ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 60, 63, and 266

[EPA–HQ–OAR–2016–0677; FRL–10003–67–OAR]

RIN 2060–AT09

EPA Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources

AGENCY: Environmental Protection Agency.

ACTION: Proposed rule.

SUMMARY: This action proposes editorial and technical revisions to the Environmental Protection Agency's Method 23 (Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources). Proposed revisions include incorporating isotope dilution for quantifying all target compounds and changing the method quality control from the current prescriptive format to a more flexible performance-based approach with specified performance criteria. We are also proposing revisions that will expand the list of target compounds of Method 23 to include polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The proposed revisions will improve the accuracy of Method 23 and will provide flexibility to stack testers and analytical laboratories who measure semivolatile organic compounds (SVOC) from stationary sources while ensuring that the stack testing community can consistently implement the method across emissions sources and facilities.

DATES: *Comments.* Comments must be received on or before March 16, 2020.

ADDRESSES: *Comments:* Submit your comments, identified by Docket ID No. EPA–HQ–OAR–2016–0677, at *https://www.regulations.gov.* Follow the online instructions for submitting comments. Once submitted, comments cannot be edited or removed from *Regulations.gov.* See **SUPPLEMENTARY INFORMATION** section for details about how the Environmental Protection Agency (EPA) treats submitted comments. *Regulations.gov* is our preferred method of receiving comments. However, the following other submission methods are also accepted:

- *Email: a-and-r-docket@epa.gov.* Include Docket ID No. EPA–HQ–OAR–2016–0677 in the subject line of the message.
- *Fax:* (202) 566–9744. Attention Docket ID No. EPA–HQ–OAR–2016–0677.
- *Mail:* To ship or send mail via the United States Postal Service, use the following address: U.S. Environmental Protection Agency, EPA Docket Center, Docket ID No. EPA–HQ–OAR–2016–0677, Mail Code 28221T, 1200 Pennsylvania Avenue NW, Washington, DC 20460.
- *Hand/Courier Delivery:* Use the following Docket Center address if you are using express mail, commercial delivery, hand delivery, or courier: EPA Docket Center, EPA WJC West Building, Room 3334, 1301 Constitution Avenue NW, Washington, DC 20004. Delivery verification signatures will be available only during regular business hours.

FOR FURTHER INFORMATION CONTACT: Dr. Raymond Merrill, Office of Air Quality Planning and Standards, Air Quality Assessment Division (E143–02), Environmental Protection Agency, Research Triangle Park, NC 27711; telephone number: (919) 541–5225; fax number: (919) 541–0516; email address: *merrill.raymond@epa.gov.*

SUPPLEMENTARY INFORMATION:

Public Participation

A. Written Comments

Submit your comments, identified by Docket ID No. EPA–HQ–OAR–2016–0677, at *https://www.regulations.gov* (our preferred method), or the other methods identified in the **ADDRESSES** section. Once submitted, comments cannot be edited or removed from the docket. The EPA may publish any comment received to its public docket. Do not submit electronically any information you consider to be Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. Multimedia submissions (audio, video, etc.) must be accompanied by a written comment. The written comment is considered the official comment and should include discussion of all points you wish to make. The EPA will generally not consider comments or comment contents located outside of the primary submission (*i.e.,* on the Web, cloud, or other file sharing system). For additional submission methods, the full EPA public comment policy, information about CBI or multimedia submissions, and general guidance on making effective comments, please visit *https://www.epa.gov/dockets/commenting-epa-dockets.*

Submitting CBI: Clearly mark the part or all of the information that you claim to be CBI. For CBI information in a disk or CD–ROM that you mail to the EPA, mark the outside of the disk or CD–ROM as CBI and then identify electronically within the disk or CD–ROM the specific information that is claimed as CBI. In addition to one complete version of the comment that includes information claimed as CBI, a copy of the comment that does not contain the information claimed as CBI must be submitted for inclusion in the public docket. Information marked as CBI will not be disclosed except in accordance with procedures set forth in Title 40 Code of Federal Regulations (CFR) part 2.

Do not submit information that you consider to be CBI or otherwise protected through *https://www.regulations.gov* or email. Send or deliver information identified as CBI to only the following address: OAQPS Document Control Officer (Room C404–02), U.S. EPA, Research Triangle Park, NC 27711, Attention Docket ID No. EPA–HQ–OAR–2016–0677.

If you have any questions about CBI or the procedures for claiming CBI, please consult the person identified in the **FOR FURTHER INFORMATION CONTACT** section.

Docket: All documents in the docket are listed in the *https://www.regulations.gov* index. Although listed in the index, some information is not publicly available, *e.g.,* CBI (Confidential Business Information) or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, will be publicly available only in hard copy. Publicly available docket materials are available either electronically in *https://www.regulations.gov* or in hard copy at the EPA Docket Center, EPA/DC, EPA WJC West Building, Room 3334, 1301 Constitution Ave. NW, Washington, DC. This Docket Facility is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566–1744, and the telephone number for the Air Docket is (202) 566–1742.

B. Participation at Public Hearing

Public hearing. If a public hearing is requested by January 21, 2020, then we will hold a public hearing at the EPA William Jefferson Clinton (WJC) East Building, 1201 Constitution Avenue NW, Washington, DC 20004. If a public hearing is requested, additional details about the public hearing will be provided in a separate **Federal Register** notice and on our website at *https://www3.epa.gov/ttn/emc/methods.* To request a hearing, to register to speak at a hearing, or to inquire if a hearing will be held, please contact Raymond Merrill

by email at *merrill.raymond@epa.gov* or phone at (919) 541–5225. The last day to pre-register in advance to speak at the public hearing will be January 27, 2020. If held, the public hearing will convene at 9:00 a.m. (local time) and will conclude at 4:00 p.m. (local time).

Because this hearing is being held at a U.S. government facility, individuals planning to attend the hearing should be prepared to show valid picture identification to the security staff in order to gain access to the meeting room. Please note that the REAL ID Act, passed by Congress in 2005, established new requirements for entering federal facilities. For purposes of the REAL ID Act, EPA will accept government-issued IDs, including drivers' licenses, from the District of Columbia and all states and territories except from American Samoa. If your identification is issued by American Samoa, you must present an additional form of identification to enter the federal building where the public hearing will be held. Acceptable alternative forms of identification include: Federal employee badges, passports, enhanced driver's licenses, and military identification cards. For additional information for the status of your state regarding REAL ID, go to: *https://www.dhs.gov/real-id-enforcement-brieffrequently-asked-questions.* Any objects brought into the building need to fit through the security screening system, such as a purse, laptop bag, or small backpack. Demonstrations will not be allowed on federal property for security reasons.

Table of Contents

The following outline is provided to aid in locating information in this preamble.

I. General Information

A. Does this action apply to me?

The proposed amendments to Method 23 apply to industries that are subject to certain provisions of parts 60, 62, 63, 79, and 266. The source categories and entities potentially affected are listed in Table 1. This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be regulated by this action. This table lists the types of entities that EPA is now aware could potentially be affected by this action. Other types of entities not listed in the table could also be regulated.

TABLE 1—POTENTIALLY AFFECTED SOURCE CATEGORIES

Category	NAICSY [a]	Examples of regulated entities
Industry	332410	Fossil fuel steam generators.
	332410	Industrial, commercial, institutional steam generating units.
	562213	Municipal Waste Combustors.
	322110	Hazardous Waste Combustors.
	325211	Polyvinyl Chloride Resins Manufacturing.
	327310	Portland cement plants.
	324122	Asphalt Shingle and Coating Materials Manufacturing.
	331314	Secondary aluminum plants.
	327120	Clay Building Material and Refractories Manufacturing.
	331410	Nonferrous Metal (except Aluminum) Smelting and Refining.

[a] North American Industry Classification System.

If you have any questions regarding the applicability of the proposed changes to Method 23, contact the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

B. Where can I get a copy of this document and other related information?

The docket number for this action is Docket ID No. EPA–HQ–OAR–2016–0677. In addition to being available in the docket, an electronic copy of the proposed method revisions is available on the Technology Transfer Network (TTN) website at *https://www3.epa.gov/ttn/emc/methods/.* The TTN provides information and technology exchange in various areas of air pollution control.

II. Background

The EPA's Method 23 (Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources) is our current reference test method for determination

of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) emitted from stationary sources.

The EPA promulgated Method 23 (Appendix A of 40 CFR part 60, Test Methods) on February 13, 1991 (56 FR 5758). Since promulgation, the measurement of PCDDs and PCDFs has evolved as analytical laboratories, EPA, and state entities have developed new standard operating procedures and methods to reflect improvements in sampling and analytical techniques. Examples of newer PCDD/PCDF methods include:

- Office of Land and Emergency Management (OLEM) Solid Waste (SW) SW–846 EPA Method 8290A, Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS);
- Office of Water (OW) EPA Method 1613, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS; and
- California Environmental Protection Agency Air Resources Board (CARB) Method 428, Determination of Polychlorinated Dibenzo-p-Dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyls Emissions from Stationary Sources.

Beginning in 2016, the EPA held a series of informal discussions with stakeholders in the measurement community to identify technical issues related to the sampling and analysis of PCDD and PCDF and potential revisions to Method 23. The stakeholders consisted of a cross section of interested parties including representatives from state regulatory entities, various EPA offices, analytical laboratories, emission testing firms, analytical standards vendors, instrument vendors, and others with experience in sampling and analysis of PCDD and PCDF and with the equipment, materials, and performance of Method 23 and other PCDD/PCDF methods. In the discussions, EPA also sought stakeholder input regarding their experience combining procedures for sampling and analysis of PCDD and PCDF with procedures for sampling and analysis of PAHs and PCBs emitted from stationary sources. The docket contains summaries of the stakeholder discussions.

III. Incorporation by Reference

The EPA proposes to incorporate by reference ASTM D6911–15 and ASTM D4840–99(2018)e1 in Method 23. The ASTM D6911–15 includes a guide for packaging and shipping environmental samples for laboratory analysis and ASTM D4840–99(2018)e1 includes a standard guide for sample chain-of-custody procedures. These standards were developed and adopted by the American society for Testing and Materials and may be obtained from *https://www.astm.org* or from the ASTM at 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428–2959.

IV. Summary of Proposed Revisions to Method 23

In this action, we are proposing technical revisions and editorial changes to clarify and update the requirements and procedures specified in Method 23. We are also proposing to reformat the method to conform with EPA's current method format (see *https://www.epa.gov/measurements-modeling/method-development#format*). We are proposing to expand the applicability of Method 23 to include procedures for sampling and analyzing PAHs and PCBs. In addition, we are proposing revisions to various sections of the CFR that either require Method 23 or require the analysis of PCDDs/PCDFs, PAHs, or PCBs.

Our intent for the proposed revisions is to ensure that Method 23 is implemented consistently and to update the method procedures to include performance-based quality requirements that add flexibility rather than the prescriptive requirements currently described in the method.

The primary focus of the proposed revisions to Method 23 is to change the method from a prescriptive method to a performance-based method, which will allow users to have flexibility in implementing the method (*e.g.,* choice of gas chromatograph (GC) column, the procedures used for sample cleanup) while still meeting performance criteria that the EPA believes are necessary for demonstrating and documenting the quality of the measurements for the target compounds. The proposed revisions also address concerns over recovery of target compounds from particulate matter by requiring a pre-extraction filter spike recovery procedure and acceptance criteria for the filter spike recovery. These new requirements resolve the concerns that led to the criteria in 40 CFR 63.1208 that required Administrator approval prior to use of Method 23 for measurement of PCDDs/PCDFs.

The EPA's second focus for the proposed revisions is to convert the method entirely to quantitation based on isotope dilution. These revisions to the method are possible because additional isotopically labeled standards for the target compounds have become available from vendors since the original promulgation of Method 23.

The third major focus for the EPA's proposed revision to Method 23 is to include options for combining sampling and analysis of PCDDs/PCDFs with PAHs and PCBs to allow the measurement of toxic SVOC. In addition, adding PCBs and PAHs to the list of target compounds measured by Method 23 is responsive to multiple requests for alternative method approval from facilities and source test teams that are responding to EPA information collection requests (ICRs).

The EPA's proposed amendments to Method 23 are presented below for each section of Method 23.

A. Section 1.0

In this action, EPA is proposing to rename section 1.0 from ''Applicability and Principle'' to ''Scope and Application,'' and revise the text to expand the target compounds for Method 23 to include PCBs and PAHs. We are also proposing to add statements that emphasize the need for working knowledge of the EPA Methods 1 through 5 of appendices A–1, A–2, and A–3 to 40 CFR part 60, and the use of high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) when applying Method 23. We are also proposing language to specify that Method 23 is performance-based and to allow users to modify parts of the method to overcome interferences or to substitute alternative materials and equipment provided that all performance criteria in the method are met.

B. Section 2.0

The EPA is proposing to rename section 2.0 from ''Apparatus'' to ''Summary of Method,'' and revise section 2.0 with language to provide an overview of the method's sampling and analytical procedures. We are also proposing to move the current language in section 2.0, which describes the materials needed to conduct Method 23, to a proposed new section 6.0.

C. Section 3.0

The current version of Method 23 does not include definitions of key terms and variables used in Method 23. In this action, we are proposing to add a new section 3.0 titled ''Definitions,'' absent in the current promulgated version of Method 23. We are providing definitions to acronyms and technical terms to improve the clarity of the method principles and procedures. We also propose to move language from the

current section 3.0 to a proposed new section 7.0.

D. Section 4.0

The current version of Method 23 does not discuss the conditions that can potentially interfere with measurements obtained when using the method. In this action, we are proposing to add a new section 4.0 titled ''Interferences,'' that would present the potential causes and recommendations for avoiding or mitigating interferences or sample contamination. We also propose to move language from the current section 4.0 to a proposed new section 8.0.

E. Section 5.0

Currently, Method 23 does not provide procedures for safety. In this action, we are proposing to add a new section 5.0 titled ''Safety,'' that would present the health hazards and procedures for minimizing risks to field and laboratory personnel when conducting Method 23. We also propose to move language from the current section 5.0 to a proposed new section 11.0.

F. Section 6.0

In this action, we are proposing to renumber and move the text in section 2.0 (Apparatus) of the current method to section 6.0 titled ''Equipment and Supplies,'' and to make clarifying edits and technical revisions to the specifications in this section. Table 2 of this preamble identifies the proposed new numbering for the subsections currently in section 2.0 and Table 3 of this preamble identifies new specifications (and the associated subsection) we are proposing to include in section 6.0.

TABLE 2—CROSSWALK FOR PROPOSED REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Proposed section
Filter holder	2.1.1	6.1.3
Condenser	2.1.2	6.1.7
Water circulating bath	2.1.3	6.1.8
Absorbent module	2.1.4	6.1.9
Fitting cap	2.2.1	6.2.1
Wash bottles	2.2.2	6.2.2
Filter storage container	2.2.4	6.2.4
Field balance	2.2.5	6.2.5
Aluminum foil	2.2.6	6.2.6
Glass sample storage containers	2.2.9	6.2.8
Extraction thimble	2.3.4	6.3.3.3
Pasteur pipette	2.3.5	6.4.1
GC oven	2.3.10.1	6.5.1.1
Temperature monitor for GC oven	2.3.10.2	6.5.1.2
GC Flow system	2.3.10.3	6.5.1.3
Capillary column	2.3.10.4	6.5.2
Mass spectrometer	2.3.11	6.5.3
Mass spectrometer data system	2.3.12	6.5.4

TABLE 3—PROPOSED ADDITIONAL SPECIFICATIONS FOR SECTION 6.0

Description	Proposed section
Probe liner	6.1.2
Filter heating system	6.1.4
Filter temperature sensor	6.1.5
Sample transfer line	6.1.6
Impingers	6.1.10
Soxhlet extraction apparatus	6.3.3.1
Moisture trap of extraction apparatus	6.3.3.2
Kuderna-Danish concentrator	6.3.4
Heating mantle	6.3.3.4
Chromatography column	6.4.2
Injection port	6.5.1.4
PCDD/PCDF column system	6.5.2.1
PAH column system	6.5.2.2
PCB column system	6.5.2.3

In this section, we are also proposing to:

- Prohibit the use of brominated flame-retardant coated tape in assembling the sampling train to avoid sample contamination;
- Revise the specification for a rotary evaporator with specifications for a Kuderna-Danish concentrator to avoid the loss of higher vapor pressure target compounds;
- Remove specifications for the graduated cylinder to improve the accuracy of moisture measurements and to make Method 23 more consistent with other isokinetic sampling methods; and
- Remove the volume requirement for wash bottles to allow greater flexibility in field sample recovery.

We are also proposing to move language from Method 23's current section 6.0 to a proposed new section 10.0.

G. Section 7.0

In this action, the EPA is proposing to renumber and move the text in section 3.0 (Reagents) of the current method to a new section 7.0 titled ''Reagents, Media and Standards,'' and to make clarifying edits and technical revisions to the specifications in this section. Table 4 of this preamble identifies the

proposed new numbering for the subsections currently in section 3.0 and Table 5 of this preamble identifies new specifications (and the associated subsection) we are proposing to include in section 7.

