning documents.

10.1.5.5 If the instrument operating conditions, such as incident power or nebulizer gas flow rate, are changed, or if a new torch injector tube with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

10.1.5.6 After completing the initial optimization of operating conditions, and before analyzing samples, the laboratory should establish and initially verify an interelement spectral interference correction routine to be used during sample analysis with interference check standards that closely match the anticipated properties of the expected sample matrices, i.e., for saltwater type matrices the interference check standard should contain components that match the salinities of the proposed sample matrix. A general description of spectral interferences and the analytical requirements for background correction, in particular, are discussed in Sec. 4.2.

10.1.5.7 Before daily calibration, and after the instrument warmup period, the nebulizer gas flow rate should be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas flow rate should be the same (< 2% change) from day to day.

10.2 For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power, to obtain stable operation and precise measurements.

10.3 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.4), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument calibration by analyzing appropriate QC samples as follows.

10.3.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be

prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

10.3.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

10.3.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses should not proceed or the previous ten samples should be reanalyzed.

10.3.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.4. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.3.3.

Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated sample concentration range. For all multi-point calibration scenarios, the lowest non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4 for recommendations on how to determine the linear dynamic range. The guidance in this section and Sec. 10.3.3 provide options for defining the lower limit of quantitation.

10.3.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multi-point calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired

target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

10.3.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined by the lowest standard in the calibration curve.

10.3.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ± 30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

10.3.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data.

The low-level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples, may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

10.4 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach.

The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ± 30% of its true value should be achieved for the lowest concentration standard.

10.5 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metal determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must either use an internal standard or be matrix-matched with the standards. Solubilization and digestion procedures are presented in Chapter Three, "Inorganic Analytes."

11.2 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Sec. 7.4. Flush the system with the calibration blank (Sec. 7.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should be prepared as detailed in Sec. 10.3.2.

11.3 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.3.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.3.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.3.4) be analyzed after every ten samples and at the end of the analysis batch.

11.4 Rinse the system with the calibration blank solution (Sec. 7.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration. Analyze the samples and record the results.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All results should be reported with up to three significant figures.

12.2 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Sec. 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In an EPA round-robin study, seven laboratories applied the ICP technique to acid-digested water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations. These data are provided for guidance purposes only.

13.3 Performance data for aqueous solutions and solid samples from a multilaboratory study are provided in Tables 5 and 6. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste*

Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. NW, Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. C. L. Jones, *et al*., "An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050," EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, NV, 1987.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678 x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227 x2	17
Molybdenum	202.030	5.3
Nickel	231.604 x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980 x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856 x2	1.2

TABLE 1
(continued)

[a] The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity. Other wavelengths may be substituted (e.g., in the case of an interference) if they provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b] The estimated instrumental detection limits shown are provided for illustrative purposes only. Each laboratory must determine IDLs and MDLs, as necessary, for their specific application of the method. These IDLs represent radial plasma data and axial plasma IDLs may be lower.

[c] Highly dependent on operating conditions and plasma position.

TABLE 2

POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelenth (nm)	Interferant[a,b]									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al at 1000 mg/L	Cu at 200 mg/L	Mn at 200 mg/L
Ca at 1000 mg/L	Fe at 1000 mg/L	Ti at 200 mg/L
Cr at 200 mg/L	Mg at 1000 mg/L	V at 200 mg/L

[b] The data shown above as analyte concentration equivalents are not the actual observed concentrations. To obtain those data, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3

MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As and Mo
IV	Al, Ca, Cr, K, Na, Ni, Li, and Sr
V	Ag[a], Mg, Sb, and Tl
VI	P

[a] See the note in Sec. 7.4.

TABLE 4

EXAMPLE ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (µg/L)	Mean Conc. (µg/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (µg/L)	Mean Conc. (µg/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (µg/L)	Mean Conc. (µg/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

These data are provided for guidance purposes only.

[a] Not all elements were analyzed by all laboratories.

[b] RSD = relative standard deviation.

[c] Results for Se are from two laboratories.

[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

EXAMPLE ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS

Element	Mean Conc. (mg/L)	n	RSD (%)	Accuracy (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

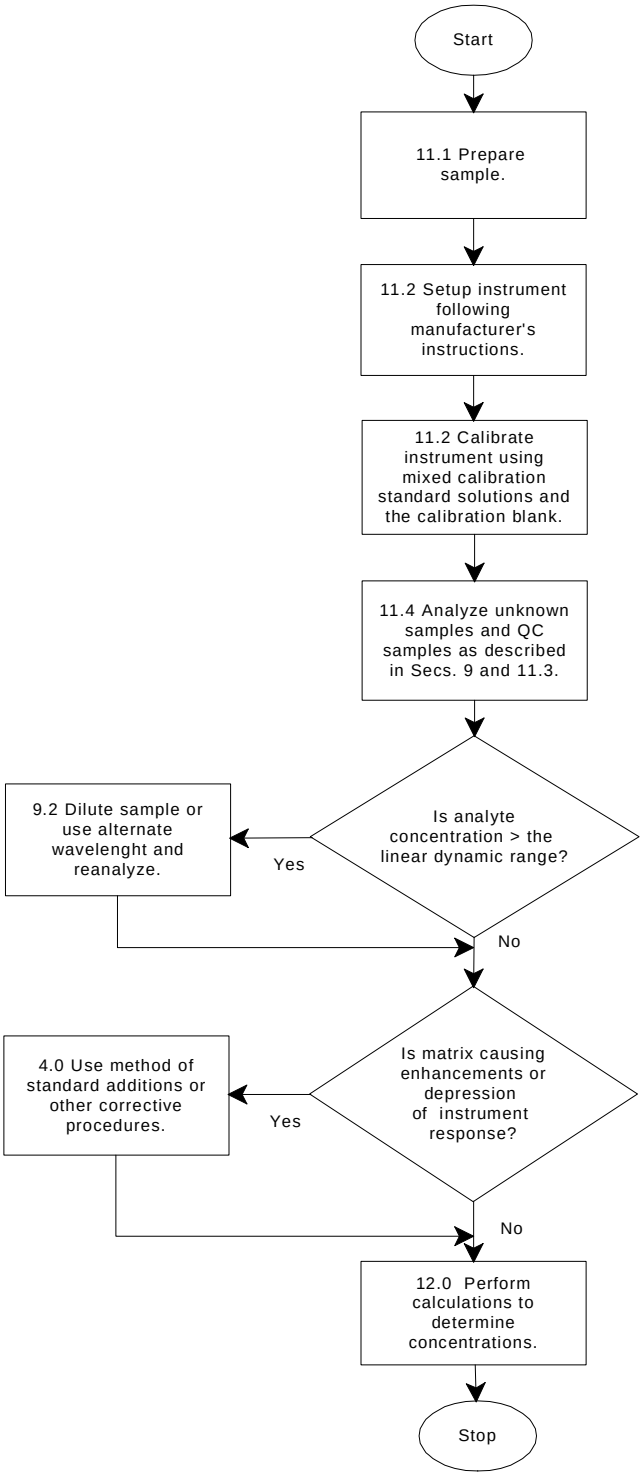
These performance values are independent of sample preparation because the labs analyzed portions of the same solutions and are provided for illustrative purposes only.
n= Number of measurements.
Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.
These data are provided for guidance purposes only.

TABLE 6

EXAMPLE ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS

	Spiked Coal Fly Ash (NIST-SRM 1633a)				Spiked Electroplating Sludge			
Element	Mean Conc. (mg/L)	n	RSD (%)	Bias (% AA)	Mean Conc. (mg/L)	n	RSD (%)	Bias (% AA)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

These performance values are independent of sample preparation because the labs analyzed portions of the same digests and are provided for illustrative purposes only.
n = Number of measurements.
Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.
These data are provided for guidance purposes only.


Start
11.1 Prepare sample.
11.2 Setup instrument following manufacturer's instructions.
11.2 Calibrate instrument using mixed calibration standard solutions and the calibration blank.
11.4 Analyze unknown samples and QC samples as described in Secs. 9 and 11.3.
Is analyte concentration > the linear dynamic range?
Yes
9.2 Dilute sample or use alternate wavelenght and reanalyze.
No
Is matrix causing enhancements or depression of instrument response?
Yes
4.0 Use method of standard additions or other corrective procedures.
No
12.0 Perform calculations to determine concentrations.
Stop

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Revision Log:

Revision: 21		**Effective Date:** This version
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Cross Reference	Reflect current procedure	Added reference Analysis #6142, 6123, 6125, 10801…
Scope	Clarification	Reworded section.
Sample Collection, Preservation and Handling	Reflect current procedure	Changed sample storage temperature to 0° to 6°C, but not frozen.
Reagents and Standards	Reflect current procedure	Added reference to 1-P-QM-FOR-9009182.
Procedure	Reflect current procedure	Add boiling stones to the batch blank and LCS for the fish samples.
Block Digestor Instructions	Reflect current procedure No longer used	Hold and press the star key. Deleted test pertaining to the control panel grey buttons.
Quality Assurance/Quality Control	Reflect current procedure	Added reference to ICP/MS Analysis #6142, 6123, 6125, 10801, …. for batch requirements.

Revision: 20		**Effective Date:** Jan 22, 2013
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Throughout Document	Reflect re-identification of documents in EtQ	Replaced all prior Level 1, 2, 3, and 4 document numbers (analyses excluded) with EDR numbers
Safety Precautions and Waste Handling	Reflect current procedure	Added the use of designated dispensing equipment for HNO3 and HCL Added test pertaining to hazardous flags
Procedure	Reflects current procedure	Removed paint chip section. Deleted text pertaining to reducing the weight of paint chips. Paint chips will be digested as normal digestion per this procedure.
Procedure 2	Reflects current procedure	Added text pertaining to adding PTFE boiling stones to the LCS. Added text pertaining to entering the weights of the Blank and LCS in the LLENS.

Reference:

1. Test Methods for Evaluating Solid Wastes, SW-846 Method 3050B, December 1996.

2. *Chemical Hygiene Plan*, current version.

Cross Reference:

Document	Document Title
Analysis #6142, 6123, 6125, 10801, 6126, 6127, 6129, 6128, 6132, 6131, 6133, 6134, 6140, 6136, 6137, 6138, 6143, 6139, 6135, 6124, 6141, 6146, 6144, 6147, 6145, …	Metals by Inductively Coupled Plasma Mass Spectrometry for SW-846 Methods 6020/6020A (aqueous, solid, tissue), CLP 5.2 (aqueous, solid, tissue) and EPA 200.8 (aqueous)
Analysis #6966, 1643, 6935, 7914, 6946, 6947, 1650, 6949, 6952, 6951, 6953, 1654, 1662, 1656, 1657, 6958, 6960, 1667, 6961,10145, 6955, 6944, 6936, 6969, 7968, …	Metals by Inductively Coupled Plasma Atomic Emissions Spectroscopy for SW-846 Methods 6010A/B/C (aqueous, solid, tissue), CLP 2.1(water/solid/tissue), CLP 4.0(water/solid/tissue), CLP 5.2 (water/solid/tissue) and EPA 200.7(aqueous)
1-P-QM-FOR-9009182	Working Instructions for Prep Solutions and Standards

Purpose:

This digestion procedure is for the preparation of solid samples for analysis by ICP and ICP/MS following SW-846 protocol.

Scope:

This method is used for preparation of metals in solid samples for analysis by ICP and ICP/MS.

Basic Principles:

A representative sample is digested with repeated additions of nitric acid (HNO3) and hydrogen peroxide (H2O2). Hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. The resultant digestate is diluted and analyzed.

This method is not a total digestion technique for most samples; it is a very strong acid digestion that dissolves almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure.

Definitions:

1. ACS – American Chemical Society
2. D – Sample Duplicate
3. DOC – Demonstration of Capability
4. IDOC – Initial Demonstration of Capability
5. LCS/LCSD – Laboratory Control Sample/ Laboratory Control Sample Duplicate
6. LCSW– Laboratory Control Sample Water
7. LLENS - the computer program that integrates a PC with an analytical balance to collect data directly from the balance. The program organizes the data and transmits the readings to the LIMS.
8. LIMS – Laboratory Information Management Systems
9. LLI Sample ID – unique 7-digit number assigned to a client sample.
10. LOQ – Limit of Quantitation
11. MDL – Method Detection Limit
12. MS (R) – Matrix Spike
13. MSD (M) – Matrix spike duplicate

14. PB/PBW–Preparation Blank/ Preparation Blank Water

15. QC – Quality Control

16. Method Blank - equivalent to a Preparation Blank. A designated sample designed to monitor for sample contamination during the analysis process. A volume of reagent laboratory water is typically used to monitor water sample analysis, while solids blanks consist of a purified solid matrix or just the reagents used in the test. The blank demonstrates that no artifacts were introduced during the analysis process.

17. SOP- Standard Operating Procedure

18. U or US – unspiked background sample

Interferences:

When analyzing sample by ICP-MS using this digestion procedure we follow the instrument manufacturer's guidelines to eliminate polyatomic interferences typically caused by Chlorine. The process we follow involves the use of a collision/reaction cell on the ICP-MS. Below is a description of how the collision/reaction cell works.

Reaction Process - The primary method of interference removal is through a reaction event. When using a reaction gas, either the target interference is more reactive than the target analyte, leading to preferential removal of the interferent or (less commonly) the target analyte is more reactive and is converted to a new species at a different mass which is free from any existing or newly-formed overlap

Collision Process - The primary method of interference removal is through a non-reactive event. This process of interference removal is kinetic energy discrimination (KED). Energy Discrimination is most commonly used with an inert gas, which means the interference removal process is not affected by reactions in the cell.

Safety Precautions and Waste Handling:

All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state and local laws and regulations.

See *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

Preparing samples for inorganic analysis involves working with concentrated acids and other chemicals which are dangerous if not handled carefully:

Nitric acid (HNO3) – This acid can cause skin burns. Add nitric acid to samples in a hood or use the designated dispensing equipment to avoid exposure to toxic fumes.

Hydrochloric acid (HCl) – This acid can cause skin burns. Never mix HCI with concentrated H2SO4 to avoid a violent reaction. Always use in a fume hood or use the designated dispensing equipment.

Hydrogen peroxide (H2O2) - This is a strong oxidizing agent and causes severe burns. Avoid contact with skin.

When diluting strong acids, never add water to acid; always add acid to water.

Store concentrated acids in the prep room acid lockers. Only acids are to be stored in these lockers. (Store solvents in the flammable liquid storage cabinet.) Some concentrated acids are kept in the acid reagent bottles on prep room counters. Fill reagent bottles in an operating fume hood using caution to avoid spills.

Perform acid digestions in hoods that are turned on and have active alarms. Notify a supervisor immediately if the hood is malfunctioning or the alarm sounds.

Samples that contain dust may be hazardous. Open in a fume hood.

When a hazardous flag is added indicating possible cyanide, special precautions are required to avoid exposure to hydrogen cyanide gas. Contact your supervisor prior to adding acid. Always open these samples and add the acid in a hood.

Use spill pillows to absorb large acid spills (small spills are cleaned with wet paper towels.) Use SPILL-X-A powder or equivalent to neutralize any remaining acid and then rinse the area thoroughly with water. Spill pillows and SPILL-X-A are stored on the prep room shelf.

Dispose of acid waste properly. Collect all acid digestions, waste solutions, and expired reagent solutions in waste containers. When the acid waste containers are full, a designated acid waste handler transfers the waste to the acid neutralization tank.

Personnel Training and Qualifications:

All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and a documented Demonstration of Capability (DOC).

Initially, each employee performing this digestion procedure must work with an experienced employee for a period of time until they can independently set up batches and perform the necessary steps outlined in this procedure. Proficiency is measured through documentation of the critical steps in this procedure, over checking of data as well as an IDOC.

The IDOC and the DOC consists of four laboratory control samples that are carried through all steps of the analysis and meet the defined acceptance criteria. The criteria include the calculation of mean accuracy and standard deviation.

Sample Collection, Preservation, and Handling:

Solid samples require no chemical preservation.

Samples must be submitted in glass or plastic containers and stored at 0° to 6°C, but not frozen, prior to digestion. Samples must be digested within 6 months (180 days) of sample collection.

Digested samples are stored in polypropylene bottles at room temperature.

Apparatus and Equipment:

1. Polypropylene containers and covers (digestion vessels) - certified clean and Class A equivalent

2. Whatman No. 41 filter paper or equivalent

3. Funnels

4. Environmental Express HotBlock (block digestor) - adjustable and capable of maintaining a temperature of 90 to 95°C

5. Balance capable of reading 0.01 g

6. Chemware Ultra-Pure PTFE boiling stones, or equivalent.

7. Computer and software LLENS (Lancaster Laboratories Electronic Notebook System)

Reagents and Standards:

For reagent preparation, shelf life, and storage conditions, see Form 1-P-QM-FOR-9009182.

1. Nitric acid (HNO_3) _ Fisher, Trace Metal Grade, or equivalent. Store at room temperature. Re-evaluate annually.

2. Nitric acid (1:1) – Add 500 mL of HNO_3 to 500 mL of reagent water. Store in polypropylene at room temperature. Expires 6 months from date of preparation. (Different volumes are acceptable but ratios must stay the same.)

3. Hydrogen peroxide, 30% (H_2O_2) – Fisher, Certified ACS or equivalent. Store at room temperature. Re-evaluate annually.

4. Hydrochloric acid (HCl) – Baker Instra-Analyzed, or equivalent. Store at room temperature. Re-evaluate annually.

   NOTE: It is acceptable to prepare using multiples of indicated weights and volumes if ratios are maintained.

Calibration:

Not applicable.

Procedure:

1. Turn block digestor on and allow block to reach the Control Point setting that provides 90° to 95°C sample temperature. (The block temperature setting is not necessarily the sample temperature.) See below for **Block Digestor Instructions** section.

2. Weigh 1.00 to 1.05 g (to the nearest 0.01 g) of a well mixed sample into a polypropylene digestion vessel. (If the sample is watery use 5.00 to 5.05 grams for analysis. Additional information on non-standard matrices is found at the end of the procedure section.) Add 1.00 to 1.49 g of Chemware Ultra-Pure PTFE boiling stones to the digestion vessel for the blank and LCS. Enter the blank and LCS weight as 1.0000 to 100.0000 final volume in the LLENS. For sample batch spiking procedures see 1-P-QM-FOR-9009182. All spiking must be performed prior to starting the digestion procedure.

3. Add 10 mL of (1:1) HNO_3, swirl to mix, and cover with a polypropylene cover.

4. Place sample vessel in block digestor. Heat (reflux) the sample at 90° to 95°C for 10 to 15 minutes without boiling.

5. Remove vessel from digestion block and allow sample to cool.

6. Add 5 mL of concentrated HNO_3. Replace cover, return vessel to digestion block and heat for 30 minutes.

   NOTE: If brown fumes are generated (indicating oxidation of the sample by HNO_3) continue the process of adding 5 mL HNO3 and heating until no brown fumes are given off by the sample. This indicates that the reaction with HNO_3 is complete. Add the same amount of HNO_3 to the entire digestion batch.

7. With cover on, heat at 90° to 95°C without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times (add reagent water if necessary).

8. Remove vessel from digestion block and allow sample to cool.

9. Add 2 mL of reagent water and 3 mL of 30% H_2O_2. With cover on, return vessel to digestion block and heat until effervescence subsides. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

10. Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

    NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

11. With cover on, continue heating the acid-peroxide digestate at 90° to 95°C without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times (add reagent water if necessary).

12. Remove sample vessel from digestion block and allow to cool.

13. Add 10 mL of HCl. With the cover on, return vessel to digestion block and heat at 90° to 95°C for 15 minutes.

14. Remove sample vessel from digestion block.

15. If floating particulate is evident after digestion, the sample must be filtered.

    a. Filter through Whatman No. 41 filter paper into a polypropylene container.

    b. Wash sample vessel, residue, and paper thoroughly with reagent water.

    c. If any samples are filtered, the prep blank and LCS must also be filtered.

16. Adjust volume to the 100mL mark on the digestion vessel with reagent water and mix. Seal vessel with a screw cap. The sample is now ready for analysis.

NOTE: When special limits of quantitation are required by the client, use more sample weight.

For wipe samples:

When wipes are digested by this method, one blank media each must be used for the batch preparation blank, the laboratory control sample (LCS), and the laboratory control sample duplicate (LCSD). Refer to Form 1-P-QM-FOR-9009182 for the spiking of the LCS and LCSD. Digest wipes in their own batch. Use reagent water to rinse any particulate matter from the wipe container into the vessel containing the wipe before digesting. If brown fumes are evolved during wipe sample digestion, perform only two 5 mL HNO_3 additions with 30-minute refluxing each; add the same amount of HNO_3 to the entire batch. Proceed with digestion.

For fish tissue samples:

When fish tissues are digested by this method, refer to Form 1-P-QM-FOR-9009182 for the spiking of the LCS, LCSD (if needed), R (matrix spike), and M (matrix spike duplicate). Add 1.00 to 1.49 g of Chemware Ultra-Pure PTFE boiling stones to the digestion vessel for the blank and LCS. Digest fish tissues in their own batch.

Block Digestor Instructions:

1. Turn block digestor on by pressing rocker switch located on the cord.

2. Wait about 8 seconds until controller display indicates current block temperature.

3. PRESS and hold STAR (*) key.

4. The display shows Control Point temperature.

5. The digits can be changed to the desired value by pressing the up and down arrow keys while holding the (*) key.

6. Confirm Control Point temperature is set to the block temperature that provides 90° to 95°C.

   NOTE: See HotBlock Control Point Temperature Logbook to obtain control point temperature setting for the HotBlock being used. If necessary, adjust Control Point temperature to the proper setting as instructed below.

   NOTE: Polypropylene containers must not be heated above 130°C.

Calculations:

Not applicable

Statistical Information/Method Performance:

Not applicable to this procedure. See analysis method.

Quality Assurance/Quality Control:

For sample batch spiking instructions see form 1-P-QM-FOR-9009182. Refer to ICP section when prepping ICP analysis. Refer to ICP/MS section when prepping ICP/MS analysis. Prepare a method blank, sample duplicate, sample matrix spike, sample matrix spike duplicate, and laboratory control sample with every digestion batch (20 samples or less). Each piece of batch QC is digested following the procedure in this SOP. If any samples are filtered the prep blank and LCS must also be filtered.

Refer to ICP Analysis #6966, 1643, 6935, … for sample batch quality control requirements, acceptance criteria and corrective action.

Refer to ICP/MS Analysis #6142, 6123, 6125, 10801, 6126, … for sample batch quality control requirements, acceptance criteria and corrective action.

No. L-30

Semivolatile Organics and

Semivolatile Organics SIM

SW-846 Method 3640a

METHOD 3640A

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (1). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated (2). A cross-linked divinylbenzene-styrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

1.2 General cleanup application - GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (2). GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes.

1.3 Specific application - This method includes guidance for cleanup of sample extracts containing the following analytes from the RCRA Appendix VIII and Appendix IX lists:

Compound Name	CAS No.[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
Aldrin	309-00-2
4-Aminobiphenyl	92-67-1
Aniline	62-53-3
Anthracene	120-12-7
Benomyl	17804-35-2
Benzenethiol	108-98-5
Benzidine	92-87-5
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(a)pyrene	50-32-8
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Benzoic acid	65-85-0
Benzotrichloride	98-07-7
Benzyl alcohol	100-51-6
Benzyl chloride	100-44-7
alpha-BHC	319-84-6
beta-BHC	319-85-7

Compound Name	CAS No.[a]
gamma-BHC	58-89-9
delta-BHC	319-86-8
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	88-85-7
Carbazole	86-74-8
Carbendazim	10605-21-7
alpha-Chlordane	5103-71-9
gamma-Chlordane	5566-34-7
4-Chloro-3-methylphenol	59-50-7
4-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
3-Chlorophenol	108-43-0
4-Chlorophenyl phenyl ether	7005-72-3
3-Chloropropionitrile	542-76-7
Chrysene	218-01-9
2-Cresol	95-48-7
3-Cresol	108-39-4
4-Cresol	106-44-5
Cyclophosphamide	50-18-0
DDD	72-54-8
DDE	72-55-9
DDT	50-29-3
Di-n-butyl phthalate	84-74-2
Diallate	2303-16-4
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,i)pyrene	189-55-9
Dibenz(a,j)acridine	224-42-0
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzothiophene	132-65-0
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
trans-1,4-Dichloro-2-butene	110-57-6
cis-1,4-Dichloro-2-butene	1476-11-5
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	106-46-7
1,4-Dichlorobenzene	541-73-1
3,3'-Dichlorobenzidine	91-94-1
2,6-Dichlorophenol	87-65-0
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7
2,4-Dichlorophenol	120-83-2

Compound Name	CAS No.[a]
2,4-Dichlorotoluene	95-73-8
1,3-Dichloro-2-propanol	96-23-1
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Dimethoate	60-51-5
Dimethyl phthalate	131-11-3
p-Dimethylaminoazobenzene	60-11-7
7,12-Dimethyl-benz(a)anthracene	57-97-6
2,4-Dimethylphenol	105-67-9
3,3-Dimethylbenzidine	119-93-7
4,6-Dinitro-o-cresol	534-52-1
1,3-Dinitrobenzene	99-65-0
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Diphenylamine	122-39-4
Diphenyl ether	101-84-8
1,2-Diphenylhydrazine	122-66-7
Disulfoton	298-04-4
Endosulfan sulfate	1031-07-8
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Ethyl methane sulfonate	62-50-0
Ethyl methacrylate	97-63-2
Bis(2-ethylhexyl) phthalate	117-81-7
Famphur	52-85-7
Fluorene	86-73-7
Fluoranthene	206-44-0
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
cis-Isosafrole	17627-76-8
trans-Isosafrole	4043-71-4
Kepone	143-50-0
Malononitrile	109-77-3
Merphos	150-50-5
Methoxychlor	72-43-5
3-Methylcholanthrene	56-49-5

Compound Name	CAS No.[a]
2-Methylnaphthalene	91-57-6
Methyl parathion	298-00-0
4,4'-Methylene-bis(2-chloroaniline)	101-14-4
Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
2-Naphthylamine	91-59-8
1-Naphthylamine	134-32-7
5-Nitro-o-toluidine	99-55-8
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	79-46-9
4-Nitrophenol	100-02-7
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethanolamine	1116-54-7
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrolidine	930-55-2
Di-n-octyl phthalate	117-84-0
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene (PCNB)	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
1,2-Phenylenediamine	95-54-5
Phorate	298-02-2
2-Picoline	109-06-8
Pronamide	23950-58-5
Pyrene	129-00-0
Resorcinol	108-46-3
Safrole	94-59-7
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,5,6-Tetrachloronitrobenzene	117-18-0
2,3,5,6-Tetrachlorophenol	935-95-5
2,3,4,6-Tetrachlorophenol	58-90-2
Tetraethyl dithiopyrophosphate (Sulfotep)	3689-24-5
Thiosemicarbazide	79-19-6
2-Toluidine	106-49-0
4-Toluidine	95-53-4

Compound Name	CAS No.[a]
Thiourea, 1-(o-chlorophenyl)	5344-82-1
Toluene-2,4-diamine	95-80-7
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
2,4,6-Trichlorophenol	88-06-2
2,4,5-Trichlorophenol	95-95-4
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)	93-72-1
Warfarin	81-81-2

[a] Chemical Abstract Services Registry Number.

Table 1 presents average percent recovery and percent RSD data for these analytes, as well as the retention volumes of each analyte on a single GPC system. Retention volumes vary from column to column. Figure 1 provides additional information on retention volumes for certain classes of compounds. The data for the semivolatiles were determined by GC/MS, whereas, the pesticide data were determined by GC/ECD or GC/FPD. Compounds not amenable to GC were determined by HPLC. Other analytes may also be appropriate for this cleanup technique, however, recovery through the GPC should be >70%.

1.4 Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol is especially susceptible to this problem. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent, and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample extract to be cleaned up. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the estimated quantitation limits (EQLs) of the analytes of interest before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS

4.1 Gel-permeation chromatography system - GPC Autoprep Model 1002 A or B, or equivalent, Analytical Biochemical Laboratories, Inc. Systems that perform very satisfactorily have also been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Sec. 7.2.2.

4.1.1 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. (Optional) To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, attach a double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

4.1.2 Guard column - (Optional) 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

4.1.3 Bio Beads (S-X3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. The UV chromatogram of the Calibration solution should be very similar to that in Figure 2, and the backpressure should be within 6-10 psi. Also, the gel swell ratio in methylene chloride should be in the range of 4.4 - 4.8 mL/g. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

4.1.4 Ultraviolet detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

4.1.5 Strip chart recorder, recording integrator or laboratory data system.

4.1.6 Syringe - 10 mL with Luerlok fitting.

4.1.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

4.2 Analytical balance - 0.0001 g.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL

4.4 Graduated cylinders

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.1.1 Some brands of methylene chloride may contain unacceptably high levels of acid (HCl). Check the pH by shaking equal portions of methylene chloride and water, then check the pH of the water layer.

5.1.1.1 If the pH of the water layer is $\leq$ 5, filter the entire supply of solvent through a 2 in. x 15 in. glass column containing activated basic alumina. This column should be sufficient for processing approximately 20-30 liters of solvent. Alternatively, find a different supply of methylene chloride.

5.2 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.3 n-Butyl chloride, $CH_3CH_2CH_2CH_2Cl$. Pesticide quality or equivalent.

5.4 GPC Calibration Solution. Prepare a calibration solution in methylene chloride containing the following analytes (in elution order):

Compound	mg/L
corn oil	25,000
bis(2-ethylhexyl) phthalate	1,000
methoxychlor	200
perylene	20
sulfur	80

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon lined screw-cap at 4°C, and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every 6 months, or more frequently if necessary.

5.5 Corn Oil Spike for Gravimetric Screen. Prepare a solution of corn oil in methylene chloride (5 g/100 mL).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F.

7.2 GPC Setup and Calibration

7.2.1 Column Preparation

7.2.1.1 Weigh out 70 g of Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon lined cap or a 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to sufficiently cover the beads at all times. If a guard column is to be used, repeat the above with 5 g of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

7.2.1.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

7.2.1.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock if one is attached. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

7.2.1.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached) and allow the excess solvent to drain. Raise the tube to stop the flow and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

7.2.1.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight

enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

7.2.1.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat Sec. 7.2.1.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is successfully inserted.

7.2.1.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

7.2.1.8 Pack the optional 5 cm column with approximately 5 g of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

7.2.1.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

7.2.1.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as in Sec. 7.2.1.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

7.2.1.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant

and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

7.2.2 Calibration of the GPC Column

7.2.2.1 Using a 10 mL syringe, load sample loop #1 with calibration solution (Sec. 5.6). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

7.2.2.2 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace similar to Figure 2 that meets the following requirements. Differences between manufacturers' cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell, and therefore the analytical cell is not acceptable for use.

7.2.2.3 Following are criteria for evaluating the UV chromatogram for column condition.

7.2.2.3.1 Peaks must be observed, and should be symmetrical, for all compounds in the calibration solution.

7.2.2.3.2 Corn oil and phthalate peaks must exhibit >85% resolution.

7.2.2.3.3 Phthalate and methoxychlor peaks must exhibit >85% resolution.

7.2.2.3.4 Methoxychlor and perylene peaks must exhibit >85% resolution.

7.2.2.3.5 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

7.2.2.3.6 Nitroaromatic compounds are particularly prone to adsorption. For example, 4-nitrophenol recoveries may be low due to a portion of the analyte being discarded after the end of the collection time. Columns should be tested with the semivolatiles matrix spiking solution. GPC elution should continue until after perylene has eluted, or long enough to recover at least 85% of the analytes, whichever time is longer.

7.2.2.4 Calibration for Semivolatiles - Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of

bis(2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences. See Figure 2 for general guidance on retention time. Figure 1 illustrates retention volumes for different classes of compounds.

7.2.2.5 Calibration for Organochlorine Pesticides/PCBs - Determine the elution times for the phthalate, methoxychlor, perylene, and sulfur. Choose a dump time which removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection after the elution of perylene, but before sulfur elutes.

7.2.2.6 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the column pressure (should be 6-10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times, and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in Sec. 7.2.2.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

7.2.2.7 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

7.2.2.7.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

7.2.2.7.2 The retention times for bis(2-ethylhexyl) phthalate and perylene must not vary more than $\pm$5% between calibrations. If the retention time shift is >5%, take corrective action. Excessive retention time shifts are caused by:

7.2.2.7.2.1 Poor laboratory temperature control or system leaks.

7.2.2.7.2.2 An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.

7.2.2.7.2.3 Excessive laboratory temperatures, causing outgassing of the methylene chloride.

7.2.2.8 Analyze a GPC blank by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (KD) evaporator. Analyze the concentrate by whatever detectors will be used for the analysis of future samples. Exchange the solvent, if necessary. If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping, if necessary.

7.3 Extract Preparation

7.3.1 Adjust the extract volume to 10.0 mL. The solvent extract must be primarily methylene chloride. All other solvents, e.g. 1:1 methylene chloride/acetone, must be concentrated to 1 mL (or as low as possible if a precipitate forms) and diluted to 10.0 mL with methylene chloride. Thoroughly mix the extract before proceeding.

7.3.2 Filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g. a 15 mL culture tube with a Teflon lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. The latter is the preferred technique for viscous extracts or extracts with a lot of solids. Particulate larger than 5 microns may scratch the valve, which may result in a system leak and cross-contamination of sample extracts in the sample loops. Repair of the damaged valve is quite expensive.

NOTE: Viscosity of a sample extract should not exceed the viscosity of 1:1 water/glycerol. Dilute samples that exceed this viscosity.

7.4 Screening the Extract

7.4.1 Screen the extract to determine the weight of dissolved residue by evaporating a 100 µL aliquot to dryness and weighing the residue. The weight of dissolved residue loaded on the GPC column cannot exceed 0.500 g. Residues exceeding 0.500 g will very likely result in incomplete extract cleanup and contamination of the GPC switching valve (which results in cross-contamination of sample extracts).

7.4.1.1 Transfer 100 µL of the filtered extract from Sec. 7.3.2 to a tared aluminum weighing dish.

7.4.1.2 A suggested evaporation technique is to use a heat lamp. Set up a 250 watt heat lamp in a hood so that it is 8 $\pm$ 0.5 cm from a surface covered with a clean sheet of aluminum foil. Surface temperature should be 80-100°C (check temperature by placing a thermometer on the foil and under the lamp). Place the

weighing dish under the lamp using tongs. Allow it to stay under the lamp for 1 min. Transfer the weighing dish to an analytical balance or a micro balance and weigh to the nearest 0.1 mg. If the residue weight is less than 10 mg/100 µL, then further weighings are not necessary. If the residue weight is greater than 10 mg/100 µL, then determine if constant weight has been achieved by placing the weighing dish and residue back under the heat lamp for 2 or more additional 0.5 min. intervals. Reweigh after each interval. Constant weight is achieved when three weights agree within ±10%.

7.4.1.3 Repeat the above residue analysis on a blank and a spike. Add 100 µL of the same methylene chloride used for the sample extraction to a weighing dish and determine residue as above. Add 100 µL of a corn oil spike (5 g/100 mL) to another weighing dish and repeat the residue determination.

7.4.2 A residue weight of 10 mg/100 µL of extract represents 500 mg in 5 mL of extract. Any sample extracts that exceed the 10 mg/100 µL residue weight must be diluted so that the 5 mL loaded on the GPC column does not exceed 0.500 g. When making the dilution, keep in mind that a minimum volume of 8 mL is required when loading the ABC GPC unit. Following is a calculation that may be used to determine what dilution is necessary if the residue exceeds 10 mg.

$$\text{Y mL taken for dilution} = \text{10 mL final volume} \times \frac{\text{10 mg maximum}}{\text{X mg of residue}}$$

Example:

$$\text{Y mL taken for dilution} = \text{10 mL final volume} \times \frac{\text{10 mg maximum}}{\text{15 mg of residue}}$$

Y mL taken for dilution = 6.7 mL

Therefore, taking 6.7 mL of sample extract from Sec. 7.3.2, and diluting to 10 mL with methylene chloride, will result in 5 mL of diluted extract loaded on the GPC column that contains 0.500 g of residue.

NOTE: This dilution factor must be included in the final calculation of analyte concentrations. In the above example, the dilution factor is 1.5.

7.5 GPC Cleanup

7.5.1 Calibrate the GPC at least once per week following the procedure outlined in Secs. 7.2.2 through 7.2.2.6. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration UV trace.

7.5.1.1 If these criteria are not met, try cleaning the column by loading one or more 5 mL portions of butyl chloride and running it through the column. Butyl chloride or 9:1 (v/v)

methylene chloride/methanol removes the discoloration and particulate that may have precipitated out of the methylene chloride extracts. Backflushing (reverse flow) with methylene chloride to dislodge particulates may restore lost resolution. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore acceptable performance, the column must be repacked with new Bio Beads and calibrated.

7.5.2 Draw a minimum of 8 mL of extract (diluted, if necessary, and filtered) into a 10 mL syringe.

7.5.3 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5-mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes. (This should be done before sample loading.)

NOTE: Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

7.5.4 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops.

7.5.5 After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

7.5.6 After loading all the sample loops, index the GPC to the OO position, switch to the "RUN" mode and start the automated sequence. Process each sample using the collect and dump cycle times established in Sec. 7.2.2.

7.5.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

7.5.7.1 Change in solvent flow rate, caused by channeling in the column or changes in column pressure.

7.5.7.2 Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.

7.5.7.3 Leaks in the system or significant variances in room temperature.

7.6 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Sec. 4.2.1 of this chapter). See the determinative methods (Chapter Four, Sec. 4.3) for the final volume.

7.7 It should be remembered that only half of the sample extract is processed by the GPC (5 mL of the 10 mL extract is loaded onto the GPC column), and thus, a dilution factor of 2 (or 2 multiplied by any dilution factor in Sec. 7.4.2) must be used for quantitation of the sample in the determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 3600 for specific quality control procedures.

8.2 The analyst should demonstrate that the compound(s) of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for single laboratory performance data.

10.0 REFERENCES

1. Wise, R.H.; Bishop, D.F.; Williams, R.T.; Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges"; U.S. EPA Municipal Environmental Research Laboratory: Cincinnati, Ohio 45268.

2. Czuczwa, J.; Alford-Stevens, A. "Optimized Gel Permeation Chromatographic Cleanup for Soil, Sediment, Waste and Waste Oil Sample Extracts for GC/MS Determination of Semivolatile Organic Pollutants, JAOAC, submitted April 1989.

3. Marsden, P.J.; Taylor, V.; Kennedy, M.R. "Evaluation of Method 3640 Gel Permeation Cleanup"; Contract No. 68-03-3375, U.S. Environmental Protection Agency, Cincinnati, Ohio, pp. 100, 1987.

TABLE 1
GPC RECOVERY AND RETENTION VOLUMES FOR RCRA
APPENDIX VIII ANALYTES

Compound	% Rec[1]	% RSD[2]	Ret. Vol.[3] (mL)
Acenaphthene	97	2	196-235
Acenaphthylene	72	10	196-235
Acetophenone	94	7	176-215
2-Acetylaminofluorene	97	2	156-195
Aldrin	99	9	196-215
4-Aminobiphenyl	96	7	176-215
Aniline	93	4	196-235
Anthracene	89	2	196-235
Benomyl	131	8	146-195
Benzenethiol	92	11	196-235
Benzidine	95	5	176-215
Benz(a)anthracene	100	3	196-235
Benzo(b)fluoranthene	93	5	196-235
Benzo(a)pyrene	93	3	196-235
Benzo(ghi)perylene	90	6	196-235
Benzo(k)fluoranthene	91	4	196-235
Benzoic acid	66	7	176-195
Benzotrichloride	93	7	176-215
Benzyl alcohol	95	17	176-215
Benzyl chloride	99	4	176-215
alpha-BHC	84	13	196-215
beta-BHC	94	9	196-215
gamma-BHC	93	4	196-215
delta-BHC	102	7	216-255
4-Bromophenyl phenyl ether	93	1	176-215
Butyl benzyl phthalate	104	3	136-175
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	103	18	176-195
Carbazole	99	5	196-255
Carbendazim	131	8	146-195
alpha-Chlordane	97	2	196-235
gamma-Chlordane	93	2	196-215
4-Chloro-3-methylphenol	87	1	196-255
4-Chloroaniline	88	3	196-235
Chlorobenzilate	92	5	176-235
Bis(2-chloroethoxy)methane	89	1	156-195
Bis(2-chloroethyl) ether	76	2	156-215
Bis(2-chloroisopropyl) ether	83	2	156-195
2-Chloronaphthalene	89	1	196-235
2-Chlorophenol	90	1	196-215
3-Chlorophenol	86	3	196-215
4-Chlorophenol	87	2	196-215
4-Chlorophenyl phenyl ether	98	2	176-215
3-Chloropropionitrile	80	5	176-215
Chrysene	102	1	196-235
2-Cresol	91	1	196-215

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
3-Cresol	70	3	196-215
4-Cresol	88	2	196-215
Cyclophosphamide	114	10	146-185
DDD	94	4	196-235
DDE	94	2	196-235
DDT	96	6	176-215
Di-n-butyl phthalate	104	3	136-175
Diallate	97	6	156-175
Dibenzo(a,e)pyrene	94	10	216-235
Dibenzo(a,i)pyrene	99	8	216-235
Dibenz(a,j)acridine	117	9	176-195
Dibenz(a,h)anthracene	92	5	196-235
Dibenzofuran	94	1	176-235
Dibenzothiophene	94	3	196-235
1,2-Dibromo-3-chloropropane	83	2	176-215
1,2-Dibromoethane	121	8	196-215
trans-1,4-Dichloro-2-butene	107	6	176-195
cis-1,4-Dichloro-2-butene	106	6	176-215
1,2-Dichlorobenzene	81	1	196-235
1,3-Dichlorobenzene	81	1	196-235
1,4-Dichlorobenzene	81	1	196-235
3,3'-Dichlorobenzidine	98	3	176-215
2,6-Dichlorophenol	86	3	196-215
2,4-Dichlorophenoxyacetic acid (2,4-D)	80	NA	176-215
2,4-Dichlorophenol	87	2	96-215
2,4-Dichlorotoluene	70	9	196-235
1,3-Dichloro-2-propanol	73	13	176-215
Dieldrin	100	5	196-215
Diethyl phthalate	103	3	136-195
Dimethoate	79	15	146-185
3,3'-Dimethoxybenzidine[a]	15	11	156-195
Dimethyl phthalate	100	1	156-195
p-Dimethylaminoazobenzene	96	1	176-215
7,12-Dimethyl-benz(a)anthracene	77	1	176-215
2,4-Dimethylphenol	93	2	176-215
3,3'-Dimethylbenzidine	93	2	156-215
4,6-Dinitro-o-cresol	100	1	156-195
1,3-Dinitrobenzene	99	2	156-195
2,4-Dinitrophenol	118	7	176-195
2,4-Dinitrotoluene	93	4	156-195
2,6-Dinitrotoluene	101	2	156-175
Diphenylamine	95	6	176-235
Diphenyl ether	67	12	196-215
1,2-Diphenylhydrazine	92	1	176-215
Disulfoton	81	15	146-165
Endosulfan sulfate	94	2	176-195
Endosulfan I	99	8	176-215

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
Endosulfan II	92	6	196-215
Endrin	95	6	196-215
Endrin aldehyde	97	1	176-215
Endrin ketone	94	4	176-215
Ethyl methane sulfonate	62	7	176-235
Ethyl methacrylate	126	7	176-195
Bis(2-ethylhexyl) phthalate	101	1	120-145
Famphur	99	NA	126-165
Fluorene	95	1	176-235
Fluoranthene	94	1	196-235
Heptachlor	85	2	195-215
Heptachlor epoxide	91	11	156-195
Hexachlorobenzene	108	2	196-235
Hexachlorobutadiene	86	2	176-215
Hexachlorocyclopentadiene	89	3	176-215
Hexachloroethane	85	1	196-235
Hexachloropropene	91	2	196-235
Indeno(1,2,3-cd)pyrene	79	13	216-255
Isodrin	98	5	196-235
Isophorone	68	7	156-195
cis-Isosafrole	90	4	176-215
trans-Isosafrole	88	16	156-195
Kepone	102	NA	196-235
Malononitrile	111	9	156-195
Merphos	93	12	126-165
Methoxychlor	94	6	156-195
3-Methylcholanthrene	74	12	176-195
2-Methylnaphthalene	67	6	196-215
Methyl parathion	84	13	146-185
4,4'-Methylene-bis(2-chloroaniline)	96	1	176-215
Naphthalene	95	7	196-215
1,4-Naphthoquinone	73	7	176-215
2-Naphthylamine	94	8	196-235
1-Naphthylamine	96	6	196-235
5-Nitro-o-toluidine	77	2	176-195
2-Nitroaniline	96	8	176-215
3-Nitroaniline	96	2	176-215
4-Nitroaniline	103	8	176-215
Nitrobenzene	86	2	176-195
2-Nitrophenol	95	3	176-195
4-Nitrophenol	77	3	196-215
N-Nitroso-di-n-butylamine	89	4	156-175
N-Nitrosodiethanolamine	104	3	146-185
N-Nitrosodiethylamine	94	2	156-175
N-Nitrosodimethylamine	86	13	156-195
N-Nitrosodiphenylamine	99	2	156-195
N-Nitrosodi-n-propylamine	85	4	156-175

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
N-Nitrosomethylethylamine	83	7	156-175
N-Nitrosomorpholine	86	4	156-195
N-Nitrosopiperidine	84	4	156-195
N-Nitrosopyrolidine	92	1	156-175
Di-n-octyl phthalate	83	4	120-156
Parathion	109	14	146-170
Pentachlorobenzene	95	2	196-235
Pentachloroethane	74	1	196-235
Pentachloronitrobenzene (PCNB)	91	8	156-195
Pentachlorophenol	102	1	196-215
Phenacetin	100	3	156-195
Phenanthrene	94	2	196-235
Phenol	83	2	156-195
1,2-Phenylenediamine	91	1	196-215
Phorate	74	NA	116-135
2-Picoline	99	14	156-215
Pronamide	105	15	156-195
Pyrene	98	2	215-235
Resorcinol	70	6	196-215
Safrole	93	1	176-215
Streptozotocin[a]	6	48	225-245
1,2,4,5-Tetrachlorobenzene	96	2	196-235
2,3,5,6-Tetrachloro-nitrobenzene	85	9	176-215
2,3,4,6-Tetrachlorophenol	95	1	196-215
2,3,5,6-Tetrachlorophenol	96	7	196-215
Tetraethyl dithiopyrophosphate (Sulfotep)	89	14	116-135
Thiosemicarbazide	74	3	146-185
2-Toluidine	92	3	176-235
4-Toluidine	87	8	176-235
Thiourea, 1-(o-chlorophenyl)	75	11	166-185
Toluene-2,4-diamine	69	7	176-215
1,2,3-Trichlorobenzene	87	1	196-235
1,2,4-Trichlorobenzene	89	1	196-235
2,4,5-Trichlorophenol	77	1	216-235
2,4,6-Trichlorophenol	95	1	216-235
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	71	23	156-235
2,4,5-Trichlorophenoxypropionic acid	67	NA	216-215
Warfarin	94	2	166-185

NA = Not applicable, recovery presented as the average of two determinations.

[a] Not an appropriate analyte for this method.

[1] The percent recovery is based on an average of three recovery values.

[2] The % relative standard deviation is determined from three recovery values.

[3] These Retention Volumes are for guidance only as they will differ from column to column and from system to system.

Figure 1
GPC RETENTION VOLUME OF CLASSES OF ANALYTES

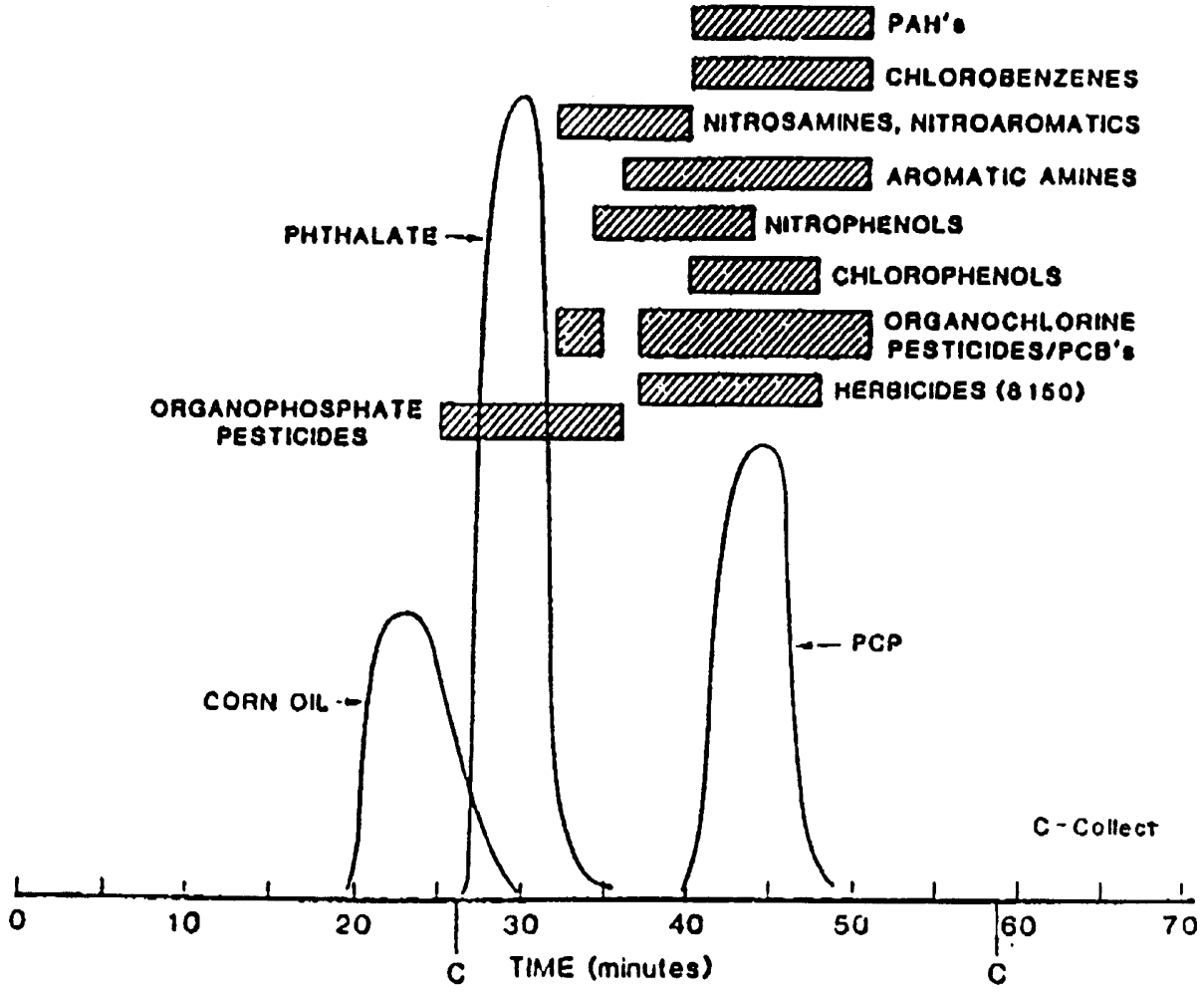
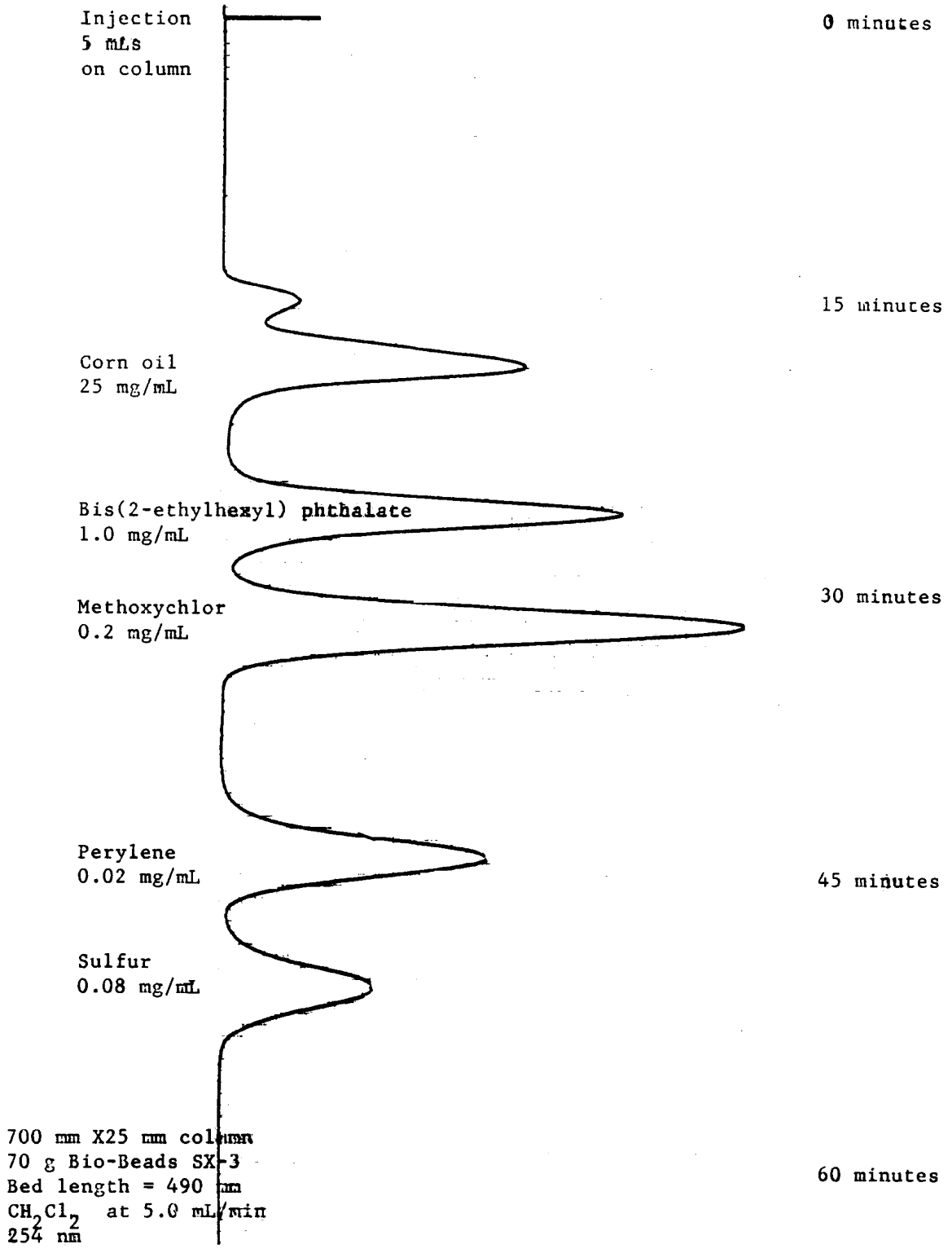
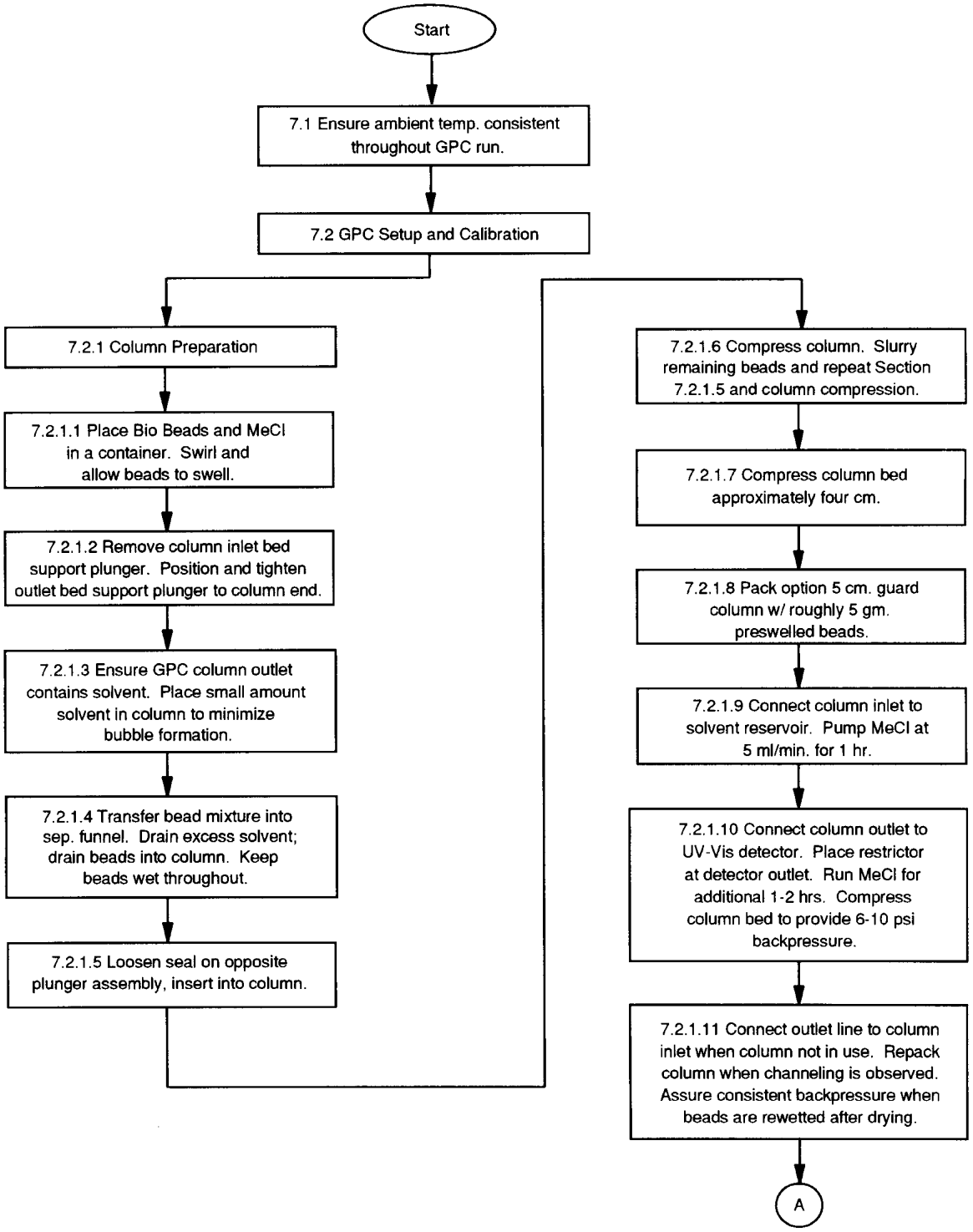
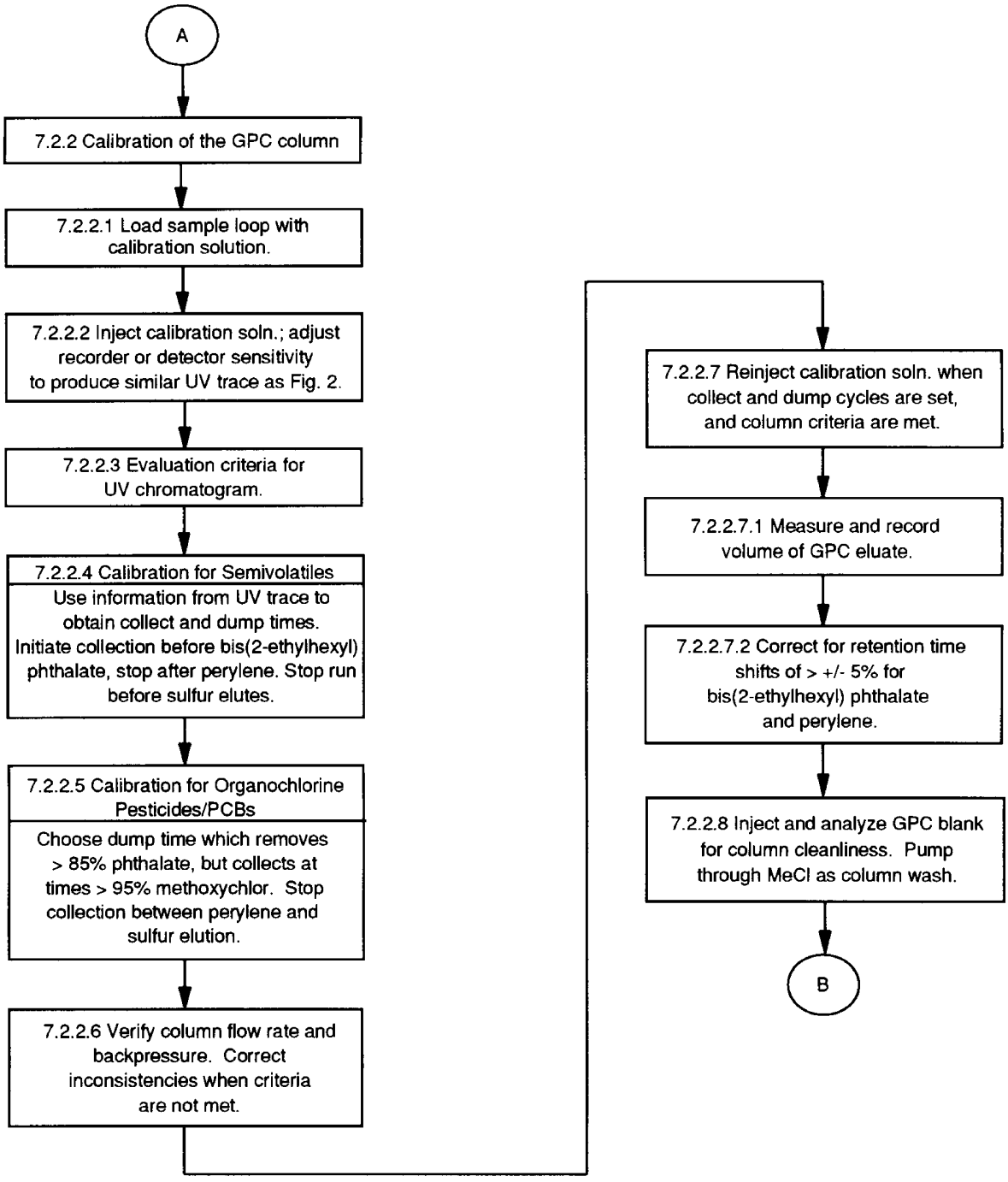
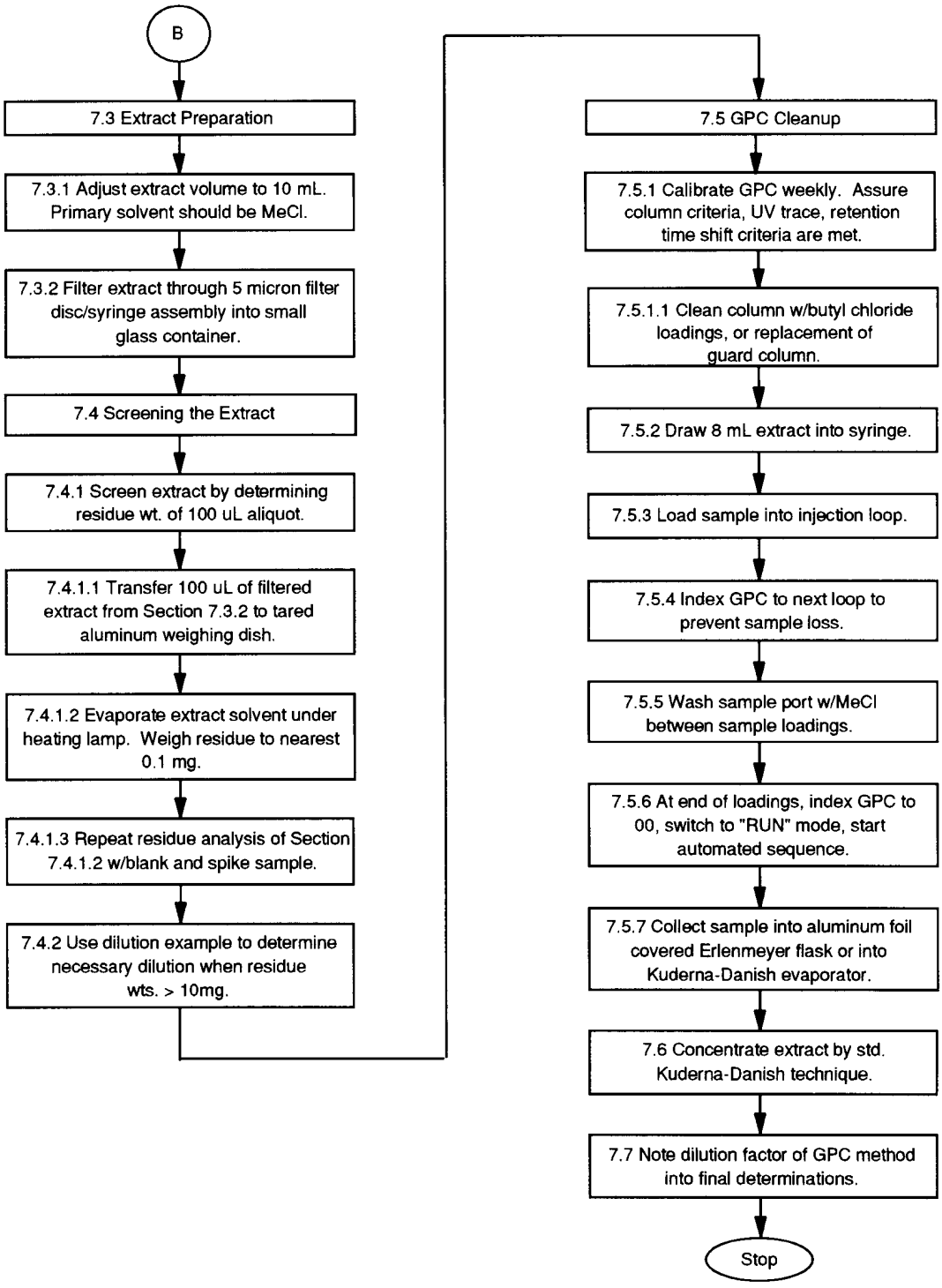


Figure 2
UV CHROMATOGRAM OF THE CALIBRATION SOLUTION




Start
7.1 Ensure ambient temp. consistent throughout GPC run.
7.2 GPC Setup and Calibration
7.2.1 Column Preparation
7.2.1.1 Place Bio Beads and MeCl in a container. Swirl and allow beads to swell.
7.2.1.2 Remove column inlet bed support plunger. Position and tighten outlet bed support plunger to column end.
7.2.1.3 Ensure GPC column outlet contains solvent. Place small amount solvent in column to minimize bubble formation.
7.2.1.4 Transfer bead mixture into sep. funnel. Drain excess solvent; drain beads into column. Keep beads wet throughout.
7.2.1.5 Loosen seal on opposite plunger assembly, insert into column.
7.2.1.6 Compress column. Slurry remaining beads and repeat Section 7.2.1.5 and column compression.
7.2.1.7 Compress column bed approximately four cm.
7.2.1.8 Pack option 5 cm. guard column w/ roughly 5 gm. preswelled beads.
7.2.1.9 Connect column inlet to solvent reservoir. Pump MeCl at 5 ml/min. for 1 hr.
7.2.1.10 Connect column outlet to UV-Vis detector. Place restrictor at detector outlet. Run MeCl for additional 1-2 hrs. Compress column bed to provide 6-10 psi backpressure.
7.2.1.11 Connect outlet line to column inlet when column not in use. Repack column when channeling is observed. Assure consistent backpressure when beads are rewetted after drying.
A


A
7.2.2 Calibration of the GPC column
7.2.2.1 Load sample loop with calibration solution.
7.2.2.2 Inject calibration soln.; adjust recorder or detector sensitivity to produce similar UV trace as Fig. 2.
7.2.2.3 Evaluation criteria for UV chromatogram.
7.2.2.4 Calibration for Semivolatiles
Use information from UV trace to obtain collect and dump times. Initiate collection before bis(2-ethylhexyl) phthalate, stop after perylene. Stop run before sulfur elutes.
7.2.2.5 Calibration for Organochlorine Pesticides/PCBs
Choose dump time which removes > 85% phthalate, but collects at times > 95% methoxychlor. Stop collection between perylene and sulfur elution.
7.2.2.6 Verify column flow rate and backpressure. Correct inconsistencies when criteria are not met.
7.2.2.7 Reinject calibration soln. when collect and dump cycles are set, and column criteria are met.
7.2.2.7.1 Measure and record volume of GPC eluate.
7.2.2.7.2 Correct for retention time shifts of > +/- 5% for bis(2-ethylhexyl) phthalate and perylene.
7.2.2.8 Inject and analyze GPC blank for column cleanliness. Pump through MeCl as column wash.
B


B
7.3 Extract Preparation
7.3.1 Adjust extract volume to 10 mL. Primary solvent should be MeCl.
7.3.2 Filter extract through 5 micron filter disc/syringe assembly into small glass container.
7.4 Screening the Extract
7.4.1 Screen extract by determining residue wt. of 100 uL aliquot.
7.4.1.1 Transfer 100 uL of filtered extract from Section 7.3.2 to tared aluminum weighing dish.
7.4.1.2 Evaporate extract solvent under heating lamp. Weigh residue to nearest 0.1 mg.
7.4.1.3 Repeat residue analysis of Section 7.4.1.2 w/blank and spike sample.
7.4.2 Use dilution example to determine necessary dilution when residue wts. > 10mg.
7.5 GPC Cleanup
7.5.1 Calibrate GPC weekly. Assure column criteria, UV trace, retention time shift criteria are met.
7.5.1.1 Clean column w/butyl chloride loadings, or replacement of guard column.
7.5.2 Draw 8 mL extract into syringe.
7.5.3 Load sample into injection loop.
7.5.4 Index GPC to next loop to prevent sample loss.
7.5.5 Wash sample port w/MeCl between sample loadings.
7.5.6 At end of loadings, index GPC to 00, switch to "RUN" mode, start automated sequence.
7.5.7 Collect sample into aluminum foil covered Erlenmeyer flask or into Kuderna-Danish evaporator.
7.6 Concentrate extract by std. Kuderna-Danish technique.
7.7 Note dilution factor of GPC method into final determinations.
Stop

No. L-31

Semivolatile Organics SIM and TEPH-alkanes

SW-846 Method 3611b

METHOD 3611B

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES

1.0 SCOPE AND APPLICATION

1.1 Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in chromatographic cleanup procedures. Method 3611 utilizes neutral pH alumina to separate petroleum wastes into aliphatic, aromatic, and polar fractions.