TABLE 4—CROSSWALK FOR PROPOSED REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Proposed section
Filter	3.1.1	7.1
Adsorbent resin	3.1.2	7.2
Glass wool	3.1.3	7.3
Water	3.1.4	7.4
Methylene chloride	3.2.2	7.6
Sodium sulfate	3.3.2	7.8.2
Basic alumina	3.3.13	7.8.9.1.2
Silica gel	3.3.14	7.8.9.3
Carbon/Celite®	3.3.17	7.8.9.4
Nitrogen	3.3.18	7.8.10

TABLE 5—PROPOSED ADDITIONAL SPECIFICATIONS FOR SECTION 7.0

Description	Proposed section
High-boiling alkanes used as keeper solvents	7.8.8
Liquid column packing materials	7.8.9
Acidic alumina	7.8.9.1.1
Florisil®	7.8.9.2
Helium	7.9.1
Spiking standards	7.9.2
Pre-sampling recovery standard solution	7.9.3
Filter recovery spike standard solution	7.9.4
Pre-extraction recovery standard solution	7.9.5
Pre-analysis recovery standard solution	7.9.6

We are proposing to replace the filter precleaning procedures of the current method with specifications for conducting a filter quality control check. We are proposing to delete unnecessary specifications presented in Table 6 to reflect modern methods. We are also proposing to rename the isotopic spiking standard mixtures to simple English names that relate the standards to their use in the proposed method.

TABLE 6—PROPOSED DELETIONS OF MATERIAL SPECIFICATIONS IN THE CURRENT METHOD 23

Material	Current section
Chromic acid cleaning solution	3.1.6
Benzene	3.3.7
Ethyl acetate	3.3.8
Nonane	3.3.11
Cyclohexane	3.3.12
Hydrogen	3.3.19
Internal standard solution	3.3.20
Surrogate standard solution	3.3.21
Recovery standard solution	3.3.22

We are also proposing to move the current section 7.0 to a proposed new section 9.0.

H. Section 8.0

In this action, the EPA is proposing to renumber and move the text in section 4.0 (Procedure) of the current method to a new section 8.0 titled ''Sample Collection, Preservation and Storage,'' and to make clarifying edits and technical revisions to the current procedures for sampling and sample recovery. As proposed, the new section 8 also would include added requirements for sample storage conditions and holding times.

Under the sampling procedures of Method 23, we are proposing revisions to the current requirements in section 4.1.1 for pretest preparations. Table 7 of this preamble identifies the new numbering to revise and replace the requirements in section 4.1.

TABLE 7—CROSSWALK FOR PROPOSED REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Proposed section
Glassware cleaning	4.1.1.1	8.1.1.1
Assembling the adsorbent module	4.1.1.2	8.1.1.2
Maintaining the sampling train components	4.1.1.3	8.1.1.3
Silica Gel	4.1.1.4	8.1.1.4

TABLE 7—CROSSWALK FOR PROPOSED REVISIONS TO CURRENT METHOD SECTIONS—Continued

Description	Current section	Proposed section
Checking and packing filters	4.1.1.5	8.1.1.5
Field preparation of the sampling train	4.1.3.1	8.1.3.1
Impinger assembly	4.1.3.2	8.1.3.2
Sampling probe and nozzle preparation	4.1.3.4	8.1.3.4

Table 8 of this preamble shows the specifications we are proposing to add to the new section 8.0. We are proposing a minimum sample volume to assure that stack testers can attain the detection limits consistent with current regulations. Sampling time requirements at each traverse point for continuous industrial processes align Method 23 with other isokinetic stationary source methods, such as Method 5. The sampling time at each traverse point for batch industrial processes ensure measurements are made for the entire process cycle. The proposed filter check requirements add details that were absent from the original Method 23 and align the method with the requirements of other isokinetic stationary source methods, such as Methods 5, 26A, and 29, also in Appendix A of this part. The proposed absorbent module orientation requirements clarify the configuration of the absorbent module to ensure that condensed moisture flows through the module into the water collection impinger. We are proposing to add filter monitoring requirements to align Method 23 with other isokinetic stationary source methods. Also, we are proposing to add adsorbent module temperature monitoring to confirm that the sorbent material was not exposed to elevated temperatures that could bias sample collection and results.

TABLE 8—PROPOSED ADDITIONAL SPECIFICATIONS FOR SECTION 8.1

Description	Proposed section
Minimum sample volume	8.1.2.1
Sampling time for continuous processes	8.1.2.2
Sampling time for batch processes	8.1.2.3
Filter assembly	8.1.3.3
Orientation of the condenser and adsorbent module	8.1.3.4
Monitoring the filter temperature	8.1.5.1
Monitoring the adsorbent module temperature	8.1.5.2

Under sample recovery procedures, we are proposing technical revisions as shown in Table 9 of this preamble. In this action, we are also proposing to add a recommendation to use clean glassware and to add specifications as shown in Table 10 of this preamble.

TABLE 9—CROSSWALK FOR PROPOSED REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Proposed section
Adsorbent module sample preparation	4.2.2	8.2.5
Preparation of Container No. 2	4.1.1.2	8.2.6
Rinsing of the filter holder and condenser	4.1.1.3	8.2.7
Weighing impinger water	4.1.1.5	8.2.8
Preparation of Container No. 3	4.1.3.1	8.2.9
Silica gel	4.1.3.2	8.2.10

TABLE 10—PROPOSED ADDITIONAL SPECIFICATIONS FOR SECTION 8.2

Description	Proposed section
Conducting a post-test leak check	8.2.1
Storage conditions for Container No. 1	8.2.4
Field sample handling, storage, and transport	8.2.11
Sample chain of custody	8.2.12

In new section 8.2.8, we propose to measure moisture by weight rather than by volume.

I. Section 9.0

In this action, the EPA is proposing to move and renumber the current section 7.0 (Quality Control) to a new section 9.0 titled ''Quality Control,'' and to make clarifying and technical revisions to the section. We are proposing to add an introductory note that addresses maintaining and documenting quality control compliance required in Method 23. We would add a new subsection that clarifies the recordkeeping and reporting necessary to demonstrate compliance with quality control requirements of this method. We are also proposing to add specifications for conducting pre-sampling, pre-extraction, and pre-analysis spike recoveries of isotopically-labeled standards and to add specifications for:

- Capillary gas chromatography columns;

- Preparing and analyzing batch blanks;
- Determining the method detection limit; and
- Assessing field train proof blanks.

We are also proposing to move language from the current section 9.0 to a proposed new section 12.0.

J. Section 10.0

In this action, the EPA is proposing to renumber and move the text in section 6.0 (Calibration) of the current method to a new section 10.0 titled ''Calibration and Standardization,'' and to make clarifying and technical revisions to the specifications for calibrating the sampling and the HRGC/HRMS systems. We are proposing to add specifications for tuning the HRGC/HRMS system, to move the specification for HRMS resolution (currently in section 5) to this proposed section, to add procedures for assessing the relative standard deviation for the mean instrument response, and to add procedures for determining the signal-to-noise ratio of the MS to bring Method 23 up to date with current laboratory practice. We are also proposing to add requirements for ion abundance ratio limits, initial calibrations, and resolution checks under the daily performance check to serve as performance indicators for analysis quality. We are also proposing to move language in the current section 10.0 to a proposed new section 16.0.

K. Section 11.0

In this action, the EPA is proposing to renumber and move the text in section 5.0 (Analysis) of the current method to a new section 11.0 titled ''Analysis Procedure,'' and to make clarifying and technical revisions to the current specifications for sample extraction and sample cleanup and fractionation. We are also proposing to add a new subsection describing how sample extract aliquots are prepared for cleanup and analysis.

We are also proposing to add the specifications and recommendations for analysis procedures shown in Table 11 of this preamble.

TABLE 11—PROPOSED ADDITIONAL SPECIFICATIONS FOR SECTION 11.0

Description	Proposed section
Preparing and operating the extraction apparatus	11.1.7 through 11.1.9.
Cooling the extraction apparatus	11.2.1.
Performing an initial extract concentration	11.2.2.
Cooling the sample extract	11.2.3.
Recommended minimum volume for PCDD/PCDF analysis	11.2.3.
Further concentration of sample (if needed) for cleanup and analysis	11.2.4.
Sample cleanup and fractionation for PAHs and PCDEs	11.3.1.
Sample cleanup and fractionation for PCDD/DFs and PCBs	11.3.2.
Addressing unresolved compounds	11.4.1.2.1.
Retention time for PCBs	11.4.3.4.5.
Chlorodiphenyl ether interference of PCDD/DFs	11.4.3.4.8.
MS lock channels	11.4.3.4.9.
Calculations of target mass and mass per dry standard cubic meter	11.4.3.5.1 and 11.4.3.5.2.
Quantifying indigenous PCDD/DFs	11.4.3.5.3.
Reporting options compound concentrations	11.4.3.5.4 through 11.4.3.5.6.
Identification criteria for PAHs	11.4.3.4.10.

L. Section 12.0

In this action, the EPA is proposing to renumber and move the text in section 9.0 (Calculations) of the current method to a new section 12.0 titled ''Data Analysis and Calculations,'' and to revise the equation variable list. We are proposing to revise the equations shown in Table 12 of this preamble to incorporate isotope dilution calculations.

TABLE 12—PROPOSED EQUATION REVISIONS FOR SECTION 12.0

Current equation	Description	Proposed section
23–2	Average relative response factor (RRF) for each compound	12.3
23–6	Concentration of individual target compound i in the extract by isotope dilution	12.7
23–9	Recovery of Labeled Compound Standards	12.10
23–10	Estimated detection limit	12.11
23–11	Total concentration	12.12

We are also proposing to remove and replace the current equations in Method 23 with the equations shown in Table 13 of this preamble to accommodate the proposed changes to the method procedures.

TABLE 13—PROPOSED ADDITIONAL EQUATIONS FOR SECTION 12.0

Equation	Description	Proposed section
23–1	Individual compound RRF for each calibration level	12.2
23–3	Percent relative standard deviation of the RRFs for a compound over the five calibration levels	12.4
23–4	Standard deviation of the RRFs for a compound over the five calibration levels	12.5
23–5	Percent difference of the RRF of the continuing calibration verification compared to the average RRF from the initial calibration for each target compound.	12.6
23–7	Concentration of individual target compound i in the sample extract	12.8

TABLE 13—PROPOSED ADDITIONAL EQUATIONS FOR SECTION 12.0—Continued

Equation	Description	Proposed section
23–8	Concentration of the Individual Target Compound or Group i in the Emission Gas	12.9

M. Section 13.0

In this action, the EPA is proposing to add a new section 13.0 titled ''Method Performance,'' that would include the specifications shown in Table 14 of this preamble.

TABLE 14—PROPOSED METHOD PERFORMANCE SPECIFICATIONS FOR SECTION 13.0

Description	Proposed section
Quality control checks of filters, adsorbent resin, glass wool, and batch blanks	13.1, 13.2, and 13.14.
Field train proof blanks	13.2.
GC column systems used to measure PCDD/F, PAH, and PCB target compounds	13.3 through 13.6.
Acceptability of detection limits	13.7.
Tuning HRGC/HRMS systems	13.8.
MS lock channels	13.9.
Initial and continuing calibrations	13.10 and 13.11.
Identification of target compounds	13.12 and 13.13.
Pre-sampling, -extraction, and –analysis spike recoveries	13.15 and 13.16.
Pre-analysis spike sensitivity requirements	13.17.
Modifications of the method	13.18 and 13.19.

N. Section 14.0

In this action, the EPA is proposing to add a new section 14.0 titled ''Pollution Prevention,'' that specifies the procedures for minimizing or preventing pollution associated with preparing and using Method 23 standards.

O. Section 15.0

In this action, the EPA is proposing to add a new section 15.0 titled ''Waste Management,'' that specifies the laboratory responsibilities for managing the waste streams associated with collecting and analyzing Method 23 samples.

P. Section 16.0

In this action, the EPA is proposing to renumber and move the text in section 10.0 (Bibliography) of the current method to a new section 16.0 titled ''References.'' We are proposing to delete previous reference numbers 3 and 4 that are no longer relevant and to add new citations for the following references:

- Fishman, V.N., Martin, G.D. and Lamparski, L.L. Comparison of a variety of gas chromatographic columns with different polarities for the separation of chlorinated dibenzo-p-dioxins and dibenzofurans by high-resolution mass spectrometry. Journal of Chromatography A 1139 (2007) 285–300.
- International Agency for Research on Cancer. Environmental Carcinogens Methods of Analysis and Exposure Measurement, Volume 11—Polychlorinated Dioxins and Dibenzofurans. IARC Scientific Publications No. 108, 1991.
- Stieglitz, L., Zwick, G., Roth, W. Investigation of different treatment techniques for PCDD/PCDF in fly ash. Chemosphere 15: 1135–1140; 1986.
- Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.
- U.S. Environmental Protection Agency. Office of Air Programs Publication No. APTD–0576: Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Research Triangle Park, NC. March 1972.
- U.S. Environmental Protection Agency. Method 1625C-Semivolatile Organic Compounds by Isotope Dilution GCMS.
- U.S. Environmental Protection Agency. Method 1613B-Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.
- U.S. Environmental Protection Agency. Method 1668C-Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS.
- Tondeur, Y., Nestrick, T., Silva, Héctor A., Vining, B., Hart, J. Analytical procedures for the determination of polychlorinated-p-dioxins, polychlorinated dibenzofurans, and hexachlorobenzene in pentachlorophenol. Chemosphere Volume 80, Issue 2, June 2010, pages 157–164.

Q. Section 17.0

In this action, the EPA is proposing to add a new section 17 titled ''Tables, Diagrams, Flow Charts, and Validation Data,'' that will contain all tables, diagrams, flow charts, and validation data referenced in Method 23. We are proposing to revise Figures 23–1 and 23–2 and to rename and/or renumber the current Method 23 tables as shown in Table 15 of this preamble.

TABLE 15—PROPOSED REVISIONS TO METHOD 23 TABLES

Current method	Proposed method
Table 1—Composition of the Sample Fortification and Recovery Standards Solutions.	Table 23–7. Composition of the Sample Fortification and Recovery Standard Solutions for PCDDs and PCDFs.
Table 2—Composition of the Initial Calibration Solutions	Table 23–11. Composition of the Initial Calibration Standard Solutions for PCDDs and PCDFs.

TABLE 15—PROPOSED REVISIONS TO METHOD 23 TABLES—Continued

Current method	Proposed method
Table 3—Elemental Compositions and Exact Masses of the Ions Monitored by High Resolution Mass Spectrometry for PCDD's and PCDF's.	Table 23–4. Elemental Compositions and Exact Masses of the Ions Monitored by High-Resolution Mass Spectrometry for PCDDs and PCDFs.
Table 4—Acceptable Ranges for Ion-Abundance Ratios of PCDD's and PCDF's.	Table 23–15. Recommended Ion Type and Acceptable Ion Abundance Ratios.
Table 5—Minimum Requirements for Initial and Daily Calibration Response Factors.	Table 23–14. Minimum Requirements for Initial and Daily Calibration Response Factors for Isotopically Labeled and Native Compounds.

We are also proposing to add Figure 23–3 (Soxhlet/Dean-Stark Extractor) and Figure 23–4 (Sample Preparation Flow Chart) and to add the tables specified in Table 16 of this preamble.

TABLE 16—ADDITIONAL PROPOSED TABLES TO METHOD 23

Proposed table	Description
23–1	Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Target Analytes.
23–2	Polycyclic Aromatic Hydrocarbon Target Analytes.
23–3	Polychlorinated Biphenyl Target Analytes.
23–5	Elemental Compositions and Exact Masses of the Ions Monitored by High-Resolution Mass Spectrometry for PAHs.
23–6	Elemental Compositions and Exact Masses of the Ions Monitored by High-Resolution Mass Spectrometry for PCBs.
23–8	Composition of the Sample Fortification and Recovery Standard Solutions for PAHs.
23–9	Composition of the Sample Fortification and Recovery Standard Solutions for PCBs.
23–10	Sample Storage Conditions and Laboratory Hold Times.
23–12	Composition of the Initial Calibration Standard Solutions for PAHs.
23–13	Composition of the Initial Calibration Standard Solutions for PCBs.
23–16	Typical DB5–MS Column Conditions.
23–17	Assignment of Pre-extraction Standards for Quantitation of Target PCBs.
23–18	Estimated Method Detection Limits for PCDDs and PCDFs.
23–19	Target Detection Limits for PAHs.
23–20	Estimated Method Detection Limits for PCBs.

V. Summary of Proposed Revisions Related to 40 CFR Parts 60, 63, and 266

A. 40 CFR Part 60—Standards of Performance for New Stationary Sources

In 40 CFR 60.17(h), we propose to incorporate by reference ASTM D4840–99(2018)e1, Standard Guide for Sample Chain-of-Custody Procedures, and to amend the reference to ASTM D6911–15, Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis, to include for use in Method 23.

In Subpart CCCC, we propose to revise § 60.2125(g)(2) and (j)(2) to realign the requirement for quantifying isomers to the reorganized section 11.4.2.4 in the proposed revision of Method 23.

In Subpart DDDD, we propose to revise § 60.2690(g)(2) and (j)(2) to realign the requirement for identifying isomers to the reorganized section 11.4.2.4 in the proposed revision of Method 23.

B. 40 CFR Part 63—National Emission Standards for Hazardous Air Pollutants for Source Categories

In 40 CFR 63.849(a)(13), we propose to replace California Air Resources Board (CARB) Method 428 with Method 23 for the measurement of PCB emissions from roof monitors not employing wet roof scrubbers.

In 40 CFR 63.1208, we propose to remove the requirement for administrator's approval to use Method 23 for measuring PCDD/PCDF emissions from hazardous waste combustors.

In 40 CFR 63.1625(b)(10), we propose to replace CARB Method 429 with Method 23 for measuring the emissions of PAH from ferromanganese electric arc furnaces.

In Subpart AAAAAAA, Table 3, we propose to replace the requirement for analysis of PAH by SW–846 Method 8270 with a requirement to use Method 23. Specifically, we are deleting ''with analysis by SW 846 Method 8270D'' in row 6 of Table 3. Since revisions to Method 23 propose to eliminate the use of methylene chloride, we also propose to remove footnote ''b'' in Table 3.

C. 40 CFR Part 266—Standards for the Management of Specific Hazardous Wastes and Specific Types of Hazardous Waste Management Facilities

In 40 CFR 266.104, we propose to add Method 23 as an alternative to SW–846 Method 0023A.

VI. Statutory and Executive Order Reviews

Additional information about these statutes and Executive Orders can be found at *https://www2.epa.gov/laws-regulations/laws-and-executive-orders.*

A. Executive Order 12866: Regulatory Planning and Review and Executive Order 13563: Improving Regulation and Regulatory Review

This action is not a significant regulatory action and was, therefore, not submitted to the Office of Management and Budget (OMB) for review.

B. Executive Order 13771: Reducing Regulations and Controlling Regulatory Costs

This action is expected to be an Executive Order 13771 deregulatory action. This proposed rule is expected to provide meaningful burden reduction by improving the accuracy of Method 23, improving data quality, and providing source testers flexibility by providing a performance-based approach and incorporating approved alternative procedures into the regulatory measurement method. This proposed action does not impose any requirements on owners/operators to

use Method 23 but provides instruction on how to use Method 23 if required to do so by an EPA source category regulation.

C. Paperwork Reduction Act (PRA)

This proposed action does not impose an information collection burden under the PRA. The revisions being proposed in this action to Method 23 do not add information collection requirements but make corrections, clarifications and updates to existing testing methodology.

D. Regulatory Flexibility Act (RFA)

I certify that this proposed action will not have a significant economic impact on a substantial number of small entities under the RFA. This action will not impose any requirements on small entities. The proposed revisions to Method 23 do not impose any requirements on regulated entities. Rather the proposed changes improve the quality of the results when required by other rules to use Method 23. Revisions proposed for Method 23 allow contemporary advances in analysis techniques to be used. Further, the proposed changes in Method 23 analysis procedures reduce the impact of this method by bringing it into alignment with other agency methods.

E. Unfunded Mandates Reform Act (UMRA)

This proposed action does not contain any unfunded mandate of $100 million or more as described in UMRA, 2 U.S.C. 1531–1538. The proposed action imposes no enforceable duty on any State, local or tribal governments or the private sector.

F. Executive Order 13132: Federalism

This proposed action does not have federalism implications. It will not have substantial direct effects on the states, on the relationship between the national government and the states, or on the distribution of power and responsibilities among the various levels of government.

G. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments

This proposed action does not have tribal implications, as specified in Executive Order 13175. It will not have substantial direct effects on the Indian Tribal Governments, on the relationship between the national government and the Indian Tribal Governments, or on the distribution of power and responsibilities among Indian Tribal Governments and the various levels of government.

H. Executive Order 13045: Protection of Children From Environmental Health Risks and Safety Risks

The EPA interprets Executive Order 13045 as applying only to those regulatory actions that concern environmental health or safety risks that the EPA has reason to believe may disproportionately affect children, per the definition of ''covered regulatory action'' in section 2–202 of the Executive Order. This proposed action is not subject to Executive Order 13045 because it does not establish or revise a standard that provides protection to children against environmental health and safety risks.

I. Executive Order 13211: Actions That Significantly Affect Energy Supply, Distribution or Use

This proposed action is not subject to Executive Order 13211, because it is not a significant regulatory action under Executive Order 12866.

J. National Technology Transfer and Advancement Act (NTTAA)

This proposed action involves technical standards. The EPA proposes to use ASTM D6911–15 (Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis) and ASTM D4840–99(2018)e1 (Standard Guide for Sample Chain-of-Custody Procedures). These ASTM standards cover best practices that guide sample shipping and tracking from collection through analysis.

These standards were developed and adopted by the American society for Testing and Materials. The standard may be obtained from *https://www.astm.org* or from the ASTM at 100 Barr Harbor Drive, P.O. box C700, West Conshohocken, PA 19428–2959.

K. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations

This proposed action will not have potential disproportionately high and adverse human health or environmental effects on minority, low-income or indigenous populations because it does not establish or revise a standard that provides protection to human health or the environment.

List of Subjects

40 CFR Part 60

Environmental protection, Air pollution control, Hazardous air pollutants, Incorporation by reference, Method 23, Polychlorinated biphenyls, Polychlorinated dibenzofurans, Polychlorinated dibenzo-p-dioxins, Polycyclic aromatic compounds, Test methods.

40 CFR Part 63

Environmental protection, Air pollution control, Method 23, New source performance, Polychlorinated biphenyls, Polychlorinated dibenzofurans, Polychlorinated dibenzo-p-dioxins, Polycyclic aromatic compounds, Test methods.

40 CFR Part 266

Environmental protection, Air pollution control, Hazardous air pollutants, Hazardous waste, Method 23, Polychlorinated biphenyls, Polychlorinated dibenzofurans, Polychlorinated dibenzo-p-dioxins, Polycyclic aromatic compounds, Test methods, Waste management.

Dated: December 17, 2019.

Andrew R. Wheeler,

Administrator.

For the reasons stated in the preamble, the Environmental Protection Agency proposes to amend title 40, chapter I of the Code of Federal Regulations as follows:

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

■ 1. The authority citation for part 60 continues to read as follows:

Authority: 42 U.S.C. 7401 *et seq.*

■ 2. In § 60.17:

■ a. Redesignate paragraphs (h)(167) through (h)(209) as (h)(168) through (h)(210);

■ b. Add paragraph (h)(167); and

■ c. Revise newly redesignated paragraph (h)(192).

The addition and revision read as follows:

§ 60.17 Incorporations by reference.

* * * * *

(h) * * *

(167) ASTM D4840–99(2018)e1 Standard Guide for Sample Chain-of-Custody Procedures, approved August 2018, IBR approved for appendix A–8: Method 30B, IBR approved for Appendix A–7: Method 23.

* * * * *

(192) ASTM D6911–15 Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis, approved January 15, 2015, IBR approved for appendix A–7: Method 23 and appendix A–8: Method 30B.

* * * * *

■ 3. In § 60.2125, revise paragraphs (g)(2) and (j)(2) to read as follows:

§ 60.2125 How do I conduct the initial and annual performance test?

* * * * *

(g) * * * (2) Quantify isomers meeting identification criteria 2, 3, 4, and 5 in Section 11.4.3.4 of Method 23, regardless of whether the isomers meet identification criteria in Section 11.4.3.4.1 of Method 23. You must quantify the isomers per Section 11.4.3.5 of Method 23. (Note: You may reanalyze the sample aliquot or split to reduce the number of isomers to meet the identification criteria in Section 11.4.3.4 of Method 23.)

* * * * *

(j) * * *

(2) Quantify isomers meeting identification criteria 2, 3, 4, and 5 in Section 11.4.3.4 of Method 23, regardless of whether the isomers meet identification Section 11.4.3.4.1 of Method 23. You must quantify the isomers per Section 11.4.3.5 of Method 23. (Note: You may reanalyze the sample aliquot or split to reduce the number of isomers to meet the identification criteria in Section 11.4.3.4 of Method 23.)

* * * * *

■ 4. In § 60.2690, revise paragraphs (g)(2) and (j)(2) to read as follows:

§ 60.2690 How do I conduct the initial and annual performance test?

* * * * *

(g) * * *

(2) Quantify isomers meeting identification criteria 2, 3, 4, and 5 in Section 11.4.3.4 of Method 23, regardless of whether the isomers meet identification Section 11.4.3.4.1 of Method 23. You must quantify the isomers per Section 11.4.3.5 of Method 23. (Note: You may reanalyze the sample aliquot or split to reduce the number of isomers to meet the identification criteria in Section 11.4.3.4 of Method 23.)

* * * * *

(j) * * *

(2) Quantify isomers meeting identification criteria 2, 3, 4, and 5 in Section 11.4.3.4 of Method 23, regardless of whether the isomers meet identification Section 11.4.3.4.1 of Method 23. You must quantify the isomers per Section 11.4.3.5 of Method 23. (Note: You may reanalyze the sample aliquot or split to reduce the number of isomers to meet the identification criteria in Section 11.4.3.4 of Method 23.); and

* * * * *

■ 5. Revise Method 23 of appendix A–7 to part 60 and to read as follows:

Appendix A–7 to Part 60—Test Methods 19 through 25E

* * * * *

Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, Polychlorinated Biphenyls, and Polycyclic Aromatic Hydrocarbons From Stationary Sources

1.0 Scope and Application

1.1 Applicability. This method applies to measuring emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), polychlorinated biphenyls (PCBs), and/or polycyclic aromatic hydrocarbons (PAHs) in emissions from stationary sources. Using this method, you can measure these analyte groups individually or in any combination using a single sample acquisition. Tables 23–1 through 23–3 of this method list the applicable targets analytes for Method 23.

1.2 Scope. This method describes the sampling and analytical procedures used to measure selected PCDDs, PCDFs, PCBs, and PAHs from stationary source air emissions. However, Method 23 incorporates by reference some of the specifications (*e.g.,* equipment and supplies) and procedures (*e.g.,* sampling and analytical) from other methods in this part that are essential to conducting Method 23. To obtain reliable samples, source sampling teams should be trained and experienced with the following additional EPA test methods: Method 1, Method 2, Method 3, Method 4, and Method 5 of appendices A–1, A–2, and A–3 to 40 CFR part 60. Laboratory analysis teams should be trained and experienced with Method 1668C found at: *https://www.epa.gov/sites/production/files/2015–09/documents/method_1668c_2010.pdf* and Method 1613B of 40 CFR part 136 appendix A.

1.3 The high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) portions of this method are for use by laboratory analysts experienced with HRGC/HRMS analysis of PCDDs, PCDFs, PCBs, and PAHs or under the close supervision of such qualified persons. Each source testing team, including the sampling and laboratory organization(s) that use this method, must demonstrate the ability to generate acceptable results that meet the performance criteria in Section 13 of this method.

1.4 This method is ''performance-based'' and includes acceptability criteria for assessing sampling and analytical procedures. Users may modify the method to overcome interferences or to substitute superior materials and equipment, provided that they meet all performance criteria in this method. Section 13 of this method presents requirements for method performance.

2.0 Summary of Method

This method identifies and determines the concentration of specific PCDD, PCDF, PCBs, and PAHs compounds. Gaseous and particulate bound target pollutants are withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber or quartz filter, and on a packed column of adsorbent material. This method is not intended to differentiate between target compounds in particle or vapor fractions. The target compounds are extracted from the combined sample collection media. Portions of the extract are chromatographically fractionated to remove interferences, separated into individual compounds or simple mixtures by HRGC, and measured with HRMS. This method uses isotopically labeled standards to improve method accuracy and precision.

3.0 Definitions

3.1 Alternate Recovery Standards. A group of isotopically labeled compounds that is not otherwise designated in this method for quality control purposes. Use alternative recovery standards to assess the recovery of a compound class relative to a step in the sampling and analysis procedure that is not already assessed as a mandatory part of this method.

3.2 Batch Blank Sample. A laboratory blank sample composed of clean filter and XAD–2 media processed and analyzed using the same procedures as a field sample.

3.3 Benzo[*a*]pyrene Toxic Equivalent Factor (B[*a*]P–TEF). One of several schemes that express the toxicity for PAH compounds in terms of the most toxic form of PAH, benzo[*a*]pyrene, as specified in applicable regulations, permits, or other requirements.

3.4 Continuing Calibration Verification Standard (CCV). The mid-point calibration standard used to verify calibration. Prepare CCV standards from a second source, when possible.

3.5 Congener. An individual compound with a common structure (dioxin, furan, or biphenyl), only differing by the number of chlorine atoms attached to the structure.

3.6 Estimated Detection Limit (EDL). The minimum qualitatively recognizable signal above background for a target compound. The EDL is a

mathematically-derived detection limit (MDL) specific to each sample analysis based on the noise signal measured near the mass of a target compound or target isomer group. Being sample specific, the EDL is affected by sample size, dilution, etc.

3.7 Estimated Possible Concentration (EPC). Report the results as EPC when the ion abundance ratio for a target analyte is outside the performance criteria. Calculate the EPC separately for each quantitation ion, if present, and report the lower value as the EPC.

3.8 Homolog. A compound belonging to a series of compounds with the same general molecular formula, differing from each other by the number of repeating units.

3.9 Isomer. An individual compound with a common structure (dioxin, furan, or biphenyl), only differing by the position of chlorine atoms attached to the structure.

3.10 Polychlorinated Biphenyl (PCB) Isomers. Any or all 209 chlorinated biphenyl congeners and their isomers. Table 23–3 of this method lists the primary target compounds and appendix A to this method provides the full list of 209 PCB congeners and isomers.

3.10.1 Monochlorobiphenyl (MoCB). Any or all three monochlorinated biphenyl isomers.

3.10.2 Dichlorobiphenyl (DiCB). Any or all 12 dichlorinated biphenyl isomers.

3.10.3 Trichlorobiphenyl (TrCB). Any or all 24 trichlorinated biphenyl isomers.

3.10.4 Tetrachlorobiphenyl (TeCB). Any or all 42 tetrachlorinated biphenyl isomers.

3.10.5 Pentachlorobiphenyl (PeCB). Any or all 46 pentachlorinated biphenyl isomers.

3.10.6 Hexachlorobiphenyl (HxCB). Any or all 42 hexachlorinated biphenyl isomers.

3.10.7 Heptachlorobiphenyl (HpCB). Any or all 24 heptachlorinated biphenyl isomers.

3.10.8 Octachlorobiphenyl (OcCB). Any or all 12 octachlorinated biphenyl isomers.

3.10.9 Nonachlorobiphenyl (NoCB). Any or all three nonachlorinated biphenyl isomers.

3.10.10 Decachlorobiphenyl (DeCB). Biphenyl fully chlorinated with ten chlorine atom substituents replacing hydrogen in the parent compound.

3.11 Polychlorinated dibenzo-p-dioxin (PCDD) isomers. Any or all 75 chlorinated dibenzo-p-dioxin isomers. There are 11 required target PCDD analytes listed in Table 23–1 of this method. This method does not measure mono- through tri-PCDDs and includes non-2,3,7,8 substituted congeners in the total homolog categories.

3.11.1 Tetrachlorodibenzo-p-dioxin (TeCDD*).* Any or all 22 tetrachlorinated dibenzo-p-dioxin isomers.

3.11.2 Pentachlorodibenzo-p-dioxin (PeCDD). Any or all 14 pentachlorinated dibenzo-p-dioxin isomers.

3.11.3 Hexachlorodibenzo-p-dioxin (HxCDD). Any or all 10 hexachlorinated dibenzo-p-dioxin isomers.

3.11.4 Heptachlorodibenzo-p-dioxin (HpCDD). Any or all two heptachlorinated dibenzo-p-dioxin isomers.

3.11.5 Octachlorodibenzo-p-dioxin (OCDD). Dibenzodioxin fully chlorinated with eight chlorine atom substituents replacing hydrogen in the parent compound.

3.12 Polychlorinated dibenzofuran (PCDF) isomers. Any or all chlorinated dibenzofuran isomers. There are 14 required target PCDF analytes listed in Table 23–1 of this method. This method does not measure mono- through tri-PCDFs and includes non-2,3,7,8 substituted congeners in the total homolog categories.

3.12.1 Tetrachlorodibenzofuran (TeCDF). Any or all 38 tetrachlorinated dibenzofuran isomers.

3.12.2 Pentachlorodibenzofuran (PeCDF). Any or all 28 pentachlorinated dibenzofuran isomers.

3.12.3 Hexachlorodibenzofuran (HxCDF). Any or all 16 hexachlorinated dibenzofuran isomers.

3.12.4 Heptachlordibenzofuran (HpCDF). Any or all four heptachlorinated dibenzofuran isomers.

3.12.5 Octachlorodibenzofuran (OCDF). Dibenzofuran fully chlorinated with eight chlorine atom substituents replacing hydrogen in the parent compound.

3.13 Polychlorinated diphenyl ethers (PCDEs). Any or all chlorinated substituted diphenyl ethers.

3.13.1 Hexachlorodiphenyl ether (HxCDPE). Any or all 42 hexachlorinated diphenyl ether isomers.

3.13.2 Heptachlorodiphenyl ether (HpCDPE). Any or all 24 heptachlorinated diphenyl ether isomers.

3.13.3 Octachlorodiphenyl ether (OCDPE). Any or all 12 octachlorinated diphenyl ether isomers.

3.13.4 Nonachlorodiphenyl ether (NCDPE). Any or all three nonachlorinated diphenyl ether isomers.

3.13.5 Decachlorodiphenyl ether (DCDPE).

3.14 Polycyclic Aromatic Hydrocarbons (PAHs). Any or all aromatic compounds with two or more fused six-member rings. Table 23–2 of this method lists the target PAH compounds for this method. You may add and analyze additional PAH compounds by adding the appropriate ^{13}C isotopically labeled compound to the pre-extraction spike mixture and by following the other requirements for target PAH compounds in this method.

3.15 Pre-analysis Standard(s). A group of isotopically labeled compounds added at a known amount immediately prior to analysis and used to correct instrument response, injection errors, instrument drift and to determine the recovery of the pre-extraction isotopically labeled spike compounds. Add pre-analysis standards to every sample (including blank, quality control sample, and calibration solutions) at a known amount.

3.16 Pre-extraction Filter Recovery Standard(s). A group of isotopically labeled compounds added at a known amount to the filter used to indicate the extraction efficiency of the filter media. Add pre-extraction filter recovery standard(s) to the filter samples just prior extraction.

3.17 Pre-extraction Standard(s). A group of isotopically labeled compounds added in a known amount to the XAD–2 adsorbent sample immediately before extraction to correct the quantity of the native target compounds present in the sample for extraction, cleanup, and concentration recovery. These isotopically labeled compounds constitute a matrix spike in each sample.