1.2 Method 3611 was formerly Method 3570 in the Second Edition of this manual.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 0.300 g of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

3.4 Mixtures of petroleum wastes containing predominantly polar solvents, i.e., chlorinated solvents or oxygenated solvents, are not appropriate for this method.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300 mm x 10 mm ID, with Pyrex® glass wool at bottom and a polytetrafluoroethylene (PTFE) stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the

glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: Appropriate sizes.

4.3 Reagent bottle: Appropriate sizes.

4.4 Muffle furnace.

4.5 Water bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Erlenmeyer flasks: 50 and 250 mL.

5.0 REAGENTS

5.1 Sodium sulfate: (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.2 Eluting solvents:

5.2.1 Methanol, CH_3OH - Pesticide quality or equivalent.

5.2.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.2.3 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 It is suggested that Method 3650, Acid-Base Partition Cleanup, be performed on the sample extract prior to alumina cleanup.

7.2 Place approximately 10 g of alumina into a chromatographic column, tap to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

7.3 Pre-elute the column with 50 mL of hexane. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1 mL sample extract onto the column using an additional 1 mL of hexane to complete the transfer. To avoid overloading the column, it is suggested that no more than 0.300 g of extractable organics be placed on the column (see Sec. 3.3).

7.4 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50 mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.5 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250 mL flask. Label this fraction "base/neutral aromatics."

7.6 Elute the column with 100 mL of methanol and collect the effluent in a 250 mL flask. Label this fraction "base/neutral polars."

7.7 Following cleanup, concentrate the fractions to the final volumes listed in the appropriate determinative method, using the techniques described in an appropriate 3500 series method. Analysis follows as specified in the determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 Rag oil is an emulsion consisting of crude oil, water, and soil particles. It has a density greater than crude oil and less than water. This material forms a layer between the crude oil and water when the crude oil is allowed to gravity separate at the refinery. A rag oil sample was analyzed by a number of laboratories according to the procedure outlined in this method. The results of these analyses by GC/MS for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1

RESULTS OF ANALYSIS FOR SELECTED COMPONENTS IN RAG OIL

Analyte	Mean Conc. (mg/kg)[a]	Standard Deviation	%RSD[b]
Naphthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	614	296	18
2-Methylnaphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methylphenanthrene	2908	2014	69
Methyldibenzothiophene	2200	1017	46
	Average Surrogate Recovery		
Nitrobenzene-d_5	58.6	11	
Terphenyl-d_{14}	83.0	2.6	
Phenol-d_6	80.5	27.6	
Naphthalene-d_8	64.5	5.0	

[a] Based on five determinations from three laboratories.

[b] Percent Relative Standard Deviation.

FIGURE 1

RECONSTRUCTED ION CHROMATOGRAM FROM GC/MS ANALYSIS OF THE AROMATIC FRACTION FROM RAG OIL

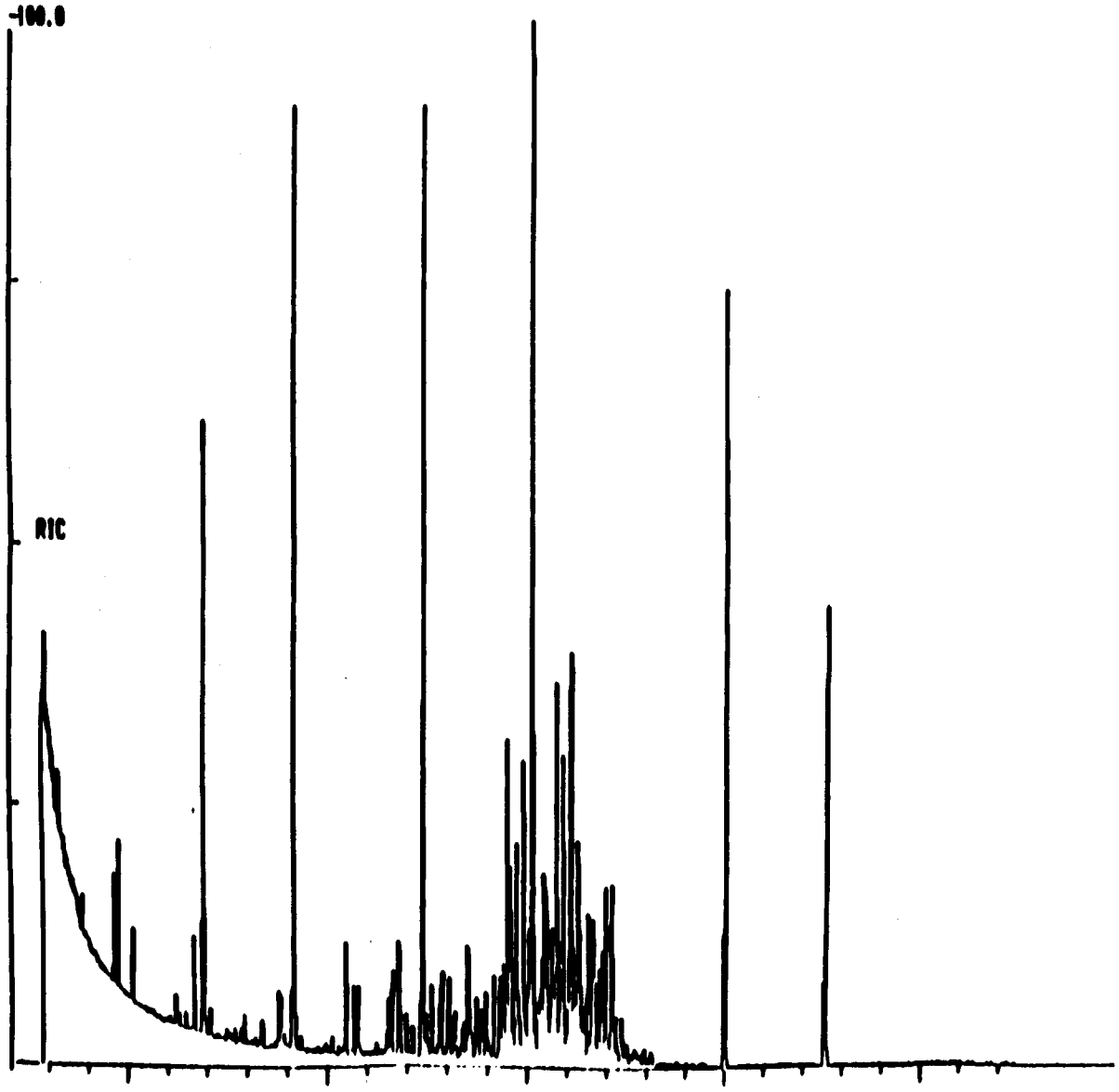
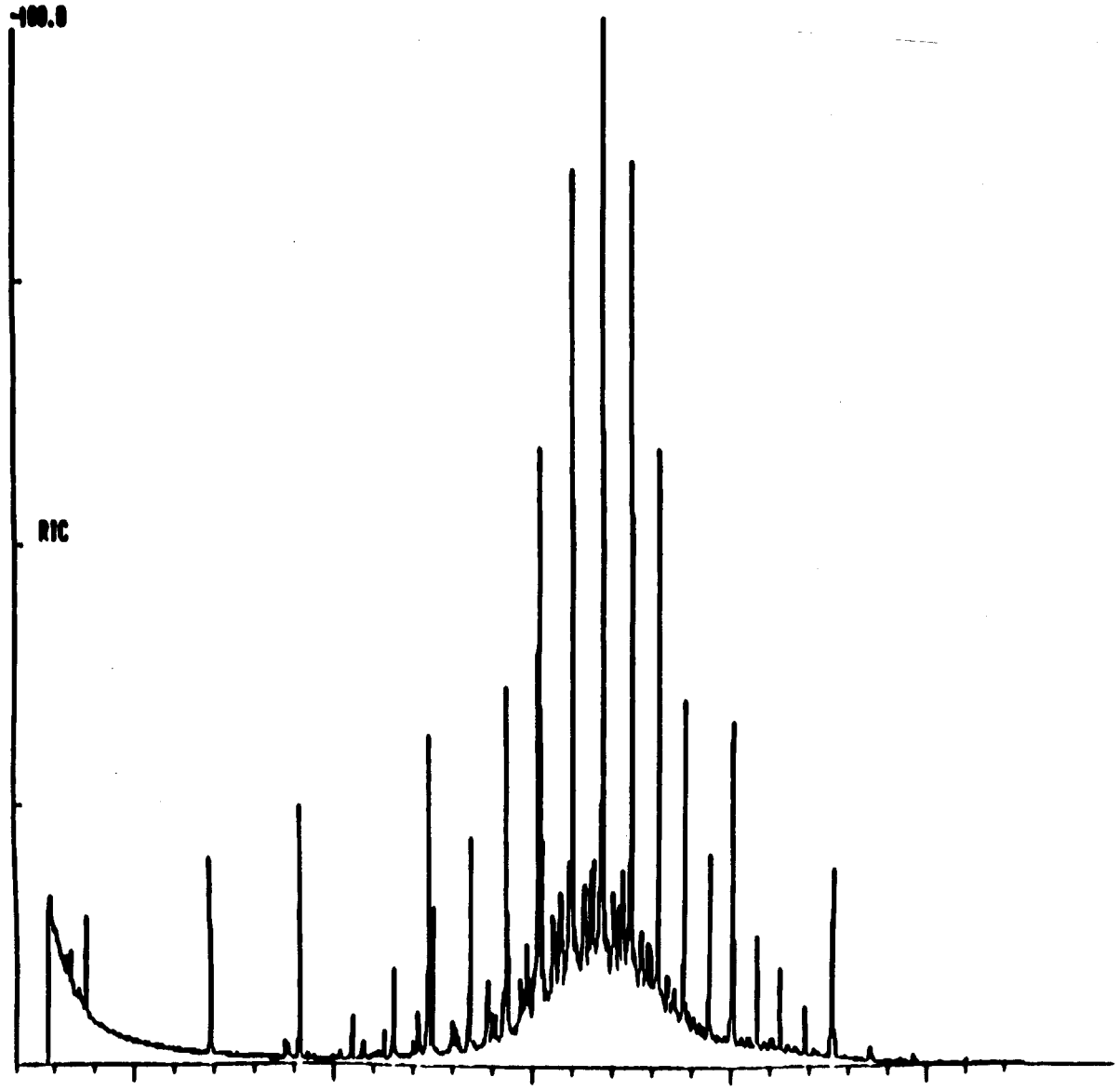
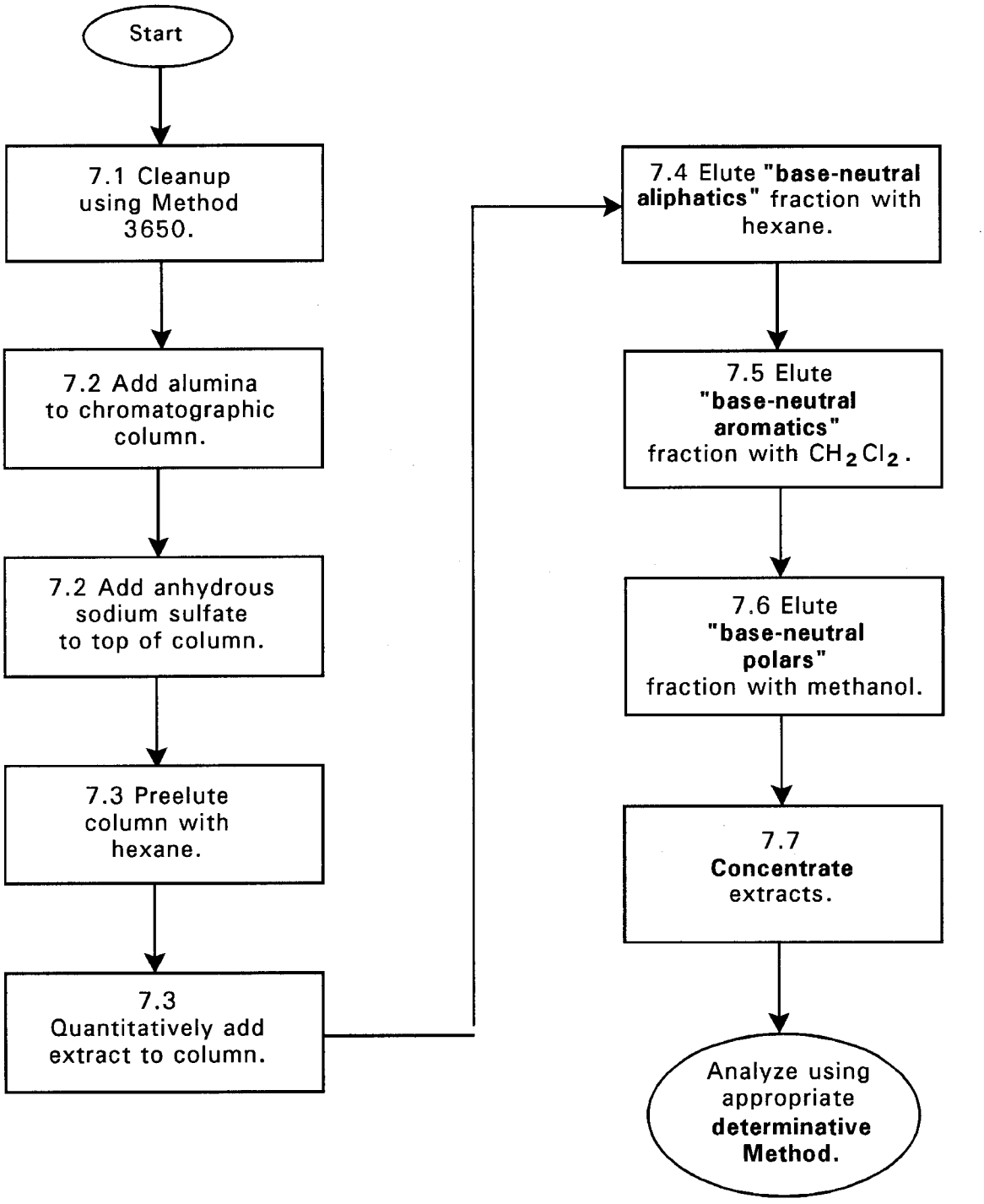


FIGURE 2

RECONSTRUCTED ION CHROMATOGRAM FROM GC/MS ANALYSIS OF THE ALIPHATIC FRACTION FROM RAG OIL



ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES



No. L-32

Semivolatile Organics and

Semivolatile Organics SIM

SW-846 Method 3630c

METHOD 3630C

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel (silicic acid) is a regenerative adsorbent of silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity. It may be used activated, after heating to 150 - 160°C, or deactivated with up to 10% water.

1.2 This method includes guidance for standard column cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds, organochlorine pesticides, and PCBs as Aroclors.

1.3 This method also provides cleanup procedures using solid-phase extraction cartridges for pentafluorobenzyl bromide-derivatized phenols, organochlorine pesticides, and PCBs. This technique also provides the best separation of PCBs from most single component organochlorine pesticides. When only PCBs are to be measured, this method can be used in conjunction with sulfuric acid/permanganate cleanup (Method 3665).

1.4 Other analytes may be cleaned up using this method if the analyte recovery meets the criteria specified in Sec. 8.0.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides the option of using either standard column chromatography techniques or solid-phase extraction cartridges. Generally, the standard column chromatography techniques use larger amounts of adsorbent and, therefore, have a greater cleanup capacity.

2.2 In the standard column cleanup protocol, the column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is accomplished with a suitable solvent(s) that leaves the interfering compounds on the column. The eluate is then concentrated (if necessary).

2.3 The cartridge cleanup protocol uses solid-phase extraction cartridges packed with 1 g or 2 g of silica gel (silicic acid) adsorbent. Each cartridge is solvent washed immediately prior to use. Aliquots of sample extracts are loaded onto the cartridges, which are then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The collected fractions may be further concentrated prior to gas chromatographic analysis.

2.4 The appropriate gas chromatographic method is listed at the end of each technique. Analysis may also be performed by gas chromatography/mass spectrometry (Method 8270).

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks. See Sec. 8 for guidance on a reagent blank check.

3.2 Phthalate ester contamination may be a problem with certain cartridges The more inert the column and/or cartridge material (i.e., glass or polytetrafluoroethylene (PTFE)), the less problem with phthalates. Phthalates create interference problems for all method analytes, not just the phthalate esters themselves.

3.3 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column - 250 mm long x 10 mm ID; with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - appropriate sizes.

4.3 Vials - 2, 10, 25 mL, glass with PTFE-lined screw-caps or crimp tops.

4.4 Muffle furnace.

4.5 Reagent bottle - appropriate sizes.

4.6 Erlenmeyer flasks - 50 and 250 mL.

4.7 Vacuum manifold: VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica gel for chromatography columns.

5.3.1 Silica Gel for Phenols and Polynuclear Aromatic Hydrocarbons: 100/200 mesh (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil.

5.3.2 Silica Gel for Organochlorine pesticides/PCBs: 100/200 mesh (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil. Deactivate it to 3.3% with reagent water in a 500 mL glass jar. Mix the contents thoroughly and allow to equilibrate for 6 hours. Store the deactivated silica gel in a sealed glass jar inside a desiccator.

5.4 Silica cartridges: 40 µm particles, 60 A pores. The cartridges with which this method was developed consist of 6 mL serological-grade polypropylene tubes, with the 1 g of silica held between two polyethylene or stainless steel frits with 20 µm pores. 2 g silica cartridges are also used in this method, and 0.5 g cartridges are available. The compound elution patterns must be verified when cartridges other than the specified size are used.

5.5 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed in order to demonstrate that there is no interference from the sodium sulfate.

5.6 Eluting solvents

5.6.1 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.6.4 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.6.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.6 Pentane, C_5H_{12} - Pesticide quality or equivalent.

5.6.7 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.6.8 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethanol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 General Guidance

7.1.1 The procedure contains two cleanup options for the derivatized phenols and organochlorine pesticides/PCBs, but only one technique for the polynuclear aromatic hydrocarbons (PAHs) (standard column chromatography). Cleanup techniques by standard column chromatography for all analytes are found in Sec. 7.2. Cleanup techniques by solid-phase cartridges for derivatized phenols and PAHs are found in Sec. 7.3. The standard column chromatography techniques are packed with a greater amount of silica gel adsorbent and, therefore, have a greater cleanup capacity. A rule of thumb relating to cleanup capacity is that 1 g of sorbent material will remove 10 to 30 mg of total interferences. (However, capacity is also dependent on the sorbent retentiveness of the interferences.) Therefore, samples that exhibit a greater degree of sample interference should be cleaned up by the standard column technique. However, both techniques have limits on the amount of interference that can be removed. If the interference is caused by high boiling material, then Method 3640 should be used prior to this method. If the interference is caused by relatively polar compounds of the same boiling range as the analytes, then multiple column or cartridge cleanups may be required. If crystals of sulfur are noted in the extract, then Method 3660 should be utilized prior to this method. The cartridge cleanup techniques are often faster and use less solvent, however they have less cleanup capacity.

7.1.2 Allow the extract to reach room temperature if it was in cold storage. Inspect the extracts visually to ensure that there are no particulates or phase separations and that the volume is as stated in the accompanying documents. Verify that the solvent is compatible with the cleanup procedures. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.1.3 If the extract solvent is methylene chloride, for most cleanup techniques, it must be exchanged to hexane. (For the PAHs, exchange to cyclohexane as per Sec. 7.2.1). Follow one of the standard concentration techniques provided in each extraction method. The volume of methylene chloride should have been reduced to 1-2 mL. Add 40 mL of hexane, a fresh boiling chip and repeat the concentration as written. The final volume required for the cleanup techniques is normally 2 mL.

7.2 Standard Column Cleanup Techniques

7.2.1 Polynuclear aromatic hydrocarbons

7.2.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. The exchange is performed by adding 4 mL of cyclohexane following reduction of the sample extract to 1-2 mL using an appropriate concentration technique (e.g., K-D using two-ball micro-snyder column) found in the 3500 series methods. The final extract volume is 2.0 mL.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost. If the extract goes to dryness, the extraction must be repeated.

7.2.1.2 Prepare a slurry of 10 g of activated silica gel (Sec. 5.3.1) in methylene chloride and place this into a 10 mm ID chromatographic column. Tap the column to

settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.2.1.3 Pre-elute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.2.1.4 Next, elute the column with 25 mL of methylene chloride/pentane (2:3)(v/v) into a flask for concentration. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC (Method 8310) or GC analysis (Method 8100). Validated components that elute in this fraction are:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

7.2.2 Derivatized Phenols

7.2.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization, as described in Method 8041. The sample extract must be in 2 mL of hexane at this point.

7.2.2.2 Place 4.0 g of activated silica gel (Sec. 5.3.1) into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.2.3 Pre-elute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.2.4 Elute the column, in order, with 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis.

7.2.3 Organochlorine Pesticides and PCBs

7.2.3.1 Transfer a 3 g portion of deactivated silica gel (Sec. 5.3.2) into a 10 mm ID glass chromatographic column and top it with 2 to 3 cm of anhydrous sodium sulfate.

7.2.3.2 Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.

7.2.3.3 Transfer the sample extract (2 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column. Elute the column with 80 mL of hexane (Fraction I) at a rate of about 5 mL/min. Remove the collection flask and set it aside for later concentration. Elute the column with 50 mL of hexane (Fraction II) and collect the eluate. Perform a third elution with 15 mL of methylene chloride (Fraction III). The elution patterns for the organochlorine pesticides, Aroclor-1016, and Aroclor-1260 are shown in Table 2.

7.2.3.4 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Fractions may be combined, as desired, depending upon the specific pesticides/PCBs of interest or level of interferences. Analyze Fraction I containing PCBs separated from most pesticides by Method 8082. Use Method 8081 to analyze for organochlorine pesticides.

7.3 Cartridge Cleanup Techniques

7.3.1 Cartridge Set-up and Conditioning

7.3.1.1 Arrange the 1 g silica cartridges (2 g for phenol cleanup) on the manifold in the closed-valve position. Other size cartridges may be used, however the data presented in the Tables are all based on 1 g cartridges for pesticides/PCBs and 2 g cartridges for phenols. Therefore, supporting recovery data must be developed for other sizes. Larger cartridges will probably require larger volumes of elution solvents.

7.3.1.2 Turn on the vacuum pump and set pump vacuum to 10 inches (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates can be controlled by opening and closing cartridge valves.

7.3.1.3 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

7.3.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

7.3.2 Derivatized Phenols

7.3.2.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane and the phenols must have undergone derivatization by pentafluorobenzyl bromide, as per the appropriate method.

7.3.2.2 Transfer the extract to the 2 g cartridge that has been conditioned as described in Sec. 7.3.1. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.2.3 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of hexane, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.2.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.3.2.5 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.2.6 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve, and collect the eluate (this is Fraction 1, and should be discarded).

NOTE: If cartridges smaller than 2 g are used, then Fraction 1 cannot be discarded, since it contains some of the phenols.

7.3.2.7 Close the cartridge valve, replace the collection vial, and add 5 mL of toluene/hexane (25/75, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2, and should be retained for analysis.

7.3.2.8 Adjust the final volume of the eluant to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL) using techniques described in an appropriate 3500 series method. Table 3 shows compound recoveries for 2 g silica cartridges. The cleaned up extracts are ready for analysis by Method 8041.

7.3.3 Organochlorine Pesticides/PCBs

NOTE: The silica cartridge procedure is appropriate when polychlorinated biphenyls are known to be present.

7.3.3.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.3.3.2 Use the 1 g cartridges conditioned as described in Sec. 7.3.1.

7.3.3.3 Transfer the extract to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.3.4 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of solvent, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.3.5 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never goes dry.

7.3.3.6 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.3.7 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 1).

7.3.3.8 Close the cartridge valve, replace the collection vial, and add 5 mL of diethyl ether/hexane (50/50, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 2).

7.3.3.9 Adjust the final volume of each of the two fractions to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL) using techniques described in an appropriate 3500 series method. The fractions may be combined prior to final adjustment of volume, if analyte fractionation is not required. Table 4 shows compound recoveries for 1 g silica cartridges. The cleaned up extracts are ready for analysis by Methods 8081 for organochlorine pesticides or 8082 for PCBs.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 A reagent blank (consisting of the elution solvents) must be passed through the column or cartridge and checked for the compounds of interest, prior to the use of this method. This same performance check is required with each new lot of adsorbent or cartridges. The level of interferences must be below the method detection limit before this method is performed on actual samples.

8.3 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. See the attached Tables for acceptable recovery data. For compounds that have not been tested, recovery must be $\geq$ 85%.

8.3.1 Before any samples are processed using the solid-phase extraction cartridges, the efficiency of the cartridge must be verified. A recovery check must be performed using standards of the target analytes at known concentration. Only lots of cartridges that meet the recovery criteria for the spiked compounds can be used to process the samples.

8.3.2 A check should also be performed on each individual lot of cartridges and for every 300 cartridges of a particular lot.

8.4 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using standard column chromatography.

9.2 Table 2 provides performance information on the fractionation of organochlorine pesticides and Aroclors using standard column chromatography.

9.3 Table 3 shows recoveries of derivatized phenols obtained using 2 g silica cartridges.

9.4 Table 4 shows recoveries and fractionation of organochlorine pesticides obtained using 1 g silica cartridges.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S EPA "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges," Project Report, December 1989.

TABLE 1

SILICA GEL FRACTIONATION OF PFBBr DERIVATIVES

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[a] Eluant composition:

Fraction 1 - 15% toluene in hexane.
Fraction 2 - 40% toluene in hexane.
Fraction 3 - 75% toluene in hexane.
Fraction 4 - 15% 2-propanol in toluene.

Data from Reference 1 (Method 604)

TABLE 2

DISTRIBUTION AND PERCENT RECOVERIES OF ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS IN SILICA GEL COLUMN FRACTIONS[a,b,c,d,e]

Compound	Fraction I		Fraction II		Fraction III		Total Recovery	
	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2
alpha-BHC[f]					82(1.7)	74(8.0)	82(1.7)	74(8.0)
beta-BHC					107(2.1)	98(12.5)	107(2.1)	98(12.5)
gamma-BHC					91(3.6)	85(10.7)	91(3.6)	85(10.7)
delta-BHC					92(3.5)	83(10.6)	92(3.5)	83(10.6)
Heptachlor	109(4.1)	118(8.7)					109(4.1)	118(8.7)
Aldrin	97(5.6)	104(1.6)					97(5.6)	104(1.6)
Heptachlor epoxide					95(4.7)	88(10.2)	95(4.7)	88(10.2)
Technical chlordane	14(5.5)	22(5.3)	19(6.8)	39(3.6)	29(5.0)	37(5.1)	62(3.3)	98(1.9)
Endosulfan I					95(5.1)	87(10.2)	95(5.1)	87(10.2)
4,4'-DDE	86(5.4)	94(2.8)					86(5.4)	94(2.8)
Dieldrin					96(6.0)	87(10.6)	96(6.0)	87(10.6)
Endrin					85(10.5)	71(12.3)	85(10.5)	71(12.3)
Endosulfan II					97(4.4)	86(10.4)	97(4.4)	86(10.4)
4,4'-DDD[f]					102(4.6)	92(10.2)	102(4.6)	92(10.2)
Endrin aldehyde					81(1.9)	76(9.5)	81(1.9)	76(9.5)
Endosulfan sulfate					93(4.9)	82(9.2)	93(4.9)	82(9.2)
4,4'-DDT[f]			86(13.4)	73(9.1)	15(17.7)	8.7(15.0)	101(5.3)	82(23.7)
4,4'-Methoxychlor					99(9.9)	82(10.7)	99(9.9)	82(10.7)
Toxaphene[f]			15(2.4)	17(1.4)	73(9.4)	84(10.7)	88(12.0)	101(10.1)
Aroclor-1016	86(4.0)	87(6.1)					86(4.0)	87(6.1)
Aroclor-1260	91(4.1)	95(5.0)					91(4.1)	95(5.0)

TABLE 2
(Continued)

[a] Effluent composition: Fraction I, 80 mL hexane; Fraction II, 50 mL hexane; Fraction III, 15 mL methylene chloride.

[b] Concentration 1 is 0.5 µg per column for BHCs, Heptachlor, Aldrin, Heptachlor epoxide, and Endosulfan I; 1.0 µg per column for Dieldrin, Endosulfan II, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Endrin, Endrin aldehyde, and Endosulfan sulfate; 5 µg per column for 4,4'-Methoxychlor and technical Chlordane; 10 µg per column for Toxaphene, Aroclor-1016, and Aroclor-1260.

[c] For Concentration 2, the amounts spiked are 10 times as high as those for Concentration 1.

[d] Values given represent the average recovery of three determinations; numbers in parentheses are the standard deviation; recovery cutoff point is 5 percent.

[e] Data obtained with standards, as indicated in footnotes b and c, dissolved in 2 mL hexane.

[f] It has been found that because of batch-to-batch variation in the silica gel material, these compounds cross over in two fractions and the amounts recovered in each fraction are difficult to reproduce.

TABLE 3

PERCENT RECOVERIES AND ELUTION PATTERNS FOR 18 PHENOLS FROM 2 g SILICA CARTRIDGES[a]

Compound	Fraction 2 Average Recovery	Percent RSD
Phenol	74.1	5.2
2-Methylphenol	84.8	5.2
3-Methylphenol	86.4	4.4
4-Methylphenol	82.7	5.0
2,4-Dimethylphenol	91.8	5.6
2-Chlorophenol	88.5	5.0
2,6-Dichlorophenol	90.4	4.4
4-Chloro-3-methylphenol	94.4	7.1
2,4-Dichlorophenol	94.5	7.0
2,4,6-Trichlorophenol	97.8	6.6
2,3,6-Trichlorophenol	95.6	7.1
2,4,5-Trichlorophenol	92.3	8.2
2,3,5-Trichlorophenol	92.3	8.2
2,3,5,6-Tetrachlorophenol	97.5	5.3
2,3,4,6-Tetrachlorophenol	97.0	6.1
2,3,4-Trichlorophenol	72.3	8.7
2,3,4,5-Tetrachlorophenol	95.1	6.8
Pentachlorophenol	96.2	8.8

[a] Silica cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL of hexane prior to use. Each experiment was performed in duplicate at three spiking concentrations (0.05 µg, 0.2 µg, and 0.4 µg per compound per cartridge). Fraction 1 was eluted with 5 mL hexane and was discarded. Fraction 2 was eluted with 5 mL toluene/hexane (25/75, v/v).

Data from Reference 2

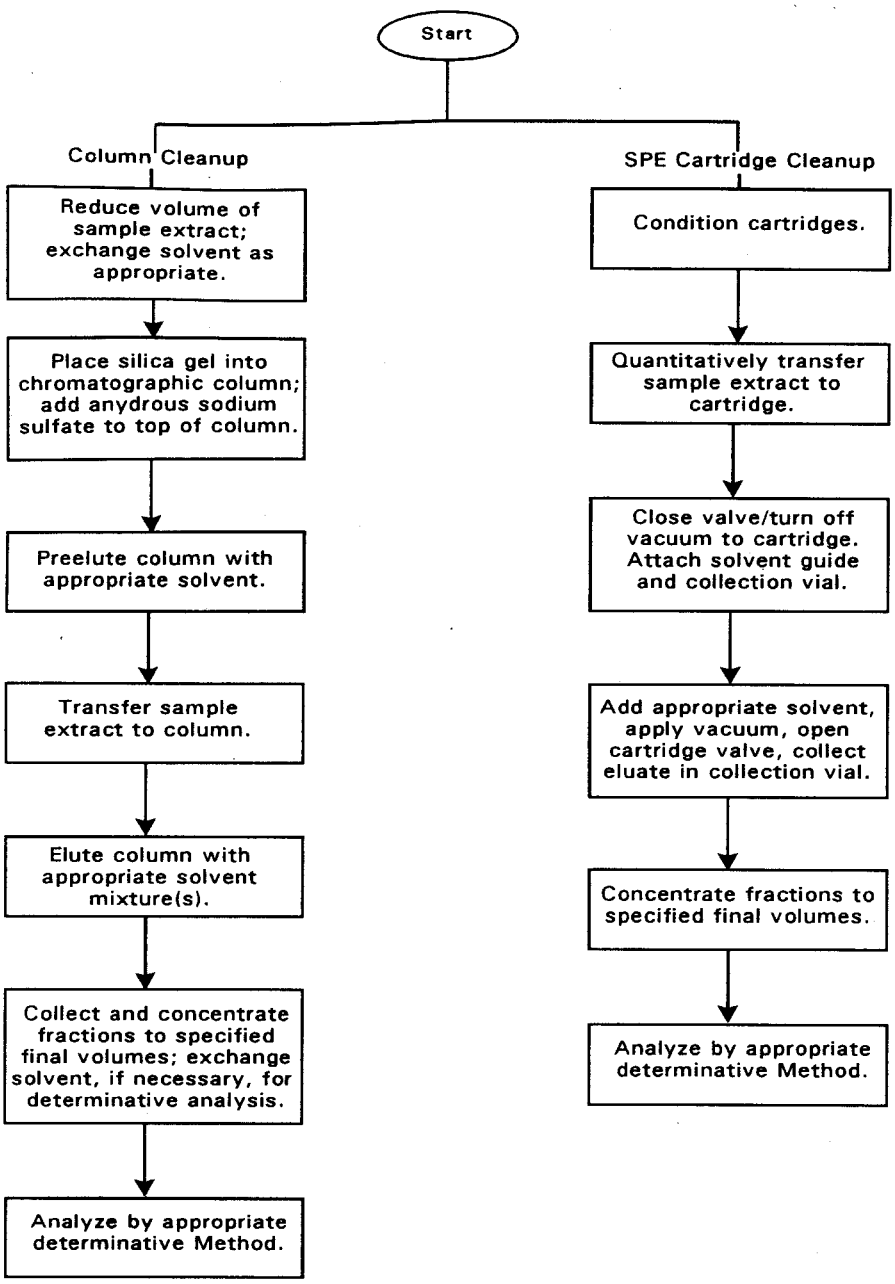
TABLE 4

PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17 ORGANOCHLORINE PESTICIDES AND AROCLORS FROM 1 g SILICA CARTRIDGES[a]

Compound	Fraction 1 Average Recovery	Fraction 1 Percent RSD	Fraction 2 Average Recovery	Fraction 2 Percent RSD
alpha-BHC	0		98.7	2.3
gamma-BHC	0		94.8	1.9
beta-BHC	0		94.3	3.0
Heptachlor	97.3	1.3	0	
delta-BHC	0		90.8	2.5
Aldrin	95.9	1.0	0	
Heptachlor epoxide	0		97.9	2.1
Endosulfan I	0		102	2.3
4,4'-DDE	99.9	1.7	0	
Dieldrin	0		92.3	2.0
Endrin	0		117	2.6
4,4'-DDD	10.7	41	92.4	3.3
Endosulfan II	0		96.0	2.2
4,4'-DDT	94.1	2.0	0	
Endrin aldehyde	0		59.7	2.6
Endosulfan sulfate	0		97.8	2.1
4,4'-Methoxychlor	0		98.0	2.4
Aroclor 1016	124			
Aroclor 1221	93.5			
Aroclor 1232	118			
Aroclor 1242	116			
Aroclor 1248	114			
Aroclor 1254	108			
Aroclor 1264	112			

[a] Silica cartridges (Supelco, Inc. lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. The organochlorine pesticides were tested separately from PCBs. Each organochlorine pesticides experiment was performed in duplicate, at three spiking concentrations (0.2 µg, 1.0 µg, and 2.0 µg per compound per cartridge). Fraction 1 was eluted with 5 mL of hexane, Fraction 2 with 5 mL of diethyl ether/hexane (50/50, v/v). PCBs were spiked at 10 µg per cartridge and were eluted with 3 mL of hexane. The values given for PCBs are the percent recoveries for a single determination.

Data from Reference 2



Note: Select specific procedures provided in the method depending on the type(s) of analytes of interest. See the method for details regarding the appropriate elution and collection procedures.

Revision Log:

Revision: 15	**Effective Date:** This version	
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Revision Log (Previous Version)	Correction	Changed analysis number from 12989**8** to 12989 in *Historical/Local Document Number* entry for version 14
Reference 4.	Reflects current references	Added reference to EPA SW-846 Method 8015D and renumbered accordingly

Revision: 14	**Effective Date:** Sep 13, 2013	
Section	**Justification**	**Changes**
Revision Log	Formatting requirement per 1-P-QM-QMA-9017356	Removed revision logs up to the previous version
Throughout Document	Reflect current practice	Changed refrigerator storage temperature from 4°± 2°C to 0° to 6°C, not frozen.
Historical/Local Document Number	Reflect current practice	Added Analysis #12989
Scope	Reflect current practice	Added Analysis #12989
Apparatus and Equipment 4	Continuity	Removed unnecessary information on trap requirements
Reagents and Standards B.1.e	Correction	Changed cat # to 563807
Reagents and Standards B.1.f	Reflect current practice	Added the fractionation RT marker stock standard
Reagents and Standards B.2.j	Clarification	Added expiration date for RT marker intermediate
Reagents and Standards B.2.k	Reflect current practice	Added fractionation RT intermediate
Reagents and Standards B.3.b	Missing information	Added without headspace
Reagents and Standards B.3.e	Enhancement	Added expected ICV concentration of 440 ppb
Reagents and Standards B.3.f	Correction	CCV expire in 24 hours. Removed 48 hr in-house study.
Reagents and Standards B.3.g	Correction	Changed volumetric flask size from 500 mL to 200 mL, and added methanol amount
Reagents and Standards B.3.h	Reflect current practice	Added C8 marker
Instrument Operating Conditions 2.	Correction	Changed sample volume from 5 mL to 25 mL
Calibration C.4	Missing information	Added correlation coefficient requirement for OA-1
Table II, III	Correction	Removed unnecessary information

Reference:

1. *Test Methods for Evaluating Solid Wastes*, SW-846 Method 8015B, December 1996.

2. *Test Methods for Evaluating Solid Wastes*, SW-846, Method 8015B Modified, December 1996.

3. *Test Methods for Evaluating Solid Wastes*, SW-846 Method 8015C, February 2007.

4. *Test Methods for Evaluating Solid Wastes,* SW-846 Method 8015D, Rev. 4, June 2003.

5. OA-1 GRO (SW-846 8015B).

6. *Test Methods for Evaluating Solid Wastes*, SW-846 Method 5035, November 2004.

7. Missouri/Iowa Method OA-1, 1993.

8. *Chemical Hygiene Plan*, current version.

Cross Reference:

Document	Document Title
Analysis #1150, 6170, 11968, 11969	Preparation of Soil and Solid Samples for GC Volatile Analyses
Analysis #8389, 8390, 6130, 6117, 6174, 7578, 7320	Preparation of Soils for Volatile Analysis by EPA SW-846 Method 5035
1-P-QM-PRO-9015470	Preparation and Analysis of Cleaning Blanks for GC and GC/MS Volatiles
1-P-QM-PRO-9015491	Statistical Calculations Used in the Analysis of Samples by EPA Methodology
1-P-QM-QMA-9015390	Demonstrations of Capability
1-P-QM-QMA-9017309	Determining Method Detection Limits and Limits of Quantitation

Scope:

This method is based on a purge and trap, gas chromatography (GC) procedure and is used to determine the concentration of gasoline range organics (GRO) in soil. Generally, this corresponds to an alkane range of approximately C6 through C12. The carbon range can be modified to comply with differing regulatory needs.

The following is a list of the various analysis numbers used to report GRO using SW846 8015B method with the exception of analysis 10599 which uses SW846 8015C. OA-1 uses the 1637, 1638 analyses and is run identically to 8015B:

Analysis Number	Description	Range	Retention Time Marker – Start of Range	Retention Time Marker – End of Range	Reporting Limit mg/kg
1637	GRO	C6 – C10	2-methylpentane	1,2,4-trimethylbenzene	1
1638	GRO, used with BTEX scan	C6 – C10	2-methylpentane	1,2,4-trimethylbenzene	1
1700	GRO – Northern CA (special reporting limit)	C6 – C12	n-hexane	Naphthalene	100 µg/kg (MDL) 1000 µg/kg (LOQ)
1725	GRO – Northern CA	C6 - C12	n-hexane	Naphthalene	1
1726	GRO – Northern CA, with BTEX	C6 - C12	n-hexane	Naphthalene	1
2765	GRO – Louisiana	C6 – C10	n-hexane	n-decane	1
2766	GRO – Louisiana, with BTEX	C6 – C10	n-hexane	n-decane	1
5550	GRO – Southern CA, with BTEX	C5 – C12	First discernable peak after the methanol/solvent front (calibration standard)	Last discernable peak in the chromatogram (Naphthalene)	1
5551	GRO – Southern CA	C5 – C12	First discernable peak after the methanol/solvent front (calibration standard)	Last discernable peak in the chromatogram (Naphthalene)	1
10599	GRO	C6 – C10	2-methylpentane	1,2,4-trimethylbenzene	1
12989	Fractionated GRO	C5 – C12	First discernable peak after the methanol/solvent front (calibration standard)	Last discernable peak in the chromatogram (Naphthalene)	1
		C5 – C6	First discernable peak after the methanol/solvent front (calibration standard)	n-hexane	1
		>C6 – C8	n-hexane	n-octane	1
		>C8 – C10	n-octane	n-decane	1
		>C10 – C12	n-decane	Naphthalene	1

This method can be run in series with a photoionization detector (PID) to analyze for BTEX and oxygenates using SW846 Method 8020 or 8021.

Basic Principles:

Soil samples are dispersed in methanol, refer to Analysis #1150, 6170, 6130, and 6117 for specifics, to dissolve volatile organic constituents. A portion of this methanol extract is diluted into reagent water and analyzed by purge and trap gas chromatography. Detection is achieved by a flame ionization detector (FID). Quantitation is performed by comparing the area of all chromatographic peaks (including resolved and unresolved components) eluting between the retention times for the start and stop of the hydrocarbon range in the sample to the total area over that same range in a gasoline standard.

Interferences:

High levels of solvents or petroleum products may contain volatile compounds that may elute within the retention time of the GRO.

Samples can become contaminated by diffusion of volatiles through the sample vial septum. A trip blank carried through sampling, storage and handling can act as a check of such contamination.

Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. To reduce carryover, the sample syringe and/or purge vessel must be rinsed between samples with reagent water. Whenever a highly concentrated sample is analyzed, it must be followed by a instrument blank to check for cross-contamination.

The trap and other parts of the system are subject to contamination. Frequent bake-out and purging of the system may be required.

Each chromatogram is reviewed for interference. If an interfering peak is observed either just prior to or immediately after the surrogate peak or the contamination level in the sample causes the integrator to improperly set the baseline, manual integration may be needed.

Safety Precautions and Waste Handling:

See *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations.

The toxicity of all compounds used in this method has not been established. However, several of the compounds are considered carcinogens. Each compound must be treated as a potential health hazard. The major route of exposure is inhalation during the handling of any stock standards while preparing secondary dilution standards. Therefore, these stocks must be prepared in a fume hood to eliminate the risk of inhaling the vapors. Information concerning the known toxicity, properties, or any special handling precautions can be found in the material safety data sheets (MSDS) available from the Safety Officer. Safety glasses and lab coats are required as personal protective wear.

The solvents utilized in this procedure are disposed of in a solvent waste container. Expired standards in methanol are disposed of as hazardous waste. All working solutions prepared in reagent water are flushed down the sink with tap water. Methanolic extracts of samples are returned to the sample storage area for future disposal. Soil sample extracts are collected and disposed of as solvent waste.

Personnel Training and Qualifications:

All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and an annual documented Demonstration of Capability (DOC).

Initially, each analyst performing instrumental analysis must work with an experienced analyst for a period of time until they can independently calibrate the instrument, use the chromatography data system to set up sequences, perform the calculations, interpret chromatograms, perform instrument maintenance, and enter data into the LIMS. Proficiency is measured through documented audits of the tasks listed and over checking of data as well as an Initial Demonstration of Capability (IDOC). Refer to 1-P-QM-QMA-9015390 for specific requirements. Demonstration of Capability is performed annually and is maintained in the analyst's training records.

Sample Collection, Preservation, and Handling:

Samples are to be collected using the recommended sampling protocol in EPA SW-846, Method 5030A and 5035B. Samples are refrigerated at 0° to 6°C, not frozen, and must be analyzed within 14 days of collection.

Samples are prepped using a 1:1 ratio of soil to methanol in accordance to Analysis #1150, 6170, or Analysis #8389, 8390, 6130, 6117, 6174, 7578, 7320.

Apparatus and Equipment:

1. Gas chromatograph – Hewlett Packard 5890 or equivalent suitable for purge and trap sample introduction

2. Detector – FID (in series with a PID if BTEX constituents are to be analyzed along with GRO)

3. GC column – DB VRX GC column, 75m × 0.45 mm × 2.55 um, or equivalent, (capable of resolving early-eluting constituents from the solvent front and ethylbenzene from *m/p*-xylene when BTEX is performed in series)

4. Purge and trap concentrator (P&T) – O.I. Analytical Model 4560 or equivalent with the following specifications. The purging chamber (sparge) is designed to accept 25 mL of sample with a water column that is at least 12 cm deep. The gaseous headspace of the chamber must be <15-mL total volume.

5. Autosampler – OI Analytical model 4551, 4552, or equivalent

6. Syringes – 5-mL and 25-mL Luer-Lok gastight syringe

7. Microsyringe – various sizes from 10 to 1000-µL gastight syringes

8. Glassware

    a. Class-A Volumetric flasks with ground-glass stopper

    b. Vials, 1.5 –mL, 15-mL, and 40 mL screw cap, with Teflon™/silicone septa

9. Stainless-steel spatula

10. Mettler top-loading balance, or equivalent, capable of accurately weighing to the nearest 0.01 g

11. Integrating system such as Chrom Perfect® by Justice Laboratory Software, or equivalent. Chrom Perfect® is a data system capable of storing and reintegrating chromatographic data and determining peak areas using a forced baseline, area summation, baseline projection, and performing baseline compensation as required.

Reagents and Standards:

A. Reagents

1. Reagent water – Reagent water is defined as water in which an interferent is not observed at or above the reporting limit for parameters of interest. In general, the reagent water supplied at the taps in the laboratory meets this criterion. If the reagent water does not meet the requirements, see your supervisor for further instructions. Reagent water must be used to prepare all sample dilutions and working standards.

2. Methanol, P&T grade or equivalent, is used to extract all solid samples for analysis and to prepare all secondary dilution standards required for this method. Store at room temperature.

B. Standards

1. Stock standards

a. All stock standards are obtained from vendors and must contain paperwork indicating: expiration date of solution, components included, and their concentrations within the solution. The vendor must present this information, as well as an indication of component's purity, for traceability issues.

b. All stocks are stored in an explosion-proof freezer at -10° to -15°C until the expiration date indicated by the vendor.

c. Gasoline Calibration Stock Standard– Gasoline standard from Restek Corporation or equivalent. Restek Cat # 30237**,** concentration certified at 5500-ppm.

d. 15,000-ppm TFT surrogate stock standard – This standard is utilized to prepare a multi-level surrogate calibration that is required by many methods. Restek Cat #54357.

e. Matrix Spike Stock Standard – Gasoline standard from Supelco or equivalent. Cat # 47516-U concentration certified at 20,000-ppm. (Alternatively, Restek Cat # 30205, concentration at 50,000-ppm)

f. Surrogate Stock Standard – This stock is purchased in two versions: 2-component and 1-component.

(1) 2-component surrogate –Restek Cat# 58097 is utilized for all continuing calibration verification (CCV) standards. Refer to the following list for each component and its concentration in this standard:

Component	Concentration (ppm)
1-Chloro-3-fluorobenzene (1C3FB)	12,500
α,α,α-Trifluorotoluene (TFT)	12,500

(2) 1-component surrogate –Restek Cat# 58098 is utilized for all sample, blanks, Laboratory Control Standard (LCS), Matrix Spike (MS), Matrix Spike Duplicate (MSD), and calibration injections. Refer to the following list for each component and its concentration in this standard:

Component	Concentration (ppm)
1C3FB	12,500

TFT is utilized as a surrogate on the FID. However, TFT is introduced to the sample during the methanol extraction (see Analyses #1150, 6170, 6130, and 6117). 1C3FB is utilized as the internal standard on the PID.

g. Custom GRO Retention Time (RT) Marker Stock – Restek cat # 563807, contains 2-methylpentane, C6 (n-hexane), toluene, 1,2,4-TMB, C10 (n-decane), and naphthalene.

h. Fractionation RT Marker Stock – Restek cat # 30451, using as C8 RT marker during Analysis # 12989 only

2. Secondary dilution standards (intermediates)

a. Secondary dilution standards are stored in an explosion-proof freezer at -10° to -15°C in Teflon-lined screw-capped vials and expire in 30 days.

b. 550-ppm gasoline calibration standard B

Prepare by diluting 1.0 mL of gasoline calibration stock standard to a final volume of 10 mL in methanol.

c. 55-ppm gasoline calibration standard A

Prepare by diluting 0.5 mL of gasoline calibration standard B to a final volume of 5 mL in methanol.

d. 75-ppm TFT calibration Standard

Prepare by diluting 0.05 mL of TFT stock standard to a final volume of 10 mL in methanol.

e. 2000-ppm Gasoline Spike Intermediate

Prepare by diluting 1.0 mL of gasoline matrix spike stock to a final volume of 10 mL in methanol.

f. 75-ppm Surrogate intermediate standard (either 1- or 2-component stock standard)

Prepare by diluting 300 µL of surrogate stock to a final volume of 50 mL in methanol.

g. 750-ppm TFT Intermediate for Methanol Preserves/Extraction

Prepare by diluting 500 µL of TFT stock to a final volume of 10 mL in methanol.

h. 750-ppb TFT Methanol Extraction Solution

(1) Prepare by diluting 2 mL of TFT Intermediate for methanol Preserves to a final volume of 2000 mL in methanol.

(2) This final methanol extraction solution is then analyzed on a GC system by taking 2 mL of this standard, with 20 µL of 1-component surrogate, and add to reagent water to a final volume of 50 mL.

(3) After analyzing the surrogate recovery is then reviewed against the statistically derived surrogate recovery windows. If the % recovery is within the acceptable windows, the solution is then used to extract blanks, LCS, and samples. If the % recovery is outside of acceptable windows, the solution is discarded and reprepped.

i. RT Marker Intermediate

Prepare by diluting 1 mL of RT stock to a final volume of 10 mL in methanol. This has an expiration date of 6 months from opening of ampule.

j. Fractionation RT marker intermediate

Prepare by diluting 1 mL of fractionation RT stock to final volume of 10 mL in methanol. This has an expiration date of 6 months from opening of ampule.

3. Working standards

a. Aqueous standards, made from the secondary dilutions, are stored at 0° to 6°C, not frozen, prepared each day of use, and expire in 24 hours unless otherwise noted. They are transferred into 40mL vials for analysis without headspace.

b. Calibration Standards—All calibration standards are prepared in 50-mL volumetric flasks, by diluting the appropriate volume of the methanolic working standard with 20 µL 1-Component Surrogate and 2 mL methanol. (See Table I for volumes used for initial calibration standard preparation and for values of each calibration level.)

c. Method Detection Limit (MDL) – Add 8 µL of the gasoline calibration standard B and 80 µL of 2-Component Surrogate, into a 500-mL volumetric flask. Add 8 mL methanol and bring to a volume with reagent water yielding the MDL standard concentration at approximately 22 ppb.

d. Initial Calibration Verification (ICV) – Add 22 µL of gasoline spike intermediate and 40 µL of 2-Component Surrogate into a 100-mL volumetric flask. Add 4 mL of methanol and bring to volume with reagent water yielding the ICV concentration at approximately 440 ppb.

e. Continuing Calibration Verification (CCV) standards

(1) Add 80 µL of gasoline standard and 80 µL of 2-Component surrogate into a 200-mL volumetric flask. Add 8 mL methanol and bring up to volume with reagent water yielding the CCV at approximately 220 ppb.

(2) The CCV concentration can vary based on set client requirements (refer to project notes).

f. RT Marker

(1) Add 100 µL of the marker intermediate and 80 µL of 2 component surrogate into a 200-mL volumetric flask. Add 8 mL methanol and bring up to volume with reagent water.

(2) The retention time marker working standards expire in 14 days from the prep date.

g. C8 Marker

(1) Add 100 µL of the fractionation RT marker intermediate and 80 µL of 2 component surrogate into a 200-mL volumetric flask. Add 8 mL methanol and bring up to volume with reagent water.

(2) The expiration date is 14 days from the prep date.

Instrument Operating Conditions:

Below are the suggested operating conditions for the autosamplers, purge and traps, and gas chromatograph.