3.18 Pre-sampling Adsorbent Standard(s). A group of isotopically labeled compounds added in a known amount to the XAD–2 adsorbent prior to sampling used to indicate the sample collection and recovery efficiency of the method.

3.19 Pre-transport Standard(s). Spiking compound(s) from the list of alternative recovery standards that can be added by the laboratory to the sample shipping containers used to transport field equipment rinse and recovery samples. The measured concentration of the pre-transport recovery standard provides a quality check on potential probe rinse sample spillage or mishandling after sample collection and during shipping.

3.20 Relative Response Factor (RRF). The response of the mass spectrometer to a known amount of an analyte relative to a known amount of an isotopically labeled standard.

3.21 2,3,7,8-Tetrachlorodibenzo-p-dioxin Toxic Equivalent Factor(s) (2,3,7,8-TeCDD–TEF). A procedure that expresses the toxicity of PCDDs, PCDFs,

and PCBs in terms of the most toxic dioxin, as specified in applicable regulations, permits, or other requirements.

4.0 Interferences

4.1 PCBs and PCDEs have similar molecular weight and chromatographic properties to PCDDs and PCDFs. PCBs produce an interfering mass-to-charge ratio (m/z) when losing chlorine (Cl_2) or Cl_4 upon fragmenting during ionization processes. PCDEs also produce interfering m/z values when losing Cl_2 in the PCDF homolog group with two fewer chlorine atoms (*i.e.,* an octachlorinated PCDE can interfere with a hexachlorinated PCDF). The latter interferences are potentially detected by monitoring an m/z corresponding to the potentially interfering PCDE; however, the fragmentation patterns of all PCDEs may not be known, complicating any attempt to quantify the extent of ether interference.

4.2 Very high amounts of other organic compounds in the matrix may interfere with the analysis. This method provides examples of column-chromatographic cleanup as procedures to reduce, but not necessarily eliminate, matrix effects due to high concentrations of organic compounds (International Agency for Research on Cancer 1991).

4.3 Target compound contaminants or related organics in solvents, reagents, glassware, isotopically labeled spiking standards, and other sample processing hardware are potential method interferences. Routinely evaluate all these materials to demonstrate that they are either free from interferences under the conditions of the analysis, or that the interference does not compromise the quality of the analysis results. Evaluate chemical interference through the preparation and analysis of batch blank samples. Use high purity reagents, solvents, and standards to minimize interference problems in sample analysis.

4.4 PAHs are subject to degradation when exposed to ultraviolet light. Take precautions to shield samples from sunlight or fluorescent light sources during sample collection, recovery, extraction, cleanup, and concentration.

5.0 Safety

Note: Develop a strict laboratory safety program for the handling of PCDDs, PCDFs, PCBs, and/or PAHs.

5.1 Compounds in the PCDD and PCDF classes such as 2,3,7,8-TeCDD are aneugenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 have toxicities comparable to that of 2,3,7,8-TeCDD.

5.2 PCBs are classified as known or suspected human or mammalian carcinogens. Be aware of the potential for inhalation and ingestion exposure to laboratory analysts.

5.3 This method recommends that the laboratory purchase dilute standard solutions of the analytes required for this method. However, if preparing primary solutions, use a hood or glove box. Laboratory personnel handling primary solutions should wear personal protective equipment including a toxic gas respirator mask fitted with charcoal filters approved by the National Institute for Occupational Safety and Health (NIOSH)/Mine Safety Health Administration (MSHA) to prevent the inhalation of airborne particulates if not working in an approved hood or glove box.

5.4 The toxicity or carcinogenicity of other reagents or chemicals used in this method is not precisely defined. However, treat each chemical as a potential health hazard and minimize exposure to these chemicals. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. Ensure that a reference file or list of internet sites that contain safety data sheets (SDS) is available to all personnel involved in the sampling and chemical analysis of samples known or suspected to contain PCDDs, PCDFs, PCBs, and PAHs.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Apparatus and materials other than those specified in this method may achieve equivalent performance. Meeting the performance requirements of this method is the responsibility of the source testing team and laboratory team.

6.1 Sampling Apparatus. Figure 23–1 of this method shows a schematic of the Method 23 sampling train. Do not use sealing greases or brominated flame retardant-coated tape in assembling the train. The train is identical to that described in section 6.1.1 of Method 5 of appendix A–3 to 40 CFR part 60 with the following additions:

6.1.1 Nozzle. The nozzle must be made of quartz or borosilicate glass or titanium. Stainless steel nozzles should not be used.

6.1.2 Probe Liner. Use either polytetrafluoroethylene (PTFE), borosilicate, or quartz glass probe liners with a heating system capable of maintaining a probe gas temperature of 120 ± 14 °C (248 ± 25 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator. Use a PTFE ferrule or single-use PTFE coated O-ring to achieve the seal at the nozzle end of the probe for stack temperatures up to about 300 °C (572 °F). Use a quartz glass liner and integrated quartz nozzle for stack temperatures between 300 and 1,200 °C (572 and 2,192 °F).

6.1.3 Filter Holder. Use a filter holder of borosilicate glass with a PTFE frit or PTFE-coated wire filter support. The holder design should provide a positive seal against leakage from the outside or around the filter. The holder should be durable, easy to load, leak-free in normal applications, and positioned immediately following the probe and cyclone bypass (or cyclone, if used) with the active side of the filter perpendicular to the source of the flow.

6.1.4 Filter Heating System. Use any heating system capable of monitoring and maintaining the temperature around the filter to ensure that the sample gas temperature exiting the filter is 120 ± 14 °C (248 ± 25 °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.5 Filter Temperature Sensor. Install a temperature sensor capable of measuring temperature to within ± 3 °C (5.4 °F) so that the sensing tip protrudes at least 1.3 centimeters (cm) (1–2 in.) into the sample gas exiting the filter. Encase the sensing tip of the sensor in glass or PTFE if needed.

6.1.6 Sample Transfer Line. The sample transfer line transports gaseous emissions from the heated filter holder to the condenser and must be heat traced and constructed of glass or PTFE with connecting fittings that form leak-free, vacuum-tight connections without using sealing greases or tapes. Keep the sample transfer lines as short as possible and maintain the lines at a temperature of 120 °C ± 14 °C (248 °F ± 25 °F) using active heating when necessary. Orient the sample transfer lines with the downstream end lower than the upstream end so that any condensate will flow away from the filter and into the condenser.

6.1.7 Condenser. Glass, water-jacketed, coil-type with compatible fittings. Orient the condenser to cause moisture to flow down to the adsorbent module to facilitate condensate drainage. Figure 23–2 of this method shows a schematic diagram of the condenser.

6.1.8 Water Circulating Bath. Use a bath pump circulating system capable of providing chilled water flow to the condenser and adsorbent module water jackets. Typically, a submersible pump is placed in the impinger ice water bath to circulate the ice water contained in the bath. Verify the function of this system by measuring the gas temperature at the entrance to the adsorbent module. Maintain this temperature at < 20 °C (68 °F).

6.1.9 Adsorbent Module. Use a water-jacketed glass container to hold up to 40 grams (g) of the solid adsorbent. Figure 23–2 of this method shows a schematic diagram of the adsorbent module. Other physical configurations of the adsorbent resin module/condenser assembly are acceptable if the configuration contains the requisite amount of solid adsorbent and maintains the minimum length-to-width adsorbent bed ratio of two-to-one. Orient the adsorbent module vertically to facilitate condensate drainage. The connecting fittings must form leak-free, vacuum-tight seals. Include a coarse glass frit in the adsorbent module to retain the adsorbent.

6.1.10 Impingers. Use five impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger must be a short-stem stem (water-dropout) design or equivalent. The second, fourth, and fifth impingers must be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1–2 in.) inside diameter (ID) glass tube extending to approximately 1.3 cm (1–2 in.) from the bottom of the flask. The third impinger must be of the Greenburg-Smith design with the standard tip. The second and third impingers must contain known quantities of water, and the fifth impinger must contain a known weight of silica gel or equivalent desiccant. Alternatively, you may omit the first impinger if you do not expect excess moisture in the sample gas.

6.2 Sample Recovery Equipment.

6.2.1 Fitting Caps. Use leak-free ground glass fittings or any similar leak-free non-contaminating fitting to cap the sections of the sampling train exposed to the sample gas. Alternatively, use PTFE tape or contaminant-free aluminum foil for this purpose (see Section 6.2.6 of this method).

6.2.2 Wash Bottles. Use PTFE bottles.

6.2.3 Probe-Liner, Probe-Nozzle, and Filter-Holder Brushes. Use inert bristle brushes with precleaned stainless steel or PTFE handles. Extensions of the probe brush must be made of stainless steel or PTFE and be at least as long as the probe. Use brushes that are properly sized and shaped to remove accumulated material from the nozzle and probe liner if used.

6.2.4 Filter Storage Container. Use a sealed filter holder, wide-mouth amber glass jar with PTFE-lined cap, or glass petri dish sealed with PTFE tape. Purchase precleaned amber glass jars and petri dishes or clean according to the glassware cleaning procedures listed in Section 8.1.1.1 of this method.

6.2.5 Field Balance. Use a weighing device capable of measurements to an accuracy of 0.5g.

6.2.6 Aluminum Foil. Use heavy duty aluminum foil cleaned by rinsing three times with hexane or toluene and stored in a pre-cleaned glass petri dish or glass jar. Do not use aluminum foil to wrap or contact filter samples due to the possibility of reaction between the sample and the aluminum.

6.2.7 Adsorbent Storage Containers. Use an air-tight container to store silica gel.

6.2.8 Glass Sample Storage Containers. Recover samples in amber glass bottles, 500- or 1000-milliliters (mL) with leak-free PTFE-lined caps. Either purchase precleaned bottles or clean containers according to glassware cleaning procedures listed in Section 8.1.1.1 of this method.

6.3 Sample Extraction Equipment.

6.3.1 Sample Containers. Use 125- and 250-mL amber glass bottles with PTFE-lined caps.

6.3.2 Test Tubes. Use glass test tubes or small (*e.g.,* 5 to 10 mL) amber vials.

6.3.3 Soxhlet/Dean-Stark Extraction Apparatus.

6.3.3.1 Soxhlet Apparatus. Use 200-mL capacity capable of holding 43 × 123-millimeter (mm) extraction thimbles, with receiving flask (typically round-bottom).

6.3.3.2 Moisture Trap. Use Dean-Stark or Barret with fluoropolymer stopcock trap to fit between the Soxhlet extractor body and the condenser as shown in Figure 23–3 of this method. Note: Dean-Stark or Barret traps are used to remove water with extraction solvents that are less dense and insoluble in water.

6.3.3.3 Extraction Thimble. Use quartz, glass, or glass fiber thimble, typically 43 × 123 mm to fit Soxhlet apparatus.

6.3.3.4 Heating Mantle. Use a hemispherical shaped heating mantle to fit round-bottom flask.

6.3.4 Kuderna-Danish Concentrator. Use an apparatus consisting of a three-ball Snyder column, a flask with leak-free joint to accept the three-ball Snyder column at the top, a leak-free joint to receive a graduated concentration tube at the bottom and a heating mantle.

6.3.5 Nitrogen Evaporative Concentrator. Use a nitrogen evaporative concentrator equipped with a water bath with the temperature controlled in the range of 30 to 60 °C (86 to 140 °F) (N-Evap Organomation Associates, Inc., South Berlin, MA, or equivalent).

6.3.6 Separatory Funnels. Use glass or PTFE 2-liter separatory funnels.

6.4 Glass Liquid Chromatography Columns.

6.4.1 Pasteur Pipettes. Use disposable pipettes, or glass serological pipettes typically 150 mm long × 6 mm ID.

6.4.2 Chromatography Columns. 200 to 300 mm long × 20 mm ID with 250-mL reservoir.

6.5 Analytical Equipment.

6.5.1 Gas Chromatograph. Use a gas chromatograph consisting of the following components:

6.5.1.1 Oven. Use an oven capable of maintaining the separation column at the proper operating temperature ± 1.0 °C (1.8 °F) and performing programmed increases in temperature at rates of at least 20 °C/min with isothermal hold.

6.5.1.2 Temperature Monitor. Use a temperature monitor to measure column oven temperature to ± 1.0 °C (1.8 °F).

6.5.1.3 Flow System. Use an electronic pressure control or equivalent gas metering system to control carrier gas flow or pressure.

6.5.1.4 Use a split/splitless injection port in the splitless mode or on-column injection port for the capillary column.

6.5.2 Capillary Gas Chromatography Columns. Use different columns for the analysis of the different target compound classes in this method, if needed. Perform the resolution checks in Sections 10.2.3.4 and 10.2.3.5 of this method to document the required resolution. Compound separation must meet the resolution specifications in Section 10.2.3.4 of this method and the identification specifications found in Section 11.4.3.4 of this method.

6.5.2.1 Recommended column systems for measuring PCDDs/PCDFs should be capable of achieving separation of the 17 PCDD/PCDF target compounds from the nearest eluting congener with no more than 10 percent peak overlap. The system must meet the performance specifications for compound separation and quantitation in calibration, performance check, and isotopically labeled standards added to field samples. Use a variety of bonded-phase capillary gas chromatography columns to meet these requirements, if needed.

Note: Fishman, et al. (see Section 16.3 of this method) demonstrated that all TEF isomers can be fully differentiated from closely eluting isomers using either of two sets of non-polar and polar stationary phase combinations. One set consisted of 5-percent phenyl methylpolysiloxane (DB–5, HP–5MS, Rtx–5MS, Equity–5) and 50-percent cyanopropylmethyl, 50-percent phenylmethylsiloxane (DB–225, SP 2331) GC columns and the other set consisted of 5-percent phenyl, 94-percent methyl, 1-percent vinyl silicone bonded-phase (DB–5MS, ZB–5MS, VF–5MS, CP–Sil 8 CB LowBleed/MS) with 50-percent cyanopropylmethyl, 50-percent phenylmethylsiloxane (SP–2331).

6.5.2.2 Use column systems for measuring PAHs that can achieve separation of anthracene and phenanthrene at m/z 178 such that the valley between the peaks does not exceed 50 percent of the taller of the two peaks, and benzo[*b*]fluoranthene and benzo[*k*]fluoranthene such that the valley between the peaks is less than 60 percent of the height of the taller peak. These requirements are achievable using a 30-m narrow bore (0.25 mm ID) 5-percent phenyl polysilphenylene-siloxane (BPX5 or equivalent) bonded-phase, fused-silica capillary column.

6.5.2.3 PCB Columns.

6.5.2.3.1 Use column systems for measuring PCBs that can achieve unique resolution and identification of the toxics for determination of a TEQ_{PCB} using TEFs (American Society of Mechanical Engineers 1984). Isomers may be unresolved if they have the same TEF and response factor and if these unresolved isomers are uniquely resolved from all other congeners. These requirements are achievable using several 30-meter (m) narrow bore (0.25 mm ID) columns including 8-percent phenyl polycarborane-siloxane (HT8), DB–XLB, and poly (50-percent n-octyl/50-percent methyl siloxane) (SPB–Octyl).

6.5.2.3.2 If using an SPB-Octyl column for PCB analysis, the column should also uniquely resolve isomers 34 from 23 and 187 from 182. Resolution for these PCBs is shown by the valley between the peaks not exceeding 40 percent of the taller of the two peaks that result when these congeners are analyzed in the same calibration sample.

6.5.3 Mass Spectrometer. Use 28 to 70 electron volt impact ionization capable of repetitive selective monitoring of 12 exact m/z values with a mass resolution defined in section 10.2.1 of this method for fragments in the range of 300 to 350 m/z. The deviation between each monitored mass lock m/z and the monoisotopic m/z (Tables 23–4, 23–5, and 23–6 of this method for PCDDs/PCDFs, PAHs, and PCBs, respectively) must be less than 5 parts per million.

6.5.4 Mass Spectrometer Data System. Use a data system compatible with the mass spectrometer and capable of sequencing and monitoring multiple groups of selected ions.

6.5.5 Analytical Balance. Use an analytical balance to measure within 0.1 milligram (mg).

7.0 Reagents, Media, and Standards

Note: The quality checks described in this section are recommended but not required. They are provided to help ensure data will meet the required performance specifications in Section 13 of this method.

7.1 Filter. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles.

7.1.1 Extraction. Conduct a quality control check on the filter lot prior to the field test to demonstrate that filters are free from contamination or interference. Perform Soxhlet extraction on a minimum of three filters with toluene for 16 hours. After extraction, allow the Soxhlet apparatus to cool. Remove the filters and remove the solvent from the filters under clean conditions (*e.g.,* a clean nitrogen stream).

7.1.2 Analysis. Analyze the individual extracts of a minimum of three filters from each lot used for sampling according to the procedures in Section 11 of this method. The blank filter check analysis must meet the performance requirements in Section 13.14 of this method.

7.2 Adsorbent Resin. Amberlite® XAD–2 resin. All adsorbent resin must meet the cleanliness criteria in Section 13.14 of this method for all target compounds on the analysis list (*i.e.,* native PCDD/PCDF, PCB, and/or PAH) following the same extraction, concentration, cleanup, and analysis steps as field samples. This method recommends using the procedures provided in appendix B to this method to clean the resin before use, if needed. However, this method allows alternative cleanup procedures that use automated extraction equipment if the adsorbent meets the required performance criteria in Section 13.14 of this method.

7.2.1 Conduct a quality control check on the cleaned adsorbent using HRGC/HRMS techniques following procedures in Section 11 of this method. The cleaned adsorbent must meet the criteria in Section 13.14 of this method. A batch blank conducted on the filter and adsorbent lot combination used for a test can serve this purpose.

7.2.2 Storage. Store adsorbent in its original purchase container, a clean wide-mouth amber glass container with a PTFE-lined cap, or in glass adsorbent modules tightly sealed with glass caps.

7.3 Glass Wool. Clean the glass wool to meet the specifications in Section 13.14 of this method. Using sequential immersion in three clean aliquots of toluene, drying in a 110 °C (230 °F) oven, and storing in a toluene-rinsed glass jar with a PTFE-lined screw cap can meet these requirements.

7.4 Water. Use deionized or distilled water meeting requirements in Section 13.14 of this method and store in its original container or in a toluene-rinsed glass container with a PTFE-lined screw cap.

7.5 Silica Gel. Indicating type, 6–16 mesh. If previously used, dry at 175 °C (347 °F) for two hours. Use new silica gel as received. As an alternative, use other types of desiccants (equivalent or better), subject to the approval of the Administrator.

7.6 Methylene Chloride. Pesticide grade or better.

7.7 Sample Recovery Reagents.

7.7.1 Acetone. Pesticide grade or better.

7.7.2 Toluene. Pesticide grade or better.

7.8 Sample Extraction and Cleanup.

7.8.1 Potassium Hydroxide. American Chemical Society (ACS) grade, 2 percent (weight/volume) in water.

7.8.2 Sodium Sulfate. Granulated or powdered, reagent grade. Use as received, include in batch blank evaluation prior to use, or purify as necessary prior to use by rinsing with methylene chloride or toluene and oven drying. The batch blank must meet the requirements in Section 13.14 of this method. Store the cleaned material in a glass container with a PTFE-lined screw cap.

7.8.3 Sulfuric Acid. Reagent grade.

7.8.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

7.8.5 Hexane. Pesticide grade or better.

7.8.6 Methanol. Pesticide grade or better.

7.8.7 Toluene. Pesticide grade or better.

7.8.8 High-Boiling Alkanes Used as Keeper Solvents (*e.g.,* tetradecane, nonane, decane). Pesticide grade. Note: Lower homologous series alkanes (nonane or decane) are necessary for higher volatility targets such as MoCBs and naphthalene to maintain retention during concentration procedures. However, do not take samples to

dryness when using these lower alkane homologs.

7.8.9 Liquid Column Chromatography Packing Materials. Use the following column chromatography packing materials, as needed, to prepare sample extracts and remove interfering compounds. Commercially prepacked cleaning columns may be available for this purpose. All procedures for preparing column chromatography packing materials are recommendations shown to meet the performance specifications required for the recovery of labeled compounds described in Section 13 of this method.

7.8.9.1 Alumina. Use either acidic or basic alumina in the cleanup of sample extracts. Use the same type of alumina for all samples in an analytical sequence, including those used to demonstrate batch blank performance.

7.8.9.1.1 Acidic Alumina (Sigma-Aldrich® 199966 or equivalent). Brockmann activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 12 hours at 130 °C (266 °F). Store in a desiccator. You may use pre-activated alumina purchased from a supplier as received.

7.8.9.1.2 Basic Alumina (Sigma-Aldrich® 19943 or equivalent). Brockmann activity grade 1. Activate by heating to 600 °C (1,112 °F) for a minimum of 24 hours. Do not heat to over 700 °C (1,292 °F) because this can lead to reduced capacity for retaining the analytes. Store at 130 °C (266 °F) in a covered flask. Use within five days of baking. Use prepacked alumina columns immediately after opening the vacuum sealed pouch or container.

7.8.9.2 Florisil®. Activated, 60–100 mesh recommended. Heat previously activated Florisil® in a glass container loosely covered with aluminum foil in an oven at 130 to 150 °C (266 to 302 °F) for a minimum of 24 hours. Upon cooling, store activated Florisil® silica prior to use in a desiccator.

7.8.9.3 Silica Gel. Use either activated, acidic or basic silica gel in the cleanup of sample extracts. Use the same type of silica gel for all samples in an analytical sequence, including those used to demonstrate batch blank performance.

7.8.9.3.1 Activated Silica Gel. Supelco® 1–3651, Bio-Sil® A, 100–200 mesh (or equivalent). Prior to use, rinse with methylene chloride and activate the silica gel by heating for at least 1 hour at 180 °C (356 °F). After cooling, rinse the silica gel sequentially with methanol and toluene. Heat the rinsed silica gel at 50 °C (122 °F) for 10 minutes, then increase the temperature gradually to 180 °C (356 °F) over 25 minutes and maintain the gel at this temperature for 90 minutes. Cool in a desiccator to room temperature and store in a glass container with a PTFE-lined screw cap.

7.8.9.3.2 Acidic Silica Gel (30 percent weight/weight). Combine 100 g of activated silica gel with 44 g of concentrated sulfuric acid in a clean screw-capped glass container and agitate thoroughly. Disperse the solids with a stirring rod until obtaining a uniform mixture. Store the mixture in a glass container with a PTFE-lined screw cap.

7.8.9.3.3 Basic Silica Gel. Combine 30 g of 1 N sodium hydroxide with 100 g of activated silica gel in a clean screw-capped glass container and agitate thoroughly. Disperse solids with a stirring rod until obtaining a uniform mixture. Store the mixture in glass container with a PTFE-lined screw cap.

7.8.9.4 Carbon/Celite® 545 (or equivalent solid support). Use a carbon-based column cleanup material (*e.g.,* one of the many Carbopack® B or C) to remove impurities from the samples prior to analysis. Thoroughly mix 9.0 g Carbopack® C and 41.0 g Celite® 545 to produce an 18-percent weight/weight mixture. Activate the mixture at 130 °C (266 °F) for a minimum of 6 hours. Store in a desiccator.

7.8.10 Nitrogen. 99.999 percent (ultra-high) purity.

7.9 Sample Analysis.

7.9.1 Helium. 99.999 percent (ultra-high) purity.

7.9.2 Spiking Standards. Prepare spiking standards quantitatively at a convenient concentration (*e.g.,*10 nanograms (ng)/mL) or use commercial standards if available, to enable accurate spiking of a labeled standard at various stages of the sample preparation. You may adjust the spiking concentrations from those recommended in Tables 23–7, 23–8 and 23–9 of this method to accommodate the concentration of target compounds anticipated in samples if the performance criteria in Section 13 of this method are met.

7.9.3 Pre-Sampling Recovery Standard Solution. Prepare stock standard solutions in nonane to enable spiking of the isotopically labelled compounds for target compound classes in Tables 23–7, 23–8, and 23–9 of this method at the mass shown under the heading ''Pre-sampling Adsorbent Standards.''

7.9.4 Pre-extraction Filter Recovery Spike Standard Solution. Prepare stock standard solutions in nonane to enable spiking of the isotopically labelled compounds for target compound classes in Tables 23–7, 23–8, and 23–9 of this method at the mass shown under the heading ''Pre-extraction Filter Recovery Spike Standards.''

7.9.5 Pre-extraction Recovery Standard Solution. Prepare stock standard solutions in nonane to enable spiking of the isotopically labelled compounds for target compound classes in Tables 23–7, 23–8, and 23–9 of this method at the mass shown under the heading ''Pre-extraction Standards.''

7.9.6 Pre-analysis Standard Solution. Prepare stock standard solutions in nonane to enable spiking of the isotopically labelled compounds for target compound classes in Tables 23–7, 23–8, and 23–9 of this method at the mass shown under the heading ''Pre-analysis Standards.''

8.0 Sample Collection, Preservation and Storage

8.1 Sampling. This method involves collection and recovery of trace concentrations of semivolatile organic compounds. Therefore, train field sampling and recovery staff in the best practices for handling and using organic solvents in field environments to recover and protect samples from contamination.

8.1.1 Pretest Preparation.

8.1.1.1 Cleaning Glassware. Clean glassware thoroughly before using. This section provides a recommended procedure, but any protocol that consistently results in contamination-free glassware meeting the batch blank criteria in Section 13.2 of this method is acceptable.

8.1.1.1.1 Soak all glassware in hot soapy water (Alconox® or equivalent).

8.1.1.1.2 Rinse with hot tap water.

8.1.1.1.3 Rinse with deionized/distilled water.

8.1.1.1.4 Rinse with methanol.

8.1.1.1.5 Rinse with toluene.

8.1.1.1.6 Baking glassware at 300 °C (572 °F) for a minimum of 2 hours may be necessary to remove contaminants or interferents from particularly dirty samples. Cool glassware after baking.

Note: Repeated baking of glassware may cause active sites on the glass surface that may irreversibly absorb target compounds.

8.1.1.1.7 Cover glassware openings with clean glass fitting caps or cleaned aluminum foil (see Section 6.2.6 of this method).

8.1.1.1.8 Rinse glassware immediately before use with acetone and toluene.

Note: To prepare heavily soiled glassware, remove surface residuals from the glassware by soaking in hot soapy water, rinsing with hot water, then soaking with a non-chromic acid oxidizing cleaning reagent in a strong acid (*e.g.,* NOCHROMIX® prepared according to manufacturer's directions). After the acid soak, rinse with hot water and repeat the

cleaning procedures in Section 8.1.1.1 of this method.

8.1.1.2 Adsorbent Module. Load the modules in a clean area to avoid contamination. Spike modules before the sampling event, but do not spike the modules in the field. Fill a module with 20 to 40 g of XAD–2. Add the pre-sampling standard spike for each of the compound classes to be measured to the top quarter of the adsorbent bed. Add sufficient spike (picograms (pg)/module) to result in the final theoretical concentrations specified in Tables 23–7, 23–8, and 23–9 of this method for PCDDs/PCDFs, PAHs, and PCBs, respectively. For samples with known or anticipated target compound concentration significantly higher or lower than the specified amount in these tables, add a pre-sampling spike amount appropriate to the expected native compound concentration, but no less than 10 times the EDL. Follow the XAD–2 with cleaned glass wool and tightly cap both ends of the module. For analysis that include PAH, use spiked modules within 14 days of preparation. See Table 23–10 of this method for storage conditions.

8.1.1.3 Sampling Train. Figure 23–1 of this method shows the complete sampling train. Follow the best practices by maintaining all sampling train components according to the procedure described in APTD–0576 Maintenance, Calibration, and Operation of Isokinetic Source-sampling Equipment (U.S. EPA 1972).

8.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air-tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container on the outside of each container. As an alternative, directly weigh the silica gel in its impinger or sampling holder just prior to sampling.

8.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container. Do not mark filters with ink or any other contaminating substance.

8.1.2 Preliminary Determinations. Use the procedures specified in Section 8.2 of Method 5 of appendix A–3 to 40 CFR part 60.

8.1.2.1 Sample Volume. Unless otherwise specified in an applicable rule, permit, or other requirement, sample for a minimum of 2 minutes at each traverse point. This method recommends sampling a minimum of 2.5 dry standard cubic meters (dscm).

8.1.2.2 For continuously operating processes, use the same sampling time at each traverse point. To avoid timekeeping errors, use an integer, or an integer plus one-half minute, for each traverse point.

8.1.2.3 For batch processes, determine the minimum operating cycle duration, dividing the sampling time evenly between the required numbers of traverse points. After sampling all traverse points once, sample each point again for the same duration of time per sampling point in reverse order until the operating cycle is completed. Sample all traverse points at least once during each test run.

8.1.3 Preparation of Sampling Train.

8.1.3.1 During field preparation and assembly of the sampling train, keep all train openings where contamination can enter sealed until just prior to assembly or until sampling is about to begin. To protect the adsorbent module from radiant heat and sunlight, you must wrap the module with aluminum foil or other suitable material capable of shielding the module from light. The XAD–2 adsorbent resin temperature must never exceed 50 °C (122 °F) because thermal decomposition will occur. Clean and prepare a complete set of sampling train components that will contact the sample for each sampling run, including one complete set to be used as a field train proof blank as described in Section 9.6 of this method.

8.1.3.2 Place approximately 100 mL of water in the second and third impingers but leave the first and fourth impingers empty. Transfer approximately 200 g or more of silica gel from its container to the fifth impinger. Weigh each impinger and the adsorbent module, including the fitting caps, to the nearest 0.5 g using the field balance and record the weight for moisture determination. Remove the aluminum foil from the adsorbent module before weighing. Keep the module out of direct sunlight and rewrap the module with foil immediately after recording the module weight.

8.1.3.3 Using tweezers or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered, and the gasket properly placed, to prevent the sample gas stream from circumventing the filter. Check the filter for tears after completing the assembly.

8.1.3.4 Prepare the inside of the sampling probe and nozzle by brushing each component while rinsing three times each with acetone and toluene. Install the selected nozzle. You may use connecting systems described in Section 6.1.2 of this method. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as shown in Figure 23–1 of this method. Orient the adsorbent module vertically so condensed moisture drains into the first impinger. See APTD–0576 Maintenance, Calibration, and Operation of Isokinetic Source-sampling Equipment (U.S. EPA 1972) for details.

8.1.3.5 Turn on the recirculation pump to the adsorbent module and condenser coil and begin monitoring the temperature of the gas entering the adsorbent module. Ensure proper temperature of the gas entering the adsorbent module before proceeding.

8.1.4 Leak-Check Procedure. Same as Section 8.4 of Method 5 of appendix A–3 to 40 CFR part 60.

8.1.5 Sampling Train Operation. Same as Sections 8.5.1 through 8.5.9 of Method 5 of appendix A–3 to 40 CFR part 60.

8.1.5.1 Monitor the filter temperature sensor and record the filter temperature during sampling to ensure a sample gas temperature exiting the filter of 120 °C ± 14 °C (248 °F ± 25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for an application of this method.

8.1.5.2 During testing, you must record the temperature of the gas entering the XAD–2 adsorbent module. The temperature of the gas must not exceed 20 °C (68 °F) for efficient capture of the target compounds.

8.2 Sample Recovery. Begin the cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with PTFE tape or clean (*e.g.,* toluene rinsed) aluminum foil. This method recommends using clean glassware prepared following Section 8.1.1.1 of this method for each sample set in a test series.

8.2.1 When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Conduct a post-test leak check. Remove the probe from the train and close off both ends with PTFE tape or clean aluminum foil. Seal off the inlet to the train with PTFE tape, a ground glass cap, or clean aluminum foil.

8.2.2 Transfer the probe and impinger assembly to the cleanup area. This method recommends cleaning and enclosing this area to minimize the chances of losing or contaminating the sample. To avoid sample contamination and unnecessary exposure to toxic chemicals, smoking or eating in the sample recovery area shall not be allowed.

8.2.3 Inspect the train prior to and during disassembly. Note and record

any abnormal conditions (*e.g.,* broken filters, colored impinger liquid). Recover and prepare samples for shipping as follows in Sections 8.2.4 through 8.2.12 of this method.

8.2.4 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. If it is necessary to remove the filter, use a pair of cleaned tweezers to handle the filter. If necessary fold the filter such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry inert bristle brush and a sharp-edged blade. Seal the container and store cool (≤ 20 ± 3 °C, 68 ± 5 °F) for transport to the laboratory.

8.2.5 Adsorbent Module Sample. Remove the module from the train, tightly cover both ends with fitting caps and PTFE tape, remove the foil, drain the recirculating water from the module, weigh and record the module weight, and label the adsorbent module. Moisture measurement in the field using the Method 23 train requires weighing the adsorbent module before the sampling run and after sampling as part of the sample recovery.

8.2.6 Container No. 2. Quantitatively recover material deposited in the nozzle, the front half of the filter holder, and the cyclone, if used, by brushing while rinsing three times with acetone followed by three rinses with toluene. Collect all the rinses in Container No. 2.

8.2.7 Rinse the back half of the filter holder three times with acetone followed by three rinses with toluene. Rinse the sample transfer line between the filter and the condenser three times with acetone followed by three rinses with toluene. If using a separate condenser and adsorbent module, rinse the condenser three times with acetone followed by three rinses with toluene. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

8.2.8 Moisture Weight. Weigh the adsorbent module, impingers, and silica gel impinger to within ± 0.5 g using the field balance and record the weights. This information is required to calculate the moisture content of the effluent gas. For PCDD/PCDF-only measurements, discard the liquid after measuring and recording the weight.

8.2.9 Container No. 3. You must save and analyze impinger water samples if PAHs and/or PCBs are the target compounds. Quantitatively recover impinger water samples for analysis if PAHs and/or PCBs are the target compounds by rinsing three times with acetone followed by three rinses with toluene. Collect impinger water and rinses in Container No. 3 and mark the level of the liquid on the container.

8.2.10 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and report its condition on the field data sheet.

8.2.11 Field Sample Handling, Preservation, Storage, and Transport. Store all field samples temporarily in cool (≤ 20 ± 3 °C, 68 ± 5 °F) and dark conditions prior to transport to the laboratory. Ship samples cool (≤ 20 ± 3 °C, 68 ± 5 °F), shielded from ultraviolet light. In addition, follow the procedures in ASTM D6911–15 (Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis) for all samples, where appropriate. To avoid contamination of the samples, pay special attention to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the adsorbent cartridges.

8.2.12 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. Follow the chain of custody procedures in ASTM D4840–99(2018)e1 (Standard Guide for Sample Chain-of-Custody Procedures) for all samples (including field samples and blanks).

8.3 Sample Storage Conditions and Laboratory Hold Times.

8.3.1 Table 23–10 of this method summarizes the sample storage conditions and laboratory hold times.

8.3.2 Store sampling train rinses and filter samples in the dark at 6 °C (43 °F) or less from the time the laboratory receives the samples until analysis.

8.3.3 You may store adsorbent samples for PCDDs/PCDFs or PCBs prior to extraction in the dark at 6 °C (43 °F) or less for up to one year from the time the laboratory receives the samples.