1. O.I. 4551 autosampler or Archon autosampler

Cool flow and chiller temperature	4°C
Rinses between samples	2
Needle depth	85% (OI only)

2. O.I. 4560 Concentrator or Tekmar LSC3000

Sample volume	25 mL
Purge	11 minutes at ambient temperature
Purge gas	He/N2 at ~40 mL/min
Sorbent trap	Tenax trap or equivalent
Desorb	Preheat to 180°C; desorb at 180°C for 4 min
Bake	10 minutes at 180°C

3. HP 5890 II Gas Chromatograph

Injector	Low dead volume injector – 220°C
Detector	FID at 250°C
GC oven	Start at 40°C and hold for 0.5 min; Ramp at 15°C/min to 140°C; Ramp at 5°C/min to 160°C; Ramp at 30°C/min to 250°C and hold for 5 min.

NOTE: Alternate parameters may be utilized, to optimize the chromatography. All QC criteria must be met, as well as maintaining proper separation and sensitivity.

4. FID gases

Column and make-up (He)	30 ± 2 mL/min
H_2 gas	35 ± 2 mL/min
Air	160 ± 5 mL/min

NOTE: Flows can be altered in order to optimize detector response.

Calibration:

A. Prior to calibration or analyzing samples utilizing the autosampler, make sure that the following is complete:

1. The autosampler is programmed and functioning properly.

2. Set the P&T and GC to the conditions specified under the Instrument Conditions section of this method. Program autosampler to start and end on the appropriate vials, then press “START.”

B. Retention Time Window

1. The gasoline range begins 0.1 minutes before the peak apex of marker compound for the start of the range, and ends 0.1 minute past the peak apex of marker compound for the end of the range. The retention times are determined by analyzing a retention time marker standard before every initial calibration and batch

2. Retention Time (RT) windows are established for the retention time marker hydrocarbons and surrogate by using ±3 standard deviation from the mean retention time for three standards injected over a 72-hour period. These marker hydrocarbons are used to determine the starting and stopping points for the GRO range to be quantitated. If the RTs for the continuing GRO standard fall outside the RT windows, update the hydrocarbon(s) midpoint retention times using that standard, the window stays the same. Also update the start and stop times used for the GRO range using the same standard. If RTs are not consistent, the cause must be investigated and corrective action taken.

C. Initial Calibration

1. The 5-point calibration (see Table I) is analyzed with gasoline concentrations ranging from approximately 27.5 to 1100 ppb (dependent on gasoline stock standard concentration). The surrogate concentration must also increase with increasing standard concentration.

2. Calibration is performed using the external standard method for FID detection.

   a. A calibration factor (CF) is calculated for each calibration level. See calculation section of this procedure.

   b. Area contributed by the surrogates is not included in the total gasoline area.

3. The percent relative standard deviation (%RSD) of the calibration factor must be ≤20% to assume linearity through the origin and use the average calibration factor (AVGCF) for quantitation. For OA-1, the correlation coefficient must be 0.995 or greater.

4. If the %RSD is >20%, a linear or quadratic calibration may be used in place of the average calibration factor as long as the correlation coefficient is greater than 0.99. At least 6 calibration levels must be utilized for a quadratic fit.

5. An ICV standard is also analyzed and must meet the same criteria established by the method. This criteria is ±15% difference for all scans except scan #10599 where the criteria is ±20%.

6. An MDL standard must be analyzed with every initial calibration. GRO must be visible for the standard to be acceptable

7. Instrument Blanks (IBLK) are analyzed to ensure the analytical system is free of contamination. Additional clean up blanks can be run as needed based on system performance.

D. Continuing Calibration Verification (CCV)

1. Prepare and analyze a CCV to ensure that the instrument is functioning correctly and that the calibration is valid.

2. The calibration curve is verified every 12 hours (or every ten field samples when run with PID in series, or if a client requires this frequency).

   A field sample is defined as any client submitted sample, matrix spike, or matrix spike duplicate sample. Blanks, LCS, and batch MS/MSD are NOT considered field samples.

3. The CCV standard criteria established by the method is ±15% difference for the calculated concentration versus the nominal concentration for all scans except Analysis #10599 where the criteria is ±20%.

4. Samples must be bracketed by acceptable CCVs, otherwise samples must be reanalyzed.

5. If the bracketing CCV fails requirements with a positive trend and GRO was below the reporting limit in the samples, then no re-analysis is required.

6. If the recovery of the GRO concentration is outside of the acceptable range, the CCV is repeated with freshly made standards.

    a. If the GRO concentration is within the acceptable range on the repeat, the standard is acceptable.

    b. If the freshly made CCVs fails and the problem appears to be instrument related, proper maintenance must be performed on the instrument that corrects the problem.

        (1) Having failed two previous CCVs, a series of two freshly made CCVs must now be analyzed and both must be within the acceptance criteria before continuing with sample analysis.

        (2) The samples associated with the failed standards must be repeated after passing CCVs.

    c. If the GRO concentration is still outside the acceptable range on the repeats, the system is recalibrated.

    d. All data must have an in-specification CCVs preceding it to be considered valid. If one CCV fails, but the second one passes, the samples still need to be repeated under the passing CCV.

Procedure:

A. Prior to analyzing samples utilizing the autosampler, make sure that the following is complete:

1. The autosampler is programmed and functioning properly.

2. Set the P&T and GC to the conditions specified under the Instrument Conditions section of this method. Program autosampler to start and end on the appropriate vials, then press "START."

3. If the system has not been calibrated, then calibrate the system (refer back to the calibration section).

B. Samples are analyzed by adding 2 mL of the sample's methanolic extract to reagent water and 20 µL of 1-component surrogate) in a 50-mL volumetric flask. Bring up to volume with reagent water. Pour into a 40-mL vial for sampling via the autosampler.

1. TFT surrogate is introduced to the sample during the methanol extraction (refer to Analyses #1150, 6170, 6130, and 6117).

2. If the prescreen of the extract indicates high levels of organics, a dilution must be made. When preparing dilutions, a constant amount of methanol (i.e., 1:25) must be maintained.

   Example: If a sample is to be analyzed at a dilution factor (df) of 250, 200 µL of the sample's extract and 1.8 mL of methanol are injected into reagent water in the 50-mL volumetric flask with 20 µL of 1-Component Surrogate.

C. Prepare a batch sequence. A batch can consist of up to 20 field samples and must contain a method blank, a laboratory control spike, and either a matrix spike/matrix spike duplicate when sufficient sample is available, or a laboratory control spike duplicate.

D. Samples must be bracketed by acceptable check standards, otherwise samples must be reanalyzed.

E. The total peak area (excluding the surrogate area) between the defined start and stop of the GRO range is used to calculate the concentration of GRO.

F. If the concentration of the analyte recovered in the sample exceeds the concentration of the highest level of the calibration, the sample must be repeated at a higher dilution.

G. The analyst must determine if carryover is present after an analysis of a sample containing high levels of analytes. It may be necessary to analyze a instrument blank to ascertain that all analytes are below the method detection limit. If they are not, the instrument blank is repeated until the system is acceptable. Refer to 1-P-QM-PRO-9015470, for more instruction on this.

Calculations:

The peak area summation of the entire gasoline pattern, excluding any surrogates and retention time markers, calculated with the dilution factor and the calibration factor will establish the concentration of GRO in the sample.

1. Calculation of GRO in a sample:

$$Conc\ (ppm) = \frac{\frac{Ar}{CF}}{1000} \times \frac{Vt}{Wt} \times DF$$

Where:

Ar = Area for the GRO in the sample

CF = Calibration factor

DF = Dilution factor (default of 25)

Wt = Weight of sample in extraction (default 10 g)

Vt = Total volume of MeOH during extraction (default 10 mL)

2. Calibration Factor (CF)

$$CF = \frac{Total\,Area}{Concentration\ (\mu g / L)}$$

3. The RPD is calculated as follows:

$$RPD = \frac{MS\ \text{Concentation} - MSD\ \text{Concentation}}{\left[\frac{MS\ \text{Concentation} + MSD\ \text{Concentation}}{2}\right]} \times 100$$

4. Refer to 1-P-QM-PRO-9015491, for further details on calculations.

Statistical Information/Method Performance:

Generate method detection limits (MDLs) and limits of quantitation (LOQs) according to 1-P-QM-QMA-9017309. Perform an MDL study on each instrument used for the analysis. Determine the MDL by taking seven spiked replicates through the entire extraction and analysis procedure. Compare and pool results to determine the final reporting MDL. The department supervisor maintains annual study data. The department supervisor requests that a QA Specialist update to the LIMS as needed. Update the department database via a download from the LIMS.

Quality Assurance/Quality Control:

A. Each batch (up to 20 samples) must contain a method blank, LCS, and either an unspiked background sample (US)/MS/MSD or an LCS/LCSD.

1. Method Blank – The method blank is analyzed once per 24 hours and is examined for possible contamination. All compounds must be less than the reporting limit of the project. If the blank values exceed these values, corrective action must be taken and the method blank reanalyzed until the criteria are met.

a. Prepare by adding 10 grams of clean sand into a 40-mL vial and extracting it with 10 mL of TFT for Methanol Extraction.

b. Then take 2 mL of this extract with 20 µL of 1-component surrogate and add to reagent water to a final volume of 50 mL.

c. The solution is then poured into 40-mL vials with screw-top Teflon-lined septa for use in the autosampler.

2. Surrogates – α,α,α-trifluorotoluene is the reported surrogate. Surrogate recovery is acceptable if the percent recovery is within the statistically derived windows. Lower recoveries are expected in diluted samples. If the surrogate recovery falls outside the acceptance window, re-extract the sample (if possible) and/or repeat the analysis. If the repeat is out of specification, report the original results and comment about the effect of the matrix on the surrogate. If the surrogate is within specifications on the repeat analysis, report the results from the repeat analysis.

3. MS and MSD—For each set of 20 field samples, extract one in triplicate, spiking the duplicate and triplicate with 55 µL of gasoline spike intermediate into sample extract. These are then diluted and analyzed as a normal sample. Approximate concentration of this standard is 11 mg/kg.

a. Results of the MS/MSD are compared to the QC limits that are statistically derived.

b. The maximum RPD (relative percent difference) allowed between the MS and MSD is 30%.

c. If any of the MS/MSD criteria fails, then an LCS is used to verify that the system is within specifications

4. LCS/ LCSD is prepared by adding 10 grams of clean sand to a 40-mL vial and adding 10 mL of TFT for methanol extraction. Spike the extraction with 55 µL of gasoline spike intermediate. Then take 2 mL of this extract with 20 µL of 1-Component Surrogate and add reagent water to a final volume of 50 mL. Approximate concentration of this standard is 440 µg/kg.

   a. If the LCS does not meet criteria, corrective action must be taken, including repeating the batch.

      Corrective action may include instrument maintenance, re-analysis of samples, or data qualification.

   b. If sufficient sample is not available to perform MS/MSD, LCS/LCSD are analyzed and must meet QC criteria.

B. QC limits for surrogates, LCS/LCSD, and MS/MSD are established through statistical analysis of historical data. The limits are evaluated every 6 months and updated as needed. The limits are maintained in the LIMS for the relevant analysis numbers.

Table I
Calibration Standards

Cal Level	Amt. Gasoline (µL)	Amt. TFT (µL)	Gas Conc. (µg/kg)*	TFT Conc. (µg/kg)
1	25 (A)	5	27.5	7.5
2	100 (A)	10	110	15
3	20 (B)	20	220	30
4	50 (B)	30	550	45
5	100 (B)	40	1110	60

* Based upon 5500-ppm gasoline stock and a 15,000-ppm TFT stock.

Appendix C

Data Validation SOPs

Appendix C

Data Validation SOPs

VALIDATION SOP

PCDDs/PCDFs
USEPA Region 2 SOP HW-25
Rev. 3, 12/10

SOP HW-25
Revision 3
December 2010

USEPA REGION II DATA VALIDATION SOP FOR EPA METHOD 1613, REVISION B
Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution (HRGC/HRMS)

PREPARED BY: _____ DATE: 12/22/10
Russell Arnone, Chemist HWSS

PEER REVIEWED BY: _____ DATE: 12/22/10
Muhammad Sheikh, Chemist, HWSS

CONCURRED BY: _____ DATE: 12/29/10
Michael Mercado, Acting Chief
Hazardous Waste Support Section

APPROVED BY: _____ DATE: 1/12/11
Robert Runyon, Chief
Hazardous Waste Support Branch

Annual Review

Reviewed by: _____ DATE: _____
Name

Reviewed by: _____ DATE: _____
Name

SOP HW-25
Revision 3
December 2010

USEPA REGION II DATA VALIDATION SOP FOR EPA METHOD 1613, REVISION B
Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution (HRGC/HRMS)

PREPARED BY: _____ DATE:_____
Russell Arnone, Chemist HWSS

PEER REVIEWED BY:_____ DATE:_____
Muhammad Sheikh, Chemist, HWSS

CONCURRED BY:_____ DATE:_____
Michael Mercado, Acting Chief
Hazardous Waste Support Section

APPROVED BY:_____ DATE:_____
Robert Runyon, Chief
Hazardous Waste Support Branch

Annual Review

Reviewed by:_____ DATE:_____
Name

Reviewed by:_____ DATE:_____
Name

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Optional Quality Control and Assurance Requirements for Validation

I.0 Introduction

This method was developed by the Engineering and Analysis division within the USEPA's Office of Science and Technology. The method is used for isomer specific determination to detect the Tetra- through octa- chlorinated dibenzo-p-dioxins and dibenzofurans associated with the Clean Water Act (CWA, as amended 1987); the Resource Conservation and Recovery Act (RECRA, as amended 1986); the Comprehensive Environmental Response, the Compensation and Liability Act (as amended in 1986); and the Safe Drinking Water Act and other dioxin and furan compounds amenable to this method.

The dioxins and furans may be determined in water, soil, sediment, sludge, tissue, and other matrices using this method. The method is based on EPA, industry, and academic methods.

2.0 Applicability

The attached Standard Operating Procedure (SOP) is applicable to chlorinated dibenzodioxin and chlorinated dibenzofuran (CDD/CDF) data obtained using EPA Method 1613B, Polychlorinated Dibenzodioxins (CDDs) and Polychlorinated Dibenzofurans (PCDFs) by Isotope Dilution using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), October 1994. Its scope is to facilitate the data validation process of the data reported by the contracting laboratory and to ensure that the data is being reviewed in a uniform manner. This SOP is based upon the quality control and quality assurance requirements specified in Method 1613B, October 1994.

3.0 Responsibilities/Scope

3.1 The reviewer must be knowledgeable of the analytical method and its QC Criteria.

3.2 The reviewer must complete the following:

3.2.1 Data Assessment Checklist - The data reviewer must read each item carefully and must check yes if there is compliance, no if there is non compliance and N/A if the question is not applicable to the data.

3.2.2 Data Assessment Narrative - The data reviewer must present professional judgement and must express concerns and comments on the validity of the overall data package. The reviewer must explain the reasons for rejecting and/or qualifying the data. Example of Data Assessment format is provided in Attachment A.

3.2.3 Communication Record Log - All communication must be in writing, and it must be documented on the Communication Record Log Sheet. A photocopy of the Communication Record Log is attached to the Data Assessment package.

3.2.4 Paperwork - Upon completion of the review the following are to be maintained with the data package and returned to the authorized person :

a. completed data assessment checklist and narrative (original)
b. Two copies of the data assessment narrative
c. Communication record Log (original and copy)

3.3 Rejection of Data - All values determined to be unacceptable on the Dioxin/Furan Analysis Data Sheet (Form I) must be flagged with an "R". The qualifier R means that due to significant QA/QC problems the analysis is invalid and it provides no information as to whether the compound is present or not. Once the data are flagged with R any further review or consideration is unnecessary. The qualifier "J" is used to indicate that due to QA/QC problems the results are considered to be estimated. The qualifier "NJ" indicates that there is presumptive evidence for the presence of the compound at an estimated value.

The data reviewer must explain in the data assessment narrative why the data was qualified. He or she must also indicate all items of contract non-compliance. When 2,3,7,8- substituted TCDD, TCDF, PeCDD and PeCDF data are rejected (flagged "R") or qualified "J" the project officer must be notified promptly. If holding times have not been exceeded reanalysis of the affected samples may be requested. All qualifications and corrections on the Analysis Data Sheet must be made in red pencil.

4.0 Definitions

CALIBRATION SOLUTION: solutions containing known amounts of selected analytes, internal standards and recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CALIBRATION VERIFICATION (VER): a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time window for each homologue.

CDD: Chlorinated Dibenzo-p-Dioxin. The isomers and congeners of tetra- through octa-chlorodibenzo-p-dioxin.

CDF: Chlorinated Dibenzofuran. The isomers and congeners of tetra- through octa-chlorodibenzofurans.

CLEAN-UP STANDARD: only one labeled analyte (2,3,7,8-TCDD) is added to all samples extracts prior to any Clean-up procedure. This standard is used to differentiate between losses of analytes or internal standards during extraction and losses that occur during the various Clean-up procedures.

CONGENER: elements of the same group in the periodic table.

DEFLECTIONS: bend or broadening of a peak

ESTIMATED DETECTION LIMIT (EDL): the concentration of a analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level.

ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC): the concentration of a given analyte that would produce a signal with a given area peak. The EMPC is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and/or confirmation ions has signal to noise in excess of 2.5 times the background level but does not meet identification criteria.

Field Blank: An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

FIELD CHAIN OF CUSTODY: see Traffic Report

GC: Gas chromatograph or gas chromatography**.**

GEL PERMEATION CHROMATOGRAPHY (GPC): removes many high molecular weight interferences that cause GC column performance to degrade. It may be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds.

HOMOLOGUE: a member or members of a particular homologous series that has the same molecular weight but not necessarily the same structural arrangement. For example, the 28 pentachlorinated dibenzofurans are homologues.

HPLC: high performance liquid chromatography

HRGC/HRMS: high resolution gas chromatography/ high resolution mass spectrometry.

INITIAL CALIBRATION STANDARD SOLUTION (CS1-CS5): analysis of analytical standards for a series of different specified concentrations. The initial calibration is used to define the linearity and dynamic range of the response of the mass

spectrometer to the target compounds.

INITIAL PRECISION AND RECOVERY (IPR): must be performed by the laboratory to establish the ability to generate acceptable precision and accuracy by analyzing four aliquots of the diluted PAR standard. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6). An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

INTEGRATED ION CURRENT: electronic output to computer from instrument to provide a hard copy of area and height of a peak that may or may not be an analyte of interest.

INTERNAL STANDARDS (IS): labeled analytes are added to every sample and are present at the same concentration in every blank, quality control sample, and calibration solution. The IS are added to the sample before extraction and are used to measure the concentration of the analytes. In Method 1613B, the ISs are $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD.

ION ABUNDANCE RATIO: mathematical comparison of selected pair of ions stipulated by the method for each target analyte. The ratio between each pair of ions must fall within established limits. These ions are needed for the identification and quantitation of target analytes.

ISOMER: chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

LABELED ANALYTE (or analog): an analyte that has isotopically carbon added to its chemical structure. These compounds are used to established identification (retention time) and used for quantitation of unlabeled analytes.

MASS/CHARGE: usually expressed as m/z.

METHOD BLANK (MB): an analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The MB is used to define the level of laboratory background contamination.

Minimum Level (ML): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point to the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and clean up procedures have been employed.

MAXIMUM CONCENTRATION LEVEL (MCL): Highest level of concentration for each analyte depending upon upper concentration of analyte. Usually used to determine upper level of the concentration range.

NON-CONGENER: elements not from the same group in the periodic table.

NON-2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure have positions other than 2,3,7,8.

ONGOING PRECISION AND RECOVERY (OPR): must be performed by the laboratory to establish the ability to maintain on a continuous basis, acceptable precision and accuracy. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table **6**).

PAR: Precision and Recovery standard. Secondary standard that is diluted and spiked to form IPR and OPR. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6).

PERCENT MOISTURE: an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at this degree including water. %M is determined from decanted samples and from samples that are not decanted.

PERCENT VALLEY: see Resolution

PERFLUOROKEROSENE (PFK): compound used to establish mass spectral instrument performance for dioxin/furan analysis.

PERFORMANCE EVALUATION MIXTURE (PEM): See Performance Evaluation (PE) Sample,

PERFORMANCE EVALUATION (PE) SAMPLE: a chemical waste, soil or water sample containing known amounts of unlabeled CDDs/PCDFs used for Quality Assurance programs. There are 3 types of PE's available. PEM Blank which consists of uncontaminated soil and used to monitor possible crossover contamination of samples in the field and laboratory. PEM Interference Fortified Blank which is a soil containing matrix interference and spiked by the laboratory with target compounds. A PEM sample(s) is a soil sample containing known amounts of unlabeled TCDD or a mixture of TCDD and other PCDD/PCDF isomers. These PEMs are used to monitor the laboratory's performance.

PCDPE: Polychlorinated Diphenylether: isomers having the same SICP and ion ratios identical to furan isomers and are monitored for interference in furan qualitative and quantitative analysis.

Quality Control Check Sample (QCS): A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

RECOVERY: a determination of the accuracy of the analytical procedure made by comparing measured values from a fortified (spiked) sample against the known spiked values. Recovery is determined by the following equation:

$$\% \text{ Recovery} = \frac{\text{measured value}}{\text{known value}} \times 100\%$$

RELATIVE RETENTION TIME (RRT): ratio of the retention time of the analyte versus the retention time of the corresponding internal standard. RRT for each analyte must be within range established by the method.

RELATIVE RESPONSE (RR): the ratio of the area response of the mass spectrometer to a known amount of an analyte (unlabeled to labeled) versus a known concentration in standard solution, plotted using linear regression. The RR is used to determine instrument performance and is used in the quantitation calculations. RR are calculated using the following equation:

$$RR = \frac{(A_n^1 + A_n^2)\, C_l}{(A_l^1 + A_l^2)\, C_n}$$

$A_n^1 + A_n^2$ are the areas of the primary and secondary m/z's for the unlabeled compound.

$A_l^1 + A_l^2$ are the areas of the primary and secondary m/z's for the labeled compound.

C_l is the concentration of the labeled compound in the calibration standard.

C_n is the concentration of the unlabeled compound in the calibration standard.

Relative Standard Deviation (RSD): The standard deviation times 100 divided by the mean. Also termed “coefficient of variation”.

RESPONSE FACTOR (RF): the ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of internal standard as measured in the initial and continuing calibrations. The RF is used to determine instrument performance using correlation coefficient and is used in the quantitation calculations. RF are calculated using the following equation:

$$RF = \frac{(A_s^1 + A_s^2)\, C_{is}}{(A_{is}^1 + A_{is}^2)\, C_s}$$

$A_s^1 + A_s^2$ are the areas of the primary and secondary m/z's for the compound to be calibrated.

$A_{is}^1 + A_{is}^2$ are the areas of the primary and secondary m/z's for the internal standard.

C_s is the concentration of the compound in the calibration standard.

C_{is} is the concentration of the internal standard.

RESOLUTION: the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RINSATE: a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SAMPLE DELIVERY GROUP (SDG): a unit within a single case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer samples within a case, received over a period of time up to 14 calendar days. Data from all samples in a SDG are due concurrently. A SDG is defined by one of the following, whichever occurs first:

- Case; or
- each 20 samples within a case; or
- each 14 day calendar period during which samples in a case are received, beginning with receipt of the first sample in the case or SDG.

SELECTED ION MONITORING (SIM): a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SICP: A plot of ion abundance versus time for each ion which provides the retention time, peak area and height. This information is used for identification and quantitation of target analyte.

SIGNAL TO NOISE (S/N) RATIO: the ratio of analyte signal to random background signal. To determine the ratio, display each characteristic ion using a window 100 scans wide, and draw a base line from the lowest point in the 100 scan window. The noise is defined as the height of the largest signal (excluding signal due to CDDs/PCDFs or other chemicals) within the 100 scan window. The signal is defined as the height of the PCDD/PCDF peak. If the data system determines the ratio, the Contractor shall demonstrate comparability between the above criteria and the automated S/N determination. Chemical noise is left to the judgement of the analyst.

2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure has other positions as well as the 2,3,7,8 positions.

TOXICITY EQUIVALENCY FACTOR (TEF): a method of converting concentrations of CDDs/PCDFs to an equivalent concentration of 2,3,7,8-TCDD to obtain an estimation of the toxicity of the entire sample. The concentrations can be found on Form I PCDD-2 in the DFLM01.1 Statement of Work for Dioxin Analysis.

TRAFFIC REPORT (TR): (may also be called Field Chain of Custody), a sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and documents sample condition and receipt by the laboratory.

TWELVE HOUR TIME PERIOD: the 12 hour time period begins with the injection of the CS3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12 hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period,

a sample or standard must be injected with 12:00 hours of the CS3 solution or the column performance solution.

UNLABEL ANALYTE: target compound that has not been isotopically altered.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR): the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample traffic report.

WINDOW DEFINING MIXTURE (WDM): a mixture containing the first and last eluting isomer for each congener. The retention time for each first and last eluting isomer establishes the retention time window for each congener. All analytes in the standards (calibrations, internal standards, recovery standards, Clean-up standard) and identified analytes in samples must have a reported retention time within the established window. It is analyzed before any calibration standard, at the beginning of each 12 hour time period or when there is a shift greater than 10 seconds between retention time of recovery standards in standards or any analysis from retention time in recent calibration verification.

YES NO N/A

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____LAB:_____
SITE:_____

I.0 Data Completeness and Deliverables

1.1 Does the Traffic Report or Field Chain of Custody list all samples? [___] ___ ___

1.2 Is the Case Narrative present? [___] ___ ___

1.3 Are the Case Number and SDG numbers contained in the case narrative? [___] ___ ___

1.4 Do the Traffic Reports, Field Chain of Custody or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical problems, or other comments affecting the quality of the data? ___ [___] ___

ACTION: Use professional judgement to evaluate the effect of the noted problems on the quality of the data.

ACTION: As per region II requirements, if any sample analyzed as a soil, contains 50% to 90% water, all data shall be flagged as estimated “J”. If a soil sample Contains more than 90% water, then qualify positive hits “J”, and non detects “UJ”.

ACTION: If sample cooler temperature was greater than 10 C, then flag all positive hits “J” And non detects “UJ”.

2.0 Reporting Requirements and Deliverables

2.1 All deliverables must be clearly labeled with the Case number and the associated sample/traffic number. Missing or illegible or incorrectly labeled items must be identified. The Project Officer must immediately be contacted and requested to ask laboratory to submit the missing or incorrect items.

2.2 The following forms were taken from the CLP SOW, DFLM01.1 and should be specified in the Project Plan. Laboratories will not always use the exact CLP format for the forms. A comparison of CLP forms must be made against the Laboratory's version. Some information may not be found on the exact form as the CLP version but may be located on another form. As long as the information is present and accessible, it is not a problem. Are these forms (CLP or lab's version) present?

a. Sample Data Summary (Form I CDD-1) [___] ___ ___

b. CDD/CDF Toxicity Equivalency Factor (Form I, CDD-2) [___] ___ ___

c. Second Column Confirmation Summary (Form I, CDD-3) [___] ___ ___

d. Total Homologue Concentration Summary (Form II CDD) [___] ___ ___

e. CDD/CDF Spiked Sample Summary (Form III CDD-1) [___] ___ ___

f. CDD/CDF Duplicate Sample Summary (Form III CDD-2) [___] ___ ___

g. CDD/CDF Method Blank Summary (Form IV-CDD) [___] ___ ___

	YES	NO	N/A
h. CDD/CDF Window Defining Mix Summary (Form V-CDD-1)	[___]	___	___
I. Chromatographic Resolution Summary (Form V CDD-2)	[___]	___	___
j. CDD/CDF Analytical Sequence Summary (Form V CDD-3)	[___]	___	___
k. Initial Calibration (Form VI, CDD-1, CDD-2)	[___]	___	___
l. Continuing Calibration (Form VII, CDD-1, Form VII, CDD-2)	[___]	___	___

ACTION: If forms are missing, contact the Project Officer to confirm which forms if any were specified in the Project Plan. If the forms are required, inform the Project Officer or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.3 GC/MS Displays
Are the following GC/MS displays present?

a.	Standard and sample SIM chromatograms. SIM and TIC chromatograms must list date and time of analysis; the file name; sample number; and instrument I.D. number	[___]	___	___
b.	Percent peak resolution valley	[___]	___	___
c.	Window Defining Mixture raw data	[___]	___	___
d.	SIM mass chromatograms must display quantitation ion, confirmation ion, and polychlorinated diphenylether ion, where applicable.	[___]	___	___
e.	Integrated area and peak height must be listed for all peaks 2.5 times above background	[___]	___	___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.4 Are the following Chain of Custody Records and in-house Laboratory Control Documents present?

a.	Chain of Custody Records	[___]	___	___
b.	Sample Shipment Records	[___]	___	___
c.	Sample log-in sheets	[___]	___	___
d.	GC/MS Standard and Sample Run Log in chronological order	[___]	___	___
e.	Sample Extraction Log	[___]	___	___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the

YES NO N/A

effect on the validity of the data. Note in the Data Assessment.

2.5 Was the sample data package paginated and one sided? [___] ___ ___

ACTION: If no, document difficulties of reviewing data caused by lack of pagination in Data Assessment.

3.0 Holding Times

3.1 Have samples been analyzed within proper holding times?

a. For aqueous samples, 30 days from VTSR to extraction? [___] ___ ___

b. For soil/sediment samples, 30 days from VTSR to extraction? [___] ___ ___

c. For fish and tissue samples, one (1) year from VTSR to extraction? [___] ___ ___

d. For all samples 45 days from time of extraction to time of analysis? [___] ___ ___

ACTION: If holding times are exceeded, flag all positive hits as estimated ("J"), and non-detects as estimated "UJ". Holding time criteria do not apply to PE samples.
If holding times are grossly exceeded (e.g. by greater than two times the specified Technical holding times), either on the first analysis or upon reanalysis, flag positive hits as estimated "J", and flag non-detects as unusable "R".

Note: The data reviewer must note whether or not technical and contractual holding times were met.

4.0 Instrument Performance

4.1 Mass Calibration - Mass calibration of the MS must be performed prior to analyzing calibration solutions, blanks, samples, and QC samples. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. Include in the narrative, minimum required resolving power of 10000 was obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm, i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

Resolving Power = $m/\triangle m$ = 380.9760/0.038 = 10025.

NOTE: The mass calibration is generally not reported. Improper mass calibration may be detected by examining ion abundance ratios for initial and continuing calibration standards. If the mass calibration is not properly performed, the standards will not have ion abundance ratios within criteria.

4.2 Window Defining Solution/ Isomer Specificity Test Standards

The Window Defining Solution must contain the first and the last isomers of each homologue CDD/CDF, (the labeled and internal standards are optional). The solution also should contain a series of other TCDD analytes for the purpose of documenting the chromatographic resolution.

4.2.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of Isomer Specificity Test Standards at the beginning of every 12 hour period. Was this performed accordingly? [___] ___ ___

YES NO N/A

ACTION: If the Isomer Specificity Test Standards was not analyzed at the required frequency, use professional judgement to determine the effect on the quality of the data. Document in Data Assessment under contract non-compliance.

4.2.2 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)? [___] ___ ___

4.2.3 Did the absolute retention time of the internal standards $^{13}C_{12}$-1,2,3,4-TCDD exceed 25.0 minutes on the DB-5 column and 15.0 minutes on the DB-225 column? (Method 1613B, Section 10.2.4) [___] ___ ___

4.2.4 Are the relative retention times of native and labeled CDD's and CDF's within the limits given in Table 2 of the method. (Method 1613B, Section 15.4.1.2) [___] ___ ___

ACTION: If no for sections 4.2.2, 4.2.3 and 4.2.4, assess the effect on the validity of the data. Note in the Data Assessment.

4.2.5 For DB-5 or equivalent, (Method 1613B, Section 15.4.2.2) the peak separation between the unlabeled 2,3,7,8-TCDD and the peaks representing any other TCDD analyte shall be resolved with a valley of $\leq$ 25 percent.
Was this criteria met? [___] ___ ___

% Valley = (x/y) x (100)

Y = The peak height of 2,3,7,8-TCDD analyte

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

ACTION: If the percent valley criteria are not met, qualify all positive data "J". Do not qualify non-detects.

4.2.6 Is the last eluting tetra chlorinated congener (1,2,8,9-TCDD) and the first eluting penta chlorinated congener (1,3,4,6,8-PeCDF) separated properly, since they elute within 15 seconds of each other? [___] ___ ___

ACTION: If one of the congener is missing, report that in the Data Assessment.

5.0 Initial 5-Point Calibration

The initial calibration standard solutions (CS1-CS5) must be analyzed prior to any sample analysis. However, initial calibration should be analyzed when the CS3 Calibration Verification (VER) or Isomer Specificity Test Standard do not meet performance criteria. The initial calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the Window Defining **Solution** and the Isomer Specificity Test Standards.

Was the initial calibration performed at the frequency specified above? [___] ___ ___

5.1 The method allows the Laboratory to perform quantitative analysis by isotope dilution and internal standard, or to combine calibration solutions.

1. Isotope Dilution: performed for the fifteen 2,3,7,8-substituted CDDs and CDFs unlabeled analytes with labeled analytes added to the samples prior to extraction and for 1,2,3,7,8,9-HXCDD and OCDF (see sections 5.2.8 and 5.2.9). The relative response (RR) is calculated

and the percent coefficient of variation must be 20% over the 5 point range (1613B sec. 10.5.4) to use the average relative response for quantitation, otherwise a calibration curve

YES NO N/A

must be used..

2. Calibration by Internal Standard: performed for non-2,3,7,8 substituted compounds having no labeled analytes in this method and for measurement of labeled compounds for intra laboratory statistics.. The response factor (RF) is calculated and the percent coefficient of variation must be 35% over the 5 point range (1613B sec. 10.6.3) to use the average response factor for quantitation, otherwise a calibration curve must be used.

3. Combined Calibration: performed by using solutions containing unlabeled, labeled compounds and internal standards. The requirements of each of the above methods are used. This method allows the laboratory to produce a single set of curves for isotope dilution and internal standard method.

5.1.1 The following MS/DS conditions must be used:

5.1.1.1 Mass calibration as per Section 4.1? [___] ___ ___

5.1.1.2 Were SIM data acquired for each of the ions listed in Table 8, including interfering ions? (see analytical method) [___] ___ ___

5.2 Were the following GC criteria met?

5.2.1 The chromatographic resolution between the 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent on the primary analysis (DB-5) column (1613B sec. 15.4.2.2). [___] ___ ___

5.2.2 The chromatographic resolution between the 2,3,7,8-TCDF and the peaks representing any other unlabeled TCDF isomers must be resolved with a valley of ≤ 25 percent on the confirmation (DB-225 or SP2330) analysis column. [___] ___ ___

5.2.3 For all calibration solutions, the relative retention time of peaks representing an unlabeled 2,3,7,8- substituted CDD or CDF must be within the limits given in table 2 of the Method. The retention times of the peaks representing non-2,3,7,8- substituted CDD or CDF's must fall within the retention time windows established by the Window Defining Solution. In addition, the absolute retention times of internal standards, $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD shall not change by more than 15 seconds between the CS3 analysis and the analysis of any other standard. [___] ___ ___

5.2.4 Are the two SIM ions for each homolog must maximize simultaneously and within 2 seconds of the corresponding labeled analyte ions?(1613B sec. 16.1) [___] ___ ___

5.2.5 The relative ion abundance criteria for CDDs/CDFs listed in Table 9 (see analytical method) must be met. [___] ___ ___

5.2.6 For all calibration solutions the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be ≥ 10. [___] ___ ___

5.2.7 The percent relative standard deviations (% RSD) for the mean response factors (RRF) from the 17 unlabeled standards must be ≤ 20%, and those for the 15 labeled reference compounds must be ≤ 35%. [___] ___ ___

5.2.8 Labeled analyte 1,2,3,7,8,9-HxCDD is used as an internal standard in this method, and can not be used to quantitate corresponding unlabeled analyte. The unlabeled 1,2,3,7,8,9-HxCDD must be

YES NO N/A

quantitated using the average of the responses of the labeled analytes of 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. The concentration of the unlabeled 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other HxCDD's. Was the unlabeled 1,2,3,7,8,9-HxCDD quantitated correctly? [___] ___ ___

5.2.9 The labeled analog of OCDF is not added to the sample because of a potential interference. Unlabeled OCDF is quantitated against the labeled OCDD. The concentration of the unlabeled OCDF is corrected for the recovery of the labeled OCDD. Was the unlabeled OCDF correctly quantitated against the labeled OCDD. [___] ___ ___

ACTION:

1. If mass calibration criteria as specified in Section 4.1 was not met, note in Data Assessment.

2. If the selected monitoring ions specified in Table 8 were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.

3. If the 25% percent valley for TCDD requirement was not met, quality positive data "J". Do not qualify non-detects. The tetra and penta (dioxins and furans) are affected. Heptas, Hexas and Octas are not affected.

4. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

5. If the ion abundance ratio for an internal or labeled standard falls outside the QC limits flag the associated positive hits with "J". No effect on the non-detects.

6. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.

7. If the %RSD for each unlabeled analyte exceeds 20%, or the %RSD for each labeled analyte exceeds 35%, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

8. If 1,2,3,7,8,9-HxCDD was not calculated using the correct HxCDD response (average) factor, either manually recalculate the values for all standards and samples or contact Project Officer to request resubmittals from the laboratory.

9. If OCDF was not calculated using the correct response factor (OCDD), either manually recalculate the values for all standards and data or contact Project Officer to request resubmittals from the laboratory.

10. Non compliance of any other criteria specified above should be evaluated using professional judgement.

5.2.10 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CDDs/CDFs and labeled standards were used. In addition, verify that the appropriate labeled standard was used for each analyte.

To recalculate the response factor, use the equation:
For target compounds (unlabeled analytes with corresponding labeled analytes):

$$RR = \frac{(A_{n1} + A_{n2}) \times Q_l}{}$$

YES NO N/A

$(A_{l1} + A_{l2}) \times Q_n$

For labeled analytes, Internal standards and cleanup standard listed in Table 6 of method 1613:

$$RF = \frac{(A_{l1} + A_{l2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times Q_l}$$

Note: There is only one m/z for $^{37}Cl_4$2,3,7,8-TCDD.

$A_{n1} + A_{n2}$ = integrated areas of the two quantitation ions of analytes of interest. (Target analyte, unlabeled compounds)

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled analytes compound.

$A_{is1} + A_{is2}$= integrated areas of the two quantitation ions of the appropriate internal standard.

Q_n = quantity of the unlabeled PCDD/PCDF analyte injected [pg]

Q_l = quantity of the appropriate labeled analytes compound [pg]

Q_{is} = quantity of the appropriate internal standard injected [pg]

ACTION: If calculations were not performed correctly, notify the Project Officer to initiate resubmittals from the laboratory.

6.0 System and Laboratory Performance (Calibration Verification and Isomer Specificity Test Standard)

At the beginning of a 12 hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all unlabeled and labeled compounds. For these tests the calibration verification (VER) standard and the isomer specificity test standards shall be used to verify all performance criteria.

Only if the laboratory meets all performance criteria may samples, blanks, and precision and recovery standards be analyzed.

6.1 Calibration Verification

6.1.1 Was the relative ion abundance for CDDs/CDFs listed in Table 9 of the analytical method met? (Method 1613B, Section 15.3.2) [___] ___ ___

6.1.2 Were the peaks representing each unlabeled and labeled compound in the verification standard present with signal to noise ratio (S/N) of $\geq$ 10? (Method 1613B, Section 15.3.3) [___] ___ ___

6.1.3 For each compound, was the concentration within the limit in Table 6 of the method? (Method 1613B, Section 15.3.5) [___] ___ ___

6.1.4 Were the absolute retention time of the internal standards $^{13}C_{12}$-1,2,3,4- TCDD and $^{13}C_{12}$1,2,3,7,8,9- HxCDD within $\pm$ 15 seconds of the retention times obtained during calibration? (Method 1613B, Section 15.4.1.1) [___] ___ ___

6.1.5 Were the relative retention times of the unlabeled and labeled CDDs and CDFs within the limits given by Table 2 of the method? (Method 1613B, Section 15.4.2.2) [___] ___ ___

YES NO N/A

6.2 Isomer Specificity Test Standard

6.2.1 Was the chromatographic resolution between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers resolved with a valley of ≤ 25 percent on the primary analysis (DB-5) column? (Method 1613**B**, Section **15**.4.2.2)
[___] ___ ___

6.2 Was the chromatographic resolution between 2,3,7,8- TCDF and the peaks representing any other unlabeled TCDF isomers resolved with a valley of ≤ 25 percent on the confirmation (DB-225 or SP2330) analysis. [___] ___ ___

ACTION:

1. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

2. If the signal noise ratio (S/N) is below control limits, use professional judgement to determine the quality of the data.

3. If an analyte concentration fell outside the acceptance criteria listed in Table 6 of the method.

   A. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte exceeds the range, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

   B. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte is below the range, flag the associated sample positive results as well as non-detects for that specific analyte as estimated ("J").

   C. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte is excessively below, ≤ 10% of the range, at the minimum, flag the associated sample positive results as well as non-detects for that specific analyte as estimated ("J"). However the validator may use professional judgement to accept or reject positive data and non-detects.

4. If the 25 percent valley for TCDD and TCDF requirement was not met, qualify positive data "J". Do not qualify non-detects. The tetras and pentas (dioxin and furans) are affected. Heptas, Hexas and Octas are not affected.

5. Non compliance of any other criteria specified above, in the method should be evaluated using professional judgement.

6.3 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CDDs/CDFs and labeled standards were used. In addition, verify the appropriate labeled standard was used for each analyte.

7.0 Sample Data

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration column.

7.l Were the following MS/DS conditions used?

7.1.1 SIM data were acquired for each of the ions listed in Table 8 (see analytical method)

		YES	NO	N/A
	including diphenylether interfering ions.	[___]	___	___
7.2	Were the following identification criteria met?			
7.2.1	For the 2,3,7,8 substituted analytes found present and the corresponding labeled compound or internal standard in the sample extract, must show relative retention times at the peak height within the limits given in Table 2. (Method 1613B, Section 16.4)	[___]	___	___
7.2.2	For non-2,3,7,8 substituted compounds (tetra through octa) found present, the retention time must be within the window established by the Window Defining Solution, for the corresponding homologue (Method 1613B, Section 16.4)	[___]	___	___
7.2.3	All specified ions listed in Table 8 for each isomer found present and the associated labeled compounds must be present in the SICP. The two SIM ions for the analyte, the labeled compound, and the internal standard must maximize simultaneously.(± 2 sec.) (Method 1613B, Section 16.1)	[___]	___	___
7.2.4	The integrated ion current for each characteristic ion of the analyte identified as positive, must be at least 2.5 times background noise and must not have saturated the detector. (Method 1613B, Section 16.2)	[___]	___	___
7.2.5	The integrated ion current for the labeled compounds, internal standards, and cleanup standard characteristic ions must be at least 10 times background noise. (Method 1613B, Section 16.2)	[___]	___	___
7.2.6	The relative ion abundance criteria for all CDDs/CDFs found present must be within the limits of Table 9, or 10% of the ratio in the midpoint CS3 calibration or calibration verification (VER) whichever is most recent.	[___]	___	___
7.2.7	The relative retention time of the unlabeled 2,3,7,8-substituted PCDD or PCDF must be within the limits given in Table 2 (Method 1613B, Section 16.4).	[___]	___	___
7.2.8	The relative ion abundance criteria for the labeled compounds, cleanup, and internal standard must be met (Table 9 - Method 1613B).	[___]	___	___
7.2.9	The analyte concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range. Was this criterion met?	[___]	___	___

NOTE: The analytical method clearly states that samples containing analytes having concentrations higher than 10 times the upper MCLs should be analyzed using a less sensitive, high resolution GC/low resolution MS method.

7.2.10	The identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected at the same time in the corresponding polychlorinated diphenylether (PCDPE) channel. Was the above condition met?	[___]	___	___

ACTION:
1. If the selected monitoring ions specified in Table 3 were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.
2. If the retention time of an analyte falls outside the retention time windows established by the associated Window Defining Mixture take the following action:

YES NO N/A

A. If the analyte has a corresponding labeled analyte and is within 2 seconds of the labeled analyte, no action taken on positive data or non-detects.

B. If the analyte has a corresponding labeled analyte and is outside 2 seconds of the labeled analyte, use professional judgement to determine qualifications for positive data or non-detects. At a minimum, "J" or "JN" positive data.

C. If the analyte does not have a corresponding labeled analyte and is outside 2 seconds of the matching unlabeled analyte from the associated calibration, use professional judgement to determine qualifications for positive data or non-detects. At a minimum, "J" or "JN" positive data.

D. If analyte meets identification criteria (7.2.2, 7.2.4, 7.2.5, 7.2.7) but does not meet ion abundance
ratio criteria (7.2.8) and is not a labeled analog, the sample must be reanalyzed on a confirmation column. If confirmation analysis was not perform, reject “R” the failing analyte.

3. If the criteria listed in section 7.2.4 and 7.2.5 are not met but all other criteria are met, qualify all positive data of the specific analyte with "J".

4. If the analytes reported positive do not meet criteria for section 7.2.6, reject “R” all positive data for these analytes. Change the positive values to EMPC (Estimated Maximum Possible Concentration). Flag "J"

5. If the labeled compounds, internal standards and cleanup standards do not meet ion abundance criteria section 7.2.6. and 7.2.7. (Table 8 - analytical method) but they meet all other criteria, flag all corresponding data with "J".

6. If the lab reported values exceeding the calibration range flag those values with "J".

7. If peak deflections >50% are visible qualify particular compound with "J".

8. If PCDF was detected but an interfering PCDPE was also detected (see Section 7.2.9) and concentration not corrected for the interference, cross out the PCDF data. The reported value of PCDF is changed to EMPC.

9. If the lab did not monitor for PCDPEs, qualify all positive furan data "JN".

7.2.10 Spot check calculations for positive data and verify that the same labeled compounds used to calculate RFs were used to calculate concentration and EMPC. Ensure that the proper CDDs/CDFs and labeled compounds were used.

To recalculate the concentration of individual CDD/CDF analytes in the sample use the following equation:

All Matrices other than water

$$Cn\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_l}{W \times (A_{l1} + A_{l2}) \times RR}$$

Water

$$Cn\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_l}{V \times (A_{l1} + A_{l2}) \times RR}$$

YES NO N/A

Where:

$A_{n1} + A_{n2}$ = integrated areas of the two quantitation ions of analyte of interest. (Target analyte)

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled analyte compound.

W = Weight (g) of sample extracted

V = Volume (L) of sample extracted

Q_l = Quantity (pg) of the appropriate labeled compound added to the sample prior to extraction.

RR = Calculated relative response from initial calibration. (see section 5.2.10)

ACTION: If the spot check calculations yielded positive hit concentrations with ≤ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the form 1's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

7.3 Clean-up procedures

Clean-up may not be necessary for relatively clean samples (drinking waters, ground waters etc). If the matrix required clean-up, the laboratory has 4 different procedures to choose from. Before using any clean-up procedure, the laboratory must demonstrate that the Initial Precision and Recovery requirements of the method can be met using the clean-up procedure.

A labeled clean-up standard $^{37}Cl_4$2,3,7,8-TCDD is added to the sample just before the back extraction with base and acid procedure. This occurs before any recommended clean-up procedures are initiated.

7.3.1 Was the percent recovery of the clean-up standard within the recommended range **listed on Table 6 of the Analytical method?** [___] ___ ___

ACTION: If no, and the recovery is less than 25%, qualify all data as estimated "J". If recovery is 0 %, qualify all positive data as estimated "J" and reject "R" all non-detects for that sample.

7.3.2 Check the chromatograms that clean-up procedure was needed for each sample. Were any clean-up procedures needed for either water or soil samples? ___ [___] ___

ACTION: If yes, check extraction log to verify which clean-up procedures if any were performed. The laboratory is not limited to only one procedure.

1. If no clean-up was performed and the chromatograms indicated that some should have been performed. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of required clean-up for complex samples in Data Assessment.

2. If one type of clean-up was performed, but the chromatograms indicate that additional clean-up should have been utilized. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of additional clean-up for complex samples in Data Assessment.

	YES	NO	N/A

7.3.3 If clean-up procedures were used, did the Laboratory perform clean-up procedures on the Initial Precision and Recovery samples as required by the method? [___] ___ ____

ACTION: If no, Use professional judgement to assess the effect of the interference on the validity of the data. Document lack of IPR documentation for clean-up procedures in Data Assessment.

8.0 Estimated Detection Limits (EDL) *If required for the project*

8.1 Was an EDL calculated for each 2,3,7,8-substituted analyte that was not identified regardless of whether other non-2,3,7,8 substituted analytes were present? [___] ___ ___

ACTION: 1. If EDL or EMPC of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

8.2 Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

$$EDL\ (pg/g) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{W \times (His^1 + His^2) \times RR}$$

WATER

$$EDL\ (pg/L) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{V \times (His^1 + His^2) \times RR}$$

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor

Qis, RR, W and V are previously defined.

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the Project Officer to request recalculations from the laboratory.

ACTION: If the spot check calculations yielded EDLs or EMPCs with $\leq$ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

9.0 Estimated Maximum Possible Concentration (EMPC) *If required for the project*

9.1 Was an EMPC calculated for 2,3,7,8-substituted analytes that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria? [___] ___ ___

9.2 Use the equation below to check EMPC calculations:

YES NO N/A

All Matrices other than water

$$EMPC\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_l \times D}{W \times (A_{l1} + A_{l2}) \times RR}$$

Water:

$$EMPC\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_l \times D}{V \times (A_{l1} + A_{l2}) \times RR}$$

Action: 1. If EDL or EMPC of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

2. If the spot check calculations yielded EDLs or EMPCs with ≤ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

3. If EDLs or EMPCs for the most toxic analytes (TEF ≥ 0.05) are above reporting limits, contact the project office to recommend sample reanalysis.

10.0 Method Blanks

10.1 Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?[___] ___ ___

10.2 If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event? [___] ___ ___

10.3 Acceptable method blanks must not contain any signal of 2,3,7,8-TCDD, or 2,3,7,8-TCDF, equivalent to a minimum levels listed in Table 2 or above one third the regulatory compliance level.. Was this criteria met? (Method 1613B, Section 9.5.2) [___] ___ ___

10.4 For other 2,3,7,8- substituted CDD/CDF isomers of each homologue, the allowable concentration in the method blank is less than minimum level listed in Table 2 (< 5 ng/Kg for soils and 50 pg/L for waters). Was this criteria met? [___] ___ ___

ACTION: 1. If the proper number of method blanks were not analyzed, document in Data Assessment. If the validator feels that the validity of the data is seriously compromised and validation of data without the method blanks would be flawed then notify the Project Officer. If decision is made to proceed with the validation process, consider the following actions: no action taken on non-detected analytes. If an analyte has a reported concentration that is > 5 times the EDL, qualify "J" and all concentrations ≤ 5 times the EDL are qualified "R" due to possibility of contamination.

2. If the method blank is contaminated with 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF or 2,3,4,7,8-PeCDF at a concentration higher than the minimum levels in Table 2, reject all contaminant compound positive data for the associated samples "R" and notify the Project Officer to initiate reanalysis.

3. A. If the method blank is contaminated with any of the analytes mentioned in Action # 2 at a concentration of less than the minimum levels in Table 2 specified in the method or of any other 2,3,7,8-substituted analytes at any concentration and the concentration in the sample is less than five times the

YES NO N/A

concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column in order to present the data as a non-detect.

B. If the concentration in the sample is higher than five times the contamination concentration in the blank, no action is needed.

11.0 Labeled Compound Recoveries

11.1 Were the samples spiked with all the labeled compounds as specified in the method? [___] ___ ___

11.2 Have labeled compounds' recoveries been within the required limits? [___] ___ ___

11.3 If not, were samples reanalyzed? [___] ___ ___

ACTION: 1. If the labeled compound recovery was below 25 percent, reject "R" all associated non- detect data (EMPC/EDL) and flag with "J" the positive data for the associated compound.

2. If the labeled compound recovery is above the upper limit (150 percent) flag associated positive data with "J". No effect on non-detects.

3. If the labeled compound recovery is less than 10%, qualify positive hits and non-detects associated with the failed labeled compound "R" (Reject). When highly toxic analytes (TEF$\geq$ 0.05) are affected, notify Project Officer to initiate reanalysis.

Recalculate the percent recovery for each labeled standard in the sample extract, Rec_l, using the formula:

$$\% Rec_l = \frac{(A_{l1} + A_{l2}) \times Q_{is} \times 100}{(A_{is1} + A_{is2}) \times RF \times Q_l}$$

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled compound.

$A_{is1} + A_{is2}$= integrated areas of the two quantitation ions of the appropriate internal standard.

Q_l = quantity of the appropriate labeled compound

Q_{is} = quantity of the appropriate internal standard injected

RF was defined, previously.

12.0 Internal Standard Area Response

There is no method criterion for the Internal Standard area response. However, because it is very critical in determining instrument sensitivity, the Internal Standard area response should be checked for every sample. The two standards $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD are referred to as Internal Standards in this method. In other Dioxin methods, the two standards are called Recovery Standards.

12.1 Are the internal standard areas for every sample and blank within the upper and lower limits of each associated initial calibration CS3?

Area upper limit= +100% of internal standard area.
Area lower limit= -50% of internal standard area. [___] ___ ___

YES NO N/A

12.2 Is the retention time of each internal standard within 15 seconds of the associated initial calibration CS3 standard? [___] ___ ___

ACTION: 1. If the internal standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the lab's labeled compound recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, flag all associated non-detect data as unusable "R" and the positive data "J".

3. If the retention time of the internal standards differs by more than 15 seconds from the initial calibration CS3, use professional judgement to determine the effect on the results. A time shift of more than 15 seconds may cause certain analytes to elute outside the retention time window established by the GC window defining/column performance check solution. A constant shift could be also the result of a leak.

NOTE: Action 1 and 2 are recommendations only since this criterion is not a method requirement. These guidelines are based on other methods, previously validated data packages and Region II recommendations. If method blanks have low area responses as well as the samples, the validator should seriously consider qualifying the data for this criterion. Action 3 is a method requirement.

13.0 Second Column Confirmation

13.1 Any sample in which 2,3,7,8-TCDF is identified on a DB-5 column, must have a confirmation analysis (Method 1613B, section 16.5). Was a second column confirmation performed? [___] ___ ___

13.2 Was the sample extract reanalyzed on a 30 m DB-225, fused silica capillary column, for 2,3,7,8-TCDF using the GC/MS conditions given in Section 10.1.1 of the analytical method? [___] ___ ___

NOTE: The concentration of 2,3,7,8-TCDF obtained from the primary column (DB-5) should only be used for qualification, due to better QC data associated with the primary column. Also note that the confirmation and quantitation of 2,3,7,8-TCDF may be accomplished on a SP-2330 GC column.

ACTION: If confirmation is missing, use professional judgement, or contact the Project Officer for assistance.

13.3 Did the second column meet the calibration and linearity specification in Sections 5.0 and 6.0 above? [___] ___ ___

ACTION: If no, refer to section 5.0 and 6.0 for appropriate action.

13.4 Was the % D of the quantitation results of the two columns less than 50? [___] ___ ___

ACTION: Note in data assessment the differences, use professional judgement to decide which column data to report for TCDF. No other action is needed since this is not a method requirement but a technical recommendation.

14.0 Sample Reanalysis

14.1 The Project Officer will evaluate the need for reanalyzing the samples with qualified data based on site-specific Data Quality Objectives.

YES NO N/A

14.2 Due to a variety of situations (see below) that may occur during sample analysis, the laboratory is required to reanalyze or re-extract and reanalyze certain samples. If a reanalysis was required but was not performed, contact the Project Officer to initiate reanalysis. List in data assessment all re-extractions and reanalyses and identify the CDD/CDF sample data summaries which must be used by the data user (when more than one analysis is submitted for a sample).

Lab must re-extract and/or re-analyzed samples when the following criteria are not met:

1. Contaminated method blank at concentrations above the minimum levels (Table 2)

2. Labeled compound recoveries outside acceptable ranges listed on Table 6 of Analytical method.

3. Exceedance of calibration range by an analyte (dilution or re-extract using a smaller aliquot).

4. Recovery of labeled compounds outside acceptable limits listed on Table 6 of the Analytical method in a diluted sample (re-extracted using a smaller aliquot).

ACTION: For criteria 1, 2, or 3, notify the Project Officer to discuss possible re-analysis of sample by the laboratory.

For criteria 4, If the calibration was verified and the re-extracted sample still does not meet labeled recovery requirements, then the method does not apply to the sample. The results are not reportable for regulatory purposes (Method 1613B, section 18.4.4). Notify the Project Officer of problem to initiate re-analysis of sample using a different method. Document in Data Assessment.

15.0 Precision and Recovery (PAR)

The laboratory is required to show initial demonstration of capability, to evaluate and document data quality. Laboratory performance is compared to established performance criteria to determine if results of analyses meet the performance characteristics of the method.

The laboratory must perform and submit data to establish the ability to generate acceptable precision and accuracy.

15.1 Did the laboratory analyzed an Initial Precision and Recovery (IPR) standard as outlined in section **9**.2 required by the analytical method? [___] ___ ___

ACTION: If no, contact the Project Officer to request resubmittals from the laboratory.

If data is not available, discuss with the Project Officer the feasibility of continuing with validation. If a decision is made to proceed with validation, use professional judgement. All data at a minimum should be qualified as estimated "J". Technically according to the method, data and system performance is unacceptable for all compounds. Analyses should not have continued as per the method. Document under contract non-compliance in Data Assessment.

15.2 Did the IPR standard deviation (s) and average concentration (x) passed criteria as outlined in Table **6** of the method? [___] ___ ___

ACTION: If no, refer to action from section 15.1.

The laboratory must analyzed an Ongoing Precision and Recovery standard (OPR) periodically, at the beginning of 12

YES NO N/A

hour shift after the analysis of the CS3 calibration verification (VER), and before the analysis of any sample in each set .

15.3 Was the Ongoing Precision and Recovery (OPR) standard analyzed at the required frequency? [___] ___ ___

15.4 Did the OPR standard passed the concentration criteria limits in Table **6** of the method? [___] ___ ___

ACTION: If no, refer to action from section 15.1. All samples that do not have a passing OPR standard are potentially affected for that analyte.

The following sections may be incorporated in the validation process on a case by case basis depending upon the requirements of the Project Plan. Sometimes a laboratory will provide data for some of the following sections on a routine basis. If not a requirement of the Project Plan, then professional judgement is needed to qualify data based on additional information**.**

16.0 Isomer Specificity and Toxicity Equivalency Factor (TEF)

NOTE: The TEF value concentrations can be found in the DFLM01.1 Statement of Work for Dioxin Analysis Form I PCDD-2.

When calculating the 2,3,7,8-TCDD Toxicity Equivalency of a sample only those 2,3,7,8 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve analyte specificity.

16.1 Did the lab include EMPC or EDL values in the toxicity equivalency calculations? [___] ___ ___

16.2 Were all samples, whose toxicity equivalency exceeded the required values were reanalyzed on a confirmation column to establish analyte specificity? [___] ___ ___

ACTION: 1. If yes, the toxicity equivalency calculations were not calculated properly, notify the Project Officer to arrange for laboratory resubmittals.

2. If the toxicity equivalency exceeded the required limits (0.7 μg/Kg for soil/ sediment, 7 ng/L for aqueous and 7 μg/Kg for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify Project Officer. Reanalysis may be initiated.

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration.

17.0 Rinsate Blank *(Region 2 QA guidelines recommend rinse blanks for all projects)*

17.1 One rinsate blank should be collected for each batch of 20 soil samples or one per day whichever is more frequent. Were rinsate blanks collected at the above frequency? [___] ___ ___

17.2 Do any rinsate blanks show the presence of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 1,2,3,7,8-PeCDD at amounts > .5 μg/L or any other analyte at levels > 1 µg/L? [___] ___ ___

ACTION: If any rinsate blank was found to be contaminated with any of the CDDs/CDFs notify the Project Officer to discuss what proper action must be taken.

If any qualification is needed due to rinsate blank contamination, follow the guidelines

YES NO N/A

outlined under Method Blanks, section 10, Actions 2 and 3.

18.0 Field Blanks

18.1 The field blanks are PEM samples (blind blanks) supplied to Laboratory at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

Were the following conditions met?

18.2 Acceptable field blanks must not contain any signal of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF equivalent to a concentration of > 20 ng/Kg. [___] ___ ___

18.3 For other 2,3,7,8 substituted CDD/CDF analytes of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method. [___] ___ ___

ACTION: When the field blank is found to be contaminated with target compounds, apply the same action as described for the Method Blank, section 10, Actions 2 and 3.

NOTE: Ask Project Officer to verify that the PEM blank (field blank) did not contain any CDD/CDF analytes and ask their assistance in the evaluation of the PEM field blank.

19.0 PEM Interference Fortified Blanks

NOTE: This type of blank may not be available at this time. In many cases, laboratories will substitute matrix spike/matrix spike duplicate (MS/MSD). If a PEM Interference Fortified blank(s) were not analyzed but MS/MSD data were submitted, skip this section and go onto to section 21.

19.1 One known blank usually an interference fortified soil/sediment sample is supplied to the Laboratory. The frequency of this QC sample is one per group of 20 environmental samples or one per samples collected over one week period, whichever occurs first. The sample is spiked by the laboratory with the appropriate volume of the matrix spiking solution and then extracted and analyzed with other samples.