8.3.4 Protect adsorbent samples destined for PAH analysis from ultraviolet light. You may store adsorbent samples for PAH analysis at 6 °C (43 °F) or less for up to 30 days from the time the laboratory receives the samples.

8.3.5 Analyze PAH extracts within 45 days of extraction.

8.3.6 You may store sample aliquots including archived extracts of PCDD/PCDF, PAH and/or PCB samples in the dark at −10 °C (14 °F) or less for up to one year.

9.0 Quality Control

Note: In recognition of advances that are occurring in sampling and analytical technology, and to allow the test team to overcome analyte sensitivity and matrix interferences, this method allows certain options to increase sample collection volume and to improve separations and the quality of the analysis results for target analytes. It is the laboratory's responsibility to establish the conditions for optimum sample extraction, cleanup, and concentration to meet the performance criteria in this method. However, you may not change the fundamental sampling and analysis techniques, isokinetic sampling with an adsorbent collection media followed by sample extraction, and HRMS detection and isotopic dilution quantification procedures. Section 13 of this method specifies the performance criteria to ensure that options employed for a sample set and analytes of interest are equal to or better than the specificity of the techniques in this method. This method recommends performing a media blank (*i.e.,* batch blank) assessment to evaluate an individual laboratory's performance against the performance criteria in this method. At a minimum, evaluate changes within the alternatives allowed in this method using a media blank sample to re-demonstrate that the performance criteria are achieved.

9.1 Record and report data and information that will allow an independent reviewer to validate the determination of each target compound concentration. At a minimum, record and report the data as described in Sections 9.1.1 through 9.1.7 of this method.

9.1.1 Sample numbers and other sample identifiers. Each sample must have a unique identifier.

9.1.2 Field sample volume.

9.1.3 Field sampling date.

9.1.4 Extraction dates.

9.1.5 Analysis dates and times.

9.1.6 Analysis sequence/run chronology.

9.1.7 Quantitation Reports.

9.1.7.1 This method does not consider EPC-flagged data to be zero concentrations. Calculate the EPC separately for each quantitation ion, if present, and report the lower value as the EPC.

9.1.7.2 In determining compliance with any PCDD and PCDF standard developed using zero for values that are below the detection level of the method, including federal emission standards using Method 23 promulgated under 40 CFR parts 60 and 63 prior to [DATE OF PUBLICATION OF THE FINAL RULE], use zero for the determination of total and weighted concentrations when the target compound is not detected. For all other circumstances, unless otherwise specified in applicable regulations, permits, or other requirements, when a target compound is measured at or below EDL, use EDL as the concentration for calculating compliance.

9.1.7.3 You must report your EDLs with analysis results.

9.1.8 Performance criteria results (See Section 13 of this method).

9.2 Isotopically Labeled Spike Recovery Results.

9.2.1 Pre-sampling Adsorbent Spike and Pre-extraction Filter Spike Recoveries. Pre-sampling adsorbent and pre-extraction filter spike recoveries must demonstrate on a per sample basis that recovery of the labeled standard achieved the requirements in Section 13 of this method. Recoveries below the acceptable range for the pre-sampling spikes may be an indication of breakthrough in the sampling train.

9.2.1.1 If the recovery of all the pre-sampling adsorbent spike standards is below 70 percent, the sampling runs are not valid, and you must repeat the invalid runs. As an alternative, you do not have to repeat the invalid sampling runs if the average pre-sampling adsorbent spike recovery is 25 percent or more and you divide the final results by the average fraction of pre-sampling adsorbent spike recovery.

9.2.1.2 If the recovery of the pre-extraction filter spike is below 70 percent, the filter sampling extraction recovery is not valid, and you must flag the test run results.

9.2.2 Pre-extraction Spike Recoveries. Pre-extraction spike recoveries must demonstrate on a per sample basis that recovery of the labeled standard achieved the requirements in Section 13 of this method. Recoveries below the acceptable range for pre-extraction spikes are an indication that sample preparation procedures did not adequately address sample and or sample matrix processing to recover native target compounds.

9.2.3 Pre-analysis Spike Recoveries. Pre-analysis spike recoveries must demonstrate on a per sample basis that adequate labeled standard signal meets the requirements in Section 13 of this method. Add pre-analysis standards to every sample (including blanks, quality control samples, and calibration solutions) in a known concentration. You may analyze archive samples to attempt meeting requirements for the compounds that do not meet the pre-analysis recovery criteria. Recoveries below the acceptable range for pre-analysis spikes are an indication that sample injection or instrument drift has failed beyond the ability to correct using pre-analysis standard results.

9.3 Capillary GC columns must be able to achieve the separation resolution specified in Sections 13.3, 13.4, and/or 13.5 of this method for the target compounds analyzed in test samples.

9.4 Batch Blank Samples. Evaluate chromatographic separation performance, spiking errors, and continuing calibration checks using a batch blank sample prepared from typical filter and absorbent media, spiked with isotopically labeled compounds and extracted identically to the procedures used to prepare samples. Analyze batch blank samples at least once during each analytical sequence or every 24 hours, whichever period is shorter. Section 13.2 of this method describes the performance criteria for field train proof blank assessment samples and batch blank samples.

9.5 Detection Limits. Calculate the EDL using the equation in Section 12.11 of this method. If the field train proof blank or the batch blank results are above the EDL, calculate and report the test-specific and compound-specific DLs equal to the sum of the EDL and the larger of the batch or field train proof blank results. If the field train proof blank and the batch blank results are equal to or less than the EDL, report the test-specific and compound-specific DLs as the EDL.

9.6 Field Train Proof Blank Assessment. Conduct at least one field train proof blank for each test series at a single facility. A field train proof blank train consists of a fully assembled train at the sampling site. Prepare and assemble the blank train in a manner identical to that described in Sections 8.1.3 and 8.1.4 of this method. The blank train must remain assembled for the same average amount of time samples are collected. Recover the blank train as described in Section 8.2 of this method. Follow all subsequent steps for blank train sample preparation and analysis used for field train samples including data reporting.

10.0 Calibration and Standardization

10.1 Sampling System. Same as Sections 6.1 and 10.1 through 10.7 of Method 5 of appendix A–3 to 40 CFR part 60.

10.2 HRGC/HRMS System.

10.2.1 Mass Resolution. Tune the HRMS instrument to a mass resolution (R) of at least 10,000 at 5 percent of the peak height or 25,000 at 50 percent of the peak height where resolution is calculated as an $R = M/\Delta M$, where M is the resolving power and ΔM is the peak width. You may use peak matching and the chosen perfluoro-kerosene (PFK) or perfluorotributylamine (FC43) reference peak to verify that the exact mass is within 5 ppm of the required value. Assess the resolution at three m/z ranges representing the low, mid and high m/z range of the masses used to measure the target compound class.

10.2.2 Initial Calibration. Calibrate the HRGC/HRMS system using a minimum of five concentrations over a range that brackets typical field sample concentrations and the concentration of isotopically labeled standards in spiked samples. Tables 23–11, 23–12, and/or 23–13 of this method, as applicable to the compound classes analyzed, show the calibration concentrations recommended by this method. Perform calibration and subsequent analyses on an absolute mass (pg/microliter (µL)) basis. The recommended calibration range ensures isotopic labels can be accurately distinguished from native compounds and provides the initial response factors that are corrected by isotopic recovery.

10.2.2.1 Lock Channels. Tables 23–4, 23–5, and 23–6 of this method provide the recommended mass spectrometer lock channels for PCDD/PCDFs, PAHs, and PCBs, respectively. You may use PFK or FC43 as your lock mass standard. Monitor the quality control check channels specified in these tables to verify instrument stability during the analysis. Flag data resulting from failure to maintain lock channel signal during analysis.

10.2.2.2 The relative standard deviation (RSD) for the mean response factor from each of the unlabeled analytes and isotopically labeled compounds used in an analysis must be less than or equal to the values in Table 23–14 of this method.

10.2.2.3 The signal-to-noise (S/N) ratio for the MS signal present in every selected ion current profile must be greater than or equal to 10 in all concentrations of calibration standards for unlabeled targets and isotopically labeled standards. The ion abundance ratios must be within the control limits in Table 23–15 of this method.

10.2.3 Daily Performance Check.

10.2.3.1 Continuing Calibration Check. Inject a mid-level calibration standard C4 from Table 23–11, 23–12, or 23–13 of this method for the compound class being analyzed at least once every 24 hours during an analysis sequence. Calculate the RRF for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRFs for the labeled compounds for a 24-hour period are within the limits of the values shown in Table 23–14 of this method. The RRF for each native compound measured in a CCV must not deviate from the initial calibration by more than the limits shown in this table.

10.2.3.2 The ion abundance ratios must be within the allowable control limits shown in Table 23–15 of this method.

10.2.3.3 Repeat the initial calibration when there is a failure to meet the requirements for acceptable continuing calibration check analysis.

10.2.3.4 Column Separation Check. Use the results from a continuing calibration check sample to verify and document the resolution required in Sections 13.3, 13.4, or 13.5 of this method for the compound classes analyzed with this method.

10.2.3.5 If you use a confirmation column, perform the resolution check in Section 10.2.3.4 of this method to document the required resolution on the confirmation column.

11.0 Analysis Procedure

11.1 Sample Extraction and Concentration. The sample extraction procedures in this method are the same for PCDD, PCDF, PCB and PAH targets. Figure 23–4 provides a flow chart showing sample container combination and extraction steps. Do not allow samples and extracts destined for PAH or PCB analysis to concentrate to dryness because the lower molecular weight PAHs and the mono- through trichlorobiphenyls may be totally or partially lost.

11.1.1 Optional Soxhlet Precleaning. Place an extraction thimble (see Section 6.3.3.3 of this method) and a plug of glass wool into the Soxhlet apparatus equipped with a Dean-Stark trap, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses from sample transfer to the extraction thimble. Retain the clean glass wool plug. Alternatively, confirm that the batch blank for reagents, materials, and media meets the performance requirements in Section 13 of this method.

11.1.2 Container No. 1 (Filter) Preparation. Spike the filter with the appropriate pre-extraction filter recovery standard solution(s) shown in Tables 23–7, 23–8, and 23–9 of this method taking care that all spike liquid is distributed on the filter. Allow the filter to air dry, then transfer the filter and the contents of Container No. 1 directly to the glass extraction thimble in the glass solvent rinse catch beaker so that the filter will be completely immersed in the solvent during extraction.

11.1.3 Adsorbent Module. Transfer the adsorbent material to the glass extraction thimble in the glass solvent rinse catch beaker. Rinse the module into the thimble in the beaker with the contents of Container No. 1. Alternatively, suspend the adsorbent module directly over the extraction thimble in a beaker, then, using a wash bottle containing methanol, flush the XAD–2 into the thimble onto the filter. Thoroughly rinse the interior of the glass module that contained the XAD–2 with toluene.

11.1.4 Container No. 2 (Acetone and Toluene Rinses). Concentrate the sample to a volume of no less than 5 mL. Concentrate samples containing toluene using a heating mantle and three-ball Snyder column or a rotary evaporator. Rinse sample Container No. 2 three times with small portions of toluene and add these to the concentrated solution and concentrate further to no less than 5 mL. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Rinse the concentrated material from Container No. 2 into the glass extraction thimble containing the filter and the XAD–2 resin.

11.1.5 Transfer the solvent contained in the collection beaker to the extraction apparatus solvent reservoir. Rinse the beaker into the Soxhlet extraction apparatus solvent reservoir three times with small portions of toluene.

11.1.6 Container No. 3 (Impinger Water and Rinses). For PAH and PCB analysis, transfer the contents of Container No. 3 to a separatory funnel. Adjust to pH 2 with 6 N sulfuric acid, if necessary. Rinse the sample container with three successive 10-mL aliquots of the toluene and these rinses to the separatory funnel. Extract the sample by vigorously shaking the separatory funnel for 5 minutes. After complete separation of the phases, remove the solvent and filter it through a bed of precleaned, dry sodium sulfate into the Soxhlet extraction apparatus solvent reservoir. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 N sodium hydroxide, re-extract the impinger water and rinses, and filter it through a bed of precleaned, dry sodium sulfate into the Soxhlet extraction apparatus solvent reservoir. Rinse the sodium sulfate into the extraction apparatus solvent reservoir with fresh solvent and discard the desiccant.

11.1.7 Add the appropriate pre-extraction spikes for the compound classes being analyzed (Tables 23–7, 23–8, and 23–9 of this method) to the extraction thimble containing the combined filter and adsorbent sample fractions. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from splashing into the solvent reservoir of the extractor. Place the extraction thimble into the Soxhlet extraction apparatus.

11.1.8 Pour additional toluene to fill the reservoir approximately two-thirds capacity. Add PTFE boiling chips and assemble the apparatus.

11.1.9 Adjust the heat source to cause the extractor to cycle approximately three times per hour. Extract the sample for sufficient time to meet the pre-extraction spike recovery performance criteria in Section 13 of this method. The solvent should cycle completely through the system a minimum of 48 times.

Note: Samples containing high carbon particulate loading, such as those collected downstream of an activated carbon injection system, may require extended extraction time or treatment such as those described in Stieglitz 1986.

11.2 Sample Aliquots for Cleanup and Analysis.

11.2.1 After extraction, allow the Soxhlet apparatus to cool.

11.2.2 Initial Extract Concentration. You may perform an initial concentration of the sample extract using the techniques (*e.g.,* Kuderna Danish, rotary evaporation, nitrogen blowdown) found to recover pre-extraction isotopically labeled compounds sufficient to meet the performance criteria in Section 13 of this method. Concentrate initial extracts in toluene using a heating mantle and three-ball Snyder column or a rotary evaporator. Concentrate the field train proof blank and batch blank samples in the same manner as samples.

Note: For samples requiring PCB or PAH analysis, you should perform the initial concentration using a three-ball Snyder column on the original extraction receiver flask. To meet isotopically label spike recoveries for low molecular weight PAHs and PCBs, do not evaporate samples to dryness.

11.2.3 Allow the sample to cool. You should use a minimum of one half of the sample extract for PCDD/PCDF analysis. You may archive the remaining sample extract or further split the extract for PCB and/or PAH analysis and archive.

11.2.4 If necessary, further concentrate the sample for cleanup and analysis using concentration techniques (*e.g.,* Kuderna Danish, rotary evaporation, nitrogen blowdown) found to recover pre-extraction isotopically labeled compounds sufficient to meet the performance criteria in Section 13 of this method.

11.3 Sample Cleanup and Fractionation. You may process a separate aliquot/split of the sample extract for each of the compound classes

analyzed by this method. Sample cleanup for each compound class may include techniques in addition to column chromatography such as acid/base back-extraction or high-performance liquid chromatography (HPLC) to isolate target compounds from interferences. This section includes a description of column chromatography shown to meet the performance criteria in Sections 9.2 and 13 of this method. The following sample cleanup and fractionation procedures are recommended but not required. You may modify cleanup column dimensions to meet manual or automated cleanup procedures as technology changes and improves. You must evaluate the cleanup and fractionation procedures used to confirm acceptable recovery of isotopically labeled standards. The alternative procedures must provide sufficient cleanup to meet method identification criteria (Section 11.4.3.4 of this method) and recovery criteria (Section 9.2 of this method). Section 13 of this method summarizes the method performance requirements.

Note: Recommendations in this section provide a cleanup approach that may allow multiple compound class measurement from a single aliquot of the original sample extract. Typically, Florisil® and alumina are used to separate PAH and chlorobiphenyl ether compounds from PCDD and PCDF target compounds. Use acid, neutral, and basic silica gel and cleanup procedures to remove nonpolar and polar interferences from samples destined for PCB and PCDD/PCDF analysis. Use Carbopack®/Celite® (or other equivalent carbon-based column material) to remove other nonpolar interferences.

11.3.1 PAH and PCDEs Fractionation and Cleanup. You may use a Florisil® column to remove PAHs and PCDEs from a sample. You may also fractionate samples using Florisil® as the first cleanup step to separate PAH for analysis.

Note: High concentrations of PAHs may interfere with mass spectrometer lock mass or saturate the source, leading to failure of performance criteria for PCDD/PCDF or PCB analysis.

11.3.1.1 Pack a 6-mm ID chromatographic column or equivalent diameter glass pipet with a glass wool plug followed by approximately 1.5 g (approximately 2 mL) of activated Florisil®. Add approximately 1 cm (approximately 1 mL) of anhydrous sodium sulfate followed by a glass wool plug to the head of the column. Pre-elute the column with 10 mL of methylene chloride followed by 10 mL of hexane and discard the eluate.

11.3.1.2 When the solvent is within 1 mm of the packing, transfer the concentrated extract (up to 5 mL) to the top of the Florisil® column, rinse the sample container twice with 1 to 2 mL of hexane, adding each rinse to the column, and elute the column with 35 mL of 5-percent dichloromethane in hexane. This fraction (Fraction 1) should contain target PCBs, and selected hydrocarbons and chlorinated monoaromatic compounds.

11.3.1.3 Elute the column with 35 mL of 15-percent of dichloromethane in hexane and collect the eluate. This fraction (Fraction 2) should contain target PCDD/PCDF compounds.

11.3.1.4 Elute the column with 50 mL of 50-percent dichloromethane in hexane. The fraction (Fraction 3) should contain target PAHs.

11.3.1.5 If necessary to remove any remaining polar organic compounds, elute the column with 70 mL of 15-percent acetone in hexane.

11.3.2 PCDD/PCDF and PCB Fractionation and Cleanup. You may remove PAHs from the original aliquot of extract used for PCDD/PCDF analysis as described in Section 11.3.1 of this method. Design the column cleanup chromatography for PCDD/PCDFs and PCBs such that two consecutive fractions are collected (one with PCDD/PCDFs and one with PCBs) without impacting the DLs. Depending on the source and sample matrix of the original sample, one or more of the following column cleanup approaches may be necessary to remove polyhalogenated diphenyl ethers. You may use any number of permutations found in the referenced literature for this cleanup if the pre-extraction standard recoveries from field and batch blank samples meet the associated performance criteria in Section 13 of this method. Alternatively, you may use an automated cleanup approach that meets the labeled spike recovery requirements in Section 13 of this method.

11.3.2.1 Silica Gel Column Chromatography. Pack one end of a glass column, approximately 20 mm ID x 230 mm long, with glass wool. Add in sequence to the glass column, 1 g of silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g of silica gel, 4 g of acid-modified silica gel, 1 g of silica gel, and 1 cm layer of anhydrous sodium sulfate. Pre-elute the column with 30 to 50 mL of hexane leaving a small quantity of hexane above the sodium sulfate layer. Discard the pre-elution hexane. Add the sample extract, dissolved in 5 mL of hexane to the head of the column. Allow the sample to flow into the column leaving a small quantity of hexane above the sodium sulfate layer. Rinse the extract container with two additional 5-mL rinses of hexane and apply each rinse to the column separately as the previous addition elutes. Elute the column with an additional 90 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 mL using the nitrogen evaporative concentrator (see Section 6.3.5 of this method).

11.3.2.2 Silver Nitrate Silica Gel Column Chromatography. Pack a column (6 mm ID, 150 mm in length) sequentially with 1 g of silica gel and 1 g of 10-percent silver nitrate silica gel followed by a layer of about 10 mm of sodium sulfate (anhydrous). Wash the column sufficiently with hexane, elute until the liquid level reaches to the upper end of the column, and then load the sample solution that is concentrated under vacuum to be about 5 mL. Wash the inner side several times with a small amount of hexane, elute with 200 mL of hexane at a flow rate about 2.5 mL/min (approximately one drop per second) to elute PCDDs.

11.3.2.3 Multi-layer Silica Gel Column Chromatography. You may use a multi-layer silica gel column in place of separate silica columns. Pack a column of 20 mm ID and 300 mm in length sequentially by the dry pack method with 0.9 g of silica gel, 3.0 g of 2-percent potassium hydroxide silica gel, 0.9 g of silica gel, 4.5 g of 44-percent sulfuric acid silica gel, 6.0 g of 22-percent sulfuric acid silica gel, 0.9 g of silica gel, 3.0 g of 10-percent silver nitrate silica gel, 2.0 g of silica gel and 6.0 g of sodium sulfate (anhydrous). Wash the column sufficiently with hexane, elute until the liquid level reaches to the upper end of the column, and then load the sample solution. Wash the inner side of the transfer vessel several times with a small amount of hexane, elute with 150–200 mL of hexane at a flow rate about 2.5 mL/min (approximately one drop per second) to elute PCDDs/PCDFs.

11.3.2.4 Basic Alumina Column Chromatography. Pack a column (20 mm ID, 300 mm in length) with approximately 6 to 12 g of basic alumina. Pre-elute the column with 50 to 100 mL of hexane. Transfer the concentrated extract from the previous column cleanup to the top of the basic alumina column. Allow the sample to flow into the column leaving a small quantity of solvent above the top of the bed. Rinse the extract container with two additional 1-mL rinses of hexane and apply each rinse to the column separately as the previous addition elutes. Elute the column with 100 mL hexane to remove the interferences. Elute the PCDDs/PCDFs from the column with 20 to 40 mL of 50-percent

methylene chloride in hexane. The ratio of methylene chloride to hexane may vary depending on the activity of the alumina used in the column preparation. Do not let the head of the column go without solvent. The first 100 mL hexane eluate is not used for subsequent PCDD/PCDF analysis. The eluate is concentrated to approximately 0.5 mL using the nitrogen evaporative concentrator.

11.3.2.5 Carbopack® C/Celite® 545 Column or Equivalent. Cut both ends from a 10 mL disposable Pasteur pipette (see Section 6.4.1 of this method) 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 Carbopack®/Celite® (see Section 7.8.9.4 of this method) 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. 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. Do not let the head of the column go without solvent. Add 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 the head of the column to complete the transfer. 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. Invert the column and elute the PCDDs/PCDFs with 20 mL of toluene. If carbon particles are present in the eluate, filter through glass-fiber filter paper. Concentrate the eluate to approximately 0.5 mL using the nitrogen evaporative concentrator for further cleanup or analysis by HRGC/HRMS.

11.4 PCDD, PCDF, PCB and PAH Analysis.

11.4.1 Analyze the sample with an HRGC/HRMS using the instrumental parameters in Sections 11.4.2 and 11.4.3 of this method.

11.4.1.1 Immediately prior to analysis, add an aliquot (typically 20 microliters (µl)) of the pre-analysis standard solution(s) from Table 23–7, 23–8, or 23–9 of this method to each sample as appropriate for the compounds you are measuring by this method.

11.4.1.2 Inject an aliquot of the sample extract into the GC. You may perform separate analyses using different GC columns for each of the target compound classes. A 1-µl aliquot of the extract is typically injected into the GC. Perform calibration and analysis for each target compound class using the same sample injection volume and concentration calculations.

11.4.1.2.1 If target compounds are not resolved sufficient from other target compounds or interferences in the sample to meet the requirements in Section 10.2.3.4 or 10.2.3.5 of this method, as applicable to the compound class being analyzed, or as otherwise specified in an applicable regulation, permit, or other requirement, analyze another aliquot of the sample using an alternative column that provides elution order to uniquely quantify the target compounds subject to interference on the first GC column.

11.4.1.2.2 You may use column systems other than those recommended in this method provided the analyst is able to demonstrate, using calibration and performance checks, that the alternative column system is able to meet the applicable specifications of Section 10.2.3.4 or 10.2.3.5 of this method.

11.4.2 Example Gas Chromatograph Operating Conditions.

11.4.2.1 Injector. Configured for capillary column, splitless, 250 °C (482 °F).

11.4.2.2 Carrier Gas. Helium, 1 to 2 mL/min.

11.4.2.3 Oven. Optimize the GC temperature program to achieve the required separation and target compound recovery for the GC column in use. Table 23–16 of this method presents the typical conditions for a DB5–MS column.

11.4.3 High-Resolution Mass Spectrometer.

11.4.3.1 Ionization Mode. Electron ionization.

11.4.3.2 Source Temperature. Maintain the source temperature in the range of 250 to 300 °C (482 to 572 °F).

11.4.3.3 Ion Monitoring Mode. Tables 23–4, 23–5, and 23–6 of this method summarize the various ions to be monitored for PCDD/PCDFs, PAHs, and PCBs, respectively.

11.4.3.4 Identification Criteria for Target Compounds. Use the following identification criteria for the characterization of target compounds in this method. The available native and isotopically labeled standards allow the unique identification of all PCDD/PCDF, PAH, and selected PCB congeners required in this method. Also see Sections 13.12 and 13.13 of this method for identification criteria for PCDD/PCDF/PCB and PAH target compounds, respectively.

11.4.3.4.1 For PCDD/PCDFs and PCBs, Table 23–15 of this method provides the integrated ion abundance ratio of primary and secondary target compound ions for the identification of target compounds. When the ion abundance ratio for a target analyte is outside the performance criteria, you may reanalyze samples on an alternative GC column to resolve chemical interferences, tune the mass spectrometer to operate at a higher mass resolution to discriminate against the interference(s), and/or reprocess an archived sample through the cleanup procedure to remove the interference(s). Report analysis results that do not meet the identification criteria as an estimated maximum possible concentration (EPC). Calculate the EPC separately for each quantitation ion, if present, and report the lower value as the EPC. This method does not consider EPC-flagged data to be zero concentrations.

Note: Some EPCs are caused by poor ion statistics when the concentration of the target compound is at or near the DL. If you use the primary ion to determine and report the target compound concentration in these cases, reanalysis of samples is not necessary.

11.4.3.4.2 The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled pre-extraction standard.

11.4.3.4.3 The signals for the two exact masses in Tables 23–4 and 23–6 of this method for PCDD/PCDFs and PCBs, respectively, must be present and must reach their maximum response within two seconds of each other.

11.4.3.4.4 Identify and quantify specific target compounds or isomers that do not have corresponding ^{13}C-labeled standards by comparing to the pre-extraction labeled standard of the same compound class with the nearest retention time to target compound.

11.4.3.4.5 For the identification of specific PCB isomers, the retention time of the native congener must be within 0.006 relative retention time (RRT) units of the pre-extraction isotopically labeled standard.

11.4.3.4.6 For qualitative identification, the S/N ratio for the GC signal present in every selected ion current profile for native compound response must be greater than or equal to 2.5. The ion abundance ratios must be within the control limits in Table 23–15 of this method for the compound class measured.

11.4.3.4.7 The confirmation of 2,3,7,8–TeCDD and 2,3,7,8–TeCDF must satisfy the separation criteria in Section

10.2.3.4 of this method and all the identification criteria specified in Sections 11.4.3.4.1 through 11.4.3.4.6 of this method.

11.4.3.4.8 Chlorodiphenyl Ether Interference. If chromatographic peaks are detected at the retention time of any PCDDs/PCDF in any of the m/z channels used to monitor chlorodiphenyl ethers, there is evidence of a positive interference and you may opt to flag data noting the interference and keep the value to calculate PCDD/PCDF concentration as EPC or conduct a complete reanalysis to remove or shift the interference. This method recommends alumina (see Section 11.3.2.4 of this method) and Florisil® (see Section 11.3.1 of this method) liquid column chromatography packing materials for removal of chlorodiphenyl ethers during sample cleanup.

11.4.3.4.9 Set the mass spectrometer lock channels as specified in Tables 23–4, 23–5, and 23–6 of this method for PCDD/PCDFs, PAHs, and PCBs, respectively. Monitor the quality control check channels to verify instrument stability during the analysis. If the signal varies by more than 25 percent from the average response, flag results for all isomers at corresponding retention time as QCF. You have the option to conduct additional cleanup procedures on an archived portion of the sample if the archive is available, or dilution the original sample and reanalysis or follow other quality review that demonstrates the target analyte and its corresponding isotopically labeled standard are equally affected by the change in the control check channels. When you conduct a complete reanalysis, reanalyze all concentration calculations based on the reanalyzed sample.

11.4.3.4.10 Identification Criteria for PAHs. The RRT between each native and labeled compound must be within 0.006 RRT units. The signals for the characteristic ion listed in Table 23–5 of this method must be present.

11.4.3.5 Quantitation. Measure the response of each native target compound and the corresponding pre-extraction standard. Use the equation in Section 12.7 of this method to sum the peak areas for the two quantitation ions monitored for each analyte and calculate the mass of the target compound(s) in the injection using the CCV RF. Use the pre-extraction recovery standard compounds to correct the homologous congener results for variations in recovery from the extraction, cleanup, and concentration steps of the analysis. Recovery of pre-extraction standards must meet minimum specifications (in Section 9.2. of this method) to ensure that the method performance and reliability have not been compromised by unacceptable losses during sample processing. Table 23–17 of this method shows the assignments for single isotopically labeled compounds for use in calculating the response factor and the concentrations of PCBs. Recoveries of all labeled standards must meet the minimum recovery specifications in this method and unacceptably low recoveries are an indication of the sample processing step that caused the low recoveries.

11.4.3.5.1 Use Eq. 23–7 to calculate the mass of each target compound or group in the extract.

11.4.3.5.2 Use Eq. 23–8 to calculate the mass per dscm of each target compound or group in the sample.

11.4.3.5.3 Quantify indigenous PCDD and PCDF in its homologous series using the corresponding native and pre-extraction standard response in its homologous series. For example, use $^{13}C_{12}$-2,3,7,8-tetra chlorinated dibenzodioxin to calculate the concentrations of all other tetra chlorinated isomers.

11.4.3.5.4 As an option or as required or specified in applicable regulations, permits, or other requirements, you may quantify any or all other PCB congeners as resolved or coeluting combinations using the response of the nearest eluting native target PCB and the response of the pre-extraction isotopic label assigned in appendix A to this method.

11.4.3.5.5 As an option or as required or specified in applicable regulations, permits, or other requirements, report the total concentration of congeners at a given level of chlorination (homolog; *i.e.,* total TrCB, total PeCB, total HxCB) by summing the concentrations of all congeners identified in the retention time window for the homologs as assigned in appendix A to this method.

11.4.3.5.6 As an option or if required in an applicable regulation, permit or other requirement, total chlorinated biphenyls (CBs) may be reported by summing all congeners identified at all window-defined congeners (WDCs) as assigned in appendix A to this method.

12.0 Data Analysis and Calculations

Note: Same as Section 12 of Method 5 of appendix A–3 to 40 CFR part 60, with the following additions.

12.1 Nomenclature.

Aai = Integrated ion current (area) of the noise for the primary and secondary m/z values at the retention time of the analyte.

A*ci = Integrated ion current (area) of the primary and secondary m/z values of the pre-extraction (internal) standard i in the calibration standard.

$A1_l$ = Integrated ion current of the primary m/z values for the isotopically labeled compound (assigned in Tables 23–4, 23–5, and 23–6 of this method).

$A1_n$ = Integrated ion current of the primary m/z values for the target native compound.

$A2_l$ = Integrated ion current of the secondary m/z's for the isotopically labeled compound. For PAH $A2_l = 0$.

$A2_n$ = Integrated ion current of the secondary m/z values for the target native compound. For PAH $A2_n = 0$.

C_l = The concentration of the labeled compound used to perform isotope recovery correction, pg/µL. Tables 23–4, 23–5, and 23–17 of this method provide the compound mass assignments.

C_n = The concentration of the target native compound, pg/µL.

C_i = Concentration of target native compound i in the sample, pg/µL.

C_{idscm} = Concentration of target native compound i in the emission gas, pg/dscm.

C_{iext} = Concentration of target native compound i in the extract, pg.

C_T = Total concentration of target compounds in the sample, pg/µL.

D = Difference in the RRF of the continuing calibration verification compared to the average RRF of the initial calibration, percent (%).

dscm = Dry standard cubic meters of gas volume sample measured by the dry gas meter, corrected to standard conditions.

H_{ai} = Summed heights of the noise at the retention time of the analyte in the two analyte channels.

H*ci = Summed heights of the noise at the primary and secondary m/z's of the pre-extraction standard i in the calibration standard.

m_i = Mass of compound i, pg.

m^*_i = Mass of pre-extraction (internal standard) compound i, pg.

n = Number of values.

NOAAT = National Oceanic and Atmospheric Administration isotopic labeled congener for PCB of interest.

R* = Recovery of labeled compound standards, %.

RRF_i = Relative response factor of a target compound at calibration level i.

RRF_{ccv} = Relative response factor of a target compound in the continuing calibration verification.

RSD = Relative standard deviation, in this case, of RRFs over the five calibration levels, %.

SD_{RRF} = Standard deviation of initial calibration RRFs.

V_{ext} = Extract volume, µL.

WHOT = World Health Organization acronym used to designate WHO isotopic labeled toxic analog.

WDC = Window-defined congener representing an isotopically labeled PCB that defines the beginning or end of a retention time window bracketing a PCB homolog level of chlorination.

12.2 Individual Compound RRF for Each Calibration Level i. The equation for the response factor of each target native compound relative to its labeled pre-extraction spike analog includes the integrated ion current of both the primary and secondary m/z values for each compound in the calibration standard. Use this equation to calculate the RRF for the continuing calibration verification for comparison to the average RRF from the initial calibration.

$$RRF_i = \frac{(A1_n + A2_n)C_l}{(A1_l + A2_l)C_n} \quad \text{Eq. 23-1}$$

12.3 Average RRF for Each Compound Over the Five Calibration Levels.

$$\overline{RRF} = \frac{1}{n}\sum_{i=1}^{n} RRF_i$$

Eq. 23-2

12.4 Percent RSD of the RRFs for a Compound Over the Five Calibration Levels. The requirement for the initial calibration RSD is in Section 13.10 and Table 23–14 of this method.

$$RSD = \frac{SD_{RRF}}{\overline{RRF}} x\ 100\%$$

Eq. 23-3

12.5 Standard Deviation of the RRFs for a Compound Over the Five Calibration Levels.

$$SD_{RRF} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1}}$$

Eq. 23-4

12.6 Percent Difference of the RRF of the Continuing Calibration Verification Compared to the Average RRF from the Initial Calibration for Each Target Compound. The requirement for the continuing calibration verification percent difference is in Section 13.11 and Table 23–14 of this method.

$$D = \frac{RRF_{ccv} - \overline{RRF}}{\overline{RRF}} x\ 100\%$$

Eq. 23-5

12.7 Concentration of Individual Target Compound i in the Extract by Isotope Dilution (pg/µL). This equation corrects for the target native compound recovery by its labeled pre-extraction spike analog. To accomplish this the pre-extraction spike, labeled compound levels must remain constant.

$$C_i = \left[\frac{C_l\,(A1_n + A2_n)}{(A1_l + A2_l)RRF_{CCV}}\right]$$

Eq. 23-6

12.8 Concentration of the Individual Target Compound i in the Sample Extract (pg).

$$C_{iext} = C_i\, V_{ext} \quad \text{Eq. 23-7}$$

12.9 Mass of the Individual Target Compound or Group i in the Emission Gas (pg/dscm).

$$C_{idscm} = \frac{C_{iext}}{dscm} \quad \text{Eq. 23-8}$$

12.10 Recovery of Labeled Compound Standards. Use this equation to determine the recovery of any labeled compounds, including pre-sampling spikes, pre-extraction filter spike, pre-extraction spikes, pre-analysis spikes. The recovery performance criteria for these spikes is in Sections 13.15, 13.16, and 13.17 of this method.

$$R^* = \frac{conc.\ found}{conc.\ spiked}\ x\ 100\%$$

Eq. 23-9

12.11 Estimated Detectable Limit (EDL).

$$EDL = \frac{2.5\ (H_{ai})\ m*_i}{H*_{ci}\ RRF_i}$$

Eq. 23-10

12.12 Total Concentration.

$$C_T = \frac{1}{n}\sum_{i=1}^{n} C_i \quad \text{Eq. 23-11}$$

Note: Unless otherwise specified in applicable regulations, permits or other requirements, count any target compounds reported as non-detected as EDL when calculating the concentration of target compounds in the sample.