19.2 Was a fortified PEM blank analyzed at the frequency described above? [___] ___ ___

19.3 Was the percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted compounds within the 50 to 150 percent control limits? [___] ___ ___

ACTION: 1. If the recovery of a 2,3,7,8-substituted analytes falls outside the 50-150 percent control limit, flag all positive and non-detect data of the same and related analytes in the same homolog series with "J". However, if the recovery is below 20%, qualify all associated non-detects "R" and positive hits as "J". Notify the Project Officer. Reanalysis may be initiated.

2. If no fortified PEM blank was analyzed, use professional judgement to assess data validity.

20.0 Matrix Spike (MS) Field Sample

Note: Matrix spike is not required by this method although Labs may routinely perform this analysis as part of internal QA/QC and submit this data as part of the package. Verify requirements with Project Officer.

		YES	NO	N/A
20.1	Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?	[___]	___	___
20.2	Was the percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted CDDs/CDFs within 60 to 140 percent?	[___]	___	___

ACTION: If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 60-140% limits of the matrix spike data may be used to flag data of the spiked sample only. The matrix spike data of the PE blank sample are more important and must be used primarily in data validation.

20.3	Was a matrix spike duplicate analyzed as per section 11.1 and 11.2?	[___]	___	___

ACTION: No action required. A matrix spike duplicate is not required. Use professional judgement if there is a large difference in concentrations reported between MS and MSD. Qualifications if any, can only be performed on the sample that was used for this criteria.

21.0 Environmental Duplicate Samples *(recommended in Region 2 for all Projects)*

NOTE: Do not confuse an environmental duplicate with a matrix spike duplicate. An environmental duplicate is a sample that has been divided into 2 parts (extracted and analyzed as two different samples) or as 2 separate samples from the same location sent by the sampling crew. This sample is not spike with any additional compounds other than those compounds required by the method for analysis of all routine samples.

21.1	For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?	[___]	___	___
21.2	Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8-substituted analytes and 50% for the rest of the analytes?	[___]	___	___

ACTION: The duplicate results can be used in conjunction of other QC data. Use professional judgement.

22.0 REFERENCES

The following references are cited in Method 1613. They are important references for technical information and are submitted here as part of this method's documentation.

1. "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", USEPA Environmental Research Laboratory, 6201 Congdon Boulevard, Duluth, NH 55804, April 1988.

2. Barnes, Donald G., Kutz, Frederick W., and Bottimore, David P., "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposure to Mixtures of Chlorinated Dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs)", Risk Assessment Forum, USEPA, Washington, DC 20460, February 1989.

3. Lamparski, L.L., and Nestrick, T.J., "Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-p-dioxin Isomers in Particulate Samples at Parts per Trillion Levels", Analytical Chemistry, 52: 2045-2054, 1980.

4. "Measurment of 2,3,7,8-Tetrachlorinated Dibenzo-p-dioxin (TCDD) and 2,3,7,8-Tetrachlorinated Dibenzofurans (TCDF) in Pulp, Sludges, Process Samples and Waste-waters from Pulp and Paper Mills",

YES NO N/A

Wright State University, Dayton, OH 45435, June 1988.

5. Method 1613-Revision **B**- Tetra through Octa- chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, USEPA, Washington, DC, 20460, October **1994**

6. "Method 613--2,3,7,8-tetrachlorodibenzo-p-dioxin", 40 CFR 136 (49 FR 43234), October 26, 1984, Section 4.1.

7. "NCASI Procedures for the Preparation and Isomer Specific Analysis of Pulp and Paper Industry Samples for 2,3,7,8 TCDD and 2,3,7,8 TCDF", National Council of the Paper Industry for Air and Stream Improvement, 260 Madison Avenue, New York, NY 10016, Technical Bulletin No.551, Pre-release Copy, July 1988.

8. Provost, L.P., and Elder, R.S., "Interpretation of Percent Recovery Data", American Laboratory, 15: 56-83, 1983

9. Stanley, John S., and Sack, Thomas M., "Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin by High Resolution Gas Chromatography/High Resolution Mass Spectrometry", USEPA EMSL, Las Vegas, Nevada 89114, EPA 600/4-86-004, January 1986.

10. Tondeur, Yves, "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-dioixin and Dibenzofurans hy High Resolution Gas Chromatography/High Resolution Mass Spectrometry", USEPA ENSL, Las Vegas, Nevada, June 1987.

11. Tondeur, Yves, "Proposed GC/MS Methodology for the Analysis of CDDs and CDFs in Special Analytical Services Samples", Triangle Laboratories, Inc., 801-10 Capitola Dr., Research Triangle Park, NC 27713, January 1988; updated by personal communication September 1988.

ATTACHMENT A

CDFs/CDD DATA ASSESSMENT

SDG No.
LABORATORY:
SITE:

DATA ASSESSMENT

The current Functional Guidelines for evaluating dioxin/furans organic data have been applied.

All data are valid and acceptable except those analytes which have been qualified with a "J" (estimated), "N" (presumptive evidence for the presence of the material), "U"(non-detects), "R" (unusable), or "JN"(presumptive evidence for the presence of the material at an estimated value). All action is detailed on the attached sheets.

Two facts should be noted by all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. "R" values should not appear on data tables because they can not be relied upon, even as a last resort. The second fact to keep in mind is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data but any value potentially contains error.

Reviewer's
Signature:_____ Date:__/__/200_

Verified By:_____ Date:___/__/200_

GENERAL COMMENTS:

HOLDING TIME:

BLANK CONTAMINATION:

WINDOW DEFINING MIXTURE:

ION ABUNDANCE:

CALIBRATIONS:

RESOLUTION:

LABELED STANDARDS PERFORMANCE:

INTERNAL STANDARDS:

PEAK IDENTIFICATION:

MATRIX SPIKE/ ENVIRONMENTAL DUPLICATE:

CONFIRMATIONS:

OTHER QC OUT OF SPECIFICATION:

SYSTEM PERFORMANCE AND OVERALL ASSESSMENT:

CONTRACT PROBLEMS NON-COMPLIANCE:

RE-EXTRACTION, REANALYSIS OR DILUTIONS:

DO NOT USE

USE FIELD DOCUMENTS:

VALIDATION SOP

PCB Congener

EDS SOP: Congener PCB, Rev.3, 7/10

Environmental Data Services
Congener PCBs (USEPA METHOD 1668A)
Data Validation Checklist

SITE:

DATE:

SDG:

	Y	N	N/A
Data Completeness and Deliverables			
Are the Field Chain of Custody Forms present for all samples?	_____	_____	_____
Are the Narrative, extraction logs, % solid worksheet, analysis logs and Cover Letter present?	_____	_____	_____
Do the Field Chain of Custody Reports or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical procedures, or other comments regarding the quality of the data?	_____	_____	_____

ACTION: Use professional judgment to evaluate the effect of the noted problems on the quality of the data.

ACTION: If any solid sample analyzed contains 50% to 90% water, all data shall be flagged as estimated "J". If a solid sample contains more than 90% water, then qualify positive hits "J" and non-detects "R".

Preservation Requirements

Is the cooler temperature ≤ 10°C for aqueous and soil samples from the time of collection until receipt at the laboratory?	_____	_____	_____

ACTION: If cooler temperature >10°C, flag non-detects as "UJ" and detects as "J".

Reporting Requirements and Deliverables

	Y	N	N/A
Are the following forms present?			
Toxic CB Congener Sample Data Summary (Form I CB-1)?	_____	_____	_____
Toxic CB Congener Toxicity Equivalency (Form I CB-2)?	_____	_____	_____
CB Congener Sample Data Summary (Form I CB-3)?	_____	_____	_____
NOTE: Form I is used for tabulating and reporting sample analyses, including dilutions, reanalyses, blanks, LCS/Ongoing Precision and Recovery (OPR) and requested matrix spike and matrix spike duplicates for target compounds.			
CB Congener Total Homologue Concentration Summary (Form II CB)?	_____	_____	_____
NOTE: Form II is used to report the concentration of the mono- through nano-chloro biphenyl homologue for each sample.			
CB Congener Method Blank Summary (Form IV CB-1)?	_____	_____	_____
NOTE: Form IV summarizes the sample associated with each method blank analysis.			
CB Congener Descriptor Switching Resolution Summary (Form V CB-1)?	_____	_____	_____
NOTE: Form V CB-1 is used to report the descriptor switching windows for each level of chlorination for each 12-hour time period and to summarize the date and time of analysis, including dilutions, reanalysis, standards, blanks, and requested MS/MSD associated with each analysis of the instrument performance check solution.			
CB Congener Ion Abundance Ratio Summary (Form V CB-2)?	_____	_____	_____
CB Congener (Labeled) Ion Abundance Ion Ratio Summary (Form V CB-3)?	_____	_____	_____
NOTE: Form V CB-2 & CB-3 are used to report the ion abundance ratios and signal-to-noise (S/N) ratios for the congeners contained in the LOC/WDM for each 12-hour time period.			
Toxic CB Congener Initial Calibration Response Factor Summary (Form VI CB-1 & CB-2)?	_____	_____	_____
Individual Congener Initial Calibration Response Factor Summary (Form VI CB-3)?	_____	_____	_____

	Y	N	N/A
NOTE: Form VI is used to report the relative response factors (RRF), average RRF, % RSD and RRT for the five or six-point initial calibration at the specific concentration levels.			
Toxic CB Congener Continuing Calibration Summary (Form VII CB-1)?	_____	_____	_____
Toxic CB Congener (Labeled) Continuing Calibration Summary (Form VII CB-2)?	_____	_____	_____
Individual Congener Continuing Calibration Summary (Form VII CB-3)?	_____	_____	_____
Toxic CB Congener Continuing Calibration Time Summary (Form VII CB-4)?	_____	_____	_____
Toxic CB Congener (Labeled) Continuing Calibration Summary (Form VII CB-5)?	_____	_____	_____
Individual Congener Continuing Calibration Summary (Form VII CB-6)?	_____	_____	_____
NOTE: Form VII is used to report the calibration verification of the HRGC/HRMS system by the analysis of specific calibration verification standard(s). This form is required for each continuing calibration (one every 12 hours of sample analysis).			
CB Congener Analytical Sequence (Form VIII CB)?	_____	_____	_____
NOTE: Form VIII is used to report the analytical sequence for CB congener analyses.			
ACTION: If deliverables are missing, contact the laboratory to request explanation/resubmittal. Note in the Data Assessment.			

Holding Times

Were the following holding times met:

Aqueous samples were extracted within 30 days of sample collection	_____	_____	_____
Solid samples were extracted within 30 days of sample collection	_____	_____	_____
All samples were analyzed within 40 days of extraction	_____	_____	_____
ACTION: If holding times are exceeded, flag all data as estimated "J". Holding time criteria do not apply to PE samples.			
If holding times from collection to extraction, or from extraction to analysis have been grossly exceeded, use professional judgment to determine whether non-detects shall be rejected.			

Column Performance **Y** **N** **N/A**

Column performance is assessed based on the evaluation of data obtained from the daily (12-hr. shift) diluted combined 209 congener solution.

The retention time for decachlorobiphenyl (PCB 209) must be greater than 55 minutes. _____ _____ _____

The column, SPB-Octyl, must uniquely resolve congeners 34 from 23 and 187 from 182, and congeners 156 and 157 must co-elute within 2 seconds at peak maximum. _____ _____ _____

An alternative Column Performance criteria when using DB-1 is as follows:

a. The retention time for decachlorobiphenyl must be greater than 55 minutes
b. The column must resolve the following congerers:
    i. 28,31 with a valley height less than 50 percent
    ii. 66,70,74,80 with a valley height less than 40 percent
    iii. 123,118 with a valley height less than 40 percent
    iv. 156,157 with a valley height less than 40 percent

NOTE: Unique resolution means a valley height of less than 40% of the shorter of the two peaks.

ACTION: If column performance criteria were not met, a detailed discussion of the problems observed and potential effects on analytical data obtained should be included in the data assessment narrative.

Initial 5-Point Calibration

The initial calibration standard solutions (CS1-CS5) must be analyzed prior to any sample analysis. These calibration standards should include all CBs listed at the concentrations specified in Table 5 of Method 1668A. They do not have to be analyzed daily provided the continuing calibration standard met all criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze samples. _____ _____ _____

SIM data were acquired for each of the ions listed in Table 7, Method 1668A _____ _____ _____

The following criteria must be met:

For all target analyte PCBs with associated labeled analogs, the two ions for each CB must maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions. _____ _____ _____

	Y	N	N/A
For the other CBs, the 2 ions for each of the CBs being quantified must maximize simultaneously.	_____	_____	_____
The relative ion abundance criteria listed in Table 8, Method 1668A must be met.	_____	_____	_____
The relative ion abundance criteria for the labeled internal and recovery standards listed in Table 8, Method 1668A must be met.	_____	_____	_____
For all calibration solutions, the signal to noise ration (S/N) for all ions of the native compounds must be greater than 10.	_____	_____	_____
For the internal and recovery standards, the signal to noise ratio for all ions must be greater than 10.	_____	_____	_____
The percent relative standard deviation (%RSD) of the five RRFs (CS1-CS5) for the CBs must not be greater than 20 percent.	_____	_____	_____

Spot- check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CBs and internal standards were used. In addition verify that the appropriate internal standard was used for each isomer.

> ACTION: If required information was not supplied, notify the lab. If unavailable, reject all associated sample data. If any calibration curve standards fail to meet any acceptance criteria, check for re-calibration and re-analysis.

Calibration by Isotopic Dilution Procedure
(Native CBs included in the Toxics/LOC CBs list)

To recalculate the response factor for targets quantitated based on isotopic dilution, use the equation:

$$RRFn = \frac{(An^1 + An^2)\ x\ Cis}{(Ais^1 + Ais^2)\ x\ Cn}$$

Where:

A_n^1 and A_n^2	=	*integrated areas of the two quantitation ions of isomer of interest*
A_{is}^1 and A_{is}^2	=	*integrated areas of the two quantitation ions of the appropriate labeled compound.*
C_{is}	=	*The concentration of the labeled compound in the calibration standard.*
Cn	=	*The concentration of the native compound in the calibration standard.*

Calibration by Internal Standard **Y N N/A**
(Native CBs not included in the Toxics/LOC CBs list)

Internal standard calibration is performed at a single point using the diluted combined 209-congener solution (Table 3, Method 1668A).

To calculate the response factor for targets based on the internal standard method, use the equation:

$$RF = \frac{(A1_S + A2_S)\, C_{is}}{(A1is + A2is)\, C_s}$$

Where:

$A1_s$ *and* $A2_s$ = *The areas of the primary and secondary m/z's for the PCB.*

$A1_{is}$ *and* $A2_{is}$ = *The areas of the primary and secondary m/z's for the internal standard.*

C_{is} = *The concentration of the internal standard.*

C_s = *The concentration of the compound in the calibration standard.*

Continuing Calibration

At the beginning of each12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all native CBs and labeled compounds. For these tests, analysis of the Cs-3 calibration verification (VER) standard (Section 7.10.1 and Table 5, Method 1668A) and the diluted compound 209-congener solution (Section 7.10.2.2 and Table 5, Method 1668A) must be used to verify all performance criteria. Adjustment and/or recalibration (Section 10, Method1668A) must be performed until all performance criteria are met. Only after all performance criteria are met, may samples, blanks, IPRs and OPRs be analyzed.

Was the continuing calibration run at the required frequency? _____ _____ _____

ACTION: If the continuing calibration standard was not analyzed at the required frequency, reject all the data.

For native Toxics and LOC CBs, the two SIM ions for each PCB must maximize simultaneously and within 3 seconds of the corresponding ions of the labeled isomers. _____ _____ _____

The two ions for each of the CBs being quantified must maximize simultaneously _____ _____ _____

	Y	N	N/A
For the continuing calibration standard solution, the signal to noise ratio (S/N) for the CB ions shall be greater than 10.	_____	_____	_____
The absolute retention times of the labeled Toxics/LOC/window defining standard congeners in the verification test must be within ± 15 seconds of the respective retention times in the calibration. Has this criteria been met?	_____	_____	_____
The relative retention times of native CBs and labeled compounds in the verification test must be within their respective RRT limits in Table 2, Method 1668A. Has the criteria been met?	_____	_____	_____
For the internal standards and the recovery standards, the signal to noise ratio (S/N) shall be greater than 10.	_____	_____	_____
The relative ion abundance criteria, Table 8, Method 1668A for all PCBs native shall be met.	_____	_____	_____
Evaluate the concentrations of the Toxics/LOC CBs in the CS-3 VER standard.			
For each compound, compare the concentration with the calibration verification limit in Table 6, Method 1668A. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. Was this criteria met?	_____	_____	_____
Spot-check continuing calibration concentrations and ion ratios. Verify that the appropriate quantitation ions were used for the unlabeled PCBs and internal standards.			

ACTION: If the required continuing calibration fail to meet any of the acceptance criteria, check for recalibration and reanalysis. If not performed, reject (“R” flag) all data associated with the analyte out of specification in the continuing calibration.

Sample Data

SIM data were acquired for each of the ions listed in Table 7, Method1668A	_____	_____	_____

Identification Criteria

A. For native Toxics and LOC CBs, the two ions for each of the PCB's being quantified must maximize simultaneously and within 3 seconds of the corresponding labeled standard.

		Y	N	N/A
	For the remaining CBs, the two ions for each of the CBs being quantified must maximize simultaneously.	_____	_____	_____
B.	The integrated ion current for each characteristic ion of the analyte identified as positive must be at least 2.5 times background noise and must have not saturated the detector.	_____	_____	_____
C.	The integrated ion current for the internal and recovery standard characteristic ions must be at least 10 times background noise.	_____	_____	_____
D.	The relative ion abundance criteria (Table 8, Method 1668A) for all PCB's found present must be met or ion ratios must be within ± 15% of the most recent CS-3 determination.	_____	_____	_____
E.	The relative retention time of the peak for a positively identified CB must be within the RRT QC limits specified in Table 2, Method 1668A, or, if an alternate column or column system is employed, within its respective RRT QC limits for the alternate column or column system.	_____	_____	_____

ACTION: Reject (“R” flag) all positive data for the analytes which do not meet criteria listed in section A.

If the criteria listed in section B are not met but all other criteria are met, qualify all positive data of the specific analyte with “J”.

If the requirements listed in section C are not met but all other requirements are met qualify the positive data of the corresponding analytes with "J".

If the analytes reported positive do not meet ion abundance criteria, section D, or do not meet RRT criteria, Section E, reject “R” all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration. _____ _____ _____

Compute the concentrations in the extract of the Native Toxics/LOC CBs, using the RRs from the calibration data and following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

Where:

C_{ex} = *The concentration of the PCB in the extract, and the other terms as defined in Section 10.5.1, Method 1668A.*

Internal Standard Quantitation and Labeled Compound Recovery

Compute the concentrations in the extract of the native compounds other than those in the Native Toxics/LOC standard, in the Labeled cleanup standard, and in the Labeled injection internal standard (except for Labeled CB178), using the response factors determined from the calibration data and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_s + A2_s)\ C_{ls}}{(A1_{is} + A2_{is})\ RF}$$

Where:

C_{ex} = *The concentration of the labeled compound in the extract. The other terms are defined on page 7 under calibration by Internal Standard.*

Using the concentration in the extract determined above, compute the percent recovery of the Labeled Toxics/LOC/window-defining CBs and the Labeled cleanup standard CBs using the following equation:

$$\text{Recovery (\%)} = \frac{\text{Concentration found (ug/mL)} \times 100}{\text{Concentration spiked (ug/mL)}}$$

The concentration of a native CB in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids as follows:

$$\text{Concentration in solid (ng/kg)} = \frac{(C_{ex} \times V_{ex})}{W_s}$$

Where:

C_{ex} = *The concentration of the compound in the extract.*

V_{ex} = *The extract volume in mL.*

W_s = *The sample weight (dry weight) in kg.*

The concentration of a native CB in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids as follows:

$$\text{Concentration in solid (ng/kg)} = \frac{(C_{ex} \times V_{ex})}{W_s}$$

Where:

C_{ex} = *The concentration of the compound in the extract.*

V_{ex} = *The extract volume in mL.*

W_s = *The sample weight (dry weight) in kg.*

Y N N/A

The concentration of a native CB in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted as follows:

$$\text{Concentration in aqueous phase (pg/L)} = \frac{(C_{ex} \times V_{ex})}{V_s}$$

Where:

C_{ex} = *The concentration of the compound in the extract.*

V_{ex} = *The extract volume in mL.*

V_s = *The sample volume in liters.*

Method Blanks

Has a method blank been extracted and analyzed with each batch of 20 samples or less, per matrix? _____ _____ _____

Was the method blank analyzed immediately after the OPR? _____ _____ _____

ACTION: If the proper number of method blanks were not analyzed, notify the contractor. If the reviewer is unavailable, reject all positive sample data. However, the reviewer may also use professional judgment to accept or reject positive sample data if no blank was run.

Were any PCBs found at a concentration greater than the PQL in the associated method blank? _____ _____ _____

ACTION: If an analyte has a reported concentration that is > 5 times the PQL, qualify "J" and all concentrations ≤ 5 times the PQL are qualified "U" due to possibility of contamination.

If the congener concentration in the sample is less than 5x the concentration in the blank, flag the congener reported value with a “U” qualifier.

If the concentration of the congener in the sample is greater than 5x the concentration in the blank, no action is needed.

Rinsate Blank

Was a rinsate blank submitted for analysis for each analytical batch not to exceed 20 samples? _____ _____ _____

Do any rinsate blanks contain concentrations of PCBs above the PQL? _____ _____ _____

	Y	N	N/A

ACTION: If an analyte has a reported concentration that is > 5x the PQL, qualify "J" and all concentrations ≤ 5x the PQL are qualified "U" due to possibility of contamination.

If the congener concentration in the sample is less than 5x the concentration in the blank, flag the congener reported value with a “U” qualifier.

If the concentration of the congener in the sample is greater than 5x the concentration in the blank, no action is needed.

Labeled Compound Recoveries

Were the samples spiked with all the internal standards as specified in the method? _____ _____ _____

Were internal standard recoveries within the method required limits (Table 6, Method1688A)? _____ _____ _____

If not, were samples reanalyzed? _____ _____ _____

ACTION: If the internal standard recovery was outside the acceptance limits (Table 6, Method 1668A) “J” flag all associated positive results.

Labeled Injection Internal Standards

Internal standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration? _____ _____ _____

Area upper limit = +100% of internal standard area.
Area lower limit = -50% of internal standard area.

Is the retention time of each internal standard within 10 seconds of the associated daily calibration standard? _____ _____ _____

ACTION: If the internal standard area is outside the upper or lower limits flag all related positive and non-detect data with “J” regardless of whether or not the labeled standard recoveries met specifications.

If extremely low area counts (<25%) are reported, qualify all associated non-detect data as unusable “R” and the positive data “J.”

If the retention time of the internal standard differs by more than 10

	Y	N	N/A

seconds from the daily calibration, use professional judgment to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the window defining mix.

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Sample ID of the sample chosen for MS/MSD analysis: _____

For every sample delivery group of 20 or fewer environmental samples was one MS/MSD pair analyzed? _____ _____ _____

NOTE: In order for the MS/MSD to be appropriate for use in qualifying or rejecting associated sample data, the spike level must be within the range of 25% to 400% of the reported sample concentration for either the aqueous or soil sample..

Is the MS recovery within the 60 to 140% acceptance range for either an aqueous or solid sample? _____ _____ _____

ACTION: qualify the value for the analyte in the sample used for the MS/MSD as estimated "J". Use professional judgment in association with signal to noise ratios and internal standard recoveries for the associated sample data to determine the effect on the quality of the associated sample data.

Does the precision of the MS/MSD analyses meet the $\leq$ 50% RPD criteria? _____ _____ _____

ACTION: Qualify the value for that analyte in the sample used for the MS/MSD as estimated "J"; use professional judgment in association with signal to noise ratios and internal standard recoveries for the associated sample data to determine the effect on the quality of the associated sample data.

Field Duplicate Samples

Sample IDs of the field duplicate pair: _____

For every batch of 20 samples or less collected there must be a sample designated as duplicate. _____ _____ _____

NOTE: For Aqueous: RPD $\leq$ 20% when target is detected in both field duplicate samples at $\geq$ 5XPQL or concentrations differ by less than 2X the PQL when detects are < 5X PQL for both field duplicate samples.

For Soil: RPD ≤ 50% when target is detected in both field duplicate samples at ≥ 5x PQL, or concentration differs by less than 2x the PQL when detects are < 5x PQL for both field duplicate samples.

	Y	N	N/A
ACTION: The duplicate results must be used in conjunction with other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.			

Ongoing Precision and Recovery (OPR)

For every batch of 20 samples or less processed by the laboratory, was an OPR processed?	_____	_____	_____
Do the calculated percent recoveries for all CBs in the associated OPR meet the acceptance limits provided in Table 6, Method 1668A?	_____	_____	_____

ACTION: If the laboratory failed to process an OPR sample with the associated field samples, qualify all target analyte results as estimated “J”.

ACTION: If any CB OPR percent recoveries failed to meet the acceptance criteria listed in Table 6, Method 1668A, qualify detects sample results as estimated "J".

Initial Precision and Recovery (IPR)

Was an initial precision and accuracy demonstration performed for the appropriate matrix as per section 9.2 of Method 1668B?	_____	_____	_____
Were the results of the IPR evaluation acceptance when compared to the acceptance limits for each analyte listed in Table 6, Method166A?	_____	_____	_____

ACTION: If IPR date was not provided by the laboratory, contact the lab to obtain the results of the IPR study.

ACTION: If the results of the laboratories IPR study do not meet the acceptance criteria for performance tests listed in Table 6, Method 1668A, contact the lab to initiate remediation of technical difficulties.

Data Validation Qualifiers

Qualifier	Description
J	Estimated value (bias undetermined) – The analyte was positively identified; but the associated numerical value is the approximate concentration of the analyte in the sample.
JH	Estimated value (potential high bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential high bias, of the analyte in the sample.
JL	Estimated value (potential low bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential low bias, of the analyte in the sample.
UJ	Estimated non-detect - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
UJL	Estimated non-detect (potential low bias) – The analyte was not detected and the report sample quantitation limit is biased low.
UJH	Estimated non-detect (potential high bias) – The analyte was not detected and the reported sample quantitation limit is biased high.
M	The analytical result reported was obtained from a sediment sample found to contain between 50 and 90 percent moisture and had no other data qualifiers added during the data validating process.
NJ	The organic analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration.
NJH	The organic analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration with a potential high bias, of the analyte concentration.
EMPC	Estimated Maximum Possible Concentration (EMPC).
R	The sample results are rejected. Due to a significant QA/QC problem, the analysis is invalid and provides no information as to whether the analyte is present or not.

VALIDATION SOP

TAL Metals

USEPA Region 2 SOP HW-2b, Rev.15, 12/12

Hazardous Waste Support Section
SOP NO. HW-2b Revision 15
ICP-MS Data Validation

Approvals:

Muhammad Hanif Sheikh — 12/20/12
Chemist, Hazardous Waste Support Section — Date

Philip Cocuzza — 12/21/12
Chief, Hazardous Waste Support Section — Date

Jon Gabry — 12/21/12
Chief, Hazardous Waste Support Branch — Date

Approving Official Annual Review — Date

NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by USEPA, and may not be relied upon to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

This document can be obtained from the USEPA's Region 2 Quality Assurance website at:

http://www.epa.gov/region2/qa/documents.htm

TABLE OF CONTENTS

LIST OF TABLES

ACRONYMS

ASB	Analytical Services Branch
CCB	Continuing Calibration Blank
CCS	Contract Compliance Screening
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
CO	Contracting Officer
CRQL	Contract Required Quantitation Limit
DF	Dilution Factor
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
EDM	EXES Data Manager
ESAT	Environmental Services Assistance Team
EXES	Electronic Data eXchange and Evaluation System
HWSS	Hazardous Waste Support Section
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Interference Check Sample
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
MDL	Method Detection Limit
NIST	National Institute of Standards and Technology
OSRTI	Office of Superfund Remediation and Technology Innovation
OSWER	Office of Solid Waste and Emergency Response
PE	Performance Evaluation
%D	Percent Difference
%R	Percent Recovery
%S	Percent Solids
PO	Project Officer
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
RSCC	Regional Sample Control Center Coordinator
SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
TR/COC	Traffic Report/Chain of Custody Documentation
USEPA	United States Environmental Protection Agency

TARGET ANALYTE LIST

Al Aluminum
Sb Antimony
As Arsenic
Ba Barium
Be Beryllium
Cd Cadmium
Ca Calcium
Cr Chromium
Co Cobalt
Cu Copper
Fe Iron
Pb Lead
Mg Magnesium
Mn Manganese
Ni Nickel
K Potassium
Se Selenium
Ag Silver
Na Sodium
Tl Thallium
V Vanadium
Zn Zinc

INTRODUCTION

This document is designed to offer the data reviewer guidance in determining the validity of analytical data generated through the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) ISM01.X Inorganic Superfund Methods (Multi-Media, Multi-Concentration), hereinafter referred to as the ISM01.2 SOW, and any future editorial revisions of ISM01.2. This guidance is somewhat limited in scope and is intended to be used as an aid in the formal technical review process.

The guidelines presented in the document will aid the data reviewer in establishing (a) if data meets the specific technical and QC criteria established in the SOW, and (b) the validity and extent of bias of any data not meeting the specific technical and QC criteria established in the SOW. It must be understood by the reviewer that acceptance of data not meeting technical requirements is based upon many factors, including, but not limited to site-specific technical requirements, the need to facilitate the progress of specific projects, and availability for re-sampling.

The reviewer should note that while this document is to be used as an aid in the formal data review process, other sources of guidance and information, as well as professional judgment, should also be used to determine the ultimate validity of data, especially in those cases where all data does not meet specific technical criteria.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process.

U	The analyte was analyzed for, but was not detected above the level of the reported sample quantitation limit.
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
J+	The result is an estimated quantity, but the result may be biased high.
J-	The result is an estimated quantity, but the result may be biased low.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.

DATA PACKAGE INSPECTION

For data obtained through the Contract Laboratory Program (CLP), the EXES Data Manager (EDM) is a useful tool in the data review process. For more information about EDM, please refer to the following Sample Management Office (SMO) website:

https://epasmoweb.fedcsc.com/help/guides/Submit%20and%20Inspect%20Data%20Quick%20Guide%20%28EXES%29.pdf

EDM will identify any missing and/or incorrect information in the data package. The CLP laboratory may submit a reconciliation package for any missing items or to correct data.
If there are any concerns regarding the data package, contact the CLP Project Officer (CLP PO) from the Region where the samples were taken. For personnel contact information, please refer to the following CLP website:

http://www.epa.gov/superfund/programs/clp/contacts.htm

HWSS DATA VALIDATION PROCESS

After downloading the data package from EDM, the data validator will use the recommendations in this SOP as well as their own professional judgment to validate the data.

The data will be saved in the following location, under the appropriate case number folder:

G:\DESADIV\HWSS\DATA VALIDATION

The file naming conventions will consist of

A. case number i.e., 12345
B. SDG name i.e., MBXY12
C. level of validation performed i.e., S2BVE

Examples: **12345_MBXY12_S2BVE.xls**

12345_MBXY12_S2BVEM.xls

When data validation is completed, the data package is uploaded for the client to download from the HWSS data delivery website:

https://epaqpx.rtp.epa.gov/hwssclpdeliverables

The completed data package includes the Executive Narrative (see Appendix B for template), the Sample Summary Report (see Appendix C for example), and the Electronic Data Deliverable (EDD) (see Appendix D for a list of the column headers included in this document).

PRELIMINARY REVIEW

This document is for the review of analytical data generated through the ISM01.2 SOW and any future editorial revisions of ISM01.2. To use this document effectively, the reviewer should have an understanding of the analytical method and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in the analysis are essential information.

It is suggested that an initial review of the data package be performed, taking into consideration all information specific to the sample data package [e.g., Modified Analysis requests, Traffic Report/Chain of Custody (TR/COC) documentation, SDG Narratives, etc.].

The reviewer should also have a copy of the Quality Assurance Project Plan (QAPP) or similar document for the project for which the samples were analyzed. The reviewer should contact the appropriate Regional Contract Laboratory Program Project Officer (CLP PO) to obtain copies of the QAPP and relevant site information. This information is necessary in determining the final usability of the analytical data.

The SDGs or Cases routinely have unique samples that require special attention from the reviewer. These include field blanks and trip blanks, field duplicates, and Performance Evaluation (PE) samples which must be identified in the sampling records. The sampling records (e.g., TR/COC records, field logs, and/or contractor tables) should identify:

1. The Region where the samples were taken, and
2. The complete list of samples with information on:
    a. Sample matrix;
    b. Field blanks*;
    c. Field duplicates*;
    d. Field spikes*;
    e. PE samples*;
    f. Shipping dates;
    g. Preservatives;
    h. Types of analysis; and
    i. Laboratories involved.

    * If applicable.

The TR/COC documentation includes sample descriptions and date(s) of sampling. The reviewer must consider lag times between sampling and start of analysis when assessing technical sample holding times.

The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, preservation, and unusual events should be documented in the SDG Narrative. The reviewer should also inspect any email or telephone/communication logs detailing any discussion of sample or analysis issues between the laboratory, the CLP Sample Management Office (SMO), and the USEPA Region.

An Example Analytical Sequence for ICP-MS

Tune
S0
S
S
S
S
S
ICV
ICB
LCS
ICSA
ICSAB
CCV
CCB
samples
CCV
CCB
samples
CCV
CCB, etc.

Preservation and Holding Times

Action:

NOTE: Apply the action to each sample for which the preservation or holding time criteria was not met.

1. If the pH of aqueous/water metal samples is > 2 at the time of sample receipt, determine if the laboratory adjusted the pH of the sample to ≤ 2 at the time of sample receipt. If not, use professional judgment to qualify the samples based on the pH of the sample and the chemistry of the metal(s) of interest. Qualify results that are ≥ Method Detection Limit (MDL) as estimated low (J-), and qualify non-detects as unusable (R).
2. If technical holding times are exceeded, use professional judgment to determine the reliability of the data, based on the magnitude of the additional time compared to the technical requirement and whether the samples were properly preserved. The expected bias would be low. Qualify results that are ≥ MDL as estimated low (J-), and qualify non-detects as unusable (R).
3. Due to limited information concerning holding times for soil/sediment samples, it is left to the discretion of the data reviewer whether to apply 180 day holding time criteria to soil/sediment samples. If they are applied, it must be clearly documented in the Data Review Narrative.
4. When the holding times are exceeded, the reviewer should comment in the Data Review Narrative on any possible consequences for the analytical results.
5. When holding times are grossly exceeded, note it for Contract Laboratory Program Project Officer (CLP PO) action.

Table 1. Technical Holding Time Actions for ICP-MS Analysis

Preservation & Holding Time Results	Action for Samples
Aqueous/water metals samples received with pH > 2 and pH not adjusted	Use professional judgment Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical Holding Time exceeded: Aqueous/water Metals > 180 days	Use professional judgment Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical Holding Time exceeded: Soil/sediment Metals > 180 days	Use professional judgment Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)

ICP-MS Tune Analysis

Action:

NOTES: For ICP-MS tunes that do not meet the technical criteria, apply the action to all samples reported from the analytical run.

1. If the ICP-MS instrument was not tuned prior to calibration, the sample data should be qualified as unusable (R).
2. If the tuning solution was not analyzed or scanned at least 5x consecutively or the tuning solution does not contain the required analytes spanning the analytical range, the reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should be recorded in the Data Review Narrative and noted for Contract Laboratory Program Project Officer (CLP PO) action.
3. If the resolution of the mass calibration is not within 0.1 u for any isotope in the tuning solution, qualify all analyte results that are ≥ Method Detection Limit (MDL) associated with that isotope as estimated (J), and all non-detects associated with that isotope as estimated (UJ). The situation should be recorded in the Data Review Narrative and noted for CLP PO action.
4. If the %RSD exceeds 5% for any isotope in the tuning solution, qualify all sample results that are ≥ MDL associated with that tune as estimated (J), and all non-detects associated with that tune as estimated (UJ). The situation should be recorded in the Data Review Narrative and noted for CLP PO action.

Table 2. ICP-MS Tune Actions for ICP-MS Analysis

ICP-MS Tune Results	Action for Samples
Tune not performed	Qualify all results as unusable (R)
Tune not performed properly	Use professional judgment
Resolution of mass calibration not within 0.1u	Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as estimated (UJ)
% RSD > 5%	Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as estimated (UJ)

Calibration

Table 3. Acceptance Criteria for ICV and CCV Standards

Analytical Method	Inorganic Analytes	ICV/CCV Low Limit (% of True Value)	ICV/CCV High Limit (% of True Value)
ICP-MS	Metals	90	110

Action:

NOTES: For initial calibrations or ICVs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.
For CCVs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the QC sample and a subsequent technically acceptable analysis of the QC sample in the analytical run.

NOTE: The data validator shall verify the correlation coefficient by calculating it using the standard concentrations and the corresponding instrument response.

1. If the instrument was not calibrated each time the instrument was set up and an ICV standard was not analyzed before field and QC samples, qualify the data as unusable (R). If the instrument was not calibrated with a blank and at least 5 calibration standards, use professional judgment to qualify results that are ≥ Method Detection Limit (MDL) as estimated (J), and non-detects as estimated (UJ). If the calibration curve does not include standards at required concentrations (e.g., a blank and at least one at or below CRQL), use professional judgment to qualify results that are ≥ MDL as estimated (J), and non-detects as estimated (UJ). If there was not at least one calibration standard at or below the CRQL for each analyte, qualify results that are ≥ MDL but < 2x the CRQL as estimated (J), and non-detects as estimated (UJ) and write it in the Contract Problem/Non-Compliance Section of the Data Review Narrative.
2. If the correlation coefficient is < 0.995, percent differences are outside the ±30% limit, or the y-intercept ≥ CRQL, qualify sample results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ). If the correlation coefficient is < 0.990, qualify results that are ≥ MDL as estimated (J) and non-detects as unusable (R).
3. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:
    a. If the ICV or CCV %R is < 75%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥ MDL as unusable (R).
    b. If the ICV or CCV %R falls within the range of 75-89%, qualify sample results that are ≥ MDL as estimated low (J-), and qualify non-detects as estimated (UJ).
    c. If the ICV or CCV %R falls within the range of 111-125%, qualify sample results that are ≥ MDL as estimated high (J+).
    d. If the ICV or CCV %R is within the range of 111-125%, non-detects should not be qualified.

e. If the ICV or CCV %R is > 125%, use professional judgment to qualify results that are ≥ MDL as estimated high (J+). Non-detects should not be qualified.
f. If the %R is > 160%, qualify all results that are ≥ MDL as unusable (R).

4. If the laboratory failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.
5. Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Narrative.
6. If calibration criteria are grossly exceeded, note this for CLP Project Officer (CLP PO) action.

NOTE: For critical samples, a further in-depth evaluation of the calibration curve may be warranted to determine if additional qualification is necessary.

Table 4. Calibration Actions for ICP-MS Analysis

Calibration Result	Action for Samples
Calibration not performed	Qualify all results as unusable (R)
Calibration incomplete	Use professional judgment Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as estimated (UJ)
Not at least one calibration standard at or below the CRQL for each analyte	Qualify results that are ≥ MDL but < 2x the CRQL as estimated (J) Qualify non-detects as estimated (UJ)
Correlation coefficient < 0.995; %D outside ±30%; y-intercept ≥ CRQL	Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as estimated (UJ)
Correlation coefficient < 0.990	Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as unusable (R)
ICV/CCV %R < 75%	Qualify results that are ≥ MDL as unusable (R) Qualify all non-detects as unusable (R)
ICV/CCV %R 75-89%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICV/CCV %R 111-125%	Qualify results that are ≥ MDL as estimated high (J+)
ICV/CCV %R > 125%	Qualify results that are ≥ MDL as estimated high (J+)
ICV/CCV %R > 160%	Qualify results that are ≥ MDL as unusable (R)

Calibration/Preparation Blanks

Action:

NOTES: For ICBs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.
For CCBs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.
For Preparation Blanks that do not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

NOTES: Convert soil sample result to mg/kg on wet weight basis to compare with the soil preparation result on Form III.
Associated samples are all samples digested with the preparation blank.

1. If the appropriate blanks were not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should then be recorded in the Data Review Narrative, and noted for Contract Laboratory Program Project Officer (CLP PO) action.
2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.
3. Some general "technical" review actions include:
    a. Any blank (including Preparation Blanks) reported with a negative result, whose value is ≤ (-MDL) but ≥ (-CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank (including Preparation Blanks) reported with a negative result, whose value is < (-CRQL) qualify results that are ≥ CRQL as estimated low (J-) and non-detects as estimated (UJ).
    b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil/sediment sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.
4. Specific "method" actions include:
    a. If the absolute value of an ICB or a CCB result is > CRQL, the analysis should be terminated. If the analysis was not terminated and the affected samples were not reanalyzed, report non-detects and results that are ≥ MDL, but ≤ CRQL as CRQL-U. For results that are > CRQL but < Blank Result, report the results at the level of the blank with a "U" qualifier. Use professional judgment to qualify results that are > Blank Result. Note this situation for CLP PO action and record it in the Data Review Narrative.

b. If the absolute value of the concentration of the Preparation Blank is ≤ CRQL, report non-detects and results that are ≥ MDL but ≤ CRQL as CRQL-U. Use professional judgment to quality results that are > CRQL.

c. If any analyte concentration in the Preparation Blank is > CRQL, the lowest concentration of that analyte in the associated samples must be 10x the Preparation Blank concentration. Otherwise, all samples associated with that blank with concentrations < 10x the Preparation Blank concentration and > CRQL should be redigested and reanalyzed. Raise the CRQL to the concentration found in the Preparation Blank and report those samples that do not require redigestion (that are ≥ MDL but ≤ CRQL) as CRQL-U. Note for CLP PO action and record in the Data Review Narrative if the laboratory failed to redigest and reanalyze the affected samples. The reviewer shall then use professional judgment to assess the data.

Table 5. Calibration/Preparation Blank Actions for ICP-MS Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB	≥ MDL but ≤ CRQL	Non-detect	No action
		≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL	Use professional judgment
ICB/CCB	> CRQL	≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL but < Blank Result	Report at level of Blank Result with a "U"
		> Blank Result	Use professional judgment
ICB/CCB	≤ (-MDL) but ≥ (-CRQL)	≥ MDL, or non-detect	Use professional judgment
ICB/CCB	< (-CRQL)	< 10x the CRQL	Qualify results that are ≥ CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)
Preparation Blank	> CRQL	≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL but < 10x the Blank Result	Qualify results as estimated high (J+)
		≥ 10x the Blank Result	No action
Preparation Blank	≥ MDL but ≤ CRQL	Non-detect	No action
		≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL	Use professional judgment
Preparation Blank	< (-CRQL)	< 10x the CRQL	Qualify results that are ≥ CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)

Inductively Coupled Plasma - Interference Check Sample (ICP-ICS)

Action:

NOTE: For an ICS for ICP-MS that does not meet the technical criteria, apply the action to all samples reported from the analytical run.

NOTE: The laboratory should have analyzed and reported ICS results for all elements being reported from the analytical run and for all interferents (target and non-target) for these reported elements.

1. The raw data may not contain results for interferents. In this case, the reviewer shall use professional judgment to qualify the data. If the data does contain results for interferents, the reviewer should apply the following actions to samples with concentrations of interferents that are comparable to, or greater than, their respective levels in the ICS:
    a. If the ICS %R for an analyte or interferent is > 120% (or greater than the true value + 2x the CRQL, as applicable) and the sample results are non-detects, the data should not be qualified.
    b. If the ICS %R for an analyte or interferent is > 120% (or greater than the true value + 2x the CRQL, as applicable) qualify sample results that are ≥ MDL as estimated high (J+). If the ICS %R (or true value) grossly exceeds the limits, use professional judgment to qualify the data.
    c. If the ICS %R for an analyte or interferent falls within the range of 50-79% (or less than the true value – 2x the CRQL, as applicable) qualify sample results that are ≥ MDL as estimated low (J-).
    d. If the ICS recovery for an analyte falls within the range of 50-79% (or less than the true value – 2x the CRQL, as applicable), the possibility of false negatives exists. Qualify sample non-detects as estimated (UJ).
    e. If the ICSAB %R for an analyte or interferent is < 50%, qualify all sample results that are ≥ MDL and all sample non-detects as unusable (R).
2. If results that are ≥ MDL are observed for analytes that are not present in the ICS solution, the possibility of false positives exists. An evaluation of the associated sample data for the affected elements should be made. For samples with comparable or higher levels of interferents and with analyte concentrations that approximate those levels found in the ICS, qualify sample results that are ≥ MDL as estimated high (J+). Non-detects should not be qualified.
3. If negative results are observed for analytes that are not present in the ICS solution, and their absolute value is ≥ MDL, the possibility of false negatives in the samples exists. An evaluation of the associated sample data for the affected analytes should be made. For samples with comparable or higher levels of interferents, qualify non-detects for the affected analytes as estimated (UJ), and results that are ≥ MDL but < 10x the absolute value of the negative result as estimated low (J-).
4. If the raw data does not contain results for the interferents, note it in the Data Review Narrative.

5. Actions regarding the interpretation and/or the subsequent qualification of ICP data due to the ICS analytical results can be extremely complex. Use professional judgment to determine the need for the associated sample data to be qualified. The reviewer may need to obtain additional information from the laboratory. All interpretive situations should then be recorded in the Data Review Narrative.
6. If the ICS acceptance criteria are grossly exceeded, note the specifics for CLP PO action.

Table 6. Interference Check Actions for ICP-MS Analysis

Interference Check Sample Results	Action for Samples
ICS %R > 120% (or greater than true value + 2x the CRQL)	Qualify results that are ≥ MDL as estimated high (J+)
ICS %R 50-79% (or less than true value – 2x the CRQL)	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICSAB %R < 50%	Qualify all sample data as unusable (R)
Potential false positives in field samples with interferents	Qualify results that are ≥ MDL as estimated high (J+)
Potential false negatives in field samples with interferents	Qualify results that are ≥ MDL but < 10x the (|negative value|) as estimated low (J-) Qualify non-detects as estimated (UJ)

Laboratory Control Sample (LCS)

Action:

If the LCS criteria are not met, the laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data associated with an LCS that does not meet the required criteria.
For an LCS that does not meet the technical criteria, apply the action to all samples in the same preparation batch.

1. **LCS:**
    a. If the LCS %R falls within the range of 40-69%, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated low (J-). If the LCS %R is > 130%, qualify sample results that are ≥ MDL as estimated high (J+).
    b. If the LCS recovery is > 130% and the sample results are non-detects, the data should not be qualified.
    c. If the LCS recovery falls within the range of 40-69%, qualify non-detects as estimated (UJ).
    d. If LCS %R is < 40%, qualify all results that are ≥ MDL as estimated low (J-) and all non-detects as unusable (R).
    e. If the LCS %R is > 150%, qualify all affected data (both detects and non-detects) as unusable (R).
2. If a laboratory fails to analyze an LCS with each SDG, or if a laboratory consistently fails to generate acceptable LCS recoveries, note this for CLP Project Officer (CLP PO) action.
3. Whenever possible, the potential effects on the data due to out-of-control LCS results should be noted in the Data Review Narrative.

Table 7. LCS Actions for ICP-MS Analysis

LCS Result	Action for Samples
%R 40-69%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
%R > 130%	Qualify results that are ≥ MDL as estimated high (J+)
%R < 40%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
%R > 150%	Qualify all results as unusable (R)

Laboratory Duplicate Sample Analysis

Action:

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to only the field sample used to prepare the duplicate sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

NOTE: Delete "*" from Form IAs.
If one value is > CRQL and the other value is non-detect, calculate the absolute difference between the value > CRQL and the MDL and use this difference to qualify sample results.
If more than one lab duplicate sample was analyzed for an SDG, then qualify the associated samples based on the worst lab duplicate analysis.

1. If the appropriate number of duplicate samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.
2. If the results from a duplicate analysis for a particular analyte fall outside the control limits for > 5x the CRQL, qualify aqueous sample results that are ≥ CRQL as estimated (J) if the RPD is between 20% - 100% and as unusable (R) if the RPD is > 100%. Qualify soil/sediment sample results that are ≥ CRQL as estimated (J) if the RPD is between 35% - 120% and as unusable (R) if the RPD is > 120%.
3. If the results from a duplicate analysis for a particular analyte fall outside the control limits for ≤ 5x the CRQL, qualify those results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ).
4. If a field blank or PE sample was used for the duplicate sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked and professional judgment exercised by the data reviewer when evaluating the data.
5. Note the potential effects on the data due to out-of-control duplicate sample results in the Data Review Narrative.

Table 8. Duplicate Sample Actions for ICP-MS Analysis

Duplicate Sample Results	Action for Samples
Aqueous: Both original sample and duplicate sample > 5x the CRQL and 20% < RPD < 100%	Qualify those results that are ≥ CRQL as estimated (J)
Aqueous: Both original sample and duplicate sample > 5x the CRQL and RPD ≥ 100%	Qualify those results that are ≥ CRQL as unusable (R)
Soil/Sediment: Both original sample and duplicate sample > 5x the CRQL and 35% < RPD < 120%	Qualify those results that are ≥ CRQL as estimated (J)
Soil/Sediment: Both original sample and duplicate sample > 5x the CRQL and RPD ≥ 120%	Qualify those results that are ≥ CRQL as unusable (R)
Original sample or duplicate sample ≤ 5x the CRQL (including non-detects) and absolute difference between sample and duplicate > CRQL	Qualify those results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ)

Spike Sample Analysis

Action:

NOTE: For a Matrix Spike that does not meet the technical criteria, apply the action to only the field sample used to prepare the Matrix Spike sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

NOTE: The final spike concentrations required for the various target analytes are presented in the methods described in the Statement of Work (SOW).

NOTE: When the sample concentration is < Method Detection Limit (MDL), use SR = 0 only for the purpose of calculating the %R. The actual spiked sample results, sample results, and %R (positive or negative) shall still be reported on Forms VA-IN and VB-IN.

NOTES: Not required for Ca, Mg, K, and Na (both matrices); Al and Fe (soil only).
If more than one spiked sample was analyzed for one SDG, then qualify the associated data based on the worst spiked sample analysis.
Disregard the out of control spike recoveries for analytes whose unspiked concentrations are ≥ 4x the spike added.
Delete "N" from Form IAs.

1. If the appropriate number of Matrix Spike samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. Note the situation in the Data Review Narrative, and for Contract Laboratory Program Project Officer (CLP PO) action.
2. If a field blank or PE sample was used for the spiked sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked and professional judgment exercised by the data reviewer when evaluating the data.
3. If the Matrix Spike recovery does not meet the evaluation criteria and a required post-digestion spike was not performed, note this for CLP PO action.
4. If the Matrix Spike %R is < 30%, verify that a post-digestion spike was analyzed if required. If the post-digestion spike %R is < 75% or is not performed, qualify sample results that are ≥ MDL as estimated low (J-) and non-detects as unusable (R). If the post-digestion spike %R is ≥ 75%, qualify sample results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ).
5. If the Matrix Spike %R is 30-74% and the sample results are ≥ MDL, verify that a post-digestion spike was analyzed if required. If the %R for the post-digestion is also < 75% or is not performed, qualify the affected data as estimated low (J-). If the %R for the post-digestion spike is ≥ 75%, qualify the affected data as estimated (J).
6. If the Matrix Spike %R falls within the range of 30-74% and the sample results are non-detects, qualify the affected data as estimated (UJ).

7. If the Matrix Spike %R is > 125% and the reported sample results are non-detects, the sample data should not be qualified.
8. If the Matrix Spike %R is > 125% and the sample results are ≥ MDL, verify that a post-digestion spike was analyzed if required. If the %R for the post-digestion spike is also > 125% or is not performed, qualify the affected data as estimated high (J+). If the %R for the post-digestion spike is ≤ 125%, qualify the affected data as estimated (J).
9. Note the potential effects on the data due to out-of-control spiked sample results in the Data Review Narrative.

Table 9. Spike Sample Actions for ICP-MS Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R < 30% Post-digestion spike %R < 75%	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R < 30% Post-digestion spike %R ≥ 75%	Qualify affected results that are ≥ MDL as estimated (J) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion Spike %R < 75%	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R ≥ 75%	Qualify affected results that are ≥ MDL as estimated (J) and affected non-detects as estimated (UJ)
Matrix Spike %R > 125% Post-digestion spike %R > 125%	Qualify affected results that are ≥ MDL as estimated high (J+)
Matrix Spike %R > 125% Post-digestion spike %R ≤ 125%	Qualify affected results that are ≥ MDL as estimated (J)
Matrix Spike %R < 30% No post-digestion spike performed	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R 30-74% No post-digestion spike performed	Qualify affected results that are ≥ MDL as estimated low (J-) and non-detects as estimated (UJ)
Matrix Spike %R > 125% No post-digestion spike performed	Qualify affected results that are ≥ MDL as estimated high (J+) Non-detects are not qualified

ICP Serial Dilution

Action:

NOTE: For a serial dilution that does not meet the technical criteria, apply the action to only the field sample used to prepare the serial dilution sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

NOTE: Serial dilution analysis is required only when the initial concentration is greater than 50x the MDL.
Delete "E" from Form IAs.

1. If the required %D criteria are not met, qualify affected aqueous results whose raw data are > MDL as estimated (J) if %D is between 10%-100% and qualify as unusable (R) if %D is ≥ 100%. Qualify affected soil/sediment results whose raw data are > MDL as estimated (J) if %D is between 15%-120% and qualify as unusable (R) if %D is ≥ 120%.
2. If evidence of positive or negative interference is found, use professional judgment to qualify the associated sample data. Note the potential effects on the reported data in the Data Review Narrative.
3. It should be noted for Contract Laboratory Program Project Officer (CLP PO) action and in the Data Review Narrative if a field blank or PE sample was used for the serial dilution analysis.

Table 10. Serial Dilution Actions for ICP-MS Analysis

Serial Dilution Result	Action for Samples
Aqueous: Sample concentration > 50x MDL and 10% < %D < 100%	Qualify affected results whose raw data are > MDL as estimated (J)
Aqueous: Sample concentration > 50x MDL and %D ≥ 100%	Qualify affected results whose raw data are > MDL as unusable (R)
Soil/Sediment: Sample concentration > 50x MDL and 15% < %D < 120%	Qualify affected results whose raw data are > MDL as estimated (J)
Soil/Sediment: Sample concentration > 50x MDL and %D ≥ 120%	Qualify affected results whose raw data are > MDL as unusable (R)
Interferences present	Use professional judgment

ICP-MS Internal Standards

Action:

NOTE: Apply the action to the affected analytes for each sample that does not meet the internal standard criteria.

1. If no internal standards were analyzed with the run, the sample data should be qualified as unusable (R). Record this in the Data Review Narrative and note for CLP Project Officer (CLP PO) action.
2. If less than five of the required internal standards were analyzed with the run, or a target analyte(s) is (are) not associated to an internal standard, the sample data, or analyte data not associated to an internal standard should be qualified as unusable (R). Record this in the Data Review Narrative and note for CLP PO action.
3. If the % Relative Intensities for all internal standards in a sample is within 60-125% of the response in the calibration blank, the sample data should not be qualified.
4. If the %RI for an internal standard in a sample is not within the 60-125% limit, qualify the data for those analytes associated with the internal standard(s) outside the limit as follows:
    a. If the sample was reanalyzed at a two-fold dilution with internal standard %RI within the limits, report the result of the diluted analysis without qualification. If the %RI of the diluted analysis was not within the 60-125% limit, report the results of the original undiluted analyses and qualify the data for all analytes that are $\geq$ Method Detection Limit (MDL) in the sample associated with the internal standard as estimated (J), and non-detected analytes associated with the internal standard as estimated (UJ).
    b. If the sample was not reanalyzed at a two-fold dilution, the reviewer should use professional judgment to determine the reliability of the data. The reviewer may determine that the results are estimated (J) or unusable (R).

Table 11. Internal Standard Actions for ICP-MS Analysis

Internal Standard Results	Action for Samples
No internal standards	Qualify all results as unusable (R)
< 5 of the required internal standards	Qualify all results as unusable (R)
Target analyte not associated with internal standard	Qualify all analyte results not associated with an internal standard as unusable (R)
% RI < 60% or > 125%, original sample reanalyzed at 2-fold dilution, and % RI of diluted sample analysis is between 60% and 125%	Do not qualify the data
% RI < 60% or > 125%, original sample reanalyzed at 2-fold dilution, and % RI of diluted sample analysis is outside the 60% to 125% limit	Qualify analytes associated with the failed internal standard that are ≥ MDL as estimated (J) and qualify associated non-detects as estimated (UJ)
Original sample not reanalyzed at 2-fold dilution	Use professional judgment Qualify sample results as estimated (J) or unusable (R)

Field Duplicates

Action:

NOTES: For field duplicates that do not meet the technical criteria, apply the action to only the field sample and its duplicate. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.
Check the Sampling Trip Report for the field duplicate pair.
Substitute MDL for CRQL when MDL > CRQL.
Do not calculate RPD when both values are non-detects.
If one value is > the CRQL and the other value is non-detect, calculate the absolute difference between the value > the CRQL and the MDL, and use this criteria to qualify the results.

1. If a field duplicate pair was collected and analyzed, calculate and report the RPD when the sample and its field duplicate values are both ≥ 5x the CRQL. Calculate and report the absolute difference when at least one value (sample or duplicate) is < 5x the CRQL.
2. When aqueous sample and duplicate values are both ≥ 5x the CRQL, and the RPD is > 20%, qualify the sample and its duplicate as estimated (J).
3. When aqueous sample and/or the duplicate value is < 5x the CRQL, and the absolute difference is > the CRQL, qualify results > the MDL as estimated (J) and non-detects as estimated (UJ).
4. When soil/sediment sample and duplicate values are both ≥ 5x the CRQL, and the RPD is > 50%, qualify the sample and its duplicate as estimated (J).
5. When soil/sediment sample and/or the duplicate value is < 5x the CRQL, and the absolute difference is > 2x the CRQL, qualify results > the MDL as estimated (J) and non-detects as estimated (UJ).

Table 12. Field Duplicate Actions for ICP-MS Analysis

Sample Type	Field Duplicate Result	Action for Samples
Aqueous	Sample and its field duplicate ≥ 5x the CRQL and RPD > 20%	Qualify sample and its duplicate as estimated (J)
	Sample and/or its field duplicate < 5x the CRQL and absolute difference > the CRQL	Qualify results > the MDL as estimated (J) Qualify non-detects as estimated (UJ)
Soil/Sediment	Sample and its field duplicate ≥ 5x the CRQL and RPD > 50%	Qualify sample and its duplicate as estimated (J)
	Sample and/or its field duplicate < 5x the CRQL and absolute difference > 2x the CRQL	Qualify results > the MDL as estimated (J) Qualify non-detects as estimated (UJ)

Field/Rinsate/Trip Blanks

Action:

NOTE: Designate "Field Blank" as such on Form IA.
Field Blank results previously rejected due to other criteria cannot be used to qualify field samples.
Do not use Rinsate Blank associated with soils to qualify water samples and vice versa.
If the MDL is > the CRQL, substitute CRQL with 2x the MDL.

1. If the appropriate blanks were not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should then be recorded in the Data Review Narrative, and noted for Contract Laboratory Program Project Officer (CLP PO) action.
2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.
3. Some general "technical" review actions include:
    a. Any blank reported with a negative result, whose value is ≤ (-MDL) but ≥ (-CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank reported with a negative result, whose value is < (-CRQL) qualify results that are ≥ CRQL as estimated low (J-) and non-detects as estimated (UJ).
    b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil/sediment sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.
4. If the absolute value of any analyte in a Field/Rinsate/Trip Blank is > the CRQL, then the CRQL shall be raised to the level in the Field/Rinsate/Trip Blank and the associated sample data below this level shall be reported as CRQL-U.
5. Sample results > the Field/Rinsate/Trip Blank value but < 10x the Field/Rinsate/Trip Blank value shall be qualified as estimated (J).
6. Sample results ≥ the MDL but ≤ the CRQL shall be reported at the CRQL value with a "U".

Table 13. Field/Rinsate/Trip Blank Actions for ICP-MS Analysis

Blank Result	Sample Result	Action for Samples
> CRQL	≥ MDL but ≤ CRQL	Report CRQL value with a "U"
	> CRQL but < Blank Result	Report at level of Blank Result with a "U"
	> Blank Result but < 10x the Blank Result	Use professional judgment to qualify results as estimated (J)

Linear Ranges

Action:

1. If any sample result was higher than the high linear range for ICP-MS and the sample was not diluted to obtain the result reported on Form I, qualify the affected results ≥ MDL as estimated (J).

Percent Solids of Sediments

Action:

1. If the percent solids in sediment for a sample are < 50%, qualify the affected results ≥ MDL as estimated (J) and the non-detects as estimated (UJ).

Regional Quality Assurance (QA) and Quality Control (QC)

Action:

Any action must be in accordance with Regional specifications and criteria for acceptable PE sample results. Note any unacceptable PE sample results for Contract Laboratory Program Project Officer (CLP PO) action.

Overall Assessment

Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.
2. Write a brief Data Review Narrative to give the user an indication of the analytical limitations of the data. Note any discrepancies between the data and the Sample Delivery Group (SDG) Narrative for Contract Laboratory Program Project Officer (CLP PO) action. If sufficient information on the intended use and required quality of the data is available, the reviewer should include an assessment of the data usability within the given context.
3. If any discrepancies are found, the laboratory may be contacted by the Region's designated representative to obtain additional information for resolution. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

Calculations for ICP-MS

Aqueous/Water Sample Concentration by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS):

The concentrations determined in the digestate are to be reported in units of µg/L:

$$Concentration\ \left(\frac{\mu g}{L}\right) = C \times \frac{V_f}{V} \times DF$$

Where,

C = Instrument value in µg/L (The average of all replicate integrations).

V_f = Final digestion volume (mL)

V = Initial aliquot amount (mL)

DF = Dilution Factor

Soil/Sediment Sample Concentration by ICP-MS:

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of mg/kg:

$$Concentration\ (drywt.)\left(\frac{mg}{kg}\right) = C \times \frac{V_f}{W \times S} \times \frac{DF}{1000}$$

Where,

C = Instrument value in µg/L (The average of all replicate integrations).

V_f = Final digestion volume (mL)

W = Initial aliquot amount (g)

S = % Solids/100 (see Exhibit D of ISM01.2 - Introduction to Analytical Methods, Section 1.6).

DF = Dilution Factor

Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation:

To calculate the adjusted MDL or adjusted CRQL for aqueous/water samples, substitute the value of the MDL (µg/L) or CRQL (µg/L) into the "C" term in the equation above. Calculate the adjusted MDL or adjusted CRQL for soil/sediment samples as follows:

$$Adjusted\ Concentration\ \left(\frac{mg}{kg}\right) = C \times \frac{W_M}{W \times S} \times \frac{V_f}{V_M} \times DF$$

Where,

C	=	MDL or CRQL (mg/kg)
W_M	=	Minimum method required aliquot amount (g) (1.00 g or 0.50 g)
W	=	Initial aliquot amount (g)
V_M	=	Method required final sample digestion volume (mL) (100 mL)
V_f	=	Final digestion volume (mL)
S	=	% Solids/100 (see Exhibit D of ISM01.2 - Introduction to Analytical Methods, Section 1.6).
DF	=	Dilution Factor

APPENDIX A: GLOSSARY

Analyte -- The element of interest, ion, or parameter an analysis seeks to determine.
Analytical Services Branch (ASB) -- Directs the Contract Laboratory Program (CLP) from within the Office of Superfund Remediation and Technical Innovation (OSRTI) in the Office of Solid Waste and Emergency Response (OSWER).
Analytical Sample -- Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, Initial Calibration Verification (ICV), Initial Calibration Blank (ICB), Continuing Calibration Verification (CCV), and Continuing Calibration Blank (CCB). Note that the following are all defined as analytical samples: undiluted and diluted samples (USEPA and non-USEPA); Matrix Spike samples; duplicate samples; serial dilution samples, analytical (post-digestion/post-distillation) spike samples; Interference Check Samples (ICSs); Laboratory Control Samples (LCSs); and Preparation Blanks.
Associated Samples -- Any sample related to a particular Quality Control (QC) analysis. For example, for Initial Calibration Verification (ICV), all samples run under the same calibration curve. For duplicates, all Sample Delivery Group (SDG) samples digested/distilled of the same matrix.
Blank -- A sample designed to assess specific sources of contamination. See individual definitions for types of blanks.
Calibration -- The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards are to be prepared using the same type of reagents or concentration of acids as used in the sample preparation.
Calibration Blank -- A blank solution containing all of the reagents in the same concentration as those used in the analytical sample preparation. This blank is not subject to the preparation method.
Calibration Curve -- A plot of instrument response versus concentration of standards.
Calibration Standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method, but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.
Case -- A finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).
Continuing Calibration Blank (CCB) -- A reagent water sample that is run 2 hours (ICP-AES, ICP-MS) or every hour (Hg, CN) and designed to detect any carryover contamination.
Contract Compliance Screening (CCS) -- A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is performed under USEPA direction by the Contract Laboratory Program (CLP) Sample Management Office (SMO) contractor.
Continuing Calibration Verification (CCV) -- A single parameter or multi-parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV can be one of the calibration standards. However, all parameters being measured by the particular system must be

represented in this standard and the standard must have the same matrix (i.e., the same amount of reagents and/or preservatives) as the samples. The CCV should have a concentration in the middle of the calibration range and shall be run every 2 hours (ICP-AES, ICP-MS) or every hour (Hg, CN).

Contract Laboratory Program (CLP) -- Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technical Innovation (OSRTI) of USEPA.

Contract Laboratory Program Project Officer (CLP PO) -- The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a CLP laboratory.

Contract Required Quantitation Limit (CRQL) -- Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

Duplicate -- A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Field Blank -- Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the laboratory. A field blank includes trip blanks, rinsate blanks, bottle blanks, equipment blanks, preservative blanks, decontamination blanks, etc.

Field Duplicate -- A duplicate sample generated in the field, not in the laboratory.

Holding Time -- The maximum amount of time samples may be held before they are processed.

Contractual -- The maximum amount of time that the Contract Laboratory Program (CLP) laboratory may hold the samples from the sample receipt date until analysis and still be in compliance with the terms of the contract, as specified in the CLP Analytical Services Statement of Work (SOW). These times are the same or less than technical holding times to allow for sample packaging and shipping.

Technical -- The maximum amount of time that samples may be held from the collection date until analysis.

Initial Calibration -- Analysis of analytical standards for a series of different specified concentrations to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

Initial Calibration Blank (ICB) -- The first blank standard run to confirm the calibration curve.

Initial Calibration Verification (ICV) -- Solution(s) prepared from stock standard solutions, metals, or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV should be traceable to National Institute of Standards and Technology (NIST) or other certified standard sources when USEPA ICV solutions are not available.

Internal Standard -- A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

Interference Check Sample (ICS) -- Verifies the contract laboratory's ability to overcome interferences typical of those found in samples.

Laboratory Control Sample (LCS) -- A control sample spiked at known level(s). LCSs are processed using the same sample preparation, reagents, and analytical methods employed for the USEPA samples received.
Matrix -- The predominant material of which the sample to be analyzed is composed. For the purposes of this document, the matrices are aqueous/water, soil/sediment, wipe, and filter.
Matrix Spike -- Introduction of a known concentration of analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology (also identified as a pre-distillation/digestion spike).
Method Detection Limit (MDL) -- The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the 7 replicates.
Narrative (SDG Narrative) -- Portion of the data package which includes laboratory, contract, Case, Sample Number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.
Office of Solid Waste and Emergency Response (OSWER) – The USEPA office that provides policy, guidance, and direction for the USEPA's solid waste and emergency response programs, including Superfund.
Percent Difference (%D) -- As used in this document and the Statement of Work (SOW), is used to compare two values. The difference between the two values divided by one of the values.
Performance Evaluation (PE) Sample -- A sample of known composition provided by USEPA for contractor analysis. Used by USEPA to evaluate Contractor performance.
Post Digestion Spike -- The addition of a known amount of standard after digestion or distillation (also identified as an analytical spike).
Preparation Blank -- An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.
Relative Percent Difference (RPD) -- As used in this document and the Statement of Work (SOW) to compare two values, the RPD is based on the mean of the two values, and is reported as an absolute value (i.e., always expressed as a positive number or zero).
Regional Sample Control Center Coordinator (RSCC) -- In USEPA Regions, coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.
Relative Standard Deviation (RSD) -- As used in this document and the Statement of Work (SOW), the mean divided by the standard deviation, expressed as a percentage.
Sample -- A single, discrete portion of material to be analyzed, which is contained in single or multiple containers and identified by a unique Sample Number.
Sample Delivery Group (SDG) -- A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

a. Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case; or
b. Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

c. Scheduled at the same level of deliverable.

In addition, all samples and/or sample fractions assigned to an SDG must be scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG. Samples may be assigned to SDGs by matrix (i.e., all soil/sediment samples in one SDG, all aqueous/water samples in another) at the discretion of the laboratory.

Sample Management Office (SMO) -- A contractor-operated facility operated under the SMO contract, awarded and administered by the USEPA. Provides necessary management, operations, and administrative support to the Contract Laboratory Program (CLP).

Serial Dilution -- The dilution of a sample by a factor of five. When corrected by the Dilution Factor (DF), the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents [Inductively Coupled Plasma (ICP) only].

Statement of Work (SOW) -- A document which specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Tune -- Analysis of a solution containing a range of isotope masses to establish Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) mass-scale accuracy, mass resolution, and precision prior to calibration.

APPENDIX B: INORGANIC DATA EXECUTIVE NARRATIVE TEMPLATE

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
DESA/HWSB/HWSS
2890, Woodbridge Avenue, Edison, NJ 08837

EXECUTIVE NARRATIVE

Case No.: **SDG No.:**
Site: **Laboratory:**

QAPP
HWSS #: **Number of Samples:**
Contractor #: **Sampling date:**

SUMMARY:

Critical: Results have an unacceptable level of uncertainty and should not be used for making decisions. Data have been qualified "R" rejected.

Major: A level of uncertainty exists that may not meet the data quality objectives for the project. A bias is likely to be present in the results. Data have been qualified "J" estimated.

Minor: The level of uncertainty is acceptable. No significant bias in the data was observed.

Critical Findings: None

Major Findings: None

Minor Findings: None

COMMENTS:

Validator's Signature: **Date:**
Name:
Affiliation:

Approver's Signature: **Date:**
Name:
Affiliation:

APPENDIX C: SAMPLE INORGANIC DATA SAMPLE SUMMARY

Case No: 00001	Contract: XYZ1234	SDG No: XY123	Lab Code: ABCD
Sample Number: XY123	Method: ICP_AES	Matrix: FLUFF	MA Number: DEFAULT
Sample Location: SOMEWHERE OUT THERE	pH: 15	Sample Date: 13322059	Sample Time: 24:03:00
% Moisture :		% Solids :	

Analyte Name	Result	Units	Dilution Factor	Lab Flag	Validation	Reportable	Validation Level
Aluminum	400	ug/L	1			Yes	S2BVEM
Antimony	40	ug/L	1	U	U	Yes	S2BVEM
Arsenic	40	ug/L	1	U	U	Yes	S2BVEM
Barium	40	ug/L	1	U	U	Yes	S2BVEM
Beryllium	40	ug/L	1	U	U	Yes	S2BVEM
Cadmium	40	ug/L	1	U	U	Yes	S2BVEM
Calcium	400	ug/L	1			Yes	S2BVEM
Chromium	40	ug/L	1	U	U	Yes	S2BVEM
Cobalt	40	ug/L	1	U	U	Yes	S2BVEM
Copper	40	ug/L	1	U	U	Yes	S2BVEM
Iron	40	ug/L	1	J	U	Yes	S2BVEM
Lead	40	ug/L	1	U	U	Yes	S2BVEM
Magnesium	400	ug/L	1			Yes	S2BVEM
Manganese	400	ug/L	1			Yes	S2BVEM
Nickel	40	ug/L	1	U	U	Yes	S2BVEM
Potassium	400	ug/L	1			Yes	S2BVEM
Selenium	40	ug/L	1	U	U	Yes	S2BVEM
Silver	40	ug/L	1	U	U	Yes	S2BVEM
Sodium	400	ug/L	1			Yes	S2BVEM
Thallium	40	ug/L	1	U	U	Yes	S2BVEM
Vanadium	40	ug/L	1	U	U	Yes	S2BVEM
Zinc	40	ug/L	1	U	U	Yes	S2BVEM

APPENDIX D: ELECTRONIC DATA DELIVERABLE TEMPLATE

DATA_PROVIDER	LAB_MATRIX_CODE	RESULT_UNIT
SYS_SAMPLE_CODE	ANAL_LOCATION	DETECTION_LIMIT_UNIT
SAMPLE_NAME	BASIS	TIC_RETENTION_TIME
SAMPLE_MATRIX_CODE	CONTAINER_ID	RESULT_COMMENT
SAMPLE_TYPE_CODE	DILUTION_FACTOR	QC_ORIGINAL_CONC
SAMPLE_SOURCE	PREP_METHOD	QC_SPIKE_ADDED
PARENT_SAMPLE_CODE	PREP_DATE	QC_SPIKE_MEASURED
SAMPLE_DEL_GROUP	LEACHATE_METHOD	QC_SPIKE_RECOVERY
SAMPLE_DATE	LEACHATE_DATE	QC_DUP_ORIGINAL_CONC
SYS_LOC_CODE	LAB_NAME_CODE	QC_DUP_SPIKE_ADDED
START_DEPTH	QC_LEVEL	QC_DUP_SPIKE_MEASURED
END_DEPTH	LAB_SAMPLE_ID	QC_DUP_SPIKE_RECOVERY
DEPTH_UNIT	PERCENT_MOISTURE	QC_RPD
CHAIN_OF_CUSTODY	SUBSAMPLE_AMOUNT	QC_SPIKE_LCL
SENT_TO_LAB_DATE	SUBSAMPLE_AMOUNT_UNIT	QC_SPIKE_UCL
SAMPLE_RECEIPT_DATE	ANALYST_NAME	QC_RPD_CL
SAMPLER	INSTRUMENT_ID	QC_SPIKE_STATUS
SAMPLING_COMPANY_CODE	COMMENT	QC_DUP_SPIKE_STATUS
SAMPLING_REASON	PRESERVATIVE	QC_RPD_STATUS
SAMPLING_TECHNIQUE	FINAL_VOLUME	BREAK_2
TASK_CODE	FINAL_VOLUME_UNIT	SYS_SAMPLE_CODE
COLLECTION_QUARTER	CAS_RN	LAB_ANL_METHOD_NAME
COMPOSITE_YN	CHEMICAL_NAME	ANALYSIS_DATE
COMPOSITE_DESC	RESULT_VALUE	TOTAL_OR_DISSOLVED
SAMPLE_CLASS	RESULT_ERROR_DELTA	COLUMN_NUMBER
CUSTOM_FIELD_1	RESULT_TYPE_CODE	TEST_TYPE
CUSTOM_FIELD_2	REPORTABLE_RESULT	TEST_BATCH_TYPE
CUSTOM_FIELD_3	DETECT_FLAG	TEST_BATCH_ID
COMMENT	LAB_QUALIFIERS	CASE
BREAK_1	VALIDATOR_QUALIFIERS	CONTRACT_NUM
SYS_SAMPLE_CODE	INTERPRETED_QUALIFIERS	SCRIBE_SAMPLE_ID
LAB_ANL_METHOD_NAME	ORGANIC_YN	SAMPLE_TIME
ANALYSIS_DATE	METHOD_DETECTION_LIMIT	FRACTION
TOTAL_OR_DISSOLVED	REPORTING_DETECTION_LIMIT	PH
COLUMN_NUMBER	QUANTITATION_LIMIT	DATA_VAL_LABEL
TEST_TYPE		

VALIDATION SOP

Titanium

USEPA Region 2 SOP HW-2a, Rev.15, 12/12

Hazardous Waste Support Section
SOP NO. HW-2a Revision 15
ICP-AES Data Validation

Approvals:

Muhammad Hanif Sheikh — 12/20/12
Muhammad Hanif Sheikh
Chemist, Hazardous Waste Support Section
Date

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Philip Cocuzza
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Date

Jon Gabry — 12/21/12
Jon Gabry
Chief, Hazardous Waste Support Branch
Date

Approving Official Annual Review
Date

NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by USEPA, and may not be relied upon to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

This document can be obtained from the USEPA's Region 2 Quality Assurance website at:

http://www.epa.gov/region2/qa/documents.htm

TABLE OF CONTENTS

LIST OF TABLES

ACRONYMS

ASB	Analytical Services Branch
CCB	Continuing Calibration Blank
CCS	Contract Compliance Screening
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
CO	Contracting Officer
CRQL	Contract Required Quantitation Limit
DF	Dilution Factor
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
EDM	EXES Data Manager
ESAT	Environmental Services Assistance Team
EXES	Electronic Data eXchange and Evaluation System
HWSS	Hazardous Waste Support Section
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Interference Check Sample
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
MDL	Method Detection Limit
NIST	National Institute of Standards and Technology
OSRTI	Office of Superfund Remediation and Technology Innovation
OSWER	Office of Solid Waste and Emergency Response
PE	Performance Evaluation
%D	Percent Difference
%R	Percent Recovery
%S	Percent Solids
PO	Project Officer
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
RSCC	Regional Sample Control Center Coordinator
SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
TR/COC	Traffic Report/Chain of Custody Documentation
USEPA	United States Environmental Protection Agency

TARGET ANALYTE LIST

Al Aluminum
Sb Antimony
As Arsenic
Ba Barium
Be Beryllium
Cd Cadmium
Ca Calcium
Cr Chromium
Co Cobalt
Cu Copper
Fe Iron
Pb Lead
Mg Magnesium
Mn Manganese
Ni Nickel
K Potassium
Se Selenium
Ag Silver
Na Sodium
Tl Thallium
V Vanadium
Zn Zinc

INTRODUCTION

This document is designed to offer the data reviewer guidance in determining the validity of analytical data generated through the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) ISM01.X Inorganic Superfund Methods (Multi-Media, Multi-Concentration), hereinafter referred to as the ISM01.2 SOW, and any future editorial revisions of ISM01.2. This guidance is somewhat limited in scope and is intended to be used as an aid in the formal technical review process.

The guidelines presented in the document will aid the data reviewer in establishing (a) if data meets the specific technical and QC criteria established in the SOW, and (b) the validity and extent of bias of any data not meeting the specific technical and QC criteria established in the SOW. It must be understood by the reviewer that acceptance of data not meeting technical requirements is based upon many factors, including, but not limited to site-specific technical requirements, the need to facilitate the progress of specific projects, and availability for re-sampling.

The reviewer should note that while this document is to be used as an aid in the formal data review process, other sources of guidance and information, as well as professional judgment, should also be used to determine the ultimate validity of data, especially in those cases where all data does not meet specific technical criteria.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process.

U	The analyte was analyzed for, but was not detected above the level of the reported sample quantitation limit.
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
J+	The result is an estimated quantity, but the result may be biased high.
J-	The result is an estimated quantity, but the result may be biased low.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.

DATA PACKAGE INSPECTION

For data obtained through the Contract Laboratory Program (CLP), the EXES Data Manager (EDM) is a useful tool in the data review process. For more information about EDM, please refer to the following Sample Management Office (SMO) website:

https://epasmoweb.fedcsc.com/help/guides/Submit%20and%20Inspect%20Data%20Quick%20Guide%20%28EXES%29.pdf

EDM will identify any missing and/or incorrect information in the data package. The CLP laboratory may submit a reconciliation package for any missing items or to correct data.
If there are any concerns regarding the data package, contact the CLP Project Officer (CLP PO) from the Region where the samples were taken. For personnel contact information, please refer to the following CLP website:

http://www.epa.gov/superfund/programs/clp/contacts.htm

HWSS DATA VALIDATION PROCESS

After downloading the data package from EDM, the data validator will use the recommendations in this SOP as well as their own professional judgment to validate the data.

The data will be saved in the following location, under the appropriate case number folder:

G:\DESADIV\HWSS\DATA VALIDATION

The file naming conventions will consist of

A. case number i.e., 12345
B. SDG name i.e., MBXY12
C. level of validation performed i.e., S2BVE

Examples: **12345_MBXY12_S2BVE.xls**

12345_MBXY12_S2BVEM.xls

When data validation is completed, the data package is uploaded for the client to download from the HWSS data delivery website:

https://epaqpx.rtp.epa.gov/hwssclpdeliverables

The completed data package includes the Executive Narrative (see Appendix B for template), the Sample Summary Report (see Appendix C for example), and the Electronic Data Deliverable (EDD) (see Appendix D for a list of the column headers included in this document).

PRELIMINARY REVIEW

This document is for the review of analytical data generated through the ISM01.2 SOW and any future editorial revisions of ISM01.2. To use this document effectively, the reviewer should have an understanding of the analytical method and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in the analysis are essential information.

It is suggested that an initial review of the data package be performed, taking into consideration all information specific to the sample data package [e.g., Modified Analysis requests, Traffic Report/Chain of Custody (TR/COC) documentation, SDG Narratives, etc.].

The reviewer should also have a copy of the Quality Assurance Project Plan (QAPP) or similar document for the project for which the samples were analyzed. The reviewer should contact the appropriate Regional Contract Laboratory Program Project Officer (CLP PO) to obtain copies of the QAPP and relevant site information. This information is necessary in determining the final usability of the analytical data.

The SDGs or Cases routinely have unique samples that require special attention from the reviewer. These include field blanks and trip blanks, field duplicates, and Performance Evaluation (PE) samples which must be identified in the sampling records. The sampling records (e.g., TR/COC records, field logs, and/or contractor tables) should identify:

1. The Region where the samples were taken, and
2. The complete list of samples with information on:
    a. Sample matrix;
    b. Field blanks*;
    c. Field duplicates*;
    d. Field spikes*;
    e. PE samples*;
    f. Shipping dates;
    g. Preservatives;
    h. Types of analysis; and
    i. Laboratories involved.

    * If applicable.

The TR/COC documentation includes sample descriptions and date(s) of sampling. The reviewer must consider lag times between sampling and start of analysis when assessing technical sample holding times.

The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, preservation, and unusual events should be documented in the SDG Narrative. The reviewer should also inspect any email or telephone/communication logs detailing any discussion of sample or analysis issues between the laboratory, the CLP Sample Management Office (SMO), and the USEPA Region.

An Example Analytical Sequence for ICP-AES

S0
S
S
S
S
S
ICV
ICB
LCS
ICSA
ICSAB
CCV
CCB
samples
CCV
CCB
samples
CCV
CCB, etc.

Preservation and Holding Times

Action:

NOTE: Apply the action to each sample for which the preservation or holding time criteria was not met.

1. If the pH of aqueous/water metal samples is > 2 at the time of sample receipt, determine if the laboratory adjusted the pH of the sample to ≤ 2 at the time of sample receipt. If not, use professional judgment to qualify the samples based on the pH of the sample and the chemistry of the metal(s) of interest. Qualify results that are ≥ Method Detection Limit (MDL) as estimated low (J-), and qualify non-detects as unusable (R).
2. If technical holding times are exceeded, use professional judgment to determine the reliability of the data, based on the magnitude of the additional time compared to the technical requirement and whether the samples were properly preserved. The expected bias would be low. Qualify results that are ≥ MDL as estimated low (J-), and qualify non-detects as unusable (R).
3. Due to limited information concerning holding times for soil/sediment, wipe, and filter samples, it is left to the discretion of the data reviewer whether to apply aqueous/water holding time criteria to soil/sediment, wipe, or filter samples. If they are applied, it must be clearly documented in the Data Review Narrative.
4. When the holding times are exceeded, the reviewer should comment in the Data Review Narrative on any possible consequences for the analytical results.
5. When holding times are grossly exceeded, note it for Contract Laboratory Program Project Officer (CLP PO) action.

Table 1. Technical Holding Time Actions for ICP-AES Analysis

Preservation & Holding Time Results	Action for Samples
Aqueous/water metals samples received with pH > 2 and pH not adjusted	Use professional judgment Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical Holding Time exceeded: Aqueous/water Metals > 180 days	Use professional judgment Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical Holding Time exceeded: Soil/sediment, wipe, filter Metals > 180 days	Use professional judgment Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)

Calibration

Table 2. Acceptance Criteria for ICVs and CCVs

Analytical Method	Inorganic Analytes	ICV/CCV Low Limit (% of True Value)	ICV/CCV High Limit (% of True Value)
ICP-AES	Metals	90	110

Action:

NOTES: For initial calibrations or ICVs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.
For CCVs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the QC sample and a subsequent technically acceptable analysis of the QC sample in the analytical run.

NOTE: The data validator shall verify the correlation coefficient by calculating it using the standard concentrations and the corresponding instrument response.

1. If the instrument was not calibrated each time the instrument was set up and an ICV standard was not analyzed before field and QC samples, qualify the data as unusable (R). If the instrument was not calibrated with a blank and at least 5 calibration standards, use professional judgment to qualify results that are ≥ Method Detection Limit (MDL) as estimated (J), and non-detects as estimated (UJ). If the calibration curve does not include standards at required concentrations (e.g., a blank and at least one at or below CRQL), use professional judgment to qualify results that are ≥ MDL as estimated (J), and non-detects as estimated (UJ). If there was not at least one calibration standard at or below the CRQL for each analyte, qualify results that are ≥ MDL but < 2x the CRQL as estimated (J), and non-detects as estimated (UJ) and write it in the Contract Problem/Non-Compliance Section of the Data Review Narrative.
2. If the correlation coefficient is < 0.995, percent differences are outside the ±30% limit, or the y-intercept ≥ CRQL, qualify sample results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ). If the correlation coefficient is < 0.990, qualify results that are ≥ MDL as estimated (J) and non-detects as unusable (R).
3. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:
    a. If the ICV or CCV %R is < 75%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥ MDL as unusable (R).
    b. If the ICV or CCV %R falls within the range of 75-89%, qualify sample results that are ≥ MDL as estimated low (J-), and qualify non-detects as estimated (UJ).
    c. If the ICV or CCV %R falls within the range of 111-125%, qualify sample results that are ≥ MDL as estimated high (J+).
    d. If the ICV or CCV %R is within the range of 111-125%, non-detects should not be qualified.

e. If the ICV or CCV %R is > 125%, use professional judgment to qualify results that are ≥ MDL as estimated high (J+). Non-detects should not be qualified.
f. If the %R is > 160%, qualify all results that are ≥ MDL as unusable (R).

4. If the laboratory failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.
5. Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Narrative.
6. If calibration criteria are grossly exceeded, note this for CLP Project Officer (CLP PO) action.

NOTE: For critical samples, a further in-depth evaluation of the calibration curve may be warranted to determine if additional qualification is necessary.

Table 3. Calibration Actions for ICP-AES Analysis

Calibration Result	Action for Samples
Calibration not performed	Qualify all results as unusable (R)
Calibration incomplete	Use professional judgment Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as estimated (UJ)
Not at least one calibration standard at or below the CRQL for each analyte	Qualify results that are ≥ MDL but < 2x the CRQL as estimated (J) Qualify non-detects as estimated (UJ)
Correlation coefficient < 0.995; %D outside ±30%; y-intercept ≥ CRQL	Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as estimated (UJ)
Correlation coefficient < 0.990	Qualify results that are ≥ MDL as estimated (J) Qualify non-detects as unusable (R)
ICV/CCV %R < 75%	Qualify results that are ≥ MDL as unusable (R) Qualify all non-detects as unusable (R)
ICV/CCV %R 75-89%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICV/CCV %R 111-125%	Qualify results that are ≥ MDL as estimated high (J+)
ICV/CCV %R > 125%	Qualify results that are ≥ MDL as estimated high (J+)
ICV/CCV %R > 160%	Qualify results that are ≥ MDL as unusable (R)

Calibration/Preparation Blanks

Action:

NOTES: For ICBs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.
For CCBs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.
For Preparation Blanks that do not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

NOTES: Convert soil sample result to mg/kg on wet weight basis to compare with the soil preparation result on Form III.
Associated samples are all samples digested with the preparation blank.

1. If the appropriate blanks were not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should then be recorded in the Data Review Narrative, and noted for Contract Laboratory Program Project Officer (CLP PO) action.
2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.
3. Some general "technical" review actions include:
    a. Any blank (including Preparation Blanks) reported with a negative result, whose value is ≤ (-MDL) but ≥ (-CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank (including Preparation Blanks) reported with a negative result, whose value is < (-CRQL) qualify results that are ≥ CRQL as estimated low (J-) and non-detects as estimated (UJ).
    b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil/sediment sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.
4. Specific "method" actions include:
    a. If the absolute value of an ICB or a CCB result is > CRQL, the analysis should be terminated. If the analysis was not terminated and the affected samples were not reanalyzed, report non-detects and results that are ≥ MDL, but ≤ CRQL as CRQL-U. For results that are > CRQL but < Blank Result, report the results at the level of the blank with a "U" qualifier. Use professional judgment to qualify results that are > Blank Result. Note this situation for CLP PO action and record it in the Data Review Narrative.

b. If the absolute value of the concentration of the Preparation Blank is ≤ CRQL, report non-detects and results that are ≥ MDL but ≤ CRQL as CRQL-U. Use professional judgment to quality results that are > CRQL.

c. If any analyte concentration in the Preparation Blank is > CRQL, the lowest concentration of that analyte in the associated samples must be 10x the Preparation Blank concentration. Otherwise, all samples associated with that blank with concentrations < 10x the Preparation Blank concentration and > CRQL should be redigested and reanalyzed. Raise the CRQL to the concentration found in the Preparation Blank and report those samples that do not require redigestion (that are ≥ MDL but ≤ CRQL) as CRQL-U. Note for CLP PO action and record in the Data Review Narrative if the laboratory failed to redigest and reanalyze the affected samples. The reviewer shall then use professional judgment to assess the data.

Table 4. Calibration/Preparation Blank Actions for ICP-AES Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB	≥ MDL but ≤ CRQL	Non-detect	No action
		≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL	Use professional judgment
ICB/CCB	> CRQL	≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL but < Blank Result	Report at level of Blank Result with a "U"
		> Blank Result	Use professional judgment
ICB/CCB	≤ (-MDL) but ≥ (-CRQL)	≥ MDL, or non-detect	Use professional judgment
ICB/CCB	< (-CRQL)	< 10x the CRQL	Qualify results that are ≥ CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)
Preparation Blank	> CRQL	≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL but < 10x the Blank Result	Qualify results as estimated high (J+)
		≥ 10x the Blank Result	No action
Preparation Blank	≥ MDL but ≤ CRQL	Non-detect	No action
		≥ MDL but ≤ CRQL	Report CRQL value with a "U"
		> CRQL	Use professional judgment
Preparation Blank	< (-CRQL)	< 10x the CRQL	Qualify results that are ≥ CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)

Inductively Coupled Plasma - Interference Check Sample (ICP-ICS)

Action:

NOTE: For an ICS that does not meet the technical criteria, apply the action to all samples analyzed in the analytical run.

NOTE: The laboratory should have analyzed and reported ICS results for all elements being reported from the analytical run and for all interferents (target and non-target) for these reported elements.

1. The raw data should, but may not, contain results for interferents. If not, the reviewer shall use professional judgment to qualify the data. If the data does contain results for interferents, the reviewer should apply the following actions to samples with concentrations of interferents that are comparable to, or greater than, their respective levels in the ICS:
    a. If the ICS %R for an analyte or interferent is > 120% (or greater than the true value + CRQL, as applicable) and the sample results are non-detects, the data should not be qualified.
    b. If the ICS %R for an analyte or interferent is > 120% (or greater than the true value + CRQL, as applicable) qualify sample results that are ≥ MDL as estimated high (J+). If the ICS %R (or true value) grossly exceeds the limits, use professional judgment to qualify the data.
    c. If the ICS %R for an analyte or interferent falls within the range of 50-79% (or less than the true value - CRQL, as applicable) qualify sample results that are ≥ MDL as estimated low (J-).
    d. If the ICS recovery for an analyte falls within the range of 50-79% (or less than the true value - CRQL, as applicable), the possibility of false negatives exists. Qualify sample non-detects as estimated (UJ).
    e. If the ICSAB %R for an analyte or interferent is < 50%, qualify all sample results that are ≥ MDL as estimated low (J-) and all sample non-detects as unusable (R).
2. If results that are ≥ MDL are observed for analytes that are not present in the ICS solution, the possibility of false positives exists. An evaluation of the associated sample data for the affected elements should be made. For samples with comparable or higher levels of interferents and with analyte concentrations that approximate those levels found in the ICS, qualify sample results that are ≥ MDL as estimated high (J+). Non-detects should not be qualified.
3. If negative results are observed for analytes that are not present in the ICS solution, and their absolute value is ≥ MDL, the possibility of false negatives in the samples exists. An evaluation of the associated sample data for the affected analytes should be made. For samples with comparable or higher levels of interferents, qualify non-detects for the affected analytes as estimated (UJ), and results that are ≥ MDL but < 10x the absolute value of the negative result as estimated low (J-).
4. In general, ICP-AES sample data can be accepted if the concentrations of Al, Ca, Fe, and Mg in the sample are found to be less than or equal to their respective concentrations in

the ICS. If these elements are present at concentrations greater than the level in the ICS, or other elements are present in the sample at > 10 mg/L, the reviewer should investigate the possibility of other interference effects as given in the ICP-AES method or as indicated by the laboratory's interelement correction factors reported on Forms XA-IN and XB-IN for that particular instrument. The analyte concentration equivalents presented in the method should be considered only as estimated values since the exact value of any analytical system is instrument-specific. Therefore, estimate the concentration produced by an interfering element. If the estimate is > 2x the CRQL, and also > 10% of the reported concentration of the affected element, qualify the affected results as estimated (J).

5. If the raw data does not contain results for the interferents, note it in the Data Review Narrative.
6. Actions regarding the interpretation and/or the subsequent qualification of ICP data due to the ICS analytical results can be extremely complex. Use professional judgment to determine the need for the associated sample data to be qualified. The reviewer may need to obtain additional information from the laboratory. All interpretive situations should then be recorded in the Data Review Narrative.
7. If the ICS acceptance criteria are grossly exceeded, note the specifics for CLP PO action.

Table 5. Interference Check Actions for ICP-AES Analysis

Interference Check Sample Results	Action for Samples
ICS %R > 120% (or greater than true value + CRQL)	Qualify results that are ≥ MDL as estimated high (J+)
ICS %R 50-79% (or less than true value - CRQL)	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICSAB %R < 50%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
Potential false positives in field samples with interferents	Qualify results that are ≥ MDL as estimated high (J+)
Potential false negatives in field samples with interferents	Qualify results that are ≥ MDL but < 10x the (|negative value|) as estimated low (J-) Qualify non-detects as estimated (UJ)

Laboratory Control Sample (LCS)

Action:

If the LCS criteria are not met, the laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data associated with an LCS that does not meet the required criteria.
For an LCS that does not meet the technical criteria, apply the action to all samples in the same preparation batch.

1. **Aqueous/Water and Soil/Sediment LCS:**
    a. If the LCS %R falls within the range of 40-69% (20-49% for Ag and Sb), qualify sample results that are ≥ Method Detection Limit (MDL) as estimated low (J-). If the LCS %R is > 130% (150% for Ag and Sb), qualify sample results that are ≥ MDL as estimated high (J+).
    b. If the LCS recovery is > 130% (150% for Ag and Sb) and the sample results are non-detects, the data should not be qualified.
    c. If the LCS recovery falls within the range of 40-69% (20-49% for Ag and Sb), qualify non-detects as estimated (UJ).
    d. If LCS %R is < 40% (<20% for Ag and Sb), qualify all results that are ≥ MDL as estimated low (J-) and all non-detects as unusable (R).
    e. If the LCS %R is > 150% (170% for Ag and Sb), qualify all affected data (both detects and non-detects) as unusable (R).
2. **Wipe/Filter LCS:**
    a. If the LCS %R is in the range of 40-69%, qualify sample results that are ≥ MDL as estimated low (J-) and qualify non-detects as estimated (UJ).
    b. If the LCS %R is < 40%, qualify all results that are ≥ MDL as estimated low (J-) and all non-detects as unusable (R).
    c. If the LCS %R is > 130% and the sample results are non-detects, do not qualify the data.
    d. If the LCS %R is > 130%, qualify all results ≥ MDL as estimated high (J+).
3. If a laboratory fails to analyze an LCS with each SDG, or if a laboratory consistently fails to generate acceptable LCS recoveries, note this for CLP Project Officer (CLP PO) action.
4. Whenever possible, the potential effects on the data due to out-of-control LCS results should be noted in the Data Review Narrative.

Table 6. LCS Actions for ICP-AES Analysis

LCS Result	Action for Samples
Aqueous/Water and Soil/Sediment %R 40-69% (20-49% Ag, Sb)	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
Aqueous/Water and Soil/Sediment %R > 130% (150% Ag, Sb)	Qualify results that are ≥ MDL as estimated high (J+)
Aqueous/Water and Soil/Sediment %R < 40% (<20% Ag, Sb)	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)
Aqueous/Water and Soil/Sediment %R > 150% (>170% Ag, Sb)	Qualify all results as unusable (R)
Wipe/Filter %R 40-69%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
Wipe/Filter %R > 130%	Qualify results that are ≥ MDL as estimated high (J+)
Wipe/Filter %R < 40%	Qualify results that are ≥ MDL as estimated low (J-) Qualify non-detects as unusable (R)

Laboratory Duplicate Sample Analysis

Action:

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to only the field sample used to prepare the duplicate sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

NOTE: The lab duplicate analysis is not required for wipe and air filter samples.
Delete "*" from Form IAs.
If one value is > CRQL and the other value is non-detect, calculate the absolute difference between the value > CRQL and the MDL and use this difference to qualify sample results.
If more than one lab duplicate sample was analyzed for an SDG, then qualify the associated samples based on the worst lab duplicate analysis.

1. If the appropriate number of duplicate samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.
2. If the results from a duplicate analysis for a particular analyte fall outside the control limits for > 5x the CRQL, qualify aqueous sample results that are ≥ CRQL as estimated (J) if the RPD is between 20% - 100% and as unusable (R) if the RPD is > 100%. Qualify soil/sediment sample results that are ≥ CRQL as estimated (J) if the RPD is between 35% - 120% and as unusable (R) if the RPD is > 120%.
3. If the results from a duplicate analysis for a particular analyte fall outside the control limits for ≤ 5x the CRQL, qualify those results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ).
4. If a field blank or PE sample was used for the duplicate sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked and professional judgment exercised by the data reviewer when evaluating the data.
5. Note the potential effects on the data due to out-of-control duplicate sample results in the Data Review Narrative.

Table 7. Duplicate Sample Actions for ICP-AES Analysis

Duplicate Sample Results	Action for Samples
Aqueous: Both original sample and duplicate sample > 5x the CRQL and 20% < RPD < 100%	Qualify those results that are ≥ CRQL as estimated (J)
Aqueous: Both original sample and duplicate sample > 5x the CRQL and RPD ≥ 100%	Qualify those results that are ≥ CRQL as unusable (R)
Soil/Sediment: Both original sample and duplicate sample > 5x the CRQL and 35% < RPD < 120%	Qualify those results that are ≥ CRQL as estimated (J)
Soil/Sediment: Both original sample and duplicate sample > 5x the CRQL and RPD ≥ 120%	Qualify those results that are ≥ CRQL as unusable (R)
Original sample or duplicate sample ≤ 5x the CRQL (including non-detects) and absolute difference between sample and duplicate > CRQL	Qualify those results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ)

Spike Sample Analysis

Action:

NOTE: For a Matrix Spike that does not meet the technical criteria, apply the action to only the field sample used to prepare the Matrix Spike sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

NOTE: Post-digestion spikes are not required for Ag.

NOTE: The final spike concentrations required for the various target analytes are presented in the methods described in the Statement of Work (SOW).

NOTE: When the sample concentration is < Method Detection Limit (MDL), use SR = 0 only for the purpose of calculating the %R. The actual spiked sample results, sample results, and %R (positive or negative) shall still be reported on Forms VA-IN and VB-IN.

NOTES: Not required for wipe and filter samples.
Not required for Ca, Mg, K, and Na (both matrices); Al and Fe (soil only).
If more than one spiked sample was analyzed for one SDG, then qualify the associated data based on the worst spiked sample analysis.
Disregard the out of control spike recoveries for analytes whose unspiked concentrations are ≥ 4x the spike added.
Delete "N" from Form IAs.

1. If the appropriate number of Matrix Spike samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. Note the situation in the Data Review Narrative, and for Contract Laboratory Program Project Officer (CLP PO) action.
2. If a field blank or PE sample was used for the spiked sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked and professional judgment exercised by the data reviewer when evaluating the data.
3. If the Matrix Spike recovery does not meet the evaluation criteria and a required post-digestion spike was not performed, note this for CLP PO action.
4. If the Matrix Spike %R is < 30%, verify that a post-digestion spike was analyzed (if required). If the post-digestion spike %R is < 75% or is not performed, qualify sample results that are ≥ MDL as estimated low (J-) and non-detects as unusable (R). If the post-digestion spike %R is ≥ 75%, qualify sample results that are ≥ MDL as estimated (J) and non-detects as estimated (UJ).
5. If the Matrix Spike %R is 30-74% and the sample results are ≥ MDL, verify that a post-digestion spike was analyzed (if required). If the %R for the post-digestion is also < 75% or is not performed, qualify the affected data as estimated low (J-). If the %R for the post-digestion spike is ≥ 75%, qualify the affected data as estimated (J).

6. If the Matrix Spike %R falls within the range of 30-74% and the sample results are non-detects, qualify the affected data as estimated (UJ).
7. If the Matrix Spike %R is > 125% and the reported sample results are non-detects, the sample data should not be qualified.
8. If the Matrix Spike %R is > 125% and the sample results are ≥ MDL, verify that a post-digestion spike was analyzed if required. If the %R for the post-digestion spike is also > 125% or is not performed, qualify the affected data as estimated high (J+). If the %R for the post-digestion spike is ≤ 125%, qualify the affected data as estimated (J).
9. Note the potential effects on the data due to out-of-control spiked sample results in the Data Review Narrative.

Table 8. Spike Sample Actions for ICP-AES Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R < 30% Post-digestion spike %R < 75%	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R < 30% Post-digestion spike %R ≥ 75%	Qualify affected results that are ≥ MDL as estimated (J) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion Spike %R < 75%	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R ≥ 75%	Qualify affected results that are ≥ MDL as estimated (J) and affected non-detects as estimated (UJ)
Matrix Spike %R > 125% Post-digestion spike %R > 125%	Qualify affected results that are ≥ MDL as estimated high (J+)
Matrix Spike %R > 125% Post-digestion spike %R ≤ 125%	Qualify affected results that are ≥ MDL as estimated (J)
Matrix Spike %R < 30% No post-digestion spike performed (e.g., not required for Ag)	Qualify affected results that are ≥ MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R 30-74% No post-digestion spike performed (e.g., not required for Ag)	Qualify affected results that are ≥ MDL as estimated low (J-) and non-detects as estimated (UJ)
Matrix Spike %R > 125% No post-digestion spike performed (e.g., not required for Ag)	Qualify affected results that are ≥ MDL as estimated high (J+) Non-detects are not qualified

ICP Serial Dilution

Action:

NOTE: For a serial dilution that does not meet the technical criteria, apply the action to only the field sample used to prepare the serial dilution sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

NOTE: Serial dilution analysis is required only when the initial concentration is greater than 50x the MDL.
Delete "E" from Form IAs.

1. If the required %D criteria are not met, qualify affected aqueous results whose raw data are > MDL as estimated (J) if %D is between 10%-100% and qualify as unusable (R) if %D is ≥ 100%. Qualify affected soil/sediment results whose raw data are > MDL as estimated (J) if %D is between 15%-120% and qualify as unusable (R) if %D is ≥ 120%.
2. If evidence of positive or negative interference is found, use professional judgment to qualify the associated sample data. Note the potential effects on the reported data in the Data Review Narrative.
3. It should be noted for Contract Laboratory Program Project Officer (CLP PO) action and in the Data Review Narrative if a field blank or PE sample was used for the serial dilution analysis.

Table 9. Serial Dilution Actions for ICP-AES Analysis

Serial Dilution Result	Action for Samples
Aqueous: Sample concentration > 50x MDL and 10% < %D < 100%	Qualify affected results whose raw data are > MDL as estimated (J)
Aqueous: Sample concentration > 50x MDL and %D ≥ 100%	Qualify affected results whose raw data are > MDL as unusable (R)
Soil/Sediment: Sample concentration > 50x MDL and 15% < %D < 120%	Qualify affected results whose raw data are > MDL as estimated (J)
Soil/Sediment: Sample concentration > 50x MDL and %D ≥ 120%	Qualify affected results whose raw data are > MDL as unusable (R)
Interferences present	Use professional judgment

Field Duplicates

Action:

NOTES: For field duplicates that do not meet the technical criteria, apply the action to only the field sample and its duplicate. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.
Check the Sampling Trip Report for the field duplicate pair.
Substitute MDL for CRQL when MDL > CRQL.
Do not calculate RPD when both values are non-detects.
If one value is > the CRQL and the other value is non-detect, calculate the absolute difference between the value > the CRQL and the MDL, and use this criteria to qualify the results.

1. If a field duplicate pair was collected and analyzed, calculate and report the RPD when the sample and its field duplicate values are both ≥ 5x the CRQL. Calculate and report the absolute difference when at least one value (sample or duplicate) is < 5x the CRQL.
2. When aqueous sample and duplicate values are both ≥ 5x the CRQL, and the RPD is > 20%, qualify the sample and its duplicate as estimated (J).
3. When aqueous sample and/or the duplicate value is < 5x the CRQL, and the absolute difference is > the CRQL, qualify results > the MDL as estimated (J) and non-detects as estimated (UJ).
4. When soil/sediment sample and duplicate values are both ≥ 5x the CRQL, and the RPD is > 50%, qualify the sample and its duplicate as estimated (J).
5. When soil/sediment sample and/or the duplicate value is < 5x the CRQL, and the absolute difference is > 2x the CRQL, qualify results > the MDL as estimated (J) and non-detects as estimated (UJ).

Table 10. Field Duplicate Actions for ICP-AES Analysis

Sample Type	Field Duplicate Result	Action for Samples
Aqueous	Sample and its field duplicate ≥ 5x the CRQL and RPD > 20%	Qualify sample and its duplicate as estimated (J)
	Sample and/or its field duplicate < 5x the CRQL and absolute difference > the CRQL	Qualify results > the MDL as estimated (J) Qualify non-detects as estimated (UJ)
Soil/Sediment	Sample and its field duplicate ≥ 5x the CRQL and RPD > 50%	Qualify sample and its duplicate as estimated (J)
	Sample and/or its field duplicate < 5x the CRQL and absolute difference > 2x the CRQL	Qualify results > the MDL as estimated (J) Qualify non-detects as estimated (UJ)

Field/Rinsate/Trip Blanks

Action:

NOTE: Designate "Field Blank" as such on Form IA.
Field Blank results previously rejected due to other criteria cannot be used to qualify field samples.
Do not use Rinsate Blank associated with soils to qualify water samples and vice versa.
If the MDL is > the CRQL, substitute CRQL with 2x the MDL.

1. If the appropriate blanks were not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the laboratory. The situation should then be recorded in the Data Review Narrative, and noted for Contract Laboratory Program Project Officer (CLP PO) action.
2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.
3. Some general "technical" review actions include:
    a. Any blank reported with a negative result, whose value is ≤ (-MDL) but ≥ (-CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank reported with a negative result, whose value is < (-CRQL) qualify results that are ≥ CRQL as estimated low (J-) and non-detects as estimated (UJ).
    b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil/sediment sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.
4. If the absolute value of any analyte in a Field/Rinsate/Trip Blank is > the CRQL, then the CRQL shall be raised to the level in the Field/Rinsate/Trip Blank and the associated sample data below this level shall be reported as CRQL-U.
5. Sample results > the Field/Rinsate/Trip Blank value but < 10x the Field/Rinsate/Trip Blank value shall be qualified as estimated (J).
6. Sample results ≥ the MDL but ≤ the CRQL shall be reported at the CRQL value with a "U".

Table 11. Field/Rinsate/Trip Blank Actions for ICP-AES Analysis

Blank Result	Sample Result	Action for Samples
> CRQL	≥ MDL but ≤ CRQL	Report CRQL value with a "U"
	> CRQL but < Blank Result	Report at level of Blank Result with a "U"
	> Blank Result but < 10x the Blank Result	Use professional judgment to qualify results as estimated (J)

Linear Ranges

Action:

1. If any sample result was higher than the high linear range for ICP-AES and the sample was not diluted to obtain the result reported on Form I, qualify the affected results ≥ MDL as estimated (J).

Percent Solids of Sediments

Action:

1. If the percent solids in sediment for a sample are < 50%, qualify the affected results ≥ MDL as estimated (J) and the non-detects as estimated (UJ).

Regional Quality Assurance (QA) and Quality Control (QC)

Action:

Any action must be in accordance with Regional specifications and criteria for acceptable PE sample results. Note any unacceptable PE sample results for Contract Laboratory Program Project Officer (CLP PO) action.

Overall Assessment

Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.
2. Write a brief Data Review Narrative to give the user an indication of the analytical limitations of the data. Note any discrepancies between the data and the Sample Delivery Group (SDG) Narrative for Contract Laboratory Program Project Officer (CLP PO) action. If sufficient information on the intended use and required quality of the data is available, the reviewer should include an assessment of the data usability within the given context.
3. If any discrepancies are found, the laboratory may be contacted by the Region's designated representative to obtain additional information for resolution. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

Calculations for ICP-AES

Aqueous/Water Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES):

The concentrations determined in the digestate are to be reported in units of µg/L:

$$Concentration\ \left(\frac{\mu g}{L}\right) = C \times \frac{V_f}{V} \times DF$$

Where,

C = Instrument value in µg/L (The average of all replicate exposures).

V_f = Final digestion volume (mL)

V = Initial aliquot amount (mL)

DF = Dilution Factor

Soil/Sediment Samples by ICP-AES:

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of mg/kg:

$$Concentration\ (drywt.)\left(\frac{mg}{kg}\right) = C \times \frac{V_f}{W \times S} \times \frac{DF}{1000}$$

Where,

C = Instrument value in µg/L (The average of all replicate exposures).

V_f = Final digestion volume (mL)

W = Initial aliquot amount (g)

S = % Solids/100 (see Exhibit D of ISM01.2 - Introduction to Analytical Methods, Section 1.6).

DF = Dilution Factor

Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation:

To calculate the adjusted MDL or adjusted CRQL for aqueous/water samples, substitute the value of the MDL (µg/L) or CRQL (µg/L) into the "C" term in the equation above. Calculate the adjusted MDL or adjusted CRQL for soil/sediment samples as follows:

$$Adjusted\ Concentration\ \left(\frac{mg}{kg}\right) = C \times \frac{W_M}{W \times S} \times \frac{V_f}{V_M} \times DF$$

Where,

C	=	MDL or CRQL (mg/kg)
W_M	=	Minimum method required aliquot amount (g) (1.00 g or 0.50 g)
W	=	Initial aliquot amount (g)
V_M	=	Method required final sample digestion volume (mL) (100 mL or 50 mL)
V_f	=	Final digestion volume (mL)
S	=	% Solids/100 (see Exhibit D of ISM01.2 - Introduction to Analytical Methods, Section 1.6).
DF	=	Dilution Factor

Wipe/Filter Mass:

$$Mass\ (\mu g) = C \times V_f \times \frac{DF}{1000}$$

Where,

C	=	Instrument value in µg/L (The average of all replicate exposures).
V_f	=	Final digestion volume (mL)
DF	=	Dilution Factor

APPENDIX A: GLOSSARY

Analyte -- The element of interest, ion, or parameter an analysis seeks to determine.
Analytical Services Branch (ASB) -- Directs the Contract Laboratory Program (CLP) from within the Office of Superfund Remediation and Technical Innovation (OSRTI) in the Office of Solid Waste and Emergency Response (OSWER).
Analytical Sample -- Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, Initial Calibration Verification (ICV), Initial Calibration Blank (ICB), Continuing Calibration Verification (CCV), and Continuing Calibration Blank (CCB). Note that the following are all defined as analytical samples: undiluted and diluted samples (USEPA and non-USEPA); Matrix Spike samples; duplicate samples; serial dilution samples, analytical (post-digestion/post-distillation) spike samples; Interference Check Samples (ICSs); Laboratory Control Samples (LCSs); and Preparation Blanks.
Associated Samples -- Any sample related to a particular Quality Control (QC) analysis. For example, for Initial Calibration Verification (ICV), all samples run under the same calibration curve. For duplicates, all Sample Delivery Group (SDG) samples digested/distilled of the same matrix.
Blank -- A sample designed to assess specific sources of contamination. See individual definitions for types of blanks.
Calibration -- The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards are to be prepared using the same type of reagents or concentration of acids as used in the sample preparation.
Calibration Blank -- A blank solution containing all of the reagents in the same concentration as those used in the analytical sample preparation. This blank is not subject to the preparation method.
Calibration Curve -- A plot of instrument response versus concentration of standards.
Calibration Standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method, but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.
Case -- A finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).
Continuing Calibration Blank (CCB) -- A reagent water sample that is run 2 hours (ICP-AES, ICP-MS) or every hour (Hg, CN) and designed to detect any carryover contamination.
Contract Compliance Screening (CCS) -- A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is performed under USEPA direction by the Contract Laboratory Program (CLP) Sample Management Office (SMO) contractor.
Continuing Calibration Verification (CCV) -- A single parameter or multi-parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV can be one of the calibration standards. However, all parameters being measured by the particular system must be

represented in this standard and the standard must have the same matrix (i.e., the same amount of reagents and/or preservatives) as the samples. The CCV should have a concentration in the middle of the calibration range and shall be run every 2 hours (ICP-AES, ICP-MS) or every hour (Hg, CN).

Contract Laboratory Program (CLP) -- Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technical Innovation (OSRTI) of USEPA.

Contract Laboratory Program Project Officer (CLP PO) -- The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a CLP laboratory.

Contract Required Quantitation Limit (CRQL) -- Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

Duplicate -- A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Field Blank -- Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the laboratory. A field blank includes trip blanks, rinsate blanks, bottle blanks, equipment blanks, preservative blanks, decontamination blanks, etc.

Field Duplicate -- A duplicate sample generated in the field, not in the laboratory.

Holding Time -- The maximum amount of time samples may be held before they are processed.

Contractual -- The maximum amount of time that the Contract Laboratory Program (CLP) laboratory may hold the samples from the sample receipt date until analysis and still be in compliance with the terms of the contract, as specified in the CLP Analytical Services Statement of Work (SOW). These times are the same or less than technical holding times to allow for sample packaging and shipping.

Technical -- The maximum amount of time that samples may be held from the collection date until analysis.

Initial Calibration -- Analysis of analytical standards for a series of different specified concentrations to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

Initial Calibration Blank (ICB) -- The first blank standard run to confirm the calibration curve.

Initial Calibration Verification (ICV) -- Solution(s) prepared from stock standard solutions, metals, or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV should be traceable to National Institute of Standards and Technology (NIST) or other certified standard sources when USEPA ICV solutions are not available.

Internal Standard -- A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

Interference Check Sample (ICS) -- Verifies the contract laboratory's ability to overcome interferences typical of those found in samples.

Laboratory Control Sample (LCS) -- A control sample spiked at known level(s). LCSs are processed using the same sample preparation, reagents, and analytical methods employed for the USEPA samples received.
Matrix -- The predominant material of which the sample to be analyzed is composed. For the purposes of this document, the matrices are aqueous/water, soil/sediment, wipe, and filter.
Matrix Spike -- Introduction of a known concentration of analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology (also identified as a pre-distillation/digestion spike).
Method Detection Limit (MDL) -- The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the 7 replicates.
Narrative (SDG Narrative) -- Portion of the data package which includes laboratory, contract, Case, Sample Number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.
Office of Solid Waste and Emergency Response (OSWER) – The USEPA office that provides policy, guidance, and direction for the USEPA's solid waste and emergency response programs, including Superfund.
Percent Difference (%D) -- As used in this document and the Statement of Work (SOW), is used to compare two values. The difference between the two values divided by one of the values.
Performance Evaluation (PE) Sample -- A sample of known composition provided by USEPA for contractor analysis. Used by USEPA to evaluate Contractor performance.
Post Digestion Spike -- The addition of a known amount of standard after digestion or distillation (also identified as an analytical spike).
Preparation Blank -- An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.
Relative Percent Difference (RPD) -- As used in this document and the Statement of Work (SOW) to compare two values, the RPD is based on the mean of the two values, and is reported as an absolute value (i.e., always expressed as a positive number or zero).
Regional Sample Control Center Coordinator (RSCC) -- In USEPA Regions, coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.
Relative Standard Deviation (RSD) -- As used in this document and the Statement of Work (SOW), the mean divided by the standard deviation, expressed as a percentage.
Sample -- A single, discrete portion of material to be analyzed, which is contained in single or multiple containers and identified by a unique Sample Number.
Sample Delivery Group (SDG) -- A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

a. Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case; or
b. Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

c. Scheduled at the same level of deliverable.

In addition, all samples and/or sample fractions assigned to an SDG must be scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG. Samples may be assigned to SDGs by matrix (i.e., all soil/sediment samples in one SDG, all aqueous/water samples in another) at the discretion of the laboratory.

Sample Management Office (SMO) -- A contractor-operated facility operated under the SMO contract, awarded and administered by the USEPA. Provides necessary management, operations, and administrative support to the Contract Laboratory Program (CLP).

Serial Dilution -- The dilution of a sample by a factor of five. When corrected by the Dilution Factor (DF), the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents [Inductively Coupled Plasma (ICP) only].

Statement of Work (SOW) -- A document which specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Tune -- Analysis of a solution containing a range of isotope masses to establish Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) mass-scale accuracy, mass resolution, and precision prior to calibration.

APPENDIX B: INORGANIC DATA EXECUTIVE NARRATIVE TEMPLATE

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
DESA/HWSB/HWSS
2890, Woodbridge Avenue, Edison, NJ 08837

EXECUTIVE NARRATIVE

Case No.: **SDG No.:**
Site: **Laboratory:**

QAPP
HWSS #: **Number of Samples:**
Contractor #: **Sampling date:**

SUMMARY:

Critical: Results have an unacceptable level of uncertainty and should not be used for making decisions. Data have been qualified "R" rejected.

Major: A level of uncertainty exists that may not meet the data quality objectives for the project. A bias is likely to be present in the results. Data have been qualified "J" estimated.

Minor: The level of uncertainty is acceptable. No significant bias in the data was observed.

Critical Findings: None

Major Findings: None

Minor Findings: None

COMMENTS:

Validator's Signature: **Date:**
Name:
Affiliation:

Approver's Signature: **Date:**
Name:
Affiliation:

APPENDIX C: SAMPLE INORGANIC DATA SAMPLE SUMMARY

Case No: 00001	Contract: XYZ1234	SDG No: XY123	Lab Code: ABCD
Sample Number: XY123	Method: ICP_AES	Matrix: FLUFF	MA Number: DEFAULT
Sample Location: SOMEWHERE OUT THERE	pH: 15	Sample Date: 13322059	Sample Time: 24:03:00
% Moisture :		% Solids :	

Analyte Name	Result	Units	Dilution Factor	Lab Flag	Validation	Reportable	Validation Level
Aluminum	400	ug/L	1			Yes	S2BVEM
Antimony	40	ug/L	1	U	U	Yes	S2BVEM
Arsenic	40	ug/L	1	U	U	Yes	S2BVEM
Barium	40	ug/L	1	U	U	Yes	S2BVEM
Beryllium	40	ug/L	1	U	U	Yes	S2BVEM
Cadmium	40	ug/L	1	U	U	Yes	S2BVEM
Calcium	400	ug/L	1			Yes	S2BVEM
Chromium	40	ug/L	1	U	U	Yes	S2BVEM
Cobalt	40	ug/L	1	U	U	Yes	S2BVEM
Copper	40	ug/L	1	U	U	Yes	S2BVEM
Iron	40	ug/L	1	J	U	Yes	S2BVEM
Lead	40	ug/L	1	U	U	Yes	S2BVEM
Magnesium	400	ug/L	1			Yes	S2BVEM
Manganese	400	ug/L	1			Yes	S2BVEM
Nickel	40	ug/L	1	U	U	Yes	S2BVEM
Potassium	400	ug/L	1			Yes	S2BVEM
Selenium	40	ug/L	1	U	U	Yes	S2BVEM
Silver	40	ug/L	1	U	U	Yes	S2BVEM
Sodium	400	ug/L	1			Yes	S2BVEM
Thallium	40	ug/L	1	U	U	Yes	S2BVEM
Vanadium	40	ug/L	1	U	U	Yes	S2BVEM
Zinc	40	ug/L	1	U	U	Yes	S2BVEM

APPENDIX D: ELECTRONIC DATA DELIVERABLE TEMPLATE

DATA_PROVIDER	LAB_MATRIX_CODE	RESULT_UNIT
SYS_SAMPLE_CODE	ANAL_LOCATION	DETECTION_LIMIT_UNIT
SAMPLE_NAME	BASIS	TIC_RETENTION_TIME
SAMPLE_MATRIX_CODE	CONTAINER_ID	RESULT_COMMENT
SAMPLE_TYPE_CODE	DILUTION_FACTOR	QC_ORIGINAL_CONC
SAMPLE_SOURCE	PREP_METHOD	QC_SPIKE_ADDED
PARENT_SAMPLE_CODE	PREP_DATE	QC_SPIKE_MEASURED
SAMPLE_DEL_GROUP	LEACHATE_METHOD	QC_SPIKE_RECOVERY
SAMPLE_DATE	LEACHATE_DATE	QC_DUP_ORIGINAL_CONC
SYS_LOC_CODE	LAB_NAME_CODE	QC_DUP_SPIKE_ADDED
START_DEPTH	QC_LEVEL	QC_DUP_SPIKE_MEASURED
END_DEPTH	LAB_SAMPLE_ID	QC_DUP_SPIKE_RECOVERY
DEPTH_UNIT	PERCENT_MOISTURE	QC_RPD
CHAIN_OF_CUSTODY	SUBSAMPLE_AMOUNT	QC_SPIKE_LCL
SENT_TO_LAB_DATE	SUBSAMPLE_AMOUNT_UNIT	QC_SPIKE_UCL
SAMPLE_RECEIPT_DATE	ANALYST_NAME	QC_RPD_CL
SAMPLER	INSTRUMENT_ID	QC_SPIKE_STATUS
SAMPLING_COMPANY_CODE	COMMENT	QC_DUP_SPIKE_STATUS
SAMPLING_REASON	PRESERVATIVE	QC_RPD_STATUS
SAMPLING_TECHNIQUE	FINAL_VOLUME	BREAK_2
TASK_CODE	FINAL_VOLUME_UNIT	SYS_SAMPLE_CODE
COLLECTION_QUARTER	CAS_RN	LAB_ANL_METHOD_NAME
COMPOSITE_YN	CHEMICAL_NAME	ANALYSIS_DATE
COMPOSITE_DESC	RESULT_VALUE	TOTAL_OR_DISSOLVED
SAMPLE_CLASS	RESULT_ERROR_DELTA	COLUMN_NUMBER
CUSTOM_FIELD_1	RESULT_TYPE_CODE	TEST_TYPE
CUSTOM_FIELD_2	REPORTABLE_RESULT	TEST_BATCH_TYPE
CUSTOM_FIELD_3	DETECT_FLAG	TEST_BATCH_ID
COMMENT	LAB_QUALIFIERS	CASE
BREAK_1	VALIDATOR_QUALIFIERS	CONTRACT_NUM
SYS_SAMPLE_CODE	INTERPRETED_QUALIFIERS	SCRIBE_SAMPLE_ID
LAB_ANL_METHOD_NAME	ORGANIC_YN	SAMPLE_TIME
ANALYSIS_DATE	METHOD_DETECTION_LIMIT	FRACTION
TOTAL_OR_DISSOLVED	REPORTING_DETECTION_LIMIT	PH
COLUMN_NUMBER	QUANTITATION_LIMIT	DATA_VAL_LABEL
TEST_TYPE		

VALIDATION SOP

Mercury

EDS SOP: Mercury by CVAFS
USEPA 1631, Rev. 1, 5/14

MERCURY VIA METHOD 1631 VALIDATION SOP REVISION 1

SITE:

DATE/INITIALS:

SDG:

LABORATORY:

Data Completeness and Deliverables	**Y**	**N**	**N/A**
Have any missing deliverables been received and added to the data package?	_____	_____	_____

ACTION: Call lab for explanation/resubmittal of any missing deliverables. If the lab cannot provide them, note the effect on the data review process in the non-compliance section of the data assessment narrative.

Custody Documents and Narratives

Are chains of custody present and complete for all samples?	_____	_____	_____

ACTION: Contact lab for replacement of missing documents.

Do chains of custody or lab narratives indicate any problems with sample receipt?	_____	_____	_____

Cooler Temperatures:

_____

i.e., condition of samples, analytical problems or special notations affecting the quality of the data.

ACTION: If samples were not iced or melted ice is present in the cooler and cooler temperature was outside the range of 4°C (±2) upon receipt for aqueous and soil, -15°C (±2) for crab and clam samples note in data assessment narrative. If cooler temperature is found to be in excess of 10°C for aqueous/soil, flag all associated Hg results as estimated "J."

Holding Times **Y** **N** **N/A**

Have any mercury technical holding times, determined from date of collection to date of preparation and analyses been exceeded? _____ _____ _____

NOTE:
Aqueous: Samples to be analyzed for total or dissolved Hg only are shipped to the laboratory unpreserved in fluoropolymer bottles capped tightly and stored at 4°. Samples must be either preserved or analyzed within 48 hours of collection. Holding time for analysis is 28 days from collection. Soil: No preservatives necessary. Holding time for analysis is 28 days from collection. Clam/Crab Collection: Ziploc® bags and shipped frozen at -15°. Holding time for sample preparation is 60 days. Holding time for analysis is 28 days from the date and time of sample homogenization.

Table of Holding Crab/Crab Collection Time Violations

Sample	Date Collected	Date lab Received	Date of Tissue Preparation

Table of Holding Time Violations

Sample	Sample Matrix	Date Sampled	Date lab Received	Date Preserved	Date Digested	Date/Time Analyzed

ACTION: If holding times are exceeded, flag all data as estimated "J" for detects and "UJ" for non-detects. If holding times were grossly exceeded (i.e., more than 2x the holding time), flag all positive data as estimated and reject all non-detects as unusable "R".

Sample Preservation

Were the pH values present for aqueous samples? _____ _____ _____

Were samples properly preserved per Section 8.5.1, Method 1631 (48 hours to preservation)? _____ _____ _____

NOTE: The pH of all aqueous samples must be tested immediately before aliquotting for processing or direct analysis pH should be < 2.

	Y	N	N/A

Preservation samples may be done by adding 5 mL/L of concentrated HCl (to allow both total and Hg determination) or 5 mL/L BrCl solution, if total mercury only is to be determined.

Laboratory Sample Preparation Log

Are all sample preparation bench sheets and logs present? _____ _____ _____

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The following sample was selected for MS/MSD analysis: _____

Is a matrix spike/matrix spike duplicate summary present? _____ _____ _____

Were matrix spikes analyzed at the required frequency for each of the analytical sample groups (i.e., 10% minimum per analytical batch)? _____ _____ _____

ACTION: If any matrix spike data are missing, call the lab for explanation/re-submittal. If information is not available document the effect in narrative notes.

MS/MSD limits for aqueous and soils are as follows:

% Recovery = 71-125%
RPD = ±24%

MS/MSD limits for tissue are as follows:

% Recovery = 71-125%
RPD = ±35%

Have any matrix spike recoveries failed to meet the criteria listed above in either the MS or MSD? _____ _____ _____

Are any spike recoveries:

Less than 10%? _____ _____ _____

Between 10-70%? _____ _____ _____

Between 126-200%? _____ _____ _____

Greater than 200%? _____ _____ _____

ACTION: If less than 10%, reject all associated aqueous data; if between 10-70%, flag all associated aqueous data as estimated potential low bias "J" or "UJL"; if between 126-200%, flag as estimated "JH" all associated aqueous data not flagged with a "U"; if > 200%, reject (red-line) all associated aqueous data not flagged with a "U."

	Y	N	N/A
Have any MS/MSD relative percent difference (RPD) values failed to meet The acceptance criteria listed above?	_____	_____	_____

ACTION: If any RPD value fails to meet the method acceptance criteria, qualify all associated sample results as estimated "J" or "UJ".

Blanks

Either bubbler blanks or system blanks will be run depending on the type of system used by the laboratory.

Bubbler Blanks (bubbler systems only- if applicable)

Have at least three bubbler blanks been analyzed to demonstrate the bubbler system is free from contamination at levels that could affect data quality?	_____	_____	_____

NOTE: Multiple bubblers may be used, at least one blank per bubbler (maximum 4 bubblers).

Upon examination of the bubbler blank data, do the blanks contain positive results?	_____	_____	_____

NOTE: If the bubbler blank is found to contain more than 50 pg Hg, the system is out of control. The problem must be investigated and remedied, and the samples run on that bubbler must be reanalyzed. If the blanks from other bubblers contain < 50 pg Hg, the data associated with those bubblers remain valid.

The mean result for all bubbler blanks must be < 25 pg, the average peak area or height is subtracted from all raw data before results are calculated.

ACTION: If yes, qualify associated results as follows: "J" flag all positive mercury sample values related to highest concentration of blank contamination.

Prepare a list of samples affected.

System Blanks (flow injection systems only- if applicable)

Have at least three system blanks been analyzed to demonstrate that flow injection systems are free from contamination at levels that could affect data quality?	_____	_____	_____

NOTE: If a system blank is found to contain $\geq$ 0.50 ng/L Hg, the system is out of control. If the blanks contain < 0.50 ng/L Hg, the data associated with the blanks remain valid.

The mean result for the three system blanks must be < 0.5 ng/L Hg with a standard deviation (n-1) < 0.1 ng/L. If the mean is < 0.5 ng/L, the average peak height or area is subtracted from all raw data before results are calculated.

	Y	N	N/A
Upon examination of the system blank data, do the blanks contain positive results > the MDL?	_____	_____	_____

ACTION: "J" flag all positive mercury sample values related to the highest concentration of blank contamination.

Method Blank

Has a method blank analysis been reported for each sample delivery group not to exceed 20 samples?	_____	_____	_____

NOTE: Three method blanks should accompany each sample delivery group. The mean blank value should be used to evaluate associated sample results.

Is the method blank summary present?	_____	_____	_____
Upon evaluation of associated method blank results, do any method blank results exceed the MDL?	_____	_____	_____

ACTION: If the samples associated with the non-compliant method blank contain positive results for mercury which are < 5x that of the mean method blank value, these sample results should be qualified as "U". Non-detect results are not affected nor are sample results that are > 5x that of the contaminated method blank mean.

Trip Blank

Has a trip blank analysis been reported for each sample delivery shipment?	_____	_____	_____
Upon examination of the trip blank, does it contain any positive results ≥ MDL?	_____	_____	_____

ACTION: If the samples associated with the non-compliant trip blank contain positive results for mercury which are < 5x that of the mean trip blank value, these sample results should be qualified as "U". Non-detect results are not affected nor are sample results that are greater than 5x that of the contaminated trip blank mean.

Field Blank (Only for soil samples. Not applicable for tissue)

Has a field blank analysis been reported for each sample delivery group not to exceed 20 samples?	_____	_____	_____
Has the field blank been analyzed in the proper sequence?	_____	_____	_____

NOTE: The field blank should be analyzed immediately before analyzing samples in the batch.

	Y	N	N/A
Upon examination of the field blank, does it contain any positive results ≥ MDL?	_____	_____	_____

ACTION: If the samples associated with the non-compliant field blank contain positive results for mercury which are < 5x that of the mean field blank value, these sample results should be qualified as "U". Non-detect results are not affected nor are sample results that are greater than 5x that of the contaminated field blank mean.

Rinse Blank (Only for tissue samples. Not applicable for soil samples)

Has a rinste blank analysis been reported for each sampling event of the decontaminated homogenization equipment in the lab, not to exceed more than one per day?	_____	_____	_____
Upon examination of the rinse blank, does it contain positive target analytes ≥ the MDL?	_____	_____	_____

ACTION: If the samples associated with the non-compliant rinse blank contain positive results for mercury which are < 5x that of the rinsate blank, these sample results should be qualified as "U". Non-detect results are not affected nor are sample results that are > 5x that of the contaminated rinsate blank.

Calibration

Are raw data and summary sheets present for both initial and continuing calibrations?	_____	_____	_____
Are the % relative standard deviation (RSD) values for the initial calibration $\leq$ 15%?	_____	_____	_____

ACTION: Associated sample data for those analytes with % RSD > 15 will be qualified as estimated "J". However, if severe discrepancies exist (i.e., %RSD > 50%) validator may elect to reject associated sample results.

Check calibration factors and % RSD values back to raw data for 10% of data received.

Are mis-calculations or transcription errors found?	_____	_____	_____

NOTE: If yes, contact the laboratory.

If RSD $\leq$ 15%, calculate the recovery for the lowest standard using mean calibration factor ($CF_{m)}$. If the RSD $\leq$ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CF_m may be used to calculate the concentration of Hg in samples.

	Y	N	N/A
Is the recovery of the lowest standard in the range of 75-25%?	_____	_____	_____

ACTION: If the recovery is < 75%, flag associated data as estimated “J” for detects and “R” for non-detects. If the recovery is > 125%, flag associated positive data “J”.

Quality Control Sample (QCS)

Was a QCS analyzed as an independent check of instrument calibration after the OPR and before the method blank?	_____	_____	_____

NOTE: The laboratory must obtain QCS source from a different source used to produce the standards, Hg.

ACTION: If < 50% recovery flag all associated data as "J". If above 150% recovery flag all associated positive data as "J".

Initial Precision and Recovery (IPR)

Was an initial precision and accuracy demonstration performed for the appropriate matrix per Section 9.5 of Method 1631 (4 replicates of the IPR solution is used to compute an average percent recovery X and the standard deviation of the percent recoveries for Hg)?	_____	_____	_____
Was the results of the IPR evaluation acceptable when compared to the acceptance limit listed in Table 1 (79-121%)?	_____	_____	_____

ACTION: If IPR data was not provided by the laboratory, contact the lab to obtain the results of the IPR study.

If the result of the laboratories IPR study does not meet the acceptance criteria for performance test listed in Table 1 , contact the laboratory to initiate remediation of technical difficulties. Further sample analyses should not be performed until the laboratory satisfactorily demonstrates the IPR performance test.

Ongoing Precision and Recovery (OPR)

Was an OPR standard prepared and analyzed for each sample batch (to a maximum of 20 samples)?	_____	_____	_____
Circle on each OPR summary report percent recoveries outside control limits Listed in Table 1 (77-123%).			
Was an OPR analyzed at the beginning and end of an analytical batch run or at the end of each 12-hour shift?	_____	_____	_____

	Y	N	N/A
Is any OPR recovery:			
Less than 10%?	_____	_____	_____
Between 10% and 76%?	_____	_____	_____
Between 124% and 150%?	_____	_____	_____
Greater than 150%?	_____	_____	_____

ACTION: Less than 10%, reject (red-line) all data; between 10% and 76%, flag all associated data as estimated (J); between 124% and 150%, flag all positive (not flagged with a "U") results as estimated; greater than 150%, reject all positive results.

Compound Quantitation and Reported Detection Limits

Verify at least one detected mercury results in each sample delivery group. Recalculate from the raw data to check for calculation and transcription errors.

Were miscalculation/transcription errors found?	_____	_____	_____

ACTION: If errors are found, contact the lab for explanation/resubmittals.

Are all positive mercury results above the MDL reported with:

three significant figures?	_____	_____	_____
correct units (ng/L, ng/kg), ?		_____	_____

_____

Field Duplicates (Not applicable for tissue samples)

NOTE: To access the precision and accuracy of the sampling, sample transportation and storage techniques.

The following samples comprise the field duplicate pair: _____

Were field duplicates submitted for mercury analysis at a frequency of one per 20 sample delivery group not to exceed field samples per matrix?	_____	_____	_____

ACTION: Where both the sample and duplicate values are > 5x the PQL, acceptable sampling and analytical precision is indicated by an RPD for the two field duplicate results of $\leq$ 20%. Where one or both analytes of the field duplicate pair are < 5x the PQL, satisfactory precision is indicated if the field duplicate results agree within 2x the PQL. If the above criteria are not met for an analyte, qualify all associated sample data for that analyte as estimated "J".

Table 1

Acceptance Criteria For Performance Test

Acceptance Criterion	Section of Method 1631	Limits	Project Quantitation Limit (PQL)
Method Detection Limit	9.2.1	<0.2 ng/L	0.5 ng/L
Initial Precision and Recovery	9.2.2		
Precision(s)	9.2.2.3	+/- 21%	
Recovery (x)	9.2.2.3	79-121%	
Interlaboratory Intercomparison	9.2.2.2	75-125%	
Matrix Spike/Matrix Spike Duplicate	9.3		
Recovery	9.3.4	71-125%	
Relative Percent Difference	9.3.6	+/-24%	
Bubbler Blanks	9.4		
Maximum	9.4.1.2	<50 pg	
Mean	9.4.1.3	<25 pg	
Ongoing Precision and Recovery	9.5	77-123%	

Data Validation Qualifiers

Qualifier	Description
EMPC	Estimated Maximum Possible Concentration (EMPC).
J	Estimated value (bias undetermined) – The analyte was positively identified; but the associated numerical value is the approximate concentration of the analyte in the sample.
JH	Estimated value (potential high bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential high bias, of the analyte in the sample.
JL	Estimated value (potential low bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential low bias, of the analyte in the sample.
M	The analytical result reported was obtained from a sediment sample found to contain between 50 and 90 percent moisture and had no other data qualifiers added during the data validating process.
NJ	The organic analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration.
R	The sample results are rejected. Due to a significant QA/QC problem, the analysis is invalid and provides no information as to whether the analyte is resent or not.
U	Non-detected value – The result initially reported as positive by the laboratory was qualified as not detected per USEPA Region II validation guidance, due to an associated quality control failure.
UJ	Estimated non-detect - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
UJL	Estimated non-detect (potential low bias) – The analyte was not detected and the report sample quantitation limit is biased low.

VALIDATION SOP

Methyl Mercury

EDS SOP: Methyl Mercury by CVAFS
USEPA 1630, Rev. 1, 5/14

METHYLMERCURY VIA METHOD 1630 VALIDATION SOP REVISION 1

SITE:

DATE/INITIALS:

SDG:

LABORATORY:

Data Completeness and Deliverables	**Y**	**N**	**N/A**
Have any missing deliverables been received and added to the data package?	_____	_____	_____

ACTION: Call lab for explanation/resubmittal of any missing deliverables. If the lab cannot provide them, note the effect on the data review process in the non-compliance section of the data assessment narrative.

Custody Documents and Narratives

Are chains of custody present and complete for all samples?	_____	_____	_____

ACTION: Contact lab for replacement of missing documents.

Do chains of custody or lab narratives indicate any problems with sample receipt, condition of samples, analytical problems or special notations affecting the quality of the data? Cooler Temperatures:	_____	_____	_____

_____

ACTION: If samples were not iced/or melted ice is present in the cooler and cooler temperature was outside the range of 4°C (±2) upon receipt, for aqueous and soil, and -15°C (±2) for crab and clam samples note in data assessment narrative. If cooler temperature is found to be in excess of 10°C for aqueous and soil, flag all associated CH_3Hg results as estimated "J."

Holding Times

Have any methyl mercury technical holding times, determined from date of collection to date of preparation and analyses been exceeded (48 hours to preservation, 28 days until analysis)?	_____	_____	_____

NOTE: Properly preserved samples may be stable for 6 months, if kept cool and in the dark. However, data qualification will be performed based on the technical holding time for methyl mercury (preservation within 48 hours, analysis within 28 days).

Y N N/A

Aqueous: Samples to be analyzed for methylmercury are shipped to the Laboratory unpreserved in fluoropolymer bottles capped tightly and stored at 4°. Samples must be either preserved or analyzed within 48 hours of collection. Holding time for analysis is 28 days from collection. Soil: No preservatives necessary. Holding time for analysis is 28 days from collection. Clam/Crab Collection: Ziploc® bags and shipped frozen at -15°. Holding time for sample preparation is 60 days. Holding time for analysis is 28 days from the date and time of sample homogenization.

Table of Holding Crab/Crab Collection Time Violations

Sample	Date Collected	Date lab Received	Date of Tissue Preparation
_____	_____	_____	_____
_____	_____	_____	_____

Table of Holding Time Violations

Sample	Sample Matrix	Date Sampled	Date lab Received	Date/Time Preserved	Date/Time Digested	Date/Time Analyzed
_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____

ACTION: If holding times are exceeded, flag all data as estimated "J" for detects and "UJ" for non-detects. If holding times were grossly exceeded (i.e., more than 2x the holding time), flag all positive data as estimated and reject all non-detects as unusable "R".

Sample Preservation

Were the pH values present for aqueous samples? _____ _____ _____

Were samples properly preserved per Section 8.5, Method 1630? _____ _____ _____

Samples may be shipped to the laboratory unpreserved if (1) collected in fluoropolymer bottles (2) filled to the top with no head space (3) Capped tightly and (4) maintained at 0-4°C from the time of collection until preservation. The samples must be acid-preserved within 48 hours of sampling.

NOTE: The pH of all aqueous samples must be tested immediately before aliquotting for processing or direct analysis pH should be < 2.

Preservation samples may be done by adding 5 mL/L of concentrated HCl (to allow both total and methyl Hg determination).

Laboratory Sample Preparation Log	**Y**	**N**	**N/A**
Are all sample preparation bench sheets and logs present?	_____	_____	_____

Calibration

Are raw data and summary sheets present for the initial calibration?	_____	_____	_____
NOTE: The initial calibration must contain at least 5 points, lowest being at the minimum level (ML) (.06 ng/l) and the analysis of at least *one ethylation blank.* Are the % RSD values for the initial calibration $\leq$ 15%?	_____	_____	_____

ACTION: Associated sample data for those analytes with % RSD > 15 will be qualified as estimated “J”. However, if severe discrepancies exist (i.e., %RSD > 50%) validator may elect to reject associated sample results.

Do the ethylation blanks contain positive results > 2 pg?	_____	_____	_____

The net concentration recovery (minus ethylation blank) for the lowest standard must be in the range of 65-135% of the expected value.

ACTION: If the recovery is < 65%, flag associated data as estimated "J" for detects and "R" for non-detects. If the recovery is > 135%, flag associated data "J" for detects.

Are mis-calculations or transcription errors found?	_____	_____	_____

NOTE: If yes, contact the laboratory.

Quality Control Sample (QCS)

Was a QCS analyzed as an independent check of instrument calibration in the analytical batch?	_____	_____	_____

NOTE: The laboratory must obtain QCS source from a different source used to produce the standards, CH_3Hg.

ACTION: If < 50% recovery flag all associated data as "J". If > 150% recovery flag all associated positive data as "J".

	Y	N	N/A

Initial Precision and Recovery (IPR)

Was an initial precision and accuracy demonstration performed for the appropriate matrix per Section 9.2 of Method 1630 (4 replicates of the IPR solution is used to compute an average percent recovery X and the standard deviations of the percent recoveries for CH_3Hg)? _____ _____ _____

Were the results of the IPR evaluation acceptable when compared to the acceptance limit listed in Table 1 (69-131%)? _____ _____ _____

ACTION: If IPR data was not provided by the laboratory, contact the lab to obtain the results of the IPR study.

If the result of the laboratories IPR study does not meet the acceptance criteria for performance test listed in Table 1 of Method 1630, contact the laboratory to initiate remediation of technical difficulties. Further sample analyses should not be performed until the laboratory Satisfactorily demonstrates the IPR performance test.

Ongoing Precision and Recovery (OPR)

Was an OPR standard and an ethylation blank prepared and analyzed prior to each sample batch? _____ _____ _____

Was an OPR analyzed at the end of an analytical run or at the end of each 12- hour shift? _____ _____ _____

Circle on each OPR summary report percent recoveries outside control limits (67-133%).

Is any OPR recovery:

Less than 10%? _____ _____ _____

Between 11% and 66%? _____ _____ _____

Between 134% and 150%? _____ _____ _____

Greater than 150%? _____ _____ _____

ACTION: Less than 10%, reject (red-line) all data; between 11% and 66%, flag all associated data as estimated "J"; between 134% and 150%, flag all positive (not flagged with a “U” results as estimated; greater than 150%, reject all positive results.

Blanks	**Y**	**N**	**N/A**
Method Blank			
Has a method blank analysis been reported for each analytical batch not to exceed 20 samples?	_____	_____	_____
NOTE: Three method blanks should accompany each analytical batch. The mean blank value should be used to evaluate associated sample results.			
Is the method blank summary present?	_____	_____	_____
Upon evaluation of associated method blank results, do all method blanks meet the MDL criteria listed in Table1?	_____	_____	_____
ACTION: If the samples associated with the non-compliant method blank contain positive results for methyl mercury which are < 5x that of the mean method blank value, these sample results should be qualified as "U" non-detected. Non-detect results are not affected nor are sample results that are > 5x that of the contaminated method blank mean.			
Trip Blank			
Has a trip blank analysis been reported for each sample delivery shipment?	_____	_____	_____
Upon examination of the trip blank, does it contain any positive results ≥ MDL?	_____	_____	_____
ACTION: If the samples associated with the non-compliant trip blank contain positive results for methyl mercury which are < 5x that of the mean trip blank value, these sample results should be qualified as "U" non-detected. Non-detect results are not affected nor are sample results that are > 5x that of the contaminated trip blank.			
Field Blank (For soil samples only. Not applicable for tissue)			
Has a field blank analysis been reported for each sampling event not to exceed 20 samples?	_____	_____	_____
Has the field blank been analyzed in the proper sequence?	_____	_____	_____
NOTE: The field blank should be analyzed immediately before analyzing samples in the batch.			
Upon examination of the field blank does it contain positive results ≥MDL?	_____	_____	_____
ACTION: If the samples associated with the non-complaint field blank contain positive results for methyl mercury which are < 5x that of the field blank, these sample results should be qualified as "U" non-detected. Non-detect results are not affected nor are sample results that are > 5x that of the contaminated field blank.			
Rinse Blank (For tissue sample only. Not applicable for soil)	**Y**	**N**	**N/A**

Has a rinse blank analysis been reported for each set of decontaminated field equipment? _____ _____ _____

Upon examination of the rinse blank, does it contain positive its ≥ MDL? _____ _____ _____

ACTION: If the samples associated with the non-complaint rinsate blank contain positive results for methyl mercury which are < 5x that of the rinsate blank, these sample results should be qualified as "U" non-detected. Non-detect results are not affected nor are sample results that are > 5x that of the contaminated rinse blank.

Compound Quantitation and Reported Detection Limits

Verify at least one detected methyl mercury result in each sample delivery group. Recalculate from the raw data to check for calculation and transcription errors.

Were miscalculation/transcription errors found? _____ _____ _____

ACTION: If errors are found, contact the lab for explanation/re-submittals.

Are all positive methyl mercury results above the MDL reported with:

three significant figures? _____ _____ _____

correct units (ng/l, ng/kg)? _____ _____

_____

Field Duplicates

NOTE: To access the precision and accuracy of the sampling, sample transportation and storage techniques.

The following samples comprise the field duplicate pair: _____

Were field duplicates submitted for methyl mercury analysis at frequency of one per sample delivery group, not to exceed 20? _____ _____ _____

ACTION: Where both the sample and duplicate values are > 5x the PQL, acceptable sampling and analytical precision is indicated by an RPD for the two field duplicate results of $\leq$ 20%. Where one or both analytes of the field duplicate pair are < 5x the PQL, satisfactory precision is indicated if the field duplicate results agree within 2x the PQL. If the above criteria are not met for an analyte, qualify all associated sample data for that analyte as estimated "J".

Matrix Spike/Matrix Spike Duplicate (MS/MSD) **Y** **N** **N/A**

The following sample was selected for MS/MSD analysis: _____

Is a matrix spike/matrix spike duplicate summary present? _____ _____ _____

Were matrix spikes analyzed at the required frequency for each of the analytical sample groups (i.e., 10% minimum per analytical batch)? _____ _____ _____

ACTION: If any matrix spike data are missing, call the lab for explanation/re-submittal. If information is not available document the effect in narrative notes.

MS/MSD limits for all matrices are as follows:

% Recovery	=	65-135%
RPD	=	±35%

Have any matrix spike recoveries failed to meet the criteria listed above? _____ _____ _____

Are any spike recoveries:

Less than 10%? _____ _____ _____

Between 10-64%? _____ _____ _____

Between 136-200%? _____ _____ _____

Greater than 200%? _____ _____ _____

ACTION: If < 10%, reject all associated aqueous data; if between 10-64%, flag all associated aqueous data as estimated "JL" or "UJL", potential low bias; if between 136-200%, flag as estimated "J" all associated aqueous data not flagged with a “U”; if > 200%, reject (red-line) all associated aqueous data not flagged with a “U.”

Have any MS/MSD relative percent difference values failed to meet the acceptance criteria listed above? _____ _____ _____

ACTION: If any relative percent difference value fails to meet the method acceptance criteria, qualify all associated sample results as estimated “J” for detects or “UJ” for non-detects.

Table 1
Acceptance Criteria For Performance Test

Acceptance Criterion	Section of Method 1630	Limits	Project Quantitation Limit (PQL)
Method Detection Limit		<0.2 ng/L	0.06 ng/L
Initial Precision and Recovery	9.2.		
Precision(s)		+/- 31%	
Recovery (x)		69-131%	
Matrix Spike/Matrix Spike Duplicate	9.3		
Recovery		65-135%	
Relative Percent Difference		+/-35%	
Method Blank	9.4		
Maximum		<2 pg	
Mean		< 0.05 ng/L	
Ongoing Precision and Recovery	9.5	67-133%	

Data Validation Qualifiers

Qualifier	Description
EMPC	Estimated Maximum Possible Concentration (EMPC).
J	Estimated value (bias undetermined) – The analyte was positively identified; but the associated numerical value is the approximate concentration of the analyte in the sample.
JH	Estimated value (potential high bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential high bias, of the analyte in the sample.
JL	Estimated value (potential low bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential low bias, of the analyte in the sample.
M	The analytical result reported was obtained from a sediment sample found to contain between 50 and 90 percent moisture and had no other data qualifiers added during the data validating process.
NJ	The organic analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration.
R	The sample results are rejected. Due to a significant QA/QC problem, the analysis is invalid and provides no information as to whether the analyte is present or not.
U	Non-detected value – The result initially reported as positive by the laboratory was qualified as not detected per USEPA Region II validation guidance, due to an associated quality control failure.
UJ	Estimated non-detect - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
UJL	Estimated non-detect (potential low bias) – The analyte was not detected and the report sample quantitation limit is biased low.

VALIDATION SOP

Butyltins

EDS SOP: Organotins Prep. 8/05

STANDARD OPERATING PROCEDURE
DATA VALIDATION OF ORGANOTIN ANALYSIS

A. INTRODUCTION

This Standard Operating Procedure (SOP) provides guidance for the validation of organotin analytical data generated from the analysis of water, soils, sediments, or tissue samples. The validation procedure was based upon the EPA Region II data validation SOP for Pesticides/PCBs (EPA 1992)[1]. A copy of the analytical protocol is provided as an appendix to the QAPP.

B. DATA VALIDATION PROCEDURES

1. Holding Times

Criteria: Holding times are established for both extraction and sample analysis. For aqueous, soil and tissue matrices, the extraction must begin within 7 days from sample collection, with analysis within 40 days of extraction.

Actions: The actions are summarized in Table 1. Actions may be taken for either time from sampling to extraction or time from extraction to analysis, but not both. If neither criteria are met, the exceedance which occurs first (i.e., time to extraction, or the criteria which results in additional qualifications or the "R" qualification takes precedence.

Table 1. Summary of Actions for Holding Times

Time from Sampling to Extraction			
Matrix	0-7 days	7-14 days	> 14 days
Sediment, water and tissues	Accept	"J" positives "UJ" non-detects	"J" positives "R" non-detects
Time from Extraction to Analysis			
Matrix	0-40 days	40-80 days	> 80 days
Sediment, water and tissues	Accept	"J" positives "UJ" non-detects	"J" positives "R" non-detects

2. Initial Calibration

The gas chromotograph undergoes a 5 point initial calibration with all of the targeted analytes. The laboratory may use either a linear regression, or calculate response factors, to ensure proper linear response of the instrument.

Criteria: If linear regression is performed, the laboratory must demonstrate that the regression coefficient ("r") is greater than or equal to 0.995.

If calibration factors are used, the laboratory must demonstrate that the relative standard deviation of the calibration factors is less than 30%.

Actions: The actions are summarized in Table 2.

Table 2. Summary of Actions for Initial Calibration

Initial Calibration using Regression			
Matrix	R ≥ 0.995	0.95 < r < 0.995	R < 0.95
Sediment, water and tissues	Accept	"J" positives "UJ" non-detects	"J" positives "R" non-detects
Initial Calibration using Calibration Factors			
Matrix	RSD < 30%	30% < RSD < 80%	RSD > 80%
Sediment, water and tissues	Accept	"J" positives "UJ" non-detects	"J" positives "R" non-detects

3. Continuing Calibration

The gas chromatograph undergoes a 1 point daily calibration with all of the targeted analytes to ensure consistency with the initial calibration.

Criteria: If linear regression was used for the initial calibration, then the continuing calibration result calculated from the linear regression must agree within 25% of the nominal concentration.

If calibration factors were used for the initial calibration, the laboratory must demonstrate that the percent difference between the mean calibration factors from the continuing calibration and the average response factor from the initial calibration is less than 30%.

Actions: The actions are summarized in Table 3.

Table 3. Summary of Actions for Continuing Calibration

Calibration using Regression			
Matrix	75 – 125% of nominal value	20 – 74% or 126 – 180% of nominal value	< 20% or > 180% of nominal value
Sediment, water and tissues	Accept	"J" positives "UJ" non-detects	"J" positives "R" non-detects
Calibration using Calibration Factors			
Matrix	%D < 30%	30% < %D < 80%	%D > 80%
Sediment, water and tissues	Accept	"J" positives "UJ" non-detects	"J" positives "R" non-detects

4. Surrogate Recoveries

For soil, water and tissue samples, surrogate is added to the sample extract prior to derivitazation.

Criteria: The laboratory must demonstrate that the surrogate recovery falls between 30 and 160%. If the initial analysis fails this criterion, then the samples must be reprocessed once.

Actions: The actions are summarized in Table 4. Chromatograms should be reviewed prior to taking any action to ensure that there were not interferences or coeluting peaks which resulted in the surrogate recoveries falling outside of the control limit. If it is the Reviewer's professional opinion that the non-compliant surrogate recoveries were due to interferences or co-eluting peaks, no action may be required.

No action is required if the surrogates were diluted out.

Table 4. Summary of Actions for Surrogate Recoveries

	%R < 10%	10 < %R < 30%	30 < %R < 160%	%R > 160%
Positives	"R"	"J"	Accept	"J"
Non-Detects	"R"	"UJ"	Accept	Accept
Note: No action is taken if the surrogates are diluted out.				

5. Method and Field QC Blanks

Method blanks are prepared by the laboratories to identify the potential for laboratory contamination. Field QC blanks are provided by the field team to identify potential contamination by the targeted analytes which may be introduced during field activities.

Criteria: There should be no detected targeted analytes in the method or field QC blanks.

Actions: If the targeted analytes are reported in the method or field QC blanks, and are present at a concentration less than 5 times the blank concentrations in the samples (adjusting for matrix variation and sample size), the reported sample results are potential false-positives and should be qualified with a "U". No action is taken if the sample concentration is greater than 5 times the method or field QC blank results. Likewise, when associated samples are "not detected" for the analyte, no qualification of data is necessary.

6. Data Calculations and Reported Concentrations

The reported concentrations for the targeted analytes in at least one sample in the Sample Delivery Group should be recalculated and verified. If a discrepancy is noted, the laboratory should be contacted to provide a sample calculation. Corrective actions may be required, as appropriate.

If the laboratory employs a confirmation column to verify sample identifications, it is recommended that the Reviewer verify that the concentrations on both columns are comparable. If significant differences are noted which are attributable to interferences or coeluting peaks, the Reviewer should consider reporting the results from the confirmation column.

7. Sample Moisture Contents

If the sediment samples exhibit moisture contents in excess of 50%, the actions in Table 6 should be taken.

Table 6. Actions for Excessive Moisture Contents in Sediments

	%Moist < 50%	50 < %Moist < 90%	%Moist > 90%
Positives	Accept	"J"	"G"
Non-Detects	Accept	"UJ"	"G"

8. Project Specific Requirements

If the direction of the bias can be determined from the analytical results, then the data reviewer can apply the following data qualifiers:

- Potential high bias: JH or UJ
- Potential low bias: JL or UJL

If the direction of the bias can not be determined, or the assessment of bias is contradicted by the quality control results (e.g., holding time exceedance with high surrogate recoveries), then the overall bias is undetermined, and the "J" or "UJ" qualifiers are appropriate.

VALIDATION SOP

Semivolatile Organics

USEPA Region 2 SOP HW-22 Rev.3, 10/06

US EPA
Hazardous Waste Support Branch
Validating Semivolatile Organic Compounds
By Gas Chromatography/Mass Spectrometry
SW-846 Method 8270D

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Annual Review

Reviewed by: _____ Date: _____
Name

Reviewed by: _____ Date: _____
Name

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INTRODUCTION

Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to "SW846-Method 8270D" January 1998. Method 8270D is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. The validation methods and actions discussed in this document are based on the requirements set forth in SW846 Method 8270D, Method 8000C and the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," January 2005. This document covers technical problems specific to each fraction and sample matrix; however, situations may arise where data limitations must be assessed based on the reviewer's professional judgement.

Summary of Method

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are defined on page 5.

The reviewer must prepare a detailed data assessment to be submitted along with the completed SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data and contract non-compliance.

Reviewer Qualifications

Data reviewers must possess a working knowledge of SW846 Analytical Methods and National Functional Guidelines mentioned above.

DEFINITIONS

Acronyms

BNA - base neutral acid(another name for Semi Volatiles)
CLP - Contract Laboratory Program
CRQL - Contract Required Quantitation Limit
%D - percent difference
DCB -decachlorobiphenyl
DDD - dichlorodiphenyldichloroethane
DDE - dichlorodiphenylethane
DDT - dichlorodiphenyltrichloroethane
DoC - Date of Collection
GC - gas chromatography
GC/ECD - gas chromatograph/electron capture detector
GC/MS - gas chromatograph/mass spectrometer
GPC - gel permeation chromatography
IS - internal standard
kg - kilogram
µg - microgram
MS - matrix spike
MSD - matrix spike duplicate
ℓ - liter
mℓ - milliliter
PCB - Polychlorinated biphenyl
PE - performance evaluation
PEM - Performance Evaluation Mixture
QC - quality control
RAS - Routine Analytical Services
RIC - reconstructed ion chromatogram
RPD - relative percent difference
RRF - relative response factor
RRF - average relative response factor (from initial calibration)
RRT - relative retention time
RSD - relative standard deviation
RT - retention time
RSCC - Regional Sample Control Center
SDG - sample delivery group
SMC - system monitoring compound
SOP - standard operating procedure
SOW - Statement of Work
SVOA - semivolatile organic acid
TCL - Target Compound List
TCLP - Toxicity Characteristics Leachate Procedure

TCX -tetrachloro-m-xylene
TIC - tentatively identified compound
TOPO - Task Order Project Officer
TPO - Technical Project Officer
VOA - Volatile organic
VTSR - Validated Time of Sample Receipt

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

JN - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

LAB QUALIFIERS:

D - The positive value is the result of an analysis at a secondary dilution factor.

B - The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.

YES NO N/A

E - The concentration of this analyte exceeds the calibration range of the instrument.

A - Indicates a Tentatively Identified Compound (TIC) is a suspected adol-condensation product.

X,Y,Z- Laboratory defined flags. The data reviewer must change these qualifiers during validation so that the data user may understand their impact on the data.

I. PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____ LAB:_____

SITE NAME:_____

1.0 Data Completeness and Deliverables

1.1 Has all data been submitted in CLP deliverable format? [ ] ___ ___

ACTION: If not, note the effect on review of the data in the data assessment narrative.

2.0 Cover Letter, SDG Narrative

2.1 Is a laboratory narrative or cover letter present? [ ] ___ ___

2.2 Are case number and SDG number(s) contained in the narrative or cover letter? [ ] ___ ___

YES NO N/A

II. SEMIVOLATILE ANALYSES

1.0 Traffic Reports and Laboratory Narrative

1.1 Are the Traffic Report Forms present for all samples? [ ] ___ ___

ACTION: If no, contact lab for replacement of missing or illegible copies.

1.2 Do the Traffic Reports or Lab Narrative indicate any problems with sample receipt, condition of samples, analytical problems or special notations affecting the quality of the data? ___ [ ] ___

ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated ("J"). If a soil sample, other than TCLP, contains more than 90% water, all non-detects data are qualified as unusable (R), and detects are flagged “J”.

ACTION: If samples were not iced, or if the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (10^{o}C), flag all positive results "J" and all non-detects "UJ".

2.0 Holding Times

2.1 Have any semivolatile technical holding times, determined from date of collection to date of extraction, been exceeded? ___ [ ] ___

Continuous extraction of water samples for semivolatile analysis must be started within **7** days of the date of collection. Soil/sediment samples must be extracted within **14** days of collection. Extracts must be analyzed within

40 days of the date of extraction.

Table of Holding Time Violations

(See Traffic Report)

Sample ID	Sample Matrix	Date Sampled	Date Lab Received	Date Extracted	Date Analyzed

ACTION: If technical holding times are exceeded, flag all positive results as estimated ("J") and sample quantitation limits as estimated ("UJ"), and document in the narrative that holding times were exceeded.

If analyses were done more than 14 days beyond holding time, either on the first analysis or upon re analysis, the reviewer must use professional judgement to determine the reliability of the data and the effects of additional storage on the sample results. At a minimum, all results should be qualified "J", but the reviewer may determine that non-detect data are unusable ("R"). If holding times are exceeded by more than 28 days, all non-detect data are unusable (R).

S))Q

		YES	NO	N/A
3.0	Surrogate Recovery (Form II/Equivalent)			
3.1	Have the semi volatile surrogate recoveries been listed on CLP Surrogate Recovery forms (Form II) for each of the following matrices:			
	a. Low Water	[ ]	___	___
	b. Low/Med Soil	[ ]	___	___
3.2	If so, are all the samples listed on the appropriate Surrogate Recovery Summary forms for each matrix:			
	a. Low Water	[ ]	___	___
	b. Low/Med Soil	[ ]	___	___
	ACTION: If CLP deliverables are unavailable, document the effect(s) in data assessments. In some cases the lab may have to be contacted to obtain the data necessary to complete the validation.			
3.3	Were outliers marked correctly with an asterisk?	[ ]	___	___
	ACTION: Circle all outliers in red.			
3.4	Were two or more base neutral OR acid surrogate recoveries out of specification for any sample or method blank (Reviewer should use lab in house recovery limits. Use surrogate recovery limits from USEPA National Functional Guidlines January 2005 page 130, if in house limits are not available. See Method 8000B-43 or 80000C-24).	[ ]	___	___
	Note: Examine lab in house limits for reasonableness.			
	If yes, were samples re-analyzed?	[ ]	___	___

YES NO N/A

Were method blanks re-analyzed? [ ] ___ ___

ACTION: If all surrogate recoveries are > 10% but two within the base-neutral or acid fraction do not meet method specifications, for the affected fraction only (i.e. either base-neutral or acid compounds):

1. Flag all positive results as estimated ("J").

2. Flag all non-detects as estimated detection limits ("UJ") when recoveries are less than the lower acceptance limit.

3. If recoveries are greater than the upper acceptance limit, do not qualify non-detects.

If any base-neutral or acid surrogate has a recovery of < 10%:

1. Positive results for the fraction with < 10% surrogate recovery are qualified with "J".

2. Non-detects for that fraction should be qualified as unusable (R) .

NOTE: Professional judgement should be used to qualify data that have method blank surrogate recoveries out of specification in both original and reanalyses. Check the internal standard areas.

3.5 Are there any transcription/calculation errors between raw data and Form II? ___ [ ] ___

ACTION: If large errors exist, call lab for explanation/resubmittal, make any necessary corrections and document

YES NO N/A

effect in data assessments.

4.0 Matrix Spikes (Form III/Equivalent)

4.1 Have the semivolatile Matrix Spike and Matrix Spike Duplicate/or duplicate unspiked Sample recoveries been listed on the Recovery Form (Form III)? [ ] ___ ___

NOTE: Method 3500B/page 4 states the spiking compounds:

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

Note: Some projects may require the spiking of specific compounds of interest.

Note: See Method 8270D-sec 8.4.2 for deciding on whether to prepare and analyze duplicate samples or a martix spike/matrix spike duplicate. If samples are expected to contain target analytes, then laboratory may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratory should use a matrix spike and matrix spike duplicate pair.

4.2 Were matrix spikes analyzed at the required frequency for each of the following matrices:

a. Low Water [ ] ___ ___

b. Low Solid [ ] ___ ___

c. Med Solid [ ] ___ ___

YES NO N/A

ACTION: If any matrix spike data are missing, take the action specified in 3.2 above. It may be necessary to contact the lab to obtain the required data.

NOTE: If the data has not been reported on CLP equivalent form, then the laboratory must provide the information necessary to evaluate the spike recoveries in the MS and MSD. The required data which should have been provided by the lab include the analytes and concentrations used for spiking, background concentrations of the spiked analytes (i.e., concentrations in unspiked sample), methods and equations used to calculate the QC acceptance criteria for the spiked analytes, percent recovery data for all spiked analytes.

The data reviewer must verify that all reported equations and percent recoveries are correct before proceeding to the next section.

4.3 Were matrix spikes performed at concentration equal to 100ug/L for acid compounds, and 200ug/l for base compounds (Method 3500B-4), or those specified in project plan. [ ] ___ ___

4.4 How many semivolatile spike recoveries are outside Laboratory in house MS/MSD recovery limits (use recovery limits values in Method 8270D-43&44 Table 6 if in house values not available).

Water	Solids
____ out of ____	____ out of ____

YES NO N/A

4.5 How many RPD's for matrix spike and matrix spike duplicate recoveries are outside QC limits?

Water	Solids
____ out of ____	____ out of ____

ACTION: Circle all outliers with red pencil.

ACTION: No action is taken on MS/MSD data alone. However, using informed professional judgement, the data reviewer may use the matrix spike and matrix spike duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data.

4.6 Was a Laboratory Control Sample (LCS) analyzed with each analytical batch? [ ] ___ ___

NOTE: When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

5.0 Blanks (Form IV/Equivalent)

5.1 Is the Method Blank Summary (Form IV) present? [ ] ___ ___

5.2 Frequency of Analysis:

Has a reagent/method blank analysis been reported per 20 samples of similar matrix, or concentration level, and for each extraction batch? [ ] ___ ___

5.3 Has a method blank been analyzed either after

	YES	NO	N/A
the calibration standard or at any other time during the analytical shift for each GC/MS system used ?	[ ]	___	___

ACTION: If any method blank data are missing, call lab for explanation/resubmittal. If not available, use professional judgement to determine if the associated sample data should be qualified.

5.4 Chromatography: review the blank raw data - chromatograms (RICs), quant reports or data system printouts and spectra.			
Is the chromatographic performance (baseline stability) for each instrument acceptable for the semivolatiles?	[ ]	___	___

ACTION: Use professional judgement to determine the effect on the data.

6.0 Contamination

NOTE: "Water blanks", "drill blanks" and "distilled water blanks" are validated like any other sample and are not used to qualify the data. Do not confuse them with the other QC blanks discussed below.

6.1 Do any method/instrument/reagent blanks have positive results for target analytes and/or TICs? When applied as described below, the contaminant concentration in these blanks are multiplied by the sample dilution factor and corrected for percent moisture where necessary.	___	[ ]	___
6.2 Do any field/rinse/ blanks have positive results for target analytes and/or TICs (if required, see section 10 below)?	___	[ ]	___

ACTION: Prepare a list of the samples associated with each of the contaminated blanks. (Attach a separate sheet.)

NOTE: All field blank results associated to a particular group of samples (may exceed one per case) must be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field Blanks must be qualified for outlying surrogates, poor spectra, instrument performance or calibration QC problems.

ACTION: Follow the directions in the table below to qualify sample results due to contamination. Use the largest value from all the associated blanks. If gross contamination exists, all data in the associated samples should be qualified as unusable (R).

Blank Action for Semivolatile Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Field	Detects	Not detected	No qualification required
	< CRQL *	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification required
	= CRQL *	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification required
	> CRQL *	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report concentration of sample with a U
		≥ CRQL and ≥ blank contamination	No qualification required

NOTE: Analytes qualified "U" for blank contamination are still considered as "hits" when qualifying for calibration criteria.

NOTE: If the laboratory did not report TIC analyses, check the project plans to verify whether or not it was required.

6.3 Are there field/rinse/equipment blanks associated with every sample? [ ] ___ ___

ACTION: For low level samples, note in data assessment that there is no associated field/rinse/equipment blank. Exception: samples taken from a drinking water tap do not have associated field blanks.

6.4 Was a instrument blank analyzed after each sample/dilution which contained a target compound

	YES	NO	N/A
that exceeded the initial calibration range.	[ ]	___	___
6.5 Does the instrument blank have positive results for target analytes and/or TICs?	___	[ ]	___

Note: Use professional judgement to determine if carryover occurred and qualify analytes accordingly.

7.0 GC/MS Apparatus and Materials

	YES	NO	N/A
7.1 Did the lab use the proper gas chromatographic column for analysis of semivolatiles by Method 8270D? Check raw data, instrument logs or contact the lab to determine what type of column was used. The method requires the use of 30 m x 0.25 mm ID (or 0.32 mm ID), silicone-coated, fused silica, capillary column.	[ ]	___	___

ACTION: If the specified column, or equivalent, was not used, document the effects in the data assessment. Use professional judgement to determine the acceptability of the data.

8.0 GC/MS Instrument Performance Check (Form V/Equivalent)

	YES	NO	N/A
8.1 Are the GC/MS Instrument Performance Check Forms (Form V) present for decafluorotriphenylphosphine (DFTPP)?	[ ]	___	___

NOTE: The performance solution should also contain 4,4-DDT, pentachlorophenol, and benzidine to verify injection port inertness and column performance. The degradation of DDT to DDE and DDD must be less than 20% total and the response of pentachlorophenol and benzidine should be within normal ranges for these compounds (based upon lab experience) and show no peak degradation or tailing before samples are analyzed. (see section 5.5

YES NO N/A

page 8270D-12).

8.2 Are the enhanced bar graph spectrum and mass/charge (m/z) listing for the DFTPP provided for each twelve hour shift? [ ] ___ ___

8.3 Has an instrument performance check solution been analyzed for every twelve hours of sample analysis per instrument? [ ] ___ ___

ACTION: List date, time, instrument ID, and sample analyses for which no associated GC/MS tuning data are available.

DATE	TIME	INSTRUMENT	SAMPLE NUMBERS
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

ACTION: If lab cannot provide missing data, reject ("R") all data generated outside an acceptable twelve hour calibration interval.

ACTION: If mass assignment is in error, flag all associated sample data as unusable (R).

8.4 Have the ion abundances been normalized to m/z 198? [ ] ___ ___

8.5 Have the ion abundance criteria been met for each instrument used? [ ] ___ ___

ACTION: List all data which do not meet ion abundance criteria (attach a separate sheet).

	YES	NO	N/A
ACTION: If ion abundance criteria are not met, take action specified in section 3.2			
8.6 Are there any transcription/calculation errors between mass lists and Form Vs? (Check at least two values but if errors are found, check more.)	___	[ ]	___
8.7 Have the appropriate number of significant figures (two) been reported?	[ ]	___	___
ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and document effect in data assessments.			
8.8 Are the spectra of the mass calibration compound acceptable?	[ ]	___	___
ACTION: Use professional judgement to determine whether associated data should be accepted, qualified, or rejected.			

9.0 Target Analytes

9.1 Are the Organic Analysis Data Sheets (Form I) present with required header information on each page, for each of the following:			
a. Samples and/or fractions as appropriate	[ ]	___	___
b. Matrix spikes and matrix spike duplicates	[ ]	___	___
c. Blanks	[ ]	___	___
9.2 Has any special cleanup, such as GPC, been performed on all soil/sediment sample extracts (see section 7.2, page 8270D-14)?	[ ]	___	___

YES NO N/A

ACTION: If data suggests that extract cleanup was not performed, use professional judgement. Make note in the data assessment narrative.

9.3 Are the Reconstructed Ion Chromatograms, mass spectra for the identified compounds, and the data system printouts (Quant Reports) included in the sample package for each of the following?

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Matrix spikes and matrix spike duplicates (Mass spectra not required) [ ] ____ ___

c. Blanks [ ] ___ ___

ACTION: If any data are missing, take action specified in 3.2 above.

9.4 Are the response factors shown in the Quant Report? [ ] ___ ___

9.5 Is chromatographic performance acceptable with respect to:

Baseline stability? [ ] ___ ___

Resolution? [ ] ___ ___

Peak shape? [ ] ___ ___

Full-scale graph (attenuation)? [ ] ___ ___

Other:_____ [ ] ___ ___

ACTION: Use professional judgement to determine the acceptability of the data.

9.6 Are the lab-generated standard mass spectra of identified semivolatile compounds present for

	YES	NO	N/A
each sample?	[ ]	___	___

ACTION: If any mass spectra are missing, take action specified in 3.2 above. If the lab does not generate their own standard spectra, make a note in the data assessment narrative. If spectra are missing, reject all positive data.

9.7 Is the RRT of each reported compound within 0.06 RRT units of the standard RRT in the continuing calibration?	[ ]	___	___
9.8 Are all ions present in the standard mass spectrum at a relative intensity greater than 10% (of the most abundant ion) also present in the sample mass spectrum?	[ ]	___	___
9.9 Do the relative intensities of the characteristic ions in the sample agree within ± 30% of the corresponding relative intensities in the reference spectrum?	[ ]	___	___

ACTION: Use professional judgement to determine acceptability of data. If it is determined that incorrect identifications were made, all such data should be rejected (R), flagged "N" (Presumptive evidence of the presence of the compound) or changed to not detected (U) at the calculated detection limit. In order to be positively identified, the data must comply with the criteria listed in 9.7, 9.8, and 9.9.

ACTION: When sample carry-over is a possibility, professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification.

YES NO N/A

10.0 Tentatively Identified Compounds (TIC)

10.1 If Tentatively Identified Compounds were required for this project, are all Form Is, Part B present; and do listed TICs include scan number or retention time, estimated concentration and "JN" qualifier?

NOTE: Review sampling reports to determine if the lab was required to identify non target analytes (refer to section 7.6.2,page 8270D-21).

10.2 Are the mass spectra for the tentatively identified compounds and associated "best match" spectra included in the sample package for each of the following: [ ] ___ ___

a. Samples and/or fractions as appropriate [ ] ___ ___

b. Blanks [ ] ___ ___

ACTION: If any TIC data are missing, take action specified in 3.2 above.

ACTION: Add "JN" qualifier only to analytes identified by CAS #.

10.3 Are any target compounds from one fraction listed as TIC compounds in another (e.g., an acid compound listed as a base neutral TIC)? ___ [ ] ___

ACTION: i. Flag with "R" any target compound listed as a TIC.

ii. Make sure all rejected compounds are properly reported in the other fraction.

10.4 Are all ions present in the reference mass spectrum with a relative intensity greater than 10% (of the most abundant ion) also present in the

	YES	NO	N/A
sample mass spectrum?	[ ]	___	___
10.5 Do TIC and "best match" standard relative ion intensities agree within ± 20%?	[ ]	___	___

ACTION: Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, change the identification to "unknown" or to some less specific identification (example: "C3 substituted benzene") as appropriate and remove "JN". Also, when a compound is not found in any blank, but is a suspected artifact of a common laboratory contaminant, the result should be qualified as unusable, "R."

11.0 Compound Quantitation and Reported Detection Limits

	YES	NO	N/A
11.1 Are there any transcription/calculation errors in Form I results? Check at least two positive values. Verify that the correct internal standard, quantitation ion, and RRF were used to calculate Form I result. Were any errors found?	___	[ ]	___

NOTE: Structural isomers with similar mass spectra, but insufficient GC resolution (i.e. percent valley between the two peaks > 25%) should be reported as isomeric pairs. The reviewer should check the raw data to ensure that all such isomers were included in the quantitation (i.e., add the areas of the two coeluting peaks to calculate the total concentration).

	YES	NO	N/A
11.2 Are the method detection limits adjusted to reflect sample dilutions and, for soils, sample moisture?	[ ]	___	___

YES NO N/A

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect in data assessments.

ACTION: When a sample is analyzed at more than one dilution, the lowest detection limits are used (unless a QC exceedance dictates the use of the higher detection limit from the diluted sample data). Replace concentrations that exceed the calibration range in the original analysis by crossing out the "E" and it's associated value on the original Form I (if present) and substituting the data from the analysis of the diluted sample. Specify which Form I is to be used, then draw a red " X" across the entire page of all Form I's that should not be used, including any in the summary package.

12.0 Standards Data (GC/MS)

12.1 Are the Reconstructed Ion Chromatograms, and data system printouts (Quant, Reports) present for initial and continuing calibration? [ ] ___ ___

ACTION: If any calibration standard data are missing, take action specified in 3.2 above.

13.0 GC/MS Initial Calibration (Form VI/Equivalent)

13.1 Is the Initial Calibration Form (Form VI/ Equivalent) present and complete for the semivolatile fraction? [ ] ___ ___

ACTION: If any calibration forms or standard row data are missing, take action specified in 3.2 above.

13.2 Are all base neutral or acid RRFs > 0.050? [ ] ___ ___

YES NO N/A

Check the **average RRFs** of the four System Performance Check Compounds (SPCCs): N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. These compounds must have **average RRFs** greater than or equal to 0.05 before running samples and should not show any peak tailing.

ACTION: Circle all outliers in red.

ACTION: For any target analyte with **average RRF <0.05**

1. "R" all non-detects;

2. "J" all positive results.

13.3 Are response factors for base neutral or acid target analytes stable over the concentration range of the calibration (% Relative standard deviation [%RSD] < 15.0%)? [ ] ___ ___

NOTE: The % RSD for each individual Calibration Check Compound (CCC, Method 8270D-40 see Table 4) must be less than 30% before analysis can begin. If grater 30%, the lab must clean and recalibrate the instrument.

CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol

YES NO N/A

Benzo(a)pyrene

ACTION: If the %RSD for any CCC >30% and no corrective action taken, then "J" qualify all positive hits and "UJ" qualify all non-detects.

ACTION: Circle all outliers in red.

ACTION: If the % RSD is $\geq$ 15.0%, qualify positive results for that analyte "J" and non-detects using professional judgement. When RSD > 90%, flag all non- detect results for that analyte "R," unusable. Alternatively, the lab should calculate first or second order regression fit of the calibration curve and select the fit which introduces the least amount of error.

NOTE: Analytes previously qualified "U" due to blank contamination are still considered as "hits" when qualifying for calibration criteria.

13.4 Did the laboratory calculate the calibration curve by the least squares regression fit? ___ [ ] ___

13.5 Are there any transcription/calculation errors in the reporting of average response factors (RRF) or % RSD? (Check at least two values but if errors are found, check more.) ___ [ ] ___

ACTION: Circle Errors in red.

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and note errors in data assessments.

13.5 Do the target compounds for this SDG include Pesticides? [ ] ___ ___

YES NO N/A

13.6 If the pesticide compounds include DDT, was the percent breakdown of DDT to DDD and DDE greater than 20%? ___ [ ] ___

ACTION: If DDT percent breakdown exceeds 20%:

i. Qualify all positive results for DDT with "J". If DDT was not detected, but DDD and DDE results are positive, qualify the quantitation limit for DDT as unusable, "R".

ii. Qualify all positive results for DDD and DDE as presumptively present at an approximate concentration "JN".

14.0 GC/MS Calibration Verification (Form VII/Equivalent)

14.1 Are the Calibration Verification Forms (Form VII) present and complete for all compounds of interest? [ ] ___ ___

14.2 Has a calibration verification standard been analyzed for every twelve hours of sample analysis per instrument? [ ] ___ ___

ACTION: List below all sample analyses that were not within twelve hours of a calibration verification analysis for each instrument used.

_____

_____

_____

ACTION: If any forms are missing or no calibration verification standard has been analyzed within twelve hours of every sample analysis,

YES NO N/A

call lab for explanation/resubmittal. If continuing calibration data are not available, flag all associated sample data as unusable ("R").

14.3 Do any of the SPCCs have an RRF <0.05? ___ [ ] ___

If YES, make a note in data assessment if the lab did not take corrective action specified in section 7.4.4, page 8270D-18. [ ] ___ ___

14.4 Do any of the CCCs have a %D between the initial and continuing RRF which exceeds 20.0%?

ACTION: If yes, make a note in data assessment.

14.5 Do any semivolatile compounds have a % Difference (% D) between the initial and continuing RRF which exceeds 20.0%? ___ [ ] ___

ACTION: Circle all outliers in red.

ACTION: Qualify both positive results and non-detects for the outlier compound(s) as estimated (J). When %D is above 90%, qualify all non-detects for that analyte as "R", unusable.

14.6 Do any semivolatile compounds have a RRF < 0.05? ___ [ ] ___

ACTION: Circle all outliers in red.

ACTION: If RRF < 0.05, qualify as unusable ("R") associated non-detects and "J" associated positive values.

14.7 Are there any transcription/calculation errors in the reporting of average response factors (RRF) or percent difference (%D) between initial and continuing RRFs? (Check at least two values but if errors are found, check more). ___ [ ] ___

YES NO N/A

ACTION: Circle errors in red.

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect(s) in the data assessments.

15.0 Internal Standards (Form VIII)

15.1 Are the internal standard areas (Form VIII) of every sample and blank within the upper and lower limits (-50% to + 100%) for each continuing calibration? [ ] ___ ___

ACTION: List each outlying internal standard below.

Sample ID	IS #	Area	LowerLimit	Upper Limit

(Attach additional sheets if necessary.)

Note: Check Table 5, 8270D-41 for associated analytes.

ACTION: i. If the internal standard area count is outside the upper or lower limit, flag with "J" all positive results and non-detects (U values) quantitated with this internal standard.

ii. Non-detects associated with IS > 100% should not be qualified.

YES NO N/A

iii. If the IS area is below the lower limit (<50%), qualify all associated non-detects (U-values) "J". If extremely low area counts are reported (<25%) or if performance exhibits a major abrupt drop off, flag all associated non-detects as unusable (R).

15.2 Are the retention times of all internal standards within 30 seconds of the associated calibration standard? [ ] ___ ___

ACTION: Professional judgement should be used to qualify data if the retention times differ by more than 30 seconds.

16.0 Laboratory Control Samples (LCS)

16.1 Were any LCS samples run in order to verify analytes which failed criteria for spike recovery? [ ] ___ ___

16.2 Did the lab spike LCS sample spiked with the same analytes and the same concentrations as the matrix spike? [ ] ___ ___

16.3 Were the mean and standard deviation of all analytes within the QC acceptance ranges as shown in Table 6, 8270D-43? [ ] ___ ___

ACTION: If the recovery of any analyte falls out of the designated range, the analytical results for that compound is suspect and should be qualified "J" in the unspiked samples.

17.0 Field Duplicates

17.1 Were any field duplicates submitted for semivolatile analysis? [ ] ___ ___

S))Q
YES NO N/A

ACTION: Compare the reported results for field duplicates and calculate the relative percent difference.

ACTION: Any gross variation between field duplicate results must be addressed in the reviewer narrative. However, if large differences exist, identification of field duplicates should be confirmed by contacting the sampler.

VALIDATION SOP

Semivolatile Organics SIM

USEPA Region 2 SOP HW-35, Revision 2, 3/13

Hazardous Waste Support Section
SOP NO. HW-35 Revision 2
Semivolatile Data Validation

Approvals:

Russell Arnone — 03/28/13
Chemist, Hazardous Waste Support Section — Date

Philip Cocuzza — 3/28/13
Chief, Hazardous Waste Support Section — Date

Jon Gabry — 3/26/13
Chief, Hazardous Waste Support Branch — Date

Approving Official Annual Review — Date

NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by USEPA, and may not be relied upon to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

The guidance for data validation set forth in the quality assurance project plan (QAPP) for the project associated with the data in question will always take precedence over the data validation guidance listed herein.

Validators should note that their professional judgment supersedes any guidance listed in this document.

Government contractors to the USEPA using this document to validate data should not hesitate to contact their Contracting Officer Representative with any questions regarding data validation or data package completeness.

This document can be obtained from the USEPA's Region 2 Quality Assurance website at:

http://www.epa.gov/region2/qa/documents.htm

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ACRONYMS

%D	Percent Difference
%RSD	Percent Relative Standard Deviation
ARO	Aroclor
ASB	Analytical Services Branch
BFB	Bromofluorobenzene
CCS	Contract Compliance Screening
CCV	Continuing Calibration Verification
CF	Calibration Factor
CLP	Contract Laboratory Program
CLP PO	Contract Laboratory Program Project Officer
CRQL	Contract Required Quantitation Limit
CSF	Complete SDG File
DART	Data Assessment Rapid Transmittal
DAT	Data Assessment Tool
DCB	Decachlorobiphenyl
DFTPP	Decafluorotriphenylphosphine
DMC	Deuterated Monitoring Compound
DQA	Data Quality Assessment
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
EDM	EXES Data Manager
ESAT	Environmental Services Assistance Team
EXES	Electronic Data eXchange and Evaluation System
GC	Gas Chromatograph
GC/ECD	Gas Chromatograph/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GPC	Gel Permeation Chromatography
HWSS	Hazardous Waste Support Section
INDA	Individual Standard Mixture A
INDB	Individual Standard Mixture B
INDC	Individual Standard Mixture C
LCS	Laboratory Control Sample
MS	Matrix Spike
MSD	Matrix Spike Duplicate
OSRTI	Office of Superfund Remediation and Technology Innovation
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PEM	Performance Evaluation Mixture
QA	Quality Assurance
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan
QC	Quality Control
RAS	Routine Analytical Services

RIC	Reconstructed Ion Chromatogram
RPD	Relative Percent Difference
RRF	Relative Response Factor
$\overline{\textbf{RRF}}$	Mean Relative Response Factor
RRT	Relative Retention Time
RSCC	Regional Sample Control Center Coordinator
RSD	Relative Standard Deviation
RT	Retention Time
SAP	Sampling and Analysis Plan
SCP	Single Component Pesticide
SDG	Sample Delivery Group
SIM	Selected Ion Monitoring
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
TCL	Target Compound List
TCLP	Toxicity Characteristics Leachate Procedure
TCX	Tetrachloro-m-xylene
TIC	Tentatively Identified Compound
TOPO	Task Order Project Officer
TR/COC	Traffic Report/Chain of Custody Record
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VTSR	Validated Time of Sample Receipt

INTRODUCTION

This document is designed to offer the data reviewer guidance in determining the validity of analytical data generated through the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Multi-Media, Multi-Concentration Organics Analysis (SOM01.2), and any future editorial revisions of SOM01.2, hereinafter referred to as the SOM01.2 SOW. This guidance is somewhat limited in scope and is intended to be used as an aid in the formal technical review process.

The guidelines presented in the document will aid the data reviewer in establishing (a) if data meets the specific technical and QC criteria established in the SOW, and (b) the validity and extent of bias of any data not meeting the specific technical and QC criteria established in the SOW. It must be understood by the reviewer that acceptance of data not meeting technical requirements is based upon many factors, including, but not limited to site-specific technical requirements, the need to facilitate the progress of specific projects, and availability for re-sampling.

The reviewer should note that while this document is to be used as an aid in the formal data review process, other sources of guidance and information, as well as **professional judgment**, should also be used to determine the ultimate validity of data, especially in those cases where all data does not meet specific technical criteria.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process.

U	The analyte was analyzed for, but was not detected above the level of the reported sample quantitation limit.
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
J+	The result is an estimated quantity, but the result may be biased high.
J-	The result is an estimated quantity, but the result may be biased low.
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.

DATA PACKAGE INSPECTION

For data obtained through the Contract Laboratory Program (CLP), the EXES Data Manager (EDM) is a useful tool in the data review process. For more information about EDM, please refer to the following Sample Management Office (SMO) website:

https://epasmoweb.fedcsc.com/help/guides/Submit%20and%20Inspect%20Data%20Quick%20Guide%20%28EXES%29.pdf

EDM will identify any missing and/or incorrect information in the data package. The CLP laboratory may submit a reconciliation package for any missing items or to correct data. If there are any concerns regarding the data package, contact the CLP Project Officer (CLP PO) from the Region where the samples were taken. For personnel contact information, please refer to the following CLP website:

http://www.epa.gov/superfund/programs/clp/contacts.htm

HWSS DATA VALIDATION PROCESS

After downloading the data package from EDM, the data validator will use the recommendations in this SOP as well as their own professional judgment to validate the data.

The data will be saved in the following location, under the appropriate case number folder:

G:\DESADIV\HWSS\DATA VALIDATION

The file naming conventions will consist of

A. case number i.e., 12345
B. SDG name i.e., BXY12
C. level of validation performed i.e., S3VE

Examples: **12345_BXY12_S3VE.xls**

12345_BXY12_S3VEM.xls

When data validation is completed, the data package is uploaded for the client to download from the HWSS data delivery website:

https://epaqpx.rtp.epa.gov/hwssclpdeliverables

The completed data package includes the Executive Narrative (see Appendix B for template), the Sample Summary Report (see Appendix C for example), and the Electronic Data Deliverable (EDD) (see Appendix D for a list of the column headers included in this document).

PRELIMINARY REVIEW

This document is for the review of analytical data generated through the SOM01.2 SOW and any future editorial revisions of SOM01.2 for USEPA Region 2. To use this document effectively, the reviewer should have an understanding of the analytical method and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in the analysis are essential information.

It is suggested that an initial review of the data package be performed, taking into consideration all information specific to the sample data package [e.g., Modified Analysis requests, Traffic Report/Chain of Custody (TR/COC) documentation, SDG Narratives, etc.].

The reviewer should also have a copy of the Quality Assurance Project Plan (QAPP) or similar document for the project for which the samples were analyzed. The criteria for data validation outlined in the QAPP supersede this Standard Operating Procedure. The reviewer should contact the appropriate Regional Contract Laboratory Program Project Officer (CLP PO) to obtain copies of the QAPP and relevant site information. This information is necessary in determining the final usability of the analytical data.

The SDGs or Cases routinely have unique samples that require special attention from the reviewer. These include field blanks and trip blanks, field duplicates, and Performance Evaluation (PE) samples which must be identified in the sampling records. The sampling records (e.g., TR/COC records, field logs, and/or contractor tables) should identify:

1. The Region where the samples were taken,
2. The Case number,
3. The complete list of samples with information on:
    a. Sample matrix;
    b. Field blanks (i.e., equipment blanks or rinsate blanks) and trip blanks;
    c. Field duplicates;
    d. Field spikes;
    e. QC audit samples;
    f. Shipping dates;
    g. Preservatives; and
    h. Laboratories involved.

The TR/COC documentation includes sample descriptions and date(s) of sampling. The reviewer must consider lag times between sampling and start of analysis when assessing technical sample holding times.

The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, preservation, and unusual events should be documented in the SDG Narrative. The reviewer should also inspect any email or telephone/communication logs detailing any discussion of sample or analysis issues between the laboratory, the CLP Sample Management Office (SMO), and USEPA Region 2.

Preservation

Action:

1. Qualify aqueous sample results using preservation and technical holding time information as follows (see Table 1):
    a. If there is no evidence that the samples were properly preserved (T = 4°C ± 2°C), and the samples were extracted or analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects as estimated (J) and non-detects as estimated (UJ).
    b. If there is no evidence that the samples were properly preserved (T = 4°C ± 2°C), and the samples were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects as estimated (J) and non-detects as estimated (UJ).
    c. If the samples were properly preserved, and were extracted and analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.
    d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects as estimated (J) and non-detects as estimated (UJ). Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.
2. Qualify non-aqueous sample results using preservation and technical holding time information as follows (see Table 1):
    a. If there is no evidence that the samples were properly preserved (T = 4°C ± 2°C), and the samples were extracted or analyzed within the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects as estimated (J) and non-detects as estimated (UJ).
    b. If there is no evidence that the samples were properly preserved (T = 4°C ± 2°C), and the samples were extracted or analyzed outside the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects as estimated (J) and non-detects as estimated (UJ).
    c. If the samples were properly preserved, and were extracted and analyzed within the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.
    d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding time [14 days from sample collection for

extraction; 40 days from sample collection for analysis], qualify detects as estimated (J) and non-detects as estimated (UJ). Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

3. Whenever possible, the reviewer should comment on the effect of the holding time exceedance on the resulting data in the Data Review Narrative.
4. Use professional judgment to qualify samples whose temperature upon receipt at the laboratory is either below 2 degrees centigrade or above 6 degrees centigrade.
5. If technical holding times are grossly exceeded, use professional judgment to qualify the data.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, when technical holding times are exceeded.

Table 1. Holding Time Actions for Semivolatile Analyses

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days (for extraction) ≤ 40 days (for analysis)	J	UJ
	No	> 7 days (for extraction) > 40 days (for analysis)	J	UJ
	Yes	≤ 7 days (for extraction) ≤ 40 days (for analysis)	No qualification	
	Yes	> 7 days (for extraction) > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	Use professional judgment	
Non-Aqueous	No	≤ 14 days (for extraction) ≤ 40 days (for analysis)	J	UJ
	No	> 14 days (for extraction) > 40 days (for analysis)	J	UJ
	Yes	≤ 14 days (for extraction) ≤ 40 days (for analysis)	No qualification	
	Yes	> 14 days (for extraction) > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	Use professional judgment	

Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

Action:

NOTES: These requirements do not apply when samples are analyzed by the Selected Ion Monitoring (SIM) technique.
All mass spectrometer instrument conditions must be identical to those used during the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the method specifications are contrary to the Quality Assurance (QA) objectives, and are therefore unacceptable.

NOTES: No data should be qualified based on DFTPP failure. Instances of this should be noted in the narrative.
All ion abundance ratios must be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be up to 100% that of m/z 198.
The requirement to analyze the instrument performance check solution is optional when analysis of Polycyclic Aromatic Hydrocarbon (PAH)/pentachlorophenol is to be performed by the Selected Ion Monitoring (SIM) technique.

1. If samples are analyzed without a preceding valid instrument performance check or are analyzed 12 hours after the Instrument Performance Check, qualify all data in those samples as unusable (R).
2. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.
3. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, the reviewer must use professional judgment to assess the data. Notify the laboratory's Contract Laboratory Program Project Officer (CLP PO).
4. If ion abundance criteria are not met, use professional judgment to determine to what extent the data may be utilized. Guidelines to aid in the application of professional judgment in evaluating ion abundance criteria are discussed as follows:
    a. Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile.
    b. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 80.0% relative abundance (criteria: 10.0-60.0%) and other criteria are met, the deficiency is minor.

   c. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.
5. Note, in the Data Review Narrative, decisions to use analytical data associated with DFTPP instrument performance checks not meeting contract requirements.
6. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described in Semivolatiles Organic Analysis, Section II.D.5 of the SOM1.2 NFG, obtain additional information on the instrument performance checks. If the techniques employed are found to be at variance with the contract requirements, the performance and procedures of the laboratory may merit evaluation. Note, for CLP PO action, concerns or questions regarding laboratory performance. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than from the DFTPP peak), note this for CLP PO action.
7. Use professional judgment to determine whether associated data should be qualified based on the spectrum of the mass calibration compound.

Initial Calibration

Table 2. Semivolatile Target Compounds Exhibiting Poor Response

Compounds	
2,2'-Oxybis-(1-chloropropane)	Benzaldehyde
4-Chloroaniline	4-Nitroaniline
Hexachlorobutadiene	4,6-Dinitro-2-methylphenol
Hexachlorocyclopentadiene	N-Nitrosodiphenylamine
2-Nitroaniline	3-3'-Dichlorobenzidine
3-Nitroaniline	1,1'-Biphenyl
2,4-Dinitrophenol	Dimethylphthalate
4-Nitrophenol	Diethylphthalate
Acetophenone	1,2,4,5-Tetrachlorobenzene
Caprolactam	Carbazole
Atrazine	Butylbenzylphthalate
Di-n-butylphthalate	Di-n-octylphthalate
Bis(2-ethylhexyl)phthalate	

Action:

NOTES: The twenty-five (25) poor performing compounds are listed in Table 2 above. The relative response factor (RRF) for these compounds must be greater than or equal to 0.010. The RRF for all other semivolatile target compounds must be ≥ 0.050. Analytes previously qualified as non-detected (U) for blank contamination are still treated as "hits" when qualifying for initial calibration criteria.
If analysis by Selected Ion Monitoring (SIM) technique is requested for PAHs/pentachlorophenols, calibration standards are analyzed at 0.10, 0.20, 0.40, 0.80, and 1.0 ng/µL for each target compound of interest and the associated DMCs. Pentachlorophenol will require only a four-point initial calibration at 0.20, 0.40, 0.80, and 1.0 ng/µL

1. Qualify all semivolatile target compounds, including the compounds exhibiting poor response listed in Table 2, using the following criteria (see Table 3):
    a. If any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response listed in Table 2, and 0.050 for all other semivolatile compounds), use professional judgment for detects, based on mass spectral identification, to qualify the data as estimated (J).
    b. If any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response listed in Table 2, and 0.050 for all other semivolatile compounds), qualify non-detected compounds as unusable (R).

c. If any of the semivolatile target compounds listed in Table 2 has %RSD greater than 40.0%, qualify detects as estimated (J), and non-detected compounds using professional judgment (see Action 2).
d. For all other semivolatile target compounds, if %RSD is greater than 20.0%, qualify detects as estimated (J), and non-detected compounds using professional judgment (see Action 2).
e. If the semivolatile target compounds meet the acceptance criteria for RRF and the %RSD, no qualification of the data is necessary.
f. No qualification of the data is necessary on the DMC RRF and %RSD data alone. Use professional judgment and follow the guidelines in Action 2 to evaluate the DMC RRF and %RSD data in conjunction with the DMC recoveries to determine the need for qualification of data.

2. At the reviewer's discretion, and based on the project-specific Data Quality Objectives (DQOs), a more in-depth review may be considered using the following guidelines:
    a. If any semivolatile target compound has a %RSD greater than the maximum criterion (40.0% for the compounds listed in Table 2, and 20.0% for all other semivolatile compounds), and if eliminating either the high or the low-point of the curve does not restore the %RSD to less than or equal to the required maximum:
        i. Qualify detects for that compound(s) as estimated (J).
        ii. Qualify non-detected semivolatile target compounds using professional judgment.
    b. If the high-point of the curve is outside of the linearity criteria (e.g., due to saturation):
        i. Qualify detects outside of the linear portion of the curve as estimated (J).
        ii. No qualifiers are required for detects in the linear portion of the curve.
        iii. No qualifiers are required for semivolatile target compounds that were not detected.
    c. If the low-point of the curve is outside of the linearity criteria:
        i. Qualify low-level detects in the area of non-linearity as estimated (J).
        ii. No qualifiers are required for detects in the linear portion of the curve.
        iii. For non-detected semivolatile compounds, use the lowest point of the linear portion of the curve to determine the new quantitation limit.
3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.
4. Document in the Data Assessment Report the analytes that fail %RSD and/or RRF criteria.
5. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 3. Initial Calibration Actions for Semivolatiles Analyses

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
RRF < 0.010 (target compounds listed in Table 2) RRF < 0.050 (all other target compounds)	J (based on mass spectral identification)	R
RRF ≥ 0.010 (target compounds listed in Table 2) RRF ≥ 0.050 (all other target compounds)	No qualification	
% RSD ≤ 40.0 (target compounds listed in Table 2) % RSD ≤ 20.0 (all other target compounds)	No qualification	
% RSD > 40.0 (target compounds listed in Table 2) % RSD > 20.0 (all other target compounds)	J	Use professional judgment

Continuing Calibration Verification (CCV)

Action:

NOTES: Verify that the CCV was run at the required frequency (an opening and closing CCV must be run within 12-hour period) and the CCV was compared to the correct initial calibration. If the mid-point standard from the initial calibration is used as an opening CCV, verify that the result (RRF) of the mid-point standard was compared to the average RRF from the correct initial calibration.
The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for the new 12-hour analytical sequence, provided that all the technical acceptance criteria are met for an opening CCV (see Table 4 below). If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a DFTPP tune followed by an opening CCV is required and the next 12-hour time period begins with the DFTPP tune.
All DMCs must meet RRF $\geq$ 0.010. No qualification of the data is necessary on the DMCs RRF and %RSD/%D data alone. However, use professional judgment to evaluate the DMC and %RSD/%D data in conjunction with the DMC recoveries to determine the need of qualification the data.

1. If a CCV (opening and closing) was not run at the appropriate frequency, qualify data using professional judgment.
2. Qualify all semivolatile target compounds, including the compounds exhibiting poor response listed in Table 2 using the following criteria:
    a. For an opening CCV, if any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response, and 0.050 for all other semivolatile compounds), use professional judgment for detects, based on mass spectral identification, to qualify detects as estimated (J) and qualify non-detected compounds as unusable (R).
    b. For a closing CCV, if any semivolatile target compound has an RRF value less than 0.010, use professional judgment for detects based on mass spectral identification to qualify detects as estimated (J), and qualify non-detected compounds as unusable (R).
    c. For an opening CCV, if the Percent Difference value for any of the semivolatile target compounds listed in Table 2 is outside the ± 40.0% criterion, qualify detects as estimated (J) and non-detected compounds as estimated (UJ).
    d. For an opening CCV, if the Percent Difference value for any other semivolatile target compound is outside the ± 25.0% criterion, qualify detects as estimated (J) and non-detected compounds as estimated (UJ).
    e. For a closing CCV, if the Percent Difference value for any semivolatile target compound is outside the ± 50.0% criterion, qualify detects as estimated (J) and non-detected compounds as estimated (UJ).
    f. If the semivolatile target compounds meet the acceptable criteria for RRF and the Percent Difference, no qualification of the data is necessary.

g. No qualification of the data is necessary on the DMC RRF and the Percent Difference data alone. Use professional judgment to evaluate the DMC RRF and Percent Difference data in conjunction with the DMC recoveries to determine the need for qualification of data.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.
4. Document in the Data Assessment under Contract Problems/Non-Compliance if more than two of the required analytes failed the acceptance criteria in Table 4.
5. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 4. Continuing Calibration Verification (CCV) Actions for Semivolatile Analyses

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.010 (semivolatile target compounds listed in Table 2) RRF < 0.050 (all other semivolatile target compounds)	RRF < 0.010 (all semivolatile target compounds)	J (based on mass spectral identification)	R
RRF ≥ 0.010 (semivolatile target compounds listed in Table 2) RRF ≥ 0.050 (all other semivolatile target compounds)	RRF ≥ 0.010 (all semivolatile target compounds)	No qualification	
%D > 40.0 or < -40.0 (semivolatile target compounds listed in Table 2) %D > 25.0 or < -25.0 (all other semivolatile target compounds)	%D > 50.0 or < -50.0 (all semivolatile target compounds)	J	UJ
%D ≤ 40.0 and ≥ -40.0 (semivolatile target compounds listed in Table 2) %D ≤ 25.0 and ≥ -25.0 (all other semivolatile target compounds)	%D ≤ 50.0 and ≥ -50.0 (all semivolatile target compounds)	No qualification	

Blanks

Action:

NOTES: The concentration of non-target compounds in all blanks must be less than or equal to 10 µg/L.
The concentration of each target compound found in the method or field blanks must be less than its CRQL listed in the method, except bis(2-ethylhexyl)phthalate, which must be less than 5x its respective CRQL in low-level samples.
Data concerning the field blanks are not evaluated as part of the CCS process. If field blanks are present, the data reviewer should evaluate this data in a similar fashion as the method blanks.

NOTES: "Water blanks, "drill blanks", and "distilled water blanks" are validated like any other sample and are not used to qualify data. Do not confuse them with the other QC blanks discussed below.
All field blank results associated with a particular group of samples (may exceed one per case) must be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field blanks must be qualified for system monitoring compounds, instrument performance criteria, and spectral or calibration QC problems.
Samples taken from a drinking water tap do not have associated field blanks.
When applied as described in Table 5 below, the contaminant concentration in the blank is multiplied by the sample dilution factor.

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. In instances where more than one of the same type of blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Do not correct the results by subtracting any blank value.

1. If a semivolatile compound is found in a method blank, but not found in the sample, no qualification of the data is necessary (see Table 5).
2. If the method or field blanks contain a semivolatile Target Compound List (TCL) compound(s) at a concentration less than the CRQL (less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples) and:
    a. the sample concentration is less than the CRQL (less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples), report the CRQL value with a "U".
    b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples), no qualification is required.
3. If the method or field blanks contain a semivolatile TCL compound(s) at a concentration greater than the CRQL (greater than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples) and:

   a. the sample concentration is less than the CRQL (less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples), report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples), and less than or equal to the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U".
   c. the sample concentration is greater than or equal to the CRQL (greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples) and greater than the blank concentration, no qualification is required.
4. If the method or field blanks contain a semivolatile TCL compound(s) at a concentration equal to the CRQL (equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples) and:
   a. the sample concentration is less than or equal to the CRQL (less than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples), report the CRQL value with a "U".
   b. the sample concentration is greater than the CRQL (greater than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples), no qualification is required.
5. If gross contamination exists (i.e., saturated peaks by GC/MS) in the method or field blanks, raise the CRQL to the level of the blank contamination and report the associated sample data below this level as CRQL-U. Non-detected semivolatile target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.
6. If contaminants are found in the field blanks, the following is recommended:
   a. Review the associated method blank data to determine if the contaminant(s) was also present in the method blank.
      i. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.
      ii. If the analyte was not present in the method blank, the source of contamination may be in the storage area, in the field, or during sample transport. Consider all associated samples for possible cross-contamination.
7. Tentatively Identified Compounds (TICs) should only be considered if requested.
   a. For TICs, if the concentration in the sample is less than five times the concentration in the most contaminated associated blank (TIC concentration < 5xblank concentration), qualify the sample data as unusable (R).
8. If method blank data are unavailable, the reviewer may use professional judgment or substitute field blank data for missing method blank data.

NOTE: There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result.

Table 5. Blank Actions for Semivolatiles Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Field	Detects	Not detected	No qualification required
	< CRQL *	< CRQL*	Report CRQL value with a U
		≥ CRQL*	No qualification required
	> CRQL *	< CRQL*	Report CRQL value with a U
		≥ CRQL* and ≤ blank concentration	Report blank value for sample concentration with a U
		≥ CRQL* and > blank concentration	No qualification required
	= CRQL*	≤ CRQL*	Report CRQL value with a U
		> CRQL*	No qualification required
	Gross contamination	Detects	Report blank value for sample concentration with a U

* 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level samples.

Deuterated Monitoring Compounds (DMCs)

Table 6. Semivolatile Deuterated Monitoring Compounds (DMCs) and Recovery Limits

DMC	Recovery Limits (%) for Water Samples	Recovery Limits (%) for Soil/Sediment Samples
Phenol-d_5	39 – 106	17 – 103
Bis-(2-chloroethyl) ether-d_8	40 – 105	12 – 98
2-Chlorophenol-d_4	41 – 106	13 – 101
4-Methylphenol-d_8	25 – 111	8 – 100
Nitrobenzene-d_5	43 – 108	16 – 103
2-Nitrophenol-d_4	40 – 108	16 – 104
2,4-Dichlorophenol-d_3	37 – 105	23 – 104
4-Chloroaniline-d_4	1 – 145	1 – 145
Dimethylphthalate-d_6	47 – 114	43 – 111
Acenaphthylene-d_8	41 – 107	20 – 97
4-Nitrophenol-d_4	33 – 116	16 – 166
Fluorene-d_{10}	42 – 111	40 – 108
4,6-Dinitro-2-methylphenol-d_2	22 – 104	1 – 121
Anthracene-d_{10}	44 – 110	22 – 98
Pyrene-d_{10}	52 – 119	51 – 120
Benzo(a)pyrene-d_{12}	32 – 121	43 – 111
Fluoranthene-d_{10} (SIM)	50 – 150	50 – 150
2-Methylnaphthalene-d_{10} (SIM)	50 – 150	50 – 150

Action:

NOTES: Recoveries for DMCs in semivolatile samples and blanks must be within the limits specified in Table 6.
The recovery limits for any of the compounds listed in Table 6 may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

NOTE: Up to four (4) DMCs per sample may fail to meet the recovery limits, but all recoveries must be > 0%. As per SOM01.2, any sample which has more than 4 DMCs outside the limits must be reanalyzed.

Table 8 lists the semivolatile DMCs and their associated target compounds. If **any** DMC recovery in the semivolatiles fraction is out of specification, qualify the data considering the existence of interference in the raw data (see Table 7). Considerations include, but are not limited to:

1. For any recovery greater than the upper acceptance limit:
    a. Qualify detected associated semivolatile target compounds as estimated high (J+).
    b. Do not qualify non-detected associated semivolatile target compounds.
2. For any recovery less than the lower acceptance limit:

   a. Qualify detected associated semivolatile target compounds as estimated low (J-).
   b. Qualify non-detected associated semivolatile target compounds as estimated (UJ).
3. For any recovery within acceptance limits, no qualification of the data is necessary.
4. In the special case of a blank analysis having DMCs out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable DMC recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, note analytical problems for Contract Laboratory Program Project Officer (CLP PO) action.
5. If more than four DMCs are outside of the recovery limits for semivolatiles analysis and the sample was not reanalyzed, note under Contract Problems/Non-Compliance.

Table 7. Deuterated Monitoring Compound (DMC) Recovery Actions for Semivolatiles Analyses

Criteria	Action	
	Detected Associated Compounds	**Non-detected Associated Compounds**
%R > Upper Acceptance Limit	J+	No qualification
%R < Lower Acceptance Limit	J-	UJ
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualification	

Table 8. Semivolatile Deuterated Monitoring Compounds (DMCs) and the Associated Target Compounds

Phenol-d_5	**2-Chlorophenol-d_4**	**2-Nitrophenol-d_4**
Benzaldehyde Phenol	2-Chlorophenol	Isophorone 2-Nitrophenol
bis(2-Chloroethyl) ether-d_8	**4-Methylphenol-d_8**	**4-Chloroaniline-d_4**
bis-(2-Chloroethyl) ether 2,2'-oxybis(1-Chloropropane) bis(2-Chloroethoxy) methane	2-Methylphenol 4-Methylphenol 2,4-Dimethylphenol	4-Chloroaniline Hexachlorocyclopentadiene 3,3'-Dichlorobenzidine
Nitrobenzene-d_5	**2,4-Dichlorophenol-d_3**	**Dimethylphthalate-d_6**
Acetophenone N-Nitroso-di-n-propylamine Hexachloroethane Nitrobenzene 2,6-Dinitrotoluene 2,4-Dinitrotoluene N-Nitrosodiphenylamine	2,4-Dichlorophenol Hexachlorobutadiene 4-Chloro-3-methylphenol 2,4,6-Trichlorophenol 2,4,5-Trichlorophenol 1,2,4,5-Tetrachlorobenzene Pentachlorophenol 2,3,4,6-Tetrachlorophenol	Caprolactam 1,1'-Biphenyl Dimethylphthalate Diethylphthalate Di-n-butylphthalate Butylbenzylphthalate bis(2-ethylhexyl)phthalate Di-n-octylphthalate
Fluorene-d_{10}	**Anthracene-d_{10}**	**Pyrene-d_{10}**
Dibenzofuran Fluorene 4-Chlorophenyl-phenylether 4-Bromophenyl-phenylether Carbazole	Hexachlorobenzene Atrazine Phenanthrene Anthracene	Fluoranthene Pyrene Benzo(a)anthracene Chrysene
Acenaphthylene-d_8	**4-Nitrophenol-d_4**	**Benzo (a) pyrene-d_{12}**
Naphthalene 2-Methylnaphthalene 2-Chloronaphthalene Acenaphthylene Acenaphthene	2-Nitroaniline 3-Nitroaniline 2,4-Dinitrophenol 4-Nitrophenol 4-Nitroaniline	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene
4,6-Dinitro-2-methylphenol-d_2	**Fluoranthene-d_{10} (SIM)**	**2-Methylnapthalene-d_{10} (SIM)**
4,6-Dinitro-2-methylphenol	Fluoranthene Pyrene Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene	Napthalene 2-Methylnapthalene Acenapthylene Acenaphthene Fluorene Pentachlorophenol Phenathrene Anthracene

Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

Action:

NOTES: Data for MS and MSDs will not be present unless requested by the Region. Notify the Contract Laboratory Program Project Officer (CLP PO) if a field blank was used for the MS and MSD.

NOTE: For a Matrix Spike that does not meet criteria, apply the action to only the field sample used to prepare the Matrix Spike sample. If it is clearly stated in the data validation materials that the samples were taken through incremental sampling or some other method guaranteeing the homogeneity of the sample group, then the entire sample group may be qualified.

1. No qualification of the data is necessary on MS and MSD data alone. However, using professional judgment, the validator may use the MS and MSD results in conjunction with other QC criteria and determine the need for some qualification of the data.

Internal Standards

Action:

1. If an internal standard area count for a sample or blank is greater than 200.0% of the area for the associated standard (opening CCV or mid-point standard from initial calibration) (see Table 9):
    a. Qualify detects for compounds quantitated using that internal standard as estimated low (J-).
    b. Do not qualify non-detected associated compounds.
2. If an internal standard area count for a sample or blank is less than 50.0% of the area for the associated standard (opening CCV or mid-point standard from initial calibration):
    a. Qualify detects for compounds quantitated using that internal standard as estimated high (J+).
    b. Qualify non-detected associated compounds as unusable (R).
3. If an internal standard area count for a sample or blank is greater than or equal to 50.0%, and less than or equal to 200% of the area for the associated standard opening CCV or mid-point standard from initial calibration, no qualification of the data is necessary.
4. Absolute RTs of internal standards should not vary dramatically between samples and the associated 12-hour calibration standard (opening CCV or mid-point standard from the initial calibration). If an internal standard RT varies by more than 30.0 seconds: Examine the chromatographic profile for that sample to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Detects should not need to be qualified as unusable (R) if the mass spectral criteria are met.
5. If an internal standard RT varies by less than or equal to 30.0 seconds, no qualification of the data is necessary.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the internal standard performance criteria are grossly exceeded. Note in the Data Review Narrative potential effects on the data resulting from unacceptable internal standard performance.

Table 9. Internal Standard Actions for Semivolatiles Analyses

Criteria	Action	
	Detected Associated Compounds*	**Non-detected Associated Compounds***
Area counts > 200% of 12-hour standard (opening CCV or mid-point standard from initial calibration)	J-	No qualification
Area counts < 50% of 12-hour standard (opening CCV or mid-point standard from initial calibration)	J+	R
Area counts ≥ 50% but ≤ 200% of 12-hour standard (opening CCV or mid-point standard from initial calibration)	No qualification	
RT difference > 30.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from initial calibration)	R	
RT difference ≤ 30.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from initial calibration)	No qualification	

* For semivolatile compounds associated to each internal standard, see Table 2 - Semivolatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation in SOM01.2, Exhibit D, available at: http://www.epa.gov/superfund/programs/clp/som1.htm

Standards Data

Action:

If missing deliverables are unavailable, document the effect in the Data Assessment.

Target Compound Identification

Criteria:

1. The Relative Retention Times (RRTs) of reported compounds must be within ±0.06 RRT units of the standard RRT [opening Continuing Calibration Verification (CCV) or mid-point standard from the initial calibration].
2. Mass spectra of the sample compound and a current laboratory-generated standard [i.e., the mass spectrum from the associated calibration standard (opening CCV or mid-point standard from initial calibration)] must match according to the following criteria:
    a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.
    b. The relative intensities of these ions must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30-70%).
    c. Ions present at greater than 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.

Action:

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, qualify all such data as unusable (R).
2. Use professional judgment to qualify the data if it is determined that cross-contamination has occurred.
3. Note in the Data Review Narrative any changes made to the reported compounds or concerns regarding target compound identifications. Note, for Contract Laboratory Program Project Officer (CLP PO) action, the necessity for numerous or significant changes.

Tentatively Identified Compounds (TICs)

Action:

NOTE: Tentatively identified compounds should only be evaluated when requested by a party from outside of the Hazardous Waste Support Section (HWSS).

1. Qualify all TIC results for which there is presumptive evidence of a match (e.g. greater than or equal to 85% match) as tentatively identified (NJ), with approximated concentrations. TICs labeled "unknown" are qualified as estimated (J).
2. General actions related to the review of TIC results are as follows:
    a. If it is determined that a tentative identification of a non-target compound is unacceptable, change the tentative identification to "unknown" or another appropriate identification, and qualify the result as estimated (J).
    b. If all contractually-required peaks were not library searched and quantitated, the Region's designated representative may request these data from the laboratory.
3. In deciding whether a library search result for a TIC represents a reasonable identification, use professional judgment. If there is more than one possible match, report the result as "either compound X or compound Y". If there is a lack of isomer specificity, change the TIC result to a nonspecific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to a substituted aromatic compound).
4. The reviewer may elect to report all similar compounds as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).
5. Target compounds from other fractions and suspected laboratory contaminants should be marked as "non-reportable".
6. Other Case factors may influence TIC judgments. If a sample TIC match is poor, but other samples have a TIC with a valid library match, similar RRT, and the same ions, infer identification information from the other sample TIC results.
7. Note in the Data Review Narrative any changes made to the reported data or any concerns regarding TIC identifications.
8. Note, for Contract Laboratory Program Project Officer (CLP PO) action, failure to properly evaluate and report TICs

Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

Action:

1. When a sample is analyzed at more than one dilution, the lowest CRQLs are used unless a QC exceedance dictates the use of the higher CRQLs from the diluted sample. Replace concentrations that exceed the calibration range in the original analysis by crossing out the "E" and its corresponding value on the original Form I and substituting the data from the diluted sample.
2. If any discrepancies are found, the Region's designated representative may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate. Under these circumstances, the reviewer may determine that qualification of data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.
3. For non-aqueous samples, if the percent moisture is less than 70.0%, no qualification of the data is necessary. If the percent moisture is greater than or equal to 70.0% and less than 90.0%, qualify detects as estimated (J) and non-detects as approximated (UJ). If the percent moisture is greater than or equal to 90.0%, qualify detects as estimated (J) and non-detects as unusable (R) (see Table 10).
4. Note, for Contract Laboratory Program Project Officer (CLP PO) action, numerous or significant failures to accurately quantify the target compounds or to properly evaluate and adjust CRQLs.

Table 10. Percent Moisture Actions for Semivolatiles Analysis For Non-Aqueous Samples

Criteria	Action	
	Detected Associated Compounds	Non-detected Associated Compounds
% Moisture < 70.0	No qualification	
70.0 < % Moisture < 90.0	J	UJ
% Moisture > 90.0	J	R

Field Duplicates

Action:

NOTE: In the absence of QAPP guidance for validating data from field duplicates, the following action will be taken.

Identify which samples within the data package are field duplicates. Estimate the relative percent difference (RPD) between the values for each compound. Use professional judgment to note large RPDs (> 50%) in the narrative.

System Performance

Action:

Use professional judgment to qualify the data if it is determined that system performance has degraded during sample analyses. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any degradation of system performance which significantly affected the data.

Overall Assessment of Data

Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.
2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any inconsistency of the data with the Sample Delivery Group (SDG) Narrative. If sufficient information on the intended use and required quality of the data is available, the reviewer should include their assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

APPENDIX A: GLOSSARY

Analyte -- The element of interest, ion, or parameter an analysis seeks to determine.
Analytical Services Branch (ASB) -- Directs the Contract Laboratory Program (CLP) from within the Office of Superfund Remediation and Technical Innovation (OSRTI) in the Office of Solid Waste and Emergency Response (OSWER).
Analytical Sample -- Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, Initial Calibration Verification (ICV), Initial Calibration Blank (ICB), Continuing Calibration Verification (CCV), and Continuing Calibration Blank (CCB). Note that the following are all defined as analytical samples: undiluted and diluted samples (USEPA and non-USEPA); Matrix Spike samples; duplicate samples; serial dilution samples, analytical (post-digestion/post-distillation) spike samples; Interference Check Samples (ICSs); Laboratory Control Samples (LCSs); and Preparation Blanks.
Associated Samples -- Any sample related to a particular Quality Control (QC) analysis. For example, for Initial Calibration Verification (ICV), all samples run under the same calibration curve. For duplicates, all Sample Delivery Group (SDG) samples digested/distilled of the same matrix.
Blank -- A sample designed to assess specific sources of contamination. See individual definitions for types of blanks.
Calibration -- The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards are to be prepared using the same type of reagents or concentration of acids as used in the sample preparation.
Calibration Blank -- A blank solution containing all of the reagents in the same concentration as those used in the analytical sample preparation. This blank is not subject to the preparation method.
Calibration Curve -- A plot of instrument response versus concentration of standards.
Calibration Standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method, but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.
Case -- A finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).
Contract Compliance Screening (CCS) -- A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is performed under USEPA direction by the Contract Laboratory Program (CLP) Sample Management Office (SMO) contractor.
Continuing Calibration Verification (CCV) -- A single parameter or multi-parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV can be one of the calibration standards. However, all parameters being measured by the particular system must be represented in this standard and the standard must have the same matrix (i.e., the same amount of reagents and/or preservatives) as the samples.

Contract Laboratory Program (CLP) -- Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technical Innovation (OSRTI) of USEPA.
Contract Laboratory Program Project Officer (CLP PO) -- The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a CLP laboratory.
Contract Required Quantitation Limit (CRQL) -- Minimum level of quantitation acceptable under the contract Statement of Work (SOW).
Duplicate -- A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.
Field Blank -- Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the laboratory. A field blank includes trip blanks, rinsate blanks, bottle blanks, equipment blanks, preservative blanks, decontamination blanks, etc.
Field Duplicate -- A duplicate sample generated in the field, not in the laboratory.
Holding Time -- The maximum amount of time samples may be held before they are processed.
Contractual -- The maximum amount of time that the Contract Laboratory Program (CLP) laboratory may hold the samples from the sample receipt date until analysis and still be in compliance with the terms of the contract, as specified in the CLP Analytical Services Statement of Work (SOW). These times are the same or less than technical holding times to allow for sample packaging and shipping.
Technical -- The maximum amount of time that samples may be held from the collection date until analysis.
Initial Calibration -- Analysis of analytical standards for a series of different specified concentrations to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.
Initial Calibration Verification (ICV) -- Solution(s) prepared from stock standard solutions, metals, or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV should be traceable to National Institute of Standards and Technology (NIST) or other certified standard sources when USEPA ICV solutions are not available.
Internal Standard -- A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.
Matrix -- The predominant material of which the sample to be analyzed is composed. For the purposes of this document, the matrices are aqueous/water, soil/sediment, wipe, and filter.
Matrix Spike -- Introduction of a known concentration of analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology (also identified as a pre-distillation/digestion spike).
Method Detection Limit (MDL) -- The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the 7 replicates.

Narrative (SDG Narrative) -- Portion of the data package which includes laboratory, contract, Case, Sample Number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

Office of Solid Waste and Emergency Response (OSWER) – The USEPA office that provides policy, guidance, and direction for the USEPA's solid waste and emergency response programs, including Superfund.

Percent Difference (%D) -- As used in this document and the Statement of Work (SOW), is used to compare two values. The difference between the two values divided by one of the values.

Performance Evaluation (PE) Sample -- A sample of known composition provided by USEPA for contractor analysis. Used by USEPA to evaluate Contractor performance.

Preparation Blank -- An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

Relative Percent Difference (RPD) -- As used in this document and the Statement of Work (SOW) to compare two values, the RPD is based on the mean of the two values, and is reported as an absolute value (i.e., always expressed as a positive number or zero).

Regional Sample Control Center Coordinator (RSCC) -- In USEPA Regions, coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.

Relative Standard Deviation (RSD) -- As used in this document and the Statement of Work (SOW), the mean divided by the standard deviation, expressed as a percentage.

Sample -- A single, discrete portion of material to be analyzed, which is contained in single or multiple containers and identified by a unique Sample Number.

Sample Delivery Group (SDG) -- A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

a. Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case; or
b. Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).
c. Scheduled at the same level of deliverable.

In addition, all samples and/or sample fractions assigned to an SDG must be scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG. Samples may be assigned to SDGs by matrix (i.e., all soil/sediment samples in one SDG, all aqueous/water samples in another) at the discretion of the laboratory.

Sample Management Office (SMO) -- A contractor-operated facility operated under the SMO contract, awarded and administered by the USEPA. Provides necessary management, operations, and administrative support to the Contract Laboratory Program (CLP).

Statement of Work (SOW) -- A document which specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

APPENDIX B: ORGANIC DATA EXECUTIVE NARRATIVE TEMPLATE

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
DESA/HWSB/HWSS
2890, Woodbridge Avenue, Edison, NJ 08837

EXECUTIVE NARRATIVE

Case No. :
Site:
Number of Samples:
Analysis:

SDG No.:
Laboratory:
Sampling dates:

QAPP
HWSS #:
Contractor Document #:

SUMMARY:

Critical: Results have an unacceptable level of uncertainty and should not be used for making decisions. Data have been qualified "R" rejected.
Major: A level of uncertainty exists that may not meet the data quality objectives for the project. A bias is likely to be present in the results. Data has been qualified "J" estimated.
Minor: The level of uncertainty is acceptable. No significant bias in the data was observed.

Critical Findings:

Major Findings:

Minor Findings:

COMMENT:

Reviewer Name(s):

Approver's Signature: Date:

Name:

Affiliation: USEPA/R2/HWSB/HWSS

Page 1 of 3

APPENDIX C: SAMPLE ORGANIC DATA SAMPLE SUMMARY

Case No:	00001	Contract:	XY1234	SDG No:	XY123	Lab Code:	00001
Sample Number:	XY123	Method:	BNA	Matrix:	Water	MA Number:	
Sample Location:	SOMEWHERE OUT THERE	pH:	8.4	Sample Date:	13322059	Sample Time:	10:09:00
% Moisture :				% Solids :			

Analyte Name	Result	Units	Dilution Factor	Lab Flag	Validation	Reportable	Validation Level
Benzaldehyde	5.0	ug/L	1.0	U	U	Yes	S3VEM
Phenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
Bis(2-Chloroethyl)ether	5.0	ug/L	1.0	U	U	Yes	S3VEM
2-Chlorophenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
2-Methylphenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
2,2'-Oxybis(1-chloropropane)	5.0	ug/L	1.0	U	U	Yes	S3VEM
Acetophenone	5.0	ug/L	1.0	U	U	Yes	S3VEM
4-Methylphenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
N-Nitroso-di-n-propylamine	5.0	ug/L	1.0	U	U	Yes	S3VEM
Hexachloroethane	5.0	ug/L	1.0	U	U	Yes	S3VEM
Nitrobenzene	5.0	ug/L	1.0	U	U	Yes	S3VEM
Isophorone	5.0	ug/L	1.0	U	U	Yes	S3VEM
2-Nitrophenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
2,4-Dimethylphenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
Bis(2-chloroethoxy)methane	5.0	ug/L	1.0	U	U	Yes	S3VEM
2,4-Dichlorophenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
Naphthalene	5.0	ug/L	1.0	U	U	Yes	S3VEM
4-Chloroaniline	5.0	ug/L	1.0	U	U	Yes	S3VEM
Hexachlorobutadiene	5.0	ug/L	1.0	U	U	Yes	S3VEM
Caprolactam	5.0	ug/L	1.0	U	U	Yes	S3VEM
4-Chloro-3-methylphenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
2-Methylnaphthalene	5.0	ug/L	1.0	U	U	Yes	S3VEM
Hexachlorocyclopentadiene	5.0	ug/L	1.0	U	U	Yes	S3VEM
2,4,6-Trichlorophenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
2,4,5-Trichlorophenol	5.0	ug/L	1.0	U	U	Yes	S3VEM
1,1'-Biphenyl	5.0	ug/L	1.0	U	U	Yes	S3VEM
2-Chloronaphthalene	5.0	ug/L	1.0	U	U	Yes	S3VEM

APPENDIX D: ELECTRONIC DATA DELIVERABLE TEMPLATE

DATA_PROVIDER	LAB_MATRIX_CODE	RESULT_UNIT
SYS_SAMPLE_CODE	ANAL_LOCATION	DETECTION_LIMIT_UNIT
SAMPLE_NAME	BASIS	TIC_RETENTION_TIME
SAMPLE_MATRIX_CODE	CONTAINER_ID	RESULT_COMMENT
SAMPLE_TYPE_CODE	DILUTION_FACTOR	QC_ORIGINAL_CONC
SAMPLE_SOURCE	PREP_METHOD	QC_SPIKE_ADDED
PARENT_SAMPLE_CODE	PREP_DATE	QC_SPIKE_MEASURED
SAMPLE_DEL_GROUP	LEACHATE_METHOD	QC_SPIKE_RECOVERY
SAMPLE_DATE	LEACHATE_DATE	QC_DUP_ORIGINAL_CONC
SYS_LOC_CODE	LAB_NAME_CODE	QC_DUP_SPIKE_ADDED
START_DEPTH	QC_LEVEL	QC_DUP_SPIKE_MEASURED
END_DEPTH	LAB_SAMPLE_ID	QC_DUP_SPIKE_RECOVERY
DEPTH_UNIT	PERCENT_MOISTURE	QC_RPD
CHAIN_OF_CUSTODY	SUBSAMPLE_AMOUNT	QC_SPIKE_LCL
SENT_TO_LAB_DATE	SUBSAMPLE_AMOUNT_UNIT	QC_SPIKE_UCL
SAMPLE_RECEIPT_DATE	ANALYST_NAME	QC_RPD_CL
SAMPLER	INSTRUMENT_ID	QC_SPIKE_STATUS
SAMPLING_COMPANY_CODE	COMMENT	QC_DUP_SPIKE_STATUS
SAMPLING_REASON	PRESERVATIVE	QC_RPD_STATUS
SAMPLING_TECHNIQUE	FINAL_VOLUME	BREAK_2
TASK_CODE	FINAL_VOLUME_UNIT	SYS_SAMPLE_CODE
COLLECTION_QUARTER	CAS_RN	LAB_ANL_METHOD_NAME
COMPOSITE_YN	CHEMICAL_NAME	ANALYSIS_DATE
COMPOSITE_DESC	RESULT_VALUE	TOTAL_OR_DISSOLVED
SAMPLE_CLASS	RESULT_ERROR_DELTA	COLUMN_NUMBER
CUSTOM_FIELD_1	RESULT_TYPE_CODE	TEST_TYPE
CUSTOM_FIELD_2	REPORTABLE_RESULT	TEST_BATCH_TYPE
CUSTOM_FIELD_3	DETECT_FLAG	TEST_BATCH_ID
COMMENT	LAB_QUALIFIERS	CASE
BREAK_1	VALIDATOR_QUALIFIERS	CONTRACT_NUM
SYS_SAMPLE_CODE	INTERPRETED_QUALIFIERS	SCRIBE_SAMPLE_ID
LAB_ANL_METHOD_NAME	ORGANIC_YN	SAMPLE_TIME
ANALYSIS_DATE	METHOD_DETECTION_LIMIT	FRACTION
TOTAL_OR_DISSOLVED	REPORTING_DETECTION_LIMIT	PH
COLUMN_NUMBER	QUANTITATION_LIMIT	DATA_VAL_LABEL
TEST_TYPE		

EPA

Hazardous Waste Support Branch

Request for Standard Operating Procedure (SOP) Change

Information

Initiator Name: Elizabeth Melenbrink Date of Initiation: 8 May 2013

Department Name: HWSS SOP Number: HW-35 Revision Number: 2

SOP Title: Semivolatile Data Validation

☐ Major Revision ☒ Minor Revision

Change(s) (Use attachment if necessary):

Add to the section **HWSS DATA VALIDATION PROCESS**:

All data is initially marked as "reportable" (Y) in EDM before validation is begun. Sometimes, due to dilutions, re-analyses, or SIM/scan runs all being performed, there will be multiple results for a single analyte from a single sample. The following criteria and professional judgment are used to determine which result should be reported:

The analysis with the lower CRQL
The analysis with the better QC results
The analysis with the higher result

The analyte values and their respective CRQLs are then transferred into a single sample run. The runs that are not to be used are updated as "not reportable" or (N) in EDM.

Reason(s) for change(s):

These circumstances were not addressed in this version of the SOP.

Approval

Philip Coccuzzo	Philip Coccuzzo	5/10/13
Section Chief/Team Leader	*Signature*	*Date*
Jon Gabany		5/13/13
HWSB Branch Chief	*Signature*	*Date*

Effective Date

Date: 5/20/13

EPA

Hazardous Waste Support Branch

Request for Standard Operating Procedure (SOP) Change

Information

Initiator Name: Elizabeth Melenbrink Date of Initiation: 8 May 2013

Department Name: HWSS SOP Number: HW-35 Revision Number: 2

SOP Title: Semivolatile Data Validation

☐ Major Revision ☒ Minor Revision

Change(s) (Use attachment if necessary):

Add to the section **Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)**:

Results between the MDL and CRQL should be qualified as estimated (J).
Results less than the MDL should be reported at the CRQL and qualified (U). MDLs themselves are not reported.

Reason(s) for change(s):

These circumstances were not addressed in this version of the SOP.

Approval

Philip Coccuzza	Philip Lacuzza	5/14/13
Section Chief/Team Leader	*Signature*	*Date*
Tom Gabry		5/13/13
HWSB Branch Chief	*Signature*	*Date*

Effective Date

Date: 5/20/13

VALIDATION SOP

Aroclor PCBs
USEPA Region 2 SOP HW-37
Rev. 1

SOP NO. HW-37/Aroclor
Validation of Data
USEPA Contract Laboratory Program
Statement of Work for Organic Analysis of Low/Medium Concentration of Aroclor Organic Compounds SOM01.2

Prepared by: George Karras Date: 8/13/07
George Karras, Chemist
Hazardous Waste Support Section

Peer Reviewed by: Russell Arnone Date: 10/3/07
Russell Arnone, Chemist
Hazardous Waste Support Section

Concurred by: Linda M. Mauel Date: 10/9/07
Linda Mauel, Chief
Hazardous Waste Support Section

Approved by: Robert Runyon Date: 10/10/07
Robert Runyon, Chief
Hazardous Waste Support Branch

Annual Review

Reviewed by: _____ Date: _____
Name

Reviewed by: _____ Date: _____
Name

TABLE OF CONTENTS

INTRODUCTION

Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to the method in the "USEPA Contract Laboratory Program Statement of Work for Organics Analysis Multi-Media, Multi-Concentration, SOM01.1, May 2005". The validation procedures and actions discussed in this document are based on the requirements set forth in the "USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review, January 2005". This document attempts to cover technical problems specific to low/Medium concentration of Aroclor compounds. Situations may arise where data limitations must be assessed based on the reviewer's own professional judgement.

In addition to technical requirements, contractual requirements may also be covered in this document. While it is important that instances of contract non-compliance be addressed in the Data Assessment, the technical criteria are always used to qualify the analytical data.

Summary

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are as follows:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

JN - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate

concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Lab Qualifiers:

D - The positive value is the result of an analysis at a secondary dilution factor.

B - The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.

E - The concentration of this analyte exceeds the calibration range of the instrument.

P - Aroclor target analytes when the % Difference between the analyte concentrations obtained from the two dissimilar GC columns is greater than 25%.

C - This flag applies to Aroclors results when the identification has been confirmed by GC/MS analysis.

S - Single point calibration.

The reviewer must prepare a detailed data assessment to be submitted along with the completed SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data and contract non-compliance.

Reviewer Qualifications:

Data reviewers must possess a working knowledge of the USEPA Statement of Work SOM01.2 and National Functional Guidelines mentioned above.

YES NO N/A

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____ **LAB:**_____

SITE NAME:_____ **SDG No(s).:**_____

1.0 Chain of Custody and Sampling Trip Reports

1.1 Are the Traffic Reports/Chain-of-Custody Records present for all samples? [ ] ___ ___

ACTION: If no, contact RSCC, or the TOPO to obtain replacement of missing or illegible copies from the lab.

1.2 Is the Sampling Trip Report present for all samples? [ ] ___ ___

ACTION: If no, contact either RSCC or ask the TOPO to obtain the necessary information from the prime contractor.

2.0 Data Completeness and Deliverables

2.1 Have any missing deliverables been received and added to the data package? ___ [ ] ___

ACTION: Contact the TOPO to obtain an explanation or resubmittal of any missing deliverables from the lab. If lab cannot provide them, note the effect on the review of the data package in the Contract

	YES	NO	N/A
Problems/Non-compliance section of the Data Assessment.			
2.2 Was SMO/CLASS CCS checklist included with the package?	[ ]	___	___
2.3 Are there any discrepancies between the Traffic Reports/Chain-of-Custody Records, and Sampling Trip Report?	___	[ ]	___

ACTION: If yes, contact the TOPO to obtain an explanation or resubmittal of any missing deliverables from the laboratory.

3.0 <u>Cover Letter SDG Narrative</u>

3.1 Is the SDG Narrative or Cover Letter Present?	[ ]	___	___
3.2 Are case number, SDG number and contract number contained in the SDG Narrative or cover letter (see SOW, Exhibit B, section 2.5.1)? EPA sample numbers in the SDG, detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing the samples? Corrective action taken?	[ ]	___	___
3.3 Does the Narrative contain the following information SOM01.1, page B-12, section 2.5.1)? column used, storage of samples, case#, SDG#, analytical problems, and discrepancies between field and lab weights.	[ ]	___	___
3.5 Did the contractor record the temperature of the cooler on the Form DC-1, Item 9 - Cooler Temperature, and in the SDG Narrative?	[ ]	___	___
3.6 Does the Case Narrative contain the "verbatim" statement (page B-12, section 2.5.1 of the SOM)?	[ ]	___	___

YES NO N/A

ACTION: If "No", to any question in this section, contact the TOPO to obtain necessary resubmittals. If unavailable, document under the Contract Problems/ Non-Compliance section of the Data Assessment.

4.0 Data Validation Checklist

4.1 Check the package for the following (see SOM reporting requirements, section 2.1, page B-10):

a. Is the package paginated in ascending order starting from the SDG narrative? [ ] ___ ___

b. Are all forms and copies legible? [ ] ___ ___

c. Assembled in the order set forth in the SOW? [ ] ___ ___

d. All Aroclor Data present? [ ] ___

PART A: Low/Medium Aroclor Analyses

1.0 Sample Conditions/Problems

1.1 Do the Traffic Reports/Chain-of-Custody Records, Sampling Trip Report or Lab Narrative indicate any problems with sample receipt, condition of samples, analytical problems or special circumstances affecting the quality of the data? ___ [ ] ___

ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the temperature of the cooler was > 10° C, then flag all positive results with a "J" and all non-detects "UJ".

2.0 Holding Times

YES NO N/A

2.1 Have any Aroclor technical holding times, determined from date of collection to date of analysis, been exceeded? ___ [ ] ___

2.2 Preservation: Aqueous and Non-aqueous samples must be cooled at 4°C ± 2°C.

ACTION: Qualify sample results according to the following table.

Holding Time Actions for Low/Medium Aroclor Analyses

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days (extraction) ≤ 40 days (analysis)	J*	UJ*
	No	> 7 days (extraction) > 40 days (analysis)	J	UJ
	Yes	≤ 7 days (extraction) ≤ 40 days (analysis)	No qualification	
	Yes	> 7 days (extraction) > 40 days (analysis)	J	UJ
	Yes/No	> 28 Days (extraction)	J	R
Non-aqueous	No	≤ 14 days (extraction) ≤ 40 days (analysis)	J*	UJ*
	No	> 14 days (extraction) > 40 days (analysis)	J	UJ
	Yes	≤ 14 days (extraction) ≤ 40 days (analysis)	No qualification	
	Yes	> 14 days (extraction) > 40 days (analysis)	J	UJ
	Yes/No	> 28 Days (extraction)	J	R

* Only if cooler temperature exceeds 10°C (see ACTION in Section 1.1 above). No action required if temperature ≤ 10°C.

YES NO N/A

3.0 Surrogate Recovery (Form II ARO-1, Form II ARO-2, Form VIII ARO)

3.1 Are the Aroclor Recovery Summary Forms present? [ ] ___ ___

ACTION: Contact the TOPO to obtain an explanation/resubmittal from the lab. If missing deliverables are unavailable, document the effect in the Data Assessment.

3.2 Were the two surrogates, tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB) added to all samples, MS/MSD, LCS, blanks including standards? [ ] ___ ___

ACTION: If no, use professional judgment in qualifying data as missing surrogate analyte may not directly apply to target analytes.

3.3 Were outliers marked with an asterisk on Form II? [ ] ___ ___

ACTION: Circle all outliers with a red pencil.

If yes, were effected samples re-analyzed? [ ] ___ ___

3.4 The RTs of the surrogates in each mid-point Aroclor standards used for continuing calibration verification, all samples, including MS/MSD, LCS and all blanks must be within the calculated RT window. TCX must be within $\pm$ 0.05 minutes and DCB must be within $\pm$ 0.10 minutes of the mean retention time (RT) determined from the initial calibration and tabulated in Form VIII Pest.

Were any outliers marked with an asterisk on Form VIII ARO? ___ [ ] ___

ACTION: Circle all outliers with a red pencil. If any Surrogate is outside the required limits, qualify their associated target compounds (See Table below) as follows:

Surrogate Compound Recovery Action for Aroclors

Criteria	Action	
	Detected Target Compounds	**Non-Detected Target Compounds**
%R > 200%	J	No qualification
150% < %R $\leq$ 200%	J	No qualification
30% $\leq$ %R $\leq$ 150%	No qualification	
10% $\leq$ %R < 30%	J	UJ

YES NO N/A

%R < 10% (sample dilution not a factor)	J	R
%R < 10% (sample dilution is a factor)	J	Use Professional Judgement
RT out of RT window	Use professional judgment	
RT within RT window	No qualification	

Note: Blank analysis having surrogates out of specification:

The reviewer must give special consideration to the validity of associated samples. Basic concern is whether the blank problems represent an isolated problem with the blank alone or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence.

ACTION: Note in the Data Assessment under Contract Problems/ Non-Compliance if the Lab did not perform reanalysis and reviewer's judgment regarding blank problem.

3.5 Are there any transcription/calculation errors between raw data and Form IIs? ___ [ ] ___

ACTION: If large errors exist, ask the TOPO to obtain an explanation/resubmittal from the lab, make any necessary corrections and note errors in the data assessment.

Note: Surrogate recovery limits criteria and qualification apply to samples diluted 5X and less. For samples diluted greater than 5X, recovery criteria does not apply Because it is assumed surrogate is diluted below the quantitation range.

4.0 Matrix Spike/Matrix Spike Duplicate Recovery (Form III)

Note: Data for MS/MSD will not be present unless requested.

4.1 Are the MS/MSD Recovery Forms (Form III ARO) present? [ ] ___ ___

4.2 Was the MS/MSD analyzed at the required frequency (once per SDG, or every 20 samples, whichever is more frequent)? [ ] ___ ___

ACTION: If any MS/MSD data are missing, take action as specified in section 3.1 above.

ACTION: No action is taken on MS/MSD data alone. However, using professional judgement, the validator may use the MS and MSD results in conjunction with other QC criteria and determine the need for some qualification of the data. If Any MS/MSD % recovery or RPD is out of specification, qualify data to include the consideration of the existence of interference in the raw

YES NO N/A

data. Consideration include, but not limited to the following "Action":

Matrix Spike/Matrix Spike Duplicate Action for Aroclor

Criteria	Action	
	Detected Spike Compounds	**Non-detected Spike Compounds**
%R or RPD > Upper Acceptance Limit	J	No qualification
20% ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	Use professional judgment	
Lower Acceptance Limit ≤ %R; RPD ≤ Upper Acceptance Limit	No qualification	

Note: If it can be determined that the results of the MS/MSD affects only the sample spiked, limit qualification to only this sample. However, use professional judgment when it is determined through the MS/MSD results that the laboratory is having systematic problem in the analysis of one or more analytes that affect all associated samples.

5.0 Blanks (Form IV)

5.1 Is the Aroclor Method Blank Summary (Form IV ARO) present for aqueous and soil samples? [ ] ___ ___

5.2 Frequency of Analysis: For the analysis of AROCLOR, has a method blank been analyzed for each SDG or every 20 samples, whichever is more frequent? [ ] ___ ___

ACTION: If any blank data are missing, take action as specified above in section 3.1. If blank data is not available, reject "R" all associated positive data. However, using professional judgement, the data reviewer may substitute field blank data for missing method blank data.

5.3 A separate Form IV should be present if part of an extraction batch required sulfur removal. In such cases some samples will be listed on two blank summary forms - once under the method blank, and once under the sulfur clean-up blank (PCBLK). Was this additional blank raw data and Form IV submitted when required? [ ] ___ ___

ACTION: If Form IV sulfur clean-up blank is missing, take action as specified in section 3.1 above.

	YES	NO	N/A
5.4 Has a Aroclor instrument blank been analyzed at the beginning of every 12 hr. period following the initial calibration sequence (minimum contract requirement)?	[ ]	___	___

ACTION: If any blank data are missing, take action specified in Section 3.1.

5.5 Was the correct identification scheme used for all Aroclor blanks? (See page B-39, section 3.3.7.3 of SOM01.1 for further information)	[ ]	___	___

ACTION: Contact the TOPO to obtain resubmittals or make the required corrections on the forms. Document in the Data Assessment under Contract Problems/Non-Compliance all corrections made by the validator.

5.6 Chromatography: Review the blank raw data chromatogram, quant. Reports and data system printout. Is the chromatographic performance (baseline stability) acceptable for each instrument?	[ ]	___	___

ACTION: Use professional judgement to determine the effect on the data.

5.7 Are all detected hits for target compounds in method, and field blanks less than the CRQL?	[ ]	___	___

ACTION: IF no, an explanation and laboratory's corrective actions must be addressed in the case SDG narrative. Contact TOPO to request from Lab. revised narrative and make a note in the Contract Problems/Non-Compliance section of the Data Assessment.

6.0 Contamination

NOTE: "Water blanks", "drill blanks", and distilled water blanks" are validated like any other sample, and are not used to qualify data. Do not confuse them with the other QC blanks discussed below.

6.1 Do any method/reagent or cleanup blanks contain positive hits for target Aroclor compounds with values greater than the CRQL for that analyte?	___	[ ]	___

Note: The concentration of each target compound in the instrument blank must be less than the CRQL for that analyte.

ACTION: Make note in data assessment under Contract Problems/Non-Compliance if any blank contains hit above the CRQLs.

6.2 Do any instrument blanks contain positive Aroclor results with values greater than CRQLs?	___	[ ]	___

YES NO N/A

ACTION: Take the action specified in section 6.1.

6.3 Do any field/rinse blanks have positive Aroclor results? ___ [ ] ___

NOTE: All field blank results associated with a particular group of samples (may exceed one per case) must be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field blanks must be qualified for system monitoring compound, instrument performance criteria, spectral or calibration QC problems.

ACTION: Follow the directions in the table below to qualify results due to contamination. Use the largest value from all the associated blanks. If any blanks are grossly contaminated, all associated sample data should be qualified unusable (R).

Blank Action for Aroclor Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Field, Sulfur Cleanup, Instrument	Detects	Not detected	No qualification required
	< CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification required
	= CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	No qualification required
	> CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report concentration of sample with a U
		≥ CRQL and ≥ blank contamination	No qualification required
	Gross contamination	Detects	Qualify results as unusable R

NOTE: Analytes qualified "U" for blank contamination are treated as "hits" when qualifying for calibration criteria.
Note: When applied as described in the table above, the contaminant concentration in the blank are multiplied by the sample dilution factor.

6.4 Are there field/rinse/equipment blanks associated with every sample? [ ] ___ ___

YES NO N/A

ACTION: Note in data assessment if there's no associated field/rinse/equipment blank.

Exception: samples taken from a drinking water tap do not have associated field blanks.

7.0 Aroclor Initial and Continuing Calibration

7.1 Are the following Forms, chromatograms and data system printouts present?

a.) Form VI ARO-1/Aroclor Initial Calibration (Multipoint) [ ] ___ ___

b.) Form VI ARO-2/Aroclor Initial Calibration (Multipoint) [ ] ___ ___

c.) Form VI ARO-3/Aroclor Initial Calibration(Singlepoint) [ ] ___ ___

d.) Form VII ARO/Aroclor Calibration Verification [ ] ___ ___

e.) Form VIII ARO/Aroclor Analytical Sequence [ ] ___ ___

f.) Form X ARO/Identification Summary for Multicomponent Analysis [ ] ___ ___

7.2 **Initial Calibration**

7.2.1 Was the following contract required initial calibration sequence provided by the laboratory? [ ] ___ ___

Initial Calibration Sequence	
1.	Aroclor 1221 CS3 (400ng/ml)
2.	Aroclor 1232 CS3 (400 ng/ml)
3.	Aroclor 1242 CS3 (400 ng/ml)
4.	Aroclor 1248 CS3 (400 ng/ml)
5.	Aroclor 1254 CS3 (400 ng/ml)
6.	Aroclor 1262 CS3 (400 ng/ml)
7.	Aroclor 1268 CS3 (400 ng/ml)
8.	Aroclor1016/1260 (100 ng/ml) CS1
9.	Aroclor1016/1260 (200 ng/ml) CS1
10.	Aroclor1016/1260 (400 ng/ml) CS1
11.	Aroclor1016/1260 (800 ng/ml) CS1

YES NO N/A

12.	Aroclor1016/1260 (1600 ng/ml) CS1
13.	Instrument Blank

ACTION: If initial calibration is not performed or not performed in the proper sequence, notify the TOPO and make a note in the data assessment.

7.3 Are there any transcription/calculation errors between raw data and the Forms? ___ [ ] ___

ACTION: If large errors exist, take action specified in section 3.1 above.

7.4 Mean Retention Time (RT) and RT Window

Were the following mean RT and RT window met: [ ] ___ ___

a.) The mean RT of each of the three to five major peaks were determined from the five-point initial calibration for all Aroclors

b.) RT window was calculated as ± 0.07 for each of the three to five major peaks and ± 0.05 and ± 0.10 for the surrogates tetrachloro-m-xylene and decachlorobiphenyl, respectively.

ACTION: If no, follow the action as specified in section 3.1.

7.5 Was at least one chromatogram from each of the Aroclor standards yield peaks that give deflection between 50-100% of full scale? [ ] ___ ___

ACTION: IF no, take action as specified in section 3.1.

7.6 Was the mean Calibration Factor (CF) calculated for the three to five major peaks of each Aroclor, as well as for the surrogates, over the initial calibration range? [ ] ___ ___

7.7 Were the Percent Relative Standard Deviation (%RSD) of the Calibration Factor for the three to five major peaks < 20% of each of the Aroclor compounds and surrogates? [ ] ___ ___

ACTION: If no, take action as specified in the following Table.

Initial Calibration Action for Aroclor Analyses

	Action
Criteria	

YES NO N/A

	Detected Associated Compounds	Non-Detected Associated Compounds
Initial calibration is not performed or not performed in proper sequence	Use Professional Judgment and notify Contract Lab Program (CLP) Project Officer	
%RSD exceeds allowable limits *	J	UJ
%RSD within allowable limits *	No qualification	

* %RSD < 20.0% for Aroclors and surrogates (tetrachloro-m-xylene and decachlorobiphenyl.

7.8 **Continuing Calibration Verification (CCV) (Form VII)**

Were the Absolute Retention Time (RT) for each Aroclor and surrogate in the mid-point concentration (CS3) of the Standard used for CCV must be within the RT window determined from the initial calibration?

7.9 For opening CCV, or closing CCV that is used as an opening CCV for the next 12-hour period, the Percent Difference (%D) between the CF of each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration (CS3) of the Aroclor standards and the CF from the initial calibration must be within $\pm$15.0%.

7.10 For a closing CCV, the %D between the CF of each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration (CS3) of the Aroclor standards and the CF from the initial calibration must be within $\pm$50.0%.

7.11 No more than 14 hours may elapse from the injection of the instrument Blank that begins an analytical sequence (opening CCV) and the injection of the last mid-point concentration (CS3) of the Aroclor standards that ends an analytical sequence (closing CCV).

7.12 No more than 12 hours may elapse from the injection of the instrument blank that begins an analytical sequence (opening CCV and the injection of the last sample or blank that is part of the same analytical sequence.

Were sections 7.8 to 7.12 met? [ ] ___ ___

ACTION: If no, use the following table to qualify Aroclor data:

Continuing Calibration Verification (CCV) Action for Aroclor Analyses

YES NO N/A

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
RT out of RT Window	Use professional Judgment *	
Percent Difference not within limits ± 15% as specified in section 7.9 above	J	UJ
Percent Difference not within limits ± 50% as specified in section 7.10 above	J	UJ
Time elapsed is greater than acceptable limits as specified in section 7.11 & 7.12 above	R	
Percent Difference, time elapsed and RT are within acceptable limits	No qualification	

***** For non-detected target compounds in the affected samples, check to see if the sample chromatogram contain any peak that are close to the expected RT window of the Aroclor of interest.

If no peaks are present, consider the non-detected values to be valid and no qualification of the data is necessary.

If any peaks are present close to the expected RT window of the Aroclor of interest, qualify the non-detected values as presumptively present “N”.

For detected compounds in the affected samples, if the peaks are within the RT window, no qualification of the data is necessary. If the peaks are close to the expected RT window of the Aroclors of interest, the reviewer may take additional effort to determine if sample peaks represent the compound of interest.

For example, the reviewer can examine the data package for the presence of three or more standards containing the Aroclor of interest that were run within the analytical sequence during which the sample was analyzed. If three or more such standards are present, the RT window can be re-evaluated using the mean RT of the standards.

If the peaks in the affected sample fall within the revised window, qualify the detected Aroclor as “JN”.

If the reviewer cannot do anything with the data to resolve the problem of concern, qualify all non-detects as unuseable “R”.

8.0 Analytical Sequence Check (Form VIII-ARO)

		YES	NO	N/A
8.1	Is Form VIII-Pest present and complete for each column and each period of analyses?	[ ]	___	___

ACTION: If no, take action as specified in section 3.1

8.2	Was the proper analytical sequence followed for each initial calibration and subsequent analyses, and all standards analyzed at the required frequency for each GC/ECD instrument used?	[ ]	___	___

ACTION: If no, use professional judgment to determine the severity of the effect on the data and qualify accordingly. Generally, the effect is negligible unless the sequence was grossly altered and/or the calibration was out of QC limits.

8.3	Are the surrogate retention time (RT) from the initial calibration for TCX and DCB provided on Form VIII-Pest?	[ ]	___	___

ACTION: If no, take action as specified in section 3.1

8.4	Was the asterisk (*) applied to the RT of any blanks, samples, standards, MS/MSD, and LCS that did not meet the QC Limits of ± 0.05 minutes for TCX (tetrachloro-m-xylene) and ± 0.10 minutes for DCB (decachlorobiphenyl)?	[ ]	___	___

ACTION: If any data are missing, take action specified in 3.1 above.

If no, use professional judgment to determine the severity of the effect on the data and qualify accordingly. Document in the data assessment under Contract Problems/Non-Compliance.

9.0 **Sulfuric Acid and Gel Permeation Chromatography (GPC) Cleanup Procedures**

9.1	Was sulfuric acid added to all extracts?	[ ]	___	___

Note: Sulfuric acid cleanup is mandatory for all extracts

ACTION: If no, take action specified in section 3.1

9.2 Gel Permeation Chromatography (GPC

GPC is an optional cleanup procedure for both aqueous and non-aqueous samples that contain high molecular weight compounds that interfere with Aroclor analysis.

YES NO N/A

9.3 If GPC cleanup was performed on samples, GPC calibration is acceptable if the two UV traces meet the following requirements.

a. Peaks must be observed and should be symmetrical for all compounds in the calibration solution.

b. Corn oil and phthalate peaks should exhibit greater than 85% resolution.

c. The phthalate and Methoxychlor peaks should exhibit greater than 85% resolution.

d. Methoxychlor and perylene peaks should exhibit greater than 85% resolution.

e. Perylene and sulfur peaks must be saturated and should exhibit greater than 90% baseline resolution.

f. The RT shift is less than 5% between UV traces for bis(2-ethylhexylphthalate and perylene.

9.4 Were all above criteria met? [ ] ___ ___

ACTION: If no, examine the raw data for the presence of high molecular weight contaminants. Examine the subsequent sample data for unusual peaks and use professional judgment in qualifying the data.

10.0 Laboratory Control Samples (LCSs)

10.1 LCSs provide information on the accuracy of the analytical method and laboratory performance.

Aroclor Laboratory Control Sample Recovery - Aqueous and Non-Aqueous

Compound	% Recovery QC Limits
Aroclor 1016	50 - 150
Aroclor 1260	50 - 150
Tetrachloro-m-xylene (surrogate)	30 - 150
Decachlorobiphenyl (surrogate)	30 - 150

10.2 Were the above recoveries met? [ ] ___ ___

ACTION: If no, qualify the sample data as follows:

YES NO N/A

Criteria	ACTION	
	Detected Associated Compound	Non-Detected Associated Compound
%R> Upper Acceptance Limit	J	No qualification
%R< Lower Acceptance Limit	J	R
Lower Acceptance Limit < %R < Upper Acceptance Limit	No qualification	

11.0 Aroclor Identification (Form X ARO/Identification Summary for Multicomponent Analysis

11.1 Is Form X (ARO) complete for every sample in which Aroclor was detected? [ ] ___ ___

ACTION: Take action as specified in section 3.1 above.

11.2 The identification of a Multi component Aroclor by GC method is based primarily on RT data and pattern recognition. Were the following requirements met: [ ] ___ ___

a.) A Minimum of 3 major peaks were selected for each Aroclor. If more than one Aroclor is observed in a sample, a peak common to other Aroclor(s) must not be used to quantitate other Aroclor. Lab must choose different peaks to quantitate each Aroclor.

b.) If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram, and both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

c.) The Retention Time (RT) of both of the surrogates and reported target compounds must be within the calculated RT window of both columns.

YES NO N/A

d.) When no analytes are identified in the sample, the chromatograms of the sample extract must use the same scaling factor used for the low-point standard of the initial calibration associated with those samples.

e.) Chromatogram must display the largest peak of any Aroclor detected in the sample at less than full scale.

f.) If an extract must be diluted, chromatograms must display Aroclor peaks between 25-100% of full scale.

ACTION: If retention times (RT) or peak apex cannot be verified, contact TOPO to obtain rescaled chromatograms from the lab.

If data reviewer identifies a peak in both GC columns that fall within the appropriate RT windows, but was reported as non-detect, the compound may be false negative. If necessary, contact TOPO to instruct laboratory to re-evaluate the chromatograms.

11.3 Are there any transcription/calculation errors in Form I and Form X ARO? ___ [ ] ___

ACTION: Take action as specified in section 3.1 above.

11.4 Are the RTs of Aroclor peaks within the established RT window for analyses on both columns? [ ] ___ ___

11.5 Was the GC/MS confirmation provided for Aroclor concentration > 10 ug/ml in final extract? [ ] ___ ___

NOTE: Laboratory is required to contact SMO to determine if GC/MS confirmation is required. Check the semivolatile TIC data for presence of Aroclors.

11.6 Is the per cent difference (%D) calculated for positive results on both columns < 25%? [ ] ___ ___

Action: Reviewer must check columns for peak interferences for the positive hits. Qualify the Arclor (s) according to the following Table:

YES NO N/A

Action on Qualifying Positive Aroclor Results

Percent Differences	Qualifier
0 - 25%	None
26 - 50%	"J"
51 - 100%	"JN"
> 50% (Aroclor value < CRQL)*	"U"
> 100%	"R"

* When the Aroclor value is below CRQL and %D > 50%, raise the value to CRQL and qualify "U", undetected.

NOTE: Professional judgement must be utilized when identifying PCBs, especially when samples are highly contaminated, and possess a significant amount of matrix interference.

12.0 Target Aroclor List (TCL)

12.1 Are the Aroclor Analysis Data Sheets (Form I ARO) present with required header information on each page for samples, MS/MSD (if required), method and instrument blanks (per column & analysis)? [ ] ___ ___

12.2 Is the chromatographic performance acceptable with respect to baseline stability, full-scale attenuation, peak shape/resolution? [ ] ___ ___

ACTION: If no, take action specified in section 3.1 above.

13.0 Compound Quantitation and Reported Detection Limits

13.1 Are there any transcription/calculation errors in the Form I results? Check at least two positive results. Were any errors found? [ ] ___ ___

ACTION: If errors were found, take action as specified in section 3.1 above.

13.2 Are the contract required quantitation limits (CRQL) adjusted to reflect sample dilution? [ ] ___ ___

YES NO N/A

ACTION: If errors exist, take action as specified in section 3.1 above.

ACTION: When a sample is required to be diluted, the lowest CRQL is used (unless a QC exceedance dictates the use of the higher CRQL from the diluted sample). Replace concentration which exceed the calibration range in the original analysis by crossing out the "E" value on the original Form I and substituting it with the result from the diluted sample. Specify which Form I to use. Use a red pencil and draw a red "X" across the entire page of all Form I's that should not be used, including those in the data summary package.

At the top or bottom of the Forms, write with red pencil, "DO Not Use".

Note: If the sample dilution factor (DF) is greater than 10, an additional 10 times more concentrated than the diluted sample extract must be analyzed and reported with the sample data. If the DF is less or equal to 10, but greater than 1, the results of the original undiluted analysis must also be reported (see SOM01.1/section 10.3.3.4/page D-44/ARO).

ACTION: IF the above requirement was not met, contact the TOPO to obtain an explanation/resubmittal from the lab and make a note in the Data Assessment under Contract Problems/Non-Compliance section.

13.3 For non-aqueous samples, were the percent moisture < 70%? [ ] ___ ___

Action: If the % moisture ≥ 70.0% and < 90.0%, qualify detects as "J" and non-detects as approximated "UJ" If the % Moisture ≥ 90%, qualify detects as "J" and non-detects as "R"

14.0 Field Duplicates

14.1 Were any field duplicates submitted for Aroclor analysis? [ ] ___ ___

ACTION: Compare the reported results for field duplicates and calculate the relative percent difference.

ACTION: Any gross variation between duplicate results must be addressed in the reviewer narrative. If large differences exist,

YES NO N/A

contact the TOPO to confirm identification of field duplicates with the sampler.

YES NO N/A

Definitions

ARO - Aroclor
CCS - contract compliance screening
CF - Calibration Factor
CLASS - Contract Laboratory Analytical Services Support
CLP - Contract Laboratory Program
CRQL - Contract Required Quantitation Limit
GC/ECD - Gas Chromatography/Electron Capture Detector
kg - kilogram
µg - microgram
ℓ - liter
mℓ - milliliter
QC - quality control
RAS - Routine Analytical Services
RPD - Relative Percent Difference
RRF - Relative Response Factor
$\overline{RRF}$ - Average Relative Response Factor (from initial calibration)
RRT - Relative Retention Time
RSD - Relative Standard Deviation
RT - Retention Time
RSCC - Regional Sample Control Center
SDG - Sample Delivery Group
SOP - standard operating procedure
SOW - Statement of Work
TCL - Target Compound List
TCLP - Toxicity Characteristics Leachate Procedure
TIC - Tentatively Identified Compound
TPO - Technical Project Officer
VTSR - Validated Time of Sample Receipt
TOPO - Task Order Project Officer

YES NO N/A

References

1. USEPA Contract Laboratory Program of Work for Organic Analysis Multi-Media, Multi-Concentration, SOW/CLP/SOM01.1, October 2004
2. National Functional Guidelines for Superfund Organic Methods Data Review January 2005

VALIDATION SOP

Pesticides

EDS SOP: Organochlorine Pesticides by HRGC/HRMS
USEPA 1699, Rev. 0, 7/10

Environmental Data Services
Organochlorine Pesticides by HRGC/HRMS
USEPA 1699, Rev 0, 7/10
Data Validation Checklist

SITE:

DATE:

SDG:

	Y	N	N/A
Data Completeness and Deliverables			
Are the Field Chain of Custody Forms present for all samples?	_____	_____	_____
Is the Narrative or Cover Letter present?	_____	_____	_____
Do the Field Chain of Custody Reports or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical procedures, or other comments regarding the quality of the data?	_____	_____	_____
ACTION: Use professional judgment to evaluate the effect of the noted problems on the quality of the data.			
Reporting Requirements and Deliverables			
Are the following forms present?			
Sample Data Summary (Form I)?	_____	_____	_____
Pesticide Spiked Sample Summary?	_____	_____	_____
Pesticide Duplicate Sample Summary?	_____	_____	_____
Pesticide Method Blank Summary?	_____	_____	_____
Pesticide Relative Retention Times?	_____	_____	_____
Pesticide Analytical Sequence Summary?	_____	_____	_____
Initial Calibration Summary?	_____	_____	_____
Continuing Calibration Summaries?	_____	_____	_____

	Y	N	N/A
GC/MS Displays			
Standard and sample SIM chromatograms. Do SIM and TIC chromatograms list date and time of analysis; the file name; sample number; and instrument I.D. number?	_____	_____	_____
Percent peak resolution valley?	_____	_____	_____
Pesticide window defining mix raw data?	_____	_____	_____
Do SIM mass chromatograms display quantitation ion and confirmation ions?	_____	_____	_____
Are the integrated area and peak height listed for all peaks 2.5 times above background?	_____	_____	_____
Do all peaks show retention time at the maximum height?	_____	_____	_____
Laboratory Records			
Are the GC/MS Standard and Sample Run Log in chronological order?	_____	_____	_____
Sample Extraction Log?	_____	_____	_____

ACTION: If deliverables are missing, call the lab for explanation/ resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the reviewers narrative.

Holding Times

Were the following holding times met:

Aqueous samples were extracted within 7 days of sample collection?	_____	_____	_____
Solid samples were extracted within 7 days of sample collection?	_____	_____	_____
All samples were analyzed within 40 days of extraction?	_____	_____	_____

ACTION: If holding times are exceeded, flag all data as estimated "J".

If holding times from collection to extraction, or from extraction to analysis have been grossly exceeded, use professional judgment to determine whether non-detects shall be rejected.

	Y	N	N/A

Preservation Requirements

Is the cooler temperature ≤ 10°C for aqueous and solid samples from the time of collection until receipt at the laboratory? _____ _____ _____

ACTION: If cooler temperature >10°C, flag non-detects as "UJ and detects as "J".

Column Performance

Does the absolute retention time of Methoxychlor exceed 39 minutes on a DB-17 column? _____ _____ _____

ACTION: If column performance criteria was not met, a detailed discussion of the problems observed and potential effects on analytical data obtained should be included in the data assessment narrative.

Endrin/4,4'-DDT Breakdown

This test is run after calibration or calibration verification to assure the labeled pesticides do not decompose in the GC.

Measure and sum the peak areas for both the exact m/z's separately for 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, endrin, endrin aldehyde, and endrin ketone.

Add the summed peak areas for endrin aldehyde and endrin ketone and separately add the peak areas or 4,4'-DDD and 4,4'-DDE.

Calculate the endrin and 4,4'-DDT breakdown as follows:

Endrin breakdown (percent) $= \frac{(areas\ for\ endrin\ aldehyde + endrin\ ketone)}{areas\ for\ endrin} \times 100$

4,4'-DDT breakdown (percent) $= \frac{(areas\ for\ 4{,}4^{'}{-}DDD + 4{,}4^{'}{-}DDE)}{areas\ for\ 4{,}4^{'}{-}DDT} \times 100$

Has the individual % breakdown exceeded 20.0% for:

endrin? _____ _____ _____

4,4'-DDT? _____ _____ _____

Y N N/A

ACTION: If any % breakdown has failed the QC criteria in the breakdown check standard, qualify all sample analyses in the entire analytical sequence as described below.

a. If 4,4'-DDT breakdown is greater than 20%:

i. Qualify all positive results for DDT with "J". If DDT was not detected, but DDD and DDE are positive, then qualify the quantitation limit for DDT as unusable ("R").

b. If endrin breakdown is greater than 20.0%:

i. Qualify all positive results for DDT with "J". If endrin was not detected, but endrin aldehyde and endrin ketone are positive, then qualify the quantitation limit for endrin as unusable ("R").

Instrument Performance

Mass Calibration - Mass calibration of the MS must be performed prior to analyzing calibration solutions, blanks, samples, and QC samples. A static resolving power of at least 8,000 (10% valley definition) must be demonstrated at appropriate masses before and at the end of each shift prior to any analysis is performed at appropriate masses. If the analyses are performed on successive shifts, only the beginning of the shift static resolving power is required. Include in the narrative, minimum required resolving power of 8,000 was obtained for perfluorokerosene (PFK) ion 304.9824. This is done by first measuring peak width at 5% of the maximum. Resolving power, then is calculated using the formula,

Resolving Power = $m/\Delta m$

Was mass calibration performed at the frequency given above? _____ _____ _____

Initial 5-Point Calibration

The initial calibration standard solutions (CS1-CS5, Table 4*) must be analyzed prior to any sample analysis. However, initial calibration should be analyzed whenever the labeled compounds response in the sample does not meet all criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to perform the mass calibration.

*NOTE: All tables mentioned throughout this checklist are taken from USEPA, Method 1699, 2007

	Y	N	N/A
The following MS/DS conditions must be used:			
Is mass calibration performed as described earlier?	_____	_____	_____
Is the total scanning time $\leq$ 1 second?	_____	_____	_____
Were SIM data acquired for each of the ions listed in Table 6?	_____	_____	_____
Do the two SIM ions for each pesticide maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions?	_____	_____	_____
Do the relative ion abundances for target analyte pesticides meet criteria listed in Table 6?.	_____	_____	_____
In all calibration solutions, is the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards $\geq$ 10?	_____	_____	_____
Does the percent relative standard deviation (%RSD) for the mean response factor (RRF) from the initial calibration for unlabeled standards exceed $\pm$ 20%?	_____	_____	_____

ACTION:

1) If the %RSD for any isomer exceeds 20%, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.
2) If the ion abundance ratio for an analyte is outside the limits flag the results for that analyte R (reject).
3) If the ion abundance ratio for an internal standard or labeled analog compound falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.
4) If the signal to noise ratio (S/N) is below control limits, use professional judgment to determine quality of the data.
5) If the selected monitoring ions specified in Table 7 were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.
6) If mass calibration criteria as specified earlier is not met, specify that in narrative notes.
7) Non-compliance of all other criteria specified above should be evaluated using professional judgement.

Spot-check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled pesticides and labeled compounds were used. In addition verify that the appropriate labeled compound was used for each isomer.

Y N N/A

Formulas

Target Analytes Quantitated by Isotopic Dilution

The response of each native organochlorine pesticide relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 2, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n)\, C_l}{(A1_l + A2_l)\, C_n}$$

Where:

$A1_n$ *and* $A2_n$ = *The areas of the primary and secondary m/z's for the organochlorine pesticide.*

$A1_l$ *and* $A2_l$ = *There areas of the primary and secondary m/z's for the labeled compound.*

C_l = *The concentration of the labeled compound in the calibration standard (Table 4).*

C_n = *The concentration of the native compound in the calibration standard (Table 4).*

Target Analytes Quantitated by Internal Standard Method

Response factors – Calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_s + A2_s)\, C_{is}}{(A1_{is} + A2_{is})\, C_s}$$

Where:

$A1_s$ *and* $A2_s$ = *There areas of the primary and secondary m/z's for the organochlorine pesticide.*

$A1_{is}$ *and* $A2_{is}$ = *The areas of the primary and secondary m/z's for the internal standard.*

C_{is} = *The concentration of the internal standard (Table 4).*

C_s = *The concentration of the compound in the calibration* standard (Table 4).

Continuing Calibration (CS-4 VER)

		Y	N	N/A
	The continuing calibration must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks.			
	Was the continuing calibration run at the required frequency?	_____	_____	_____
	Were the following MS/DS conditions were used:			
A.	Was the total scanning time $\leq$1 second?	_____	_____	_____
B.	Were SIM data acquired for each of the ions listed in Table 6?	_____	_____	_____
	The following GC criteria must be met:			
C.	The two SIM ions for each pesticide must maximize simultaneously ($\pm$ 3 sec) and within 3 seconds of the corresponding ions of the labeled isomers.	_____	_____	_____
D.	For the CS-4 standard solution, the signal to noise ratio (S/N) for the unlabeled pesticide ions shall be > 10.	_____	_____	_____
E.	For the labeled analog compounds and the internal standards, the signal to noise ratio (S/N) shall be > 10.	_____	_____	_____
F.	The relative ion abundance criteria (Table 6) for all pesticides shall be met.	_____	_____	_____
G.	The relative ion abundance criteria for all labeled analog compounds and internal standards (Table 6) must be met.	_____	_____	_____
H.	The found concentration for each analyte must fall within the concentration range specified in Table 4.	_____	_____	_____
I.	The absolute retention times of the GCMS internal standards during the CS-4 (VER) test must be within $\pm$15 seconds of the RTs obtained during the initial calibration.	_____	_____	_____

		Y	N	N/A
J.	Further, the RRT of native pesticides and labeled compounds in the verification test must be within 5% of the RRT given in Table 2.	_____	_____	_____

ACTION: If any requirements listed in sections A, B, C, D, E, F, or G are not met, reject all data ("R" flag) specifically affected by the problem.

When the found concentration of the calibration verification sample falls outside the specified allowable range, all data for outlier congeners are flagged "J".

If the continuing calibration standard was not analyzed at the required frequency, reject all the data.

If any of the requirements listed in Section I are not met, use professional judgment to determine the validity of data.

Sample Data

The following MS/DS conditions were used:

Was the scanning time $\leq$1 second?	_____	_____	_____
Were SIM data acquired for each of the ions listed in Table 2?	_____	_____	_____

Identification Criteria

A.	For the organochlorine pesticides found present, the relative retention time at the maximum peak height of the analyte must be within 5% of the RTs listed in Table 2.	_____	_____	_____
B.	All specified ions listed in Table 2 (analytical method) for each pesticide found present and the labeled standards must be present in the SICP. The two SIM ions for the analyte, the labeled analog compounds and internal standards must maximize simultaneously ($\pm$2 seconds).	_____	_____	_____
C.	The integrated ion current for each characteristic ion of the analyte identified as positive must be at least 2.5 times background noise and must have not saturated the detector.	_____	_____	_____
D.	The integrated ion current for the labeled analog compound and internal standard characteristic ions must be at least 10 times background noise.	_____	_____	_____

		Y	N	N/A
E.	The relative ion abundance criteria (Table 6) for all pesticides found present must be within ±20% of the ratio in the daily CS-4 VER test.	_____	_____	_____
F.	The relative ion abundance criteria for the labeled analog compounds and internal standards must be met (Table 6), or within ±20% of the ratio in the daily CS-4 VER test.	_____	_____	_____
G.	The analyte concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range. Was the above criteria met?	_____	_____	_____
H.	Do any lock mass ion signals show peak deflections of greater than 20% in the retention time areas of any analyte?	_____	_____	_____

ACTION: Reject (flag “R”) all positive data for the analytes which do not meet criteria listed in sections A & B.

If the criteria listed in section C are not met but all other criteria are met, qualify all positive data of the specific analyte with “J”.

If the requirements listed in section D are not met but all other requirements are met qualify the positive data of the corresponding analytes with "J".

If the analytes reported positive do not meet ion abundance criteria, section E, reject “R” all positive data for these analytes.

If labeled analog compounds and internal standards do not meet ion abundance criteria (Table 6) but they meet all other criteria flag all corresponding data with "J".

If any peak deflection is greater than 20%, then qualify the associated compound with a "J".

Spot-check calculations for positive data and verify that the same labeled analog compounds used to calculate RRFs were used to calculate concentrations.		_____	_____	_____

Y N N/A

To recalculate the concentration of organochlorine pesticides in the sample use the following equations:

Isotope dilution quantation -

$$M_{ex}\ (ng/mL) = (A1_n + A2_n) \times M_{lb} / (A1_{lb} + A2_{lb}) \times RRF$$

Where:

M_{ex} = *The mass of the organochlorine pesticide in the sample extract.*

M_{lb} = *The mass of the labeled compound in the sample extract.*

$A1_n$ *and* $A2_n$ *pesticide* = *Area of the primary and secondary ion for the native organochlorine pesticide.*

$A1_{lb} + A1_{lb}$ = *Area of the primary and secondary ion for the labeled compound.*

Any peaks representing the other organochlorine pesticides are quantitated using an average of the response factors from all of the labeled organochlorine pesticides at the same level of chlorination.

Method Blanks

Has a method blank been extracted and analyzed with each batch of 20 samples, or less, per matrix? _____ _____ _____

Was the method blank analyzed immediately after analysis of the OPR to demonstrate freedom of concentration? _____ _____ _____

If pesticides are carried over from the OPR, analyze one or more aliquots of solvent between OPR and the method blank.

If samples of same matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event? _____ _____ _____

ACTION: If the proper number of method blanks were not analyzed, notify the contractor. If the reviewer is unavailable, reject all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

	Y	N	N/A
Are any organochlorine pesticides found in the method blank at a a concentration greater than the PQL?	_____	_____	_____

ACTION: If the analyte has a reported concentration that is > 5 times the PQL, no qualification is necessary. All associated positive target analyte results ≤ 5 times the PQL are flagged "J".

Rinsate Blank

Was a minimum of one rinsate blank collected for each batch of 20 samples, or one each day sampling equipment decontamination procedures are performed, whichever is more frequent?	_____	_____	_____
Do any rinsate blanks show the presence of pesticides at amounts greater than the PQL?	_____	_____	_____

ACTION: If the analyte has a reported concentration that is > 5 times the PQL, no qualification is necessary. All associated positive target analyte results ≤ 5 times the PQL are flagged "J".

Labeled Analog Recoveries

Were the samples spiked with all the labeled analog compounds as specified in the method?	_____	_____	_____
Were labeled analog compound recoveries within the required (25-150%) limits?	_____	_____	_____
If not, were samples reanalyzed?	_____	_____	_____

ACTION: If the labeled analog compound recovery was below 25%, reject "R" all associated non-detect data (EMPC/EDL) and flag with "J" all positive data. If the labeled analog compound recovery is above the upper limit (150%) flag all associated data (positive and non-detect data) with "J".

If the labeled analog compound recovery is less than 10% reject ("R" flag) all associated data.

Y N N/A

Recalculate the percent recovery for each labeled analog compound in the sample extract, (Ris), using the formula:

$$\%\ Rec_{\ 1} = \frac{(A_{11} + A_{12})\ x\ Q_{is}\ x\ 100}{(A_{is1} + A_{is12})\ x\ RRF_1\ x\ Q_1}$$

$A_{n1} + A_{n2}$ = *integrated areas of the two quantitation ions of isomer of interest. (Target analyte).*

$A_{11} + A_{12}$ = *integrated areas of the two quantitation ions of the appropriate labeled analog compound.*

$A_{is1} + A_{is2}$ = *integrated areas of the two quantitation ions of the appropriate internal standard.*

Q_n = *quantity of the unlabeled pesticide analyte injected (pg)*

Q_1 = *quantity of the appropriate labeled analog compound injected (pg)*

Q_{is} = *quantity of the appropriate internal standard injected (pg)*

Internal Standards

Are the internal standard areas for every sample and blank within the upper and lower limits of each associated CS-4 VER? _____ _____ _____

Area upper limit = +100% of recovery standard area.
Area lower limit = - 50% of recovery standard area.

Is the retention time of each internal standard within 10 seconds of the associated CS-4 VER? _____ _____ _____

ACTION: If the internal standard area is outside the upper or lower limits flag all related positive and non-detect data with "J" regardless whether the labeled analog compound recoveries met specifications or not.

If extremely low area counts (<25%) are reported flag all associated non-detect data as unusable “R” and the positive data “J”.

If the retention time of the internal standard differs by more than 10 seconds from the CS-4 use professional judgment to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window.

Y N N/A

Matrix Spike/Matrix Spike Duplicate (Field Sample)

The following sample ID was chosen for MS/MSD analysis: _____

Was a matrix spike analyzed at the frequency of one per SDG, per matrix? _____ _____ _____

Was the percent recovery of all organochlorine pesticides within 50-150% and Toxaphene 20-180% for both aqueous and solid samples? _____ _____ _____

ACTION: If problems such as interferences are observed and if the recovery of the MS is out of the 50-150% acceptance range for either an aqueous or soil sample, qualify the result for the affected target analyte in the sample used for the MS/MSD as estimated "J".

Was the relative percent difference (RPD) between the matrix spike/matrix spike duplicate <25%? _____ _____ _____

ACTION: If the precision of the MS/MSD analyses is >50% RPD, qualify the value for that analyte in the sample used for the MS/MSD as estimated "J".

Field Duplicate Samples

Sample IDs of the field duplicate pair: _____

For every batch of 20 samples or less collected, was there a sample designated as duplicate? _____ _____ _____

NOTE: For Aqueous: RPD $\leq$ 20% when target is detected in both field duplicate samples at > 5x the PQL or concentrations differ by < 2x the PQL when detects are $\leq$ 5x PQL for both field duplicate samples.

For Soil: RPD ≤ 50% when target is detected in both field duplicate samples at > 5x PQL, or concentration differs by < 2x the PQL when detects are $\leq$ 5x PQL for both field duplicate samples.

ACTION: The duplicate results must be used in conjunction with other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.

	Y	N	N/A
IPR			
Was an initial precision and accuracy demonstration performed for the appropriate matrix per Section 9.2 of Method 1699, 2007?	_____	_____	_____
Were the results of the IPR evaluation acceptable when compared to the acceptance limits for each analyte listed in Table 5?	_____	_____	_____

ACTION: If IPR data was not provided by the laboratory, contact the lab to obtain the results of the IPR study.

If the results of the laboratories IPR study do not meet the acceptance criteria for performance tests listed in Table 5, contact the laboratory to initiate remediation of technical difficulties. Further sample analyses should not be performed until the laboratory satisfactorily demonstrates the IPR performance test.

OPR			
Was an ongoing precision and recovery (OPR) standard prepared for each sample or sample set (to a maximum of 20 samples)?	_____	_____	_____
Has the OPR been analyzed prior to analysis of the samples from the same batch?	_____	_____	_____
Do the results of all OPR standard meet the acceptance criteria for all target analytes of 50-150% except Toxaphene which is 20-180% for both aqueous and soil?	_____	_____	_____

ACTION: If the laboratory failed to process an OPR sample with the associated field samples, qualify all target analyte results as estimated ”J”.

ACTION: When the observed OPR recovery is less than 10%, associated non-detect results are flagged “R” rejected and positive results are flagged “J” estimated.

When the observed OPR recovery is lower than the lowest acceptance limit but greater than 10%, associated non-detect results are flagged “UJ” estimated non-detect and positive results are flagged “J” estimated.

When the observed OPR recovery is higher than the highest acceptance limit flag only associated positive results “J” estimated.

Compute the percent recovery of the organochlorine pesticides with labeled analogs by isotope dilution.

Compute the percent recovery of each labeled compound by the internal Standard method.

Data Validation Qualifiers

Qualifier	Description
J	Estimated value (bias undetermined) – The analyte was positively identified; but the associated numerical value is the approximate concentration of the analyte in the sample.
JH	Estimated value (potential high bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential high bias, of the analyte in the sample.
JL	Estimated value (potential low bias) – The analyte was positively identified; but the associated numerical value is the approximate concentration, with a potential low bias, of the analyte in the sample.
UJ	Estimated non-detect - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
UJL	Estimated non-detect (potential low bias) – The analyte was not detected and the report sample quantitation limit is biased low.
UJH	Estimated non-detect (potential high bias) – The analyte was not detected and the reported sample quantitation limit is biased high.
M	The analytical result reported was obtained from a sediment sample found to contain between 50 and 90 percent moisture and had no other data qualifiers added during the data validating process.
NJ	The organic analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration.
NJH	The organic analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration with a potential high bias, of the analyte concentration.
EMPC	Estimated Maximum Possible Concentration (EMPC).
R	The sample results are rejected. Due to a significant QA/QC problem, the analysis is invalid and provides no information as to whether the analyte is present or not.

VALIDATION SOP

% Moisture (tissue)

EDS SOP V-14, Rev.2, 2/10 - Verification/Validation Geotechnical Data

Environmental Data Services
SOP V-14
Verification/Validation
Geotechnical

Site: _____ Project:_____
Collection Date(s): _____ SDG: _____
Verifier/Validator: _____ Date(s): _____

DIRECTIONS: Complete the checklist questions and proceed with the corresponding "Action," when necessary. Attachment 1 shall be completed to tally the number of samples exhibiting non-conformances (outliers).

Geotechnical Parameters (circle those that apply):

Grain Size	Organic Content
Specific Gravity	Water Content
Atterberg Limits	Bulk Density/In-Place Density
Consolidation	Paint Filter
Unconsolidated undrained shear strength	
Consolidated undrained shear strength	

	Y	N	N/A
I. Data Completeness and Deliverables			
1. Were all project specified deliverables received? Refer to QAPP worksheet #29 for required deliverables.	___	___	___
2. Is there evidence of proper communication procedures by laboratory and/or field personnel?	___	___	___
Action: If "no", contact the laboratory for submittal of missing or illegible information.			
II. Chain-of-Custody (COC)			
1. Are all field and laboratory COCs present and complete for all samples?	___	___	___
2. Were the project required analytical groups and corresponding analytes reported as requested on the field COCs?	___	___	___
3. Examine chain-of-custody records against the project procedural requirements specified in the QAPP. Were all project requirements met?	___	___	___
Action: If "no", contact the laboratory or field personnel as appropriate for submittal of missing or illegible information.			
III. Sample Handling and Receipt			
1. Were samples received at the appropriate temperature (0-10°C)? Record cooler temps: _____ °C	___	___	___
2. Were any deviations from project required sample handling, receipt, or storage documented?	___	___	___
Action: If "no", contact the laboratory or field personnel for submittal of missing or illegible information. Document the non-conformance and associated samples along with potential data limitations and attach to this checklist.			

Environmental Data Services
SOP V-14
Verification/Validation
Geotechnical

	Y	N	N/A
IV. Final Data / EDD			
1. Was a Case Narrative including the following present for each analysis group?			
▪ Identification of QC samples	___	___	___
▪ Communication logs	___	___	___
▪ Corrective action reports	___	___	___
▪ Documentation of corrective action results	___	___	___
▪ Documentation of laboratory method deviations	___	___	___
▪ Signatures for laboratory sign-off	___	___	___
2. Were results reported for all geotechnical analytes specified in the QAPP?	___	___	___
3. Perform a 10% transcription check, i.e., from laboratory instrument to form. Was the accuracy of transcription verified?	___	___	___
4. Compare results on Form 1s to EDD. Is the EDD free of transcription errors?	___	___	___
Action: If "no", contact the laboratory or field personnel for submittal of missing or illegible information. Document the non-conformance and associated samples along with potential data limitations and attach to this checklist.			
V. Sampling and Analytical Methods and Procedures			
1. Were required sampling and field measurement methods used and were any deviations noted (see QAPP Worksheet #21)?	___	___	___
2. Were required analytical methods used and were any deviations noted (see QAPP Worksheet #23) for?			
▪ Grain Size	___	___	___
▪ Specific Gravity	___	___	___
▪ Atterberg Limits	___	___	___
▪ Organic Content	___	___	___
▪ Water Content	___	___	___
▪ Bulk Density/In-Place Density	___	___	___
▪ Paint Filter	___	___	___
▪ Consolidation	___	___	___
▪ Unconsolidated undrained shear strength	___	___	___
▪ Consolidated undrained shear strength	___	___	___
Action: If "no", contact the laboratory or field personnel for submittal of missing or illegible information. Document the non-conformance and associated samples along with potential data limitations and attach to this checklist.			

Environmental Data Services
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	Y	N	N/A
VI. Field Duplicate			
1. Were the % RPD between sample and field duplicate within the project specified limits of <100% for?			
▪ Grain Size	___	___	___
▪ Specific Gravity	___	___	___
▪ Atterberg Limits	___	___	___
▪ Organic Content	___	___	___
▪ Water Content	___	___	___
▪ Bulk Density/In-Place Density	___	___	___
▪ Paint Filter	___	___	___
▪ Consolidation	___	___	___
▪ Unconsolidated undrained shear strength	___	___	___
▪ Consolidated undrained shear strength	___	___	___
Action: Document non-conformance and associated samples along with potential data limitations and attach to this checklist.			

VALIDATION SOP

% Lipids

EDS SOP: Rev.0, 7/14

Completeness Check

Percent Lipid Completeness Checklist for Tissue Samples Rev. 0, 07/2014

Tierra Solutions
Crab/Clam QAPP

Laboratory:
Validator/Date:

Date Collected:
Date Received by Laboratory:
Date Extracted:
Date Analyzed:

Batch Number:

Sample Delivery Group (SDG) Number :

Cooler Temps:
Preservation: N/A
Holding Time: N/A

Tissue Extraction Method: Soxhlet extraction; acid/base silica gel column followed by acid alumina.

Completeness Check Questions	Y	N	N/A
1. Are all samples in this sample delivery group (SDG) present on the bench worksheet log?			
Note: Worksheet log located in the dioxin extraction section of data package.			
2. Has a method blank been analyzed per analytical batch or every 20 samples?			
3. Spot check one sample calculation. Were errors identified during calculation check?			
Note: % lipid = [weight of residue (g)/weight of tissue (g)] x 100			
4. Did the laboratory perform a laboratory duplicate sample?			
If yes, provide below: Sample ID: _____ % RPD= _____ If no, explain below: **Note: Adequate laboratory precision is demonstrated when % RPD $\leq$ 50%.**			
5. Did the laboratory report the % lipid results for each sample on the dioxin data sheets?			
6. Is the correct number of significant figures (3) used on the data sheets?			
7. Were any problems noted?			
If yes, explain below:			

Note: Per the QAPP, field duplicates, rinse blanks, field blanks, MDLs and PQLs are not required for % lipid analyses.

Appendix D

Data Forms

Location Data Form

Project Name: **Project No.:**

Field Crew Initials:

Deployment Date & Time	Retrieval Date & Time	Sampling Zone & Location	Sampling Method	Water Depth (feet)	GPS Coordinates		Notes
					EASTING (X)	NORTHING (Y)	

Notes:

Non-Target Species Tally Form

Project Name: **Project No.:**

Field Crew Initials:

Collection Date/Time	Collection Method	Sampling Zone/Location	Species	Length (mm)	Weight (g)	Estimated Size Class	Notes

Specimen Tally Form

Project Name: **Project No.:**

Field Crew Initials:

COLLECTION DATE	COLLECTION TIME	Location ID	SPECIMEN ID	LENGTH (mm)	WEIGHT (g)	COMMENTS

Notes:
mm = millimeter(s)
g = gram(s)

Sample Processing Form

Project: _____

Sample Location: _____

Sample Date: _____ Sampled by: _____

Processing Date: _____ Processed by: _____

Sample ID	Species	Sample Type	Number of Organisms	Length (mm) / Weight (g)	Notes

Notes:

g = gram
mm = millimeters
SF = skin-on fillet; SF* = skin-off fillet (eel); WBC = whole-body composite; WBI = whole-body individual

Appendix A-2

USGS

FISH HEALTH EXAMINATION FORM DATE: ___/___/___ STATION ID# _____ FISH ID# _____

SPECIES: _____ Weight: _____(g) Length: _____(mm) Sex: _____

EXTERNAL EXAMINATION: *(check all that apply)*

BODY SURFACE:
- ☐ normal
- ☐ raised growth(s)
- ☐ reddened lesion(s)
- ☐ spinal deformities
- ☐ hemorrhagic body
- ☐ focal discoloration
- ☐ body fungus
- ☐ parasite(s) *specify:*
  - ☐ white spots
  - ☐ leech(es)
  - ☐ black spot(s)
  - ☐ Anchor worm(s)
- ☐ OTHER *specify:*

_____
_____
_____

in fixative ____ # of photos ____

HEAD and ORAL CAVITY:
- ☐ normal head
- ☐ deformed head
- ☐ upper lip growth
- ☐ lower lip growth
- ☐ swollen nare

BARBELS:
- ☐ normal
- ☐ missing
- ☐ stubbed
- ☐ deformed

☐ OTHER *specify:*

_____
_____
_____

in fixative ____ # of photos ____

EYES:

Left:	Right:
☐ normal	☐ normal
☐ exopthalmic	☐ exopthalmic
☐ opaque	☐ opaque
☐ missing	☐ missing
☐ hemorrhagic	☐ hemorrhagic
☐ emboli	☐ emboli
☐ OTHER *specify:*	☐ OTHER *specify:*
_____	_____
_____	_____
_____	_____
_____	_____
# in fixative ____	# in fixative ____
# of photos ____	# of photos ____

OPERCULA:
- ☐ normal
- ☐ slight shortening
- ☐ severe shortening

☐ OTHER *specify:* _____
_____
_____

in fixative ____ # of photos____

GILLS:

Left:		Right:	
☐ normal		☐ normal	
☐ frayed		☐ frayed	
☐ marginate		☐ marginate	
☐ pale		☐ pale	
☐ OTHER *specify:* _____	# in fixative ____	☐ OTHER *specify:* _____	# in fixative ____
_____		_____	
_____	# of photos ____	_____	# of photos ____

FINS:
- ☐ normal
- ☐ mild erosion
- ☐ severe erosion
- ☐ frayed
- ☐ hemorrhagic
- ☐ emboli

☐ OTHER *specify:* _____
_____
_____

in fixative ____
of photos ____

Appendix A-2--Continued

INTERNAL EXAMINATION: ***(check all that apply)***

LIVER:
☐normal (dark to light red)
☐tan (coffee with cream)
☐general discoloration
☐focal discoloration
☐nodules
☐OTHER *specify:* _____
_____
_____

Weight_____(0.1g) *with gallbladder intact*

in fixative ____ # of photos____

GALL BLADDER and BILE:

Color:
☐yellow
☐light-grass green
☐dark green to blue-green
☐OTHER *specify:*
_____
_____
_____
_____
_____

Fullness:
☐empty
☐partly full
☐full or distended

in fixative ____ # of photos____

GONADS:

Gender:
☐male
☐female
☐indeterminate

Stage:
☐ripe
☐spent
☐intermediate

☐OTHER *specify:* _____
_____

Weight _____(0.1g) # in fixative ____ # of photos____

SPLEEN:

☐normal (red to black)
☐granular
☐nodular
☐enlarged

☐OTHER *specify:* _____
_____

Weight_____(0.002g) # in fixative ____ # of photos____

POSTERIOR (Trunk) KIDNEY:

☐normal
☐swollen
☐mottled
☐granular
☐urolithiasis

☐OTHER *specify:* _____
_____
_____

in fixative ____ # of photos____

ANTERIOR (Head) KIDNEY:

☐normal
☐swollen
☐mottled
☐granular
☐urolithiasis

☐OTHER *specify:* _____
_____
_____

in fixative ____ # of photos____

GENERAL COMMENTS:

_____
_____
_____
_____
_____
_____
_____
_____

☐**SCALES:**

side sampled:
☐left
☐right

☐**SPINES:**

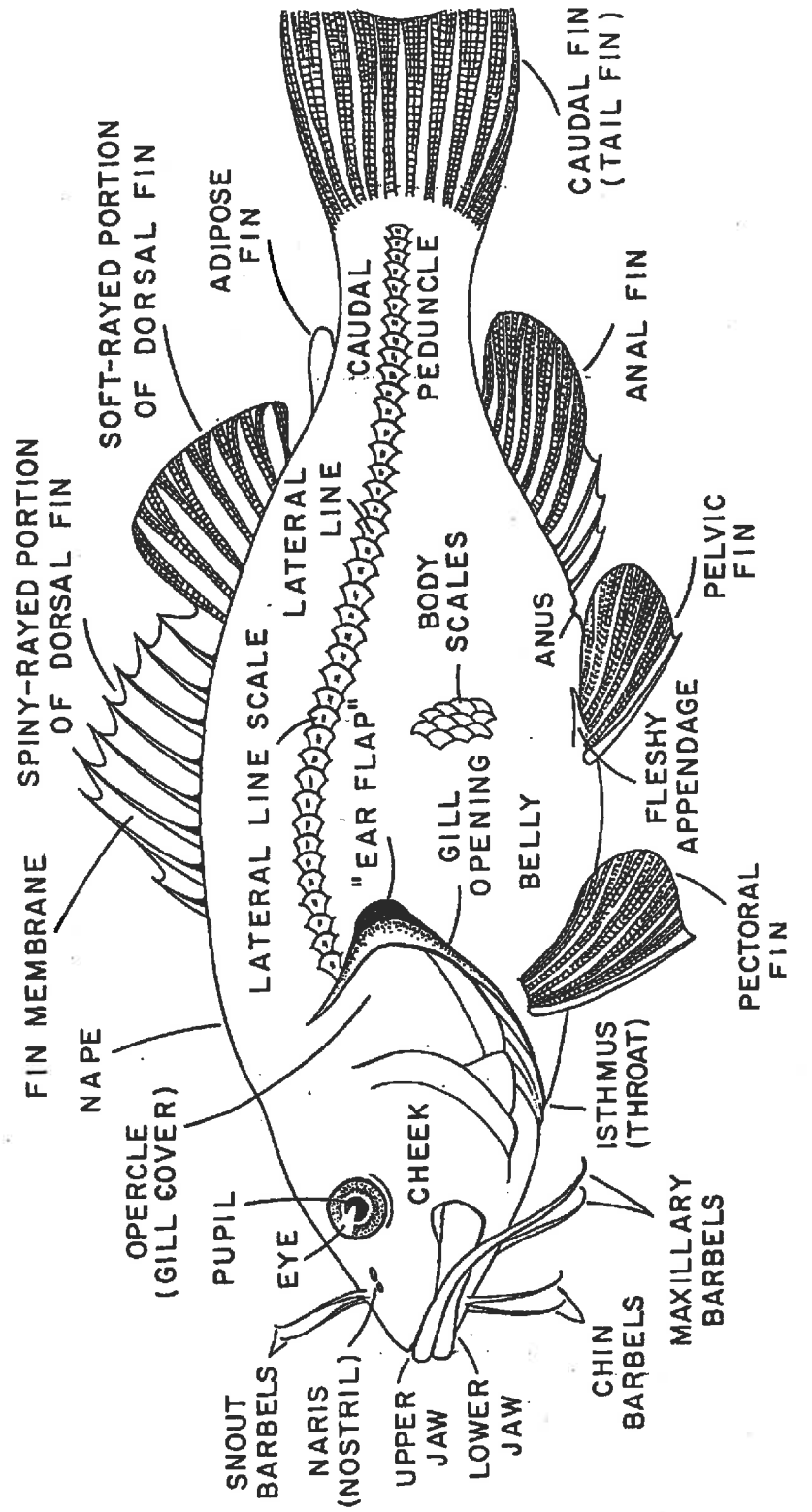
specify: _____
_____

☐OTHER:_____

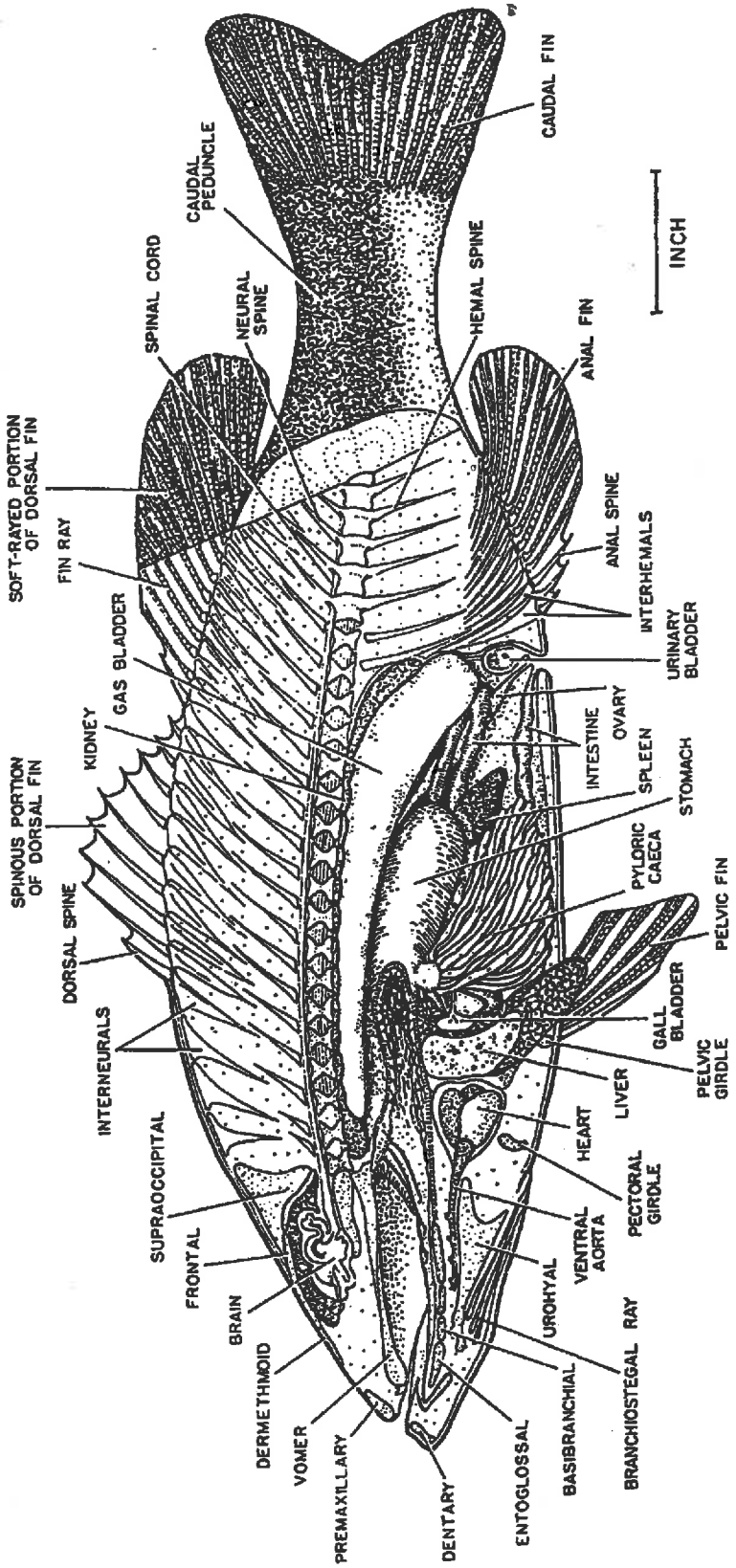
INITIALS:

RECORDER: _____
DISSECTOR: _____
REVIEWER: _____

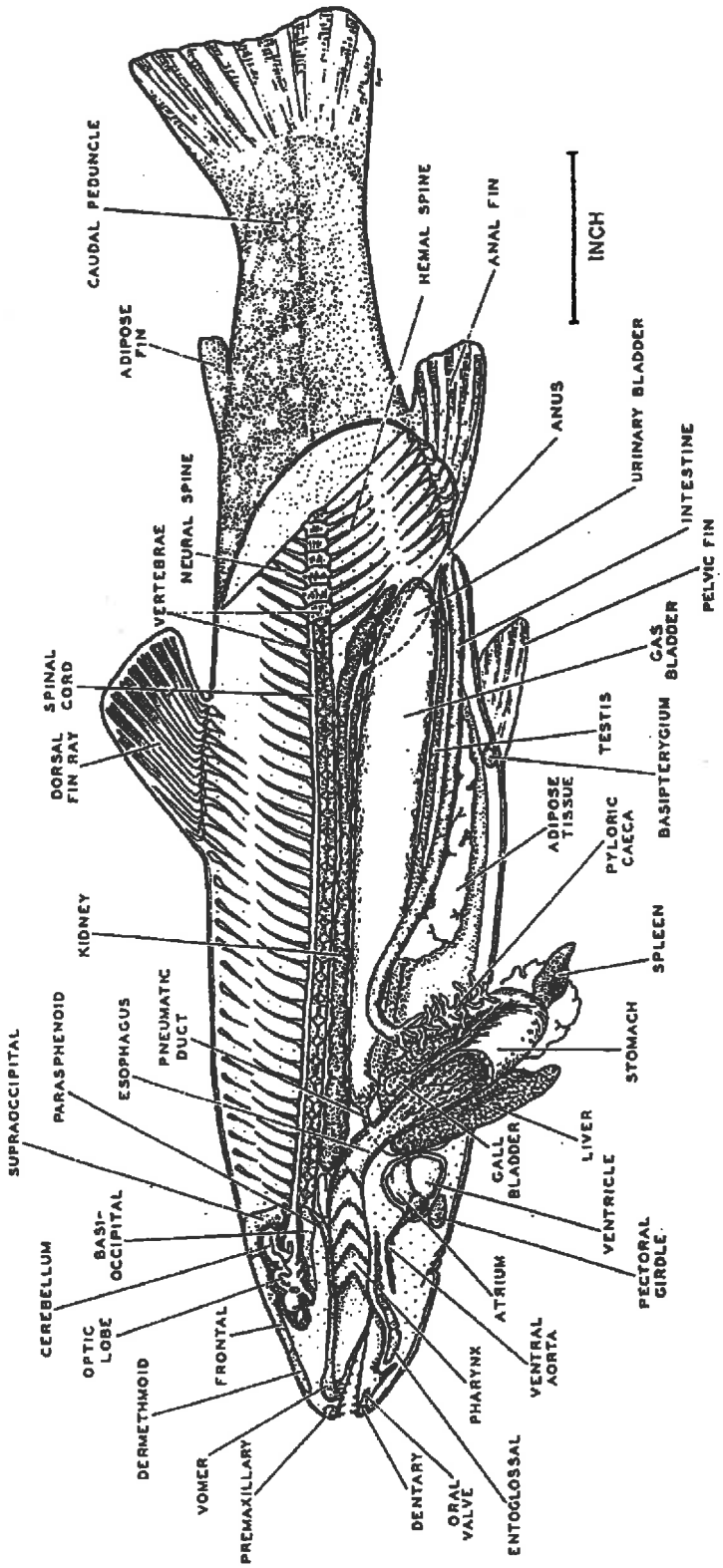
Appendix B
External and Internal Diagrams of Fish Anatomy



B-1. External features of a composite fish. From Hunn (1988)



Anatomy of a spiny-rayed bony fish, the largemouth bass, *Micropterus salmoides*



Anatomy of a soft-rayed bony fish, the brook trout, *Salvelinus fontinalis*

Protocol Modification Form

Project Name and Number: _____

Material to be Sampled: _____

Measurement Parameter: _____

Standard Procedure for Field Collection & Laboratory Analysis (cite reference):

Reason for Change in Field Procedure or Analysis Variation:

Variation from Field or Analytical Procedure:

Special Equipment, Materials or Personnel Required:

Initiator's Name: _____ Date: _____

Project Manager: _____ Date: _____

QA Manager: _____ Date: _____

USEPA Authority: _____ Date: _____