13.0 Method Performance

13.1 Residual Toluene Quality Check. If adsorbent resin is cleaned or recleaned by the laboratory, a quality control check for residual toluene must be ≤1,000 µg/g of adsorbent. See appendix B to this method for procedures to assess residual toluene.

13.2 Field Train Proof Blank and Batch Blank Sample Assessment. Conduct at least one field train proof blank for each test series at a single facility or sampling location. Analyze at least one batch blank sample during an analytical sequence or every 24 hours, whichever is shorter. Native target compound concentrations must be less than or equal to three times the EDL of the method or 10 times lower than the quantitation limit required by the end use of the data, whichever is higher. If blank assessment fails this criterion, flag sample data from this test with explanation that the blank samples failed the method criteria.

13.3 GC column systems used to measure PCDD/PCDFs must meet the column separation requirements in Section 6.5.2.1 of this method and the applicable requirements in Sections 10.2.3.4 and 11.4.3.4 of this method using calibration and batch blank performance checks. Failure to meet this chromatographic resolution criterion requires data from this analysis to be flagged explaining the potential bias of the results. A mid-concentration standard containing all of the native target PCDD/PCDFs may be used to demonstrate this requirement.

13.4 GC column systems used to measure PAHs must meet the column separation requirements in Section 6.5.2.2 of this method and the applicable requirements in Sections 10.2.3.4 and 11.4.3.4 of this method using calibration and batch blank performance checks. Failure to meet this chromatographic resolution criterion requires data from this analysis to be flagged explaining the potential bias of the results.

13.5 GC systems used to measure PCBs must meet the column separation requirements in Section 6.5.2.3 of this method and the applicable requirements in Sections 10.2.3.4 and 11.4.3.4 of this method of this method using calibration and batch blank performance checks, and be able to achieve unique resolution and identification of the toxics for determination of a TEQ_{PCB} using TEFs (American Society of Mechanical Engineers 1984).

13.6 Confirmation Column. If target compounds are not sufficiently resolved from other target compounds or interferences in the sample to meet the requirements for target compounds in Sections 13.3, 13.4, and/or 13.5 of this method, analyze another aliquot of the sample in a separate run using an alternative column that provides elution order to uniquely quantify the target compounds subject to interference on the first GC column.

13.7 Detection Limits. If the DLs as determined in Section 9.5 of this method meet the target DLs shown in Tables 23–18, 23–19, and 23–20 of this method for the target compounds determined with this method, the DLs

are considered acceptable. If the compound specific DLs are less than 50 percent of the emission standard, the DLs are acceptable. If the DL requirements are not met, you must flag native compound data that fails to meet these criteria and provide a description of the impact on the data as part of the quality narrative for the sample analyses.

13.8 Tune. Tune the HRGC/HRMS to meet the isotopic ratio criteria listed in Table 23–15 of this method.

13.9 Lock Channels. MS lock and quality control channels recommended in Tables 23–4, 23–5, and 23–6 of this method for PCDD/PCDFs, PCBs, or PAHs, respectively, must not vary >25 percent from the average response. You may use PFK or perfluorotributylamine (FC43) as your lock mass standard. You may choose lock masses within a SIM descriptor window that demonstrates the least interference. Monitor the quality control check channels specified in these tables to verify instrument stability during the analysis. Flag data resulting from failure to maintain lock channel signal or quality control check signal during analysis (QCF).

13.10 Initial Calibration.

13.10.1 The RSD for mean RRF from each of the target analytes and labeled standards in the calibration samples must not exceed the values in Table 23–14 of this method.

13.10.2 The S/N in every selected ion current profile must be ≥10 for all unlabeled targets and labeled standards in the calibration samples.

13.10.3 The ion abundance ratios must be within the control limits in Table 23–15 of this method.

13.11 Continuing Calibration.

13.11.1 The RRF for each unlabeled and labeled compound measured in a continuing calibration verification must not deviate from the initial calibration by more than the limits shown in Table 23–14 of this method.

13.11.2 The ion abundance ratios must be within the control limits in Table 23–15 of this method.

13.12 Compound Identification for PCDD/PCDFs and PCBs.

13.12.1 Target compounds must have ion abundance ratios within the control limits in Table 23–15 of this method. When the ion abundance ratio for a target analyte is outside the performance criteria, report the results as EPC (see Section 3.7 of this method). PAH target compounds have single ion identifiers with no ion abundance ratio requirement.

13.12.2 Report analysis results that do not meet the identification criteria as an EPC.

13.12.3 The Retention time (RT) for the analytes must be within 3 seconds of the corresponding labeled pre-extraction standard.

13.12.4 The monitored ions, shown in Table 23–4 of this method for a given PCDD/PCDF, must reach their maximum response within 2 seconds of each other.

13.12.5 The monitored ions, shown in Table 23–6 of this method for a given PCB, must reach their maximum response within 2 seconds of each other.

13.12.6 For the identification of specific PCB isomers, the retention time of the native congener must be within 0.006 RRT units of the pre-extraction standard RRT.

13.12.7 The chromatographic overlap of 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,7,8,9-HxCDF peaks with interference peaks must not exceed 25 percent.

13.12.8 Identify and quantify isomers that do not have corresponding labeled pre-extraction standards by comparing to the pre-extraction labeled standard of the same compound class with the nearest RT to the target compound.

13.12.9 If chromatographic peaks are detected at the RT of any PCDD/PCDF in any of the m/z channels used to monitor chlorophenyl ethers, there is evidence of interference and positive bias. Data must be flagged to indicate an interference. You may report the total with bias for the affected target. To reduce the bias, you may use a confirmatory column or perform additional clean up on an archived sample followed by reanalysis.

13.13 Compound Identification for PAHs.

13.13.1 The signals for the characteristic ion listed in Table 23–5 of this method must be present.

13.13.2 The RRT between each native and labeled compound must be within 0.006 RRT units.

13.14 Filter, Adsorbent Resin, Glass Wool, Water and Laboratory Batch Blank Quality Control Check. Target levels must be ≤ three times the EDL of the method or 10 times lower than the quantitation limit required by the end use of the data, whichever is higher.

Note: You must analyze batch blank samples at least once during each analytical sequence or every 24 hours, whichever is shorter.

13.15 Pre-sampling Spike Recovery and Pre-extraction Filter Spike Recovery. Recoveries of all pre-sampling isotopically labeled spike compounds standards added to the sample and all pre-extraction filter recovery spike compounds added to the filter must be between 70 and 130 percent (Tables 23–7, 23–8, and 23–9 of this method).

13.15.1 If the recovery of the pre-sampling spike is below 70 percent, the sampling runs are not valid, and you must repeat the invalid runs. As an alternative, you do not have to repeat the invalid sampling runs if the average pre-sampling adsorbent spike recovery is 25 percent or more and you divide the final results by the average fraction of pre-sampling adsorbent spike recovery.

13.15.2 If the recovery of the pre-extraction filter spike is below 70 percent, the sampling recovery is not valid, and you must flag the test run results.

13.16 Pre-extraction Spike Recovery. Recoveries of all pre-extraction isotopically labeled spike compounds standards added to the sample must be between 20 to 130 percent for PCDD/PCDFs and PAHs (Tables 23–7 and 23–8 of this method) and between 20 to 145 percent for PCBs (Table 23–9 of this method).

13.17 Pre-analysis Spike Sensitivity. Response of all pre-analysis isotopically labeled spike compounds must show a S/N for every selected ion current profile of ≥10. Poor sensitivity compared to initial calibration response may indicate injection errors or instrument drift.

13.18 Requirements for Equivalency. The Administrator considers any modification of this method, beyond those expressly permitted in this method as options, to be a major modification subject to application and approval of alternative test procedures following EPA Guidance Document 22 currently found at: *https://www.epa.gov/emc/emc-guideline-documents.*

13.19 Records. As part of the laboratory's quality system, the laboratory must maintain records of modification to this method.

14.0 Pollution Prevention

The target compounds used as standards in this method are prepared in extremely small amounts and pose little threat to the environment when managed properly. Prepare standards in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

15.0 Waste Management

15.1 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 for protecting the air, water, and land by minimizing and controlling all releases from fume

hoods and bench operations. The laboratory must also comply with any sewage discharge permits and regulations. The EPA's *Environmental Management Guide for Small Laboratories* (EPA 233–B–98–001) provides an overview of requirements.

15.2 Samples containing hydrogen chloride or sulfuric acid to pH <2 are hazardous and must be neutralized before being poured down a drain 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,* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 Bibliography

1. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC. December 1984. 23 p.

2. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington DC. December 1984. 25 p.

3. Fishman, V.N., Martin, G.D. and Lamparski, L.L., Comparison of a variety of gas chromatographic columns with different polarities for the separation of chlorinated dibenzo-p-dioxins and dibenzofurans by high-resolution mass spectrometry, Journal of Chromatography A 1139 (2007) 285–300.

4. International Agency for Research on Cancer. Environmental Carcinogens Methods of Analysis and Exposure Measurement, Volume 11—Polychlorinated Dioxins and Dibenzofurans. IARC Scientific Publications No. 108, 1991.

5. Stieglitz, L., Zwick, G., Roth, W. Investigation of different treatment techniques for PCDD/PCDF in fly ash. Chemosphere 15: 1135–1140; 1986.

6. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.

7. U.S. Environmental Protection Agency. Method 8290—The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW–846.

8. U.S. Environmental Protection Agency. Office of Air Programs Publication No. APTD–0576: Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Research Triangle Park, NC. March 1972.

9. U.S. Environmental Protection Agency. Method 1625C-Semivolatile Organic Compounds by Isotope Dilution GCMS.

10. U.S. Environmental Protection Agency. Method 1613B-Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.

11. U.S. Environmental Protection Agency. Method 1668C-Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS.12. Tondeur, Y., Nestrick, T., Silva, Héctor A., Vining, B., Hart, J. Analytical procedures for the determination of polychlorinated-p-dioxins, polychlorinated dibenzofurans, and hexachlorobenzene in pentachlorophenol, Chemosphere Volume 80, Issue 2, June 2010 pages 157–164.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 23–1—POLYCHLORINATED DIBENZO-P-DIOXIN AND POLYCHLORINATED DIBENZOFURAN TARGET ANALYTES

Polychlorinated dibenzo-p-dioxins	CAS [a] registry number	Polychlorinated dibenzofurans	CAS [a] registry No.
2,3,7,8-TeCDD	1746–01–6	2,3,7,8-TeCDF.	51207–31–9
1,2,3,7,8-PeCDD	40321–76–4	1,2,3,7,8-PeCDF.	57117–41–6
1,2,3,4,7,8-HxCDD	39227–28–6	2,3,4,7,8-PeCDF.	57117–31–4
1,2,3,6,7,8-HxCDD	57653–85–7	1,2,3,4,7,8-HxCDF.	70648–26–9
1,2,3,7,8,9-HxCDD	19408–74–3	1,2,3,6,7,8-HxCDF.	57117–44–9
1,2,3,4,6,7,8-HpCDD	35822–46–9	1,2,3,7,8,9-HxCDF.	72918–21–9
Total TeCDD	41903–57–5	2,3,4,6,7,8-HxCDF.	60851–34–5
Total PeCDD	36088–22–9	1,2,3,4,6,7,8-HpCDF.	67562–39–4
Total HxCDD	34465–4608	1,2,3,4,7,8,9-HpCDF.	55673–89–7
Total HpCDD	37871–00–4	Total TeCDF	55722–27–5
Total OCDD	3268–87–9	Total PeCDF	30402–15–4
		Total HxCDF	55684–94–1
		Total HpCDF	38998–75–3
		Total OCDF ..	39001–02–0

[a] Chemical Abstract Service.

TABLE 23–2—POLYCYCLIC AROMATIC HYDROCARBON TARGET ANALYTES

Polycyclic aromatic hydrocarbons	CAS[a] registry No.	Polycyclic aromatic hydrocarbons	CAS[a] registry No.
Naphthalene	91–20–3	Chrysene	218–01–9
2-Methylnapthalene	91–57–6	Benzo[*b*]fluoranthene	205–99–2
Acenaphthylene	208–96–8	Benzo[*k*]fluoranthene	207–08–9
Acenaphthene	83–32–9	Perylene	198–55–8
Fluorene	86–73–7	Benzo[*a*]pyrene	50–32–8
Anthracene	120–12–7	Benzo[*e*]pyrene	192–92–2
Phenanthrene	85–01–8	Benzo[*g,h,i*]perylene	191–24–2
Fluoranthene	206–44–0	Indeno[*1,2,3-cd*]pyrene	193–39–5
Pyrene	129–00–0	Dibenz[*a,h*]anthracene	53–70–3
Benzo[*a*]anthracene	56–55–3		

[a] Chemical Abstract Service.

TABLE 23–3—POLYCHLORINATED BIPHENYL TARGET ANALYTES

PCB congener	BZ No.[a]	CAS[b] Registry No.	PCB congener	BZ No.[a]	CAS[b] Registry No.
2,4′-DiCB	8	34883–43–7	2,2′,3,3′,4,4′-HxCB	128	38380–07–3
2,2′,5-TrCB	18	37680–65–2	2,2′,3,4,4′,5′-HxCB	138	35065–28–2
2,4,4′-TrCB	28	7012–37–5	2,2′,4,4′,5,5′-HxCB	153	35065–27–1
2,2′,3,5′-TeCB	44	41464–39–5	2,3,3′,4,4′,5-HxCB	156	38380–08–4
2,2′,5,5′-TeCB	52	35693–99–3	2,3,3′,4,4′,5′-HxCB	157	69782–90–7
2,3′,4,4′-TeCB	66	32598–10–0	2,3′,4,4′,5,5′-HxCB	167	52663–72–6
3,3′,4,4′-TeCB	77	32598–13–3	3,3′,4,4′,5,5′-HxCB	169	32774–16–6
3,4,4′,5-TeCB	81	70362–50–4	2,2′,3,3′,4,4′,5-HpCB	170	35065–30–6
2,2′,4,5,5′-PeCB	101	37680–73–2	2,2′,3,4,4′,5,5′-HpCB	180	35065–29–3
2,3,3′,4,4′-PeCB	105	32598–14–4	2,2′,3,4′,5,5′,6-HpCB	187	52663–68–0
2,3,4,4′,5-PeCB	114	74472–37–0	2,3,3′,4,4′,5,5′-HpCB	189	39635–31–9
2,3′,4,4′,5-PeCB	118	31508–00–6	2,2′,3,3′,4,4′,5,6-OcCB	195	52663–78–2
2′,3,4,4′,5-PeCB	123	65510–44–3	2,2′,3,3′,4,4′,5,5′,6-NoCB	206	40186–72–9
3,3′,4,4′,5-PeCB	126	57465–28–8	2,2′,3,3′,4,4′,5,5′,6,6′-DeCB	209	2051–24–3

[a] BZ No.: Ballschmiter and Zell 1980, or International Union of Pure and Applied Chemistry (IUPAC) number.
[b] Chemical Abstract Service.

TABLE 23–4—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH-RESOLUTION MASS SPECTROMETRY FOR PCDDS AND PCDFS

Mass[a]	Ion type[b]	Elemental composition	Target analyte[b]	Mass[a]	Ion type[b]	Elemental composition	Target analyte[b]
263.9871	LOCK	$C_5F_{10}N$	FC43	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S).
292.9825	LOCK	C_7F_{11}	PFK	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S).
303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TeCDF	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD.
305.8987	M+2	$C_{12}H_4{}^{35}Cl^{37}O$	TeCDF	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD.
313.9839	QC	$C_6F_{12}N$	FC43	392.9760	LOCK	C_9F_{15}	PFK.
315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TeCDF (S)	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S).
316.9745	M+2	$^{13}C_{12}H_4{}^{35}Cl_4O$	TeCDF (S)	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S).
317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TeCDF (S)	425.9775	QC	$C_9F_{16}N$	FC43.
319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TeCDD	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE.
321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TeCDD	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF.
325.9839	QC	$C_7F_{12}N$	FC43	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF.
327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TeCDD (S)	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S).
330.9792	QC	C_7F_{13}	PFK	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S).
331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TeCDD (S)	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD.
333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TeCDD (S)	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD.
339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF	430.9729	QC	C_9F_{17}	PFK.
341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S).
354.9792	LOCK	C_9F_{13}	PFK	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S).
351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)	442.9728	LOCK	$C_{10}F_{17}$	PFK.
353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE.
355.8546	M+2	$C_{12}H_3{}^{35}Cl_3{}^{37}ClO_2$	PeCDD	430.9729	LOCK	C_9F_{17}	PFK.
357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF.
367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF.
369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD.
375.9807	QC	$C_8F_{14}N$	FC43	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD.
375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE	463.9743	QC	$C_9F_{18}N$	FC43.
409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S).
373.8208	M+2	$C_{12}H_235Cl_5{}^{37}ClO$	HxCDF	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S).
375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE.
375.9807	QC	$C_8F_{14}N$	FC43	442.9728	QC	$C_{10}F_{17}$	PFK.

[a] The following nuclidic masses were used to calculate exact masses: H = 1.007825, C = 12.000000, ^{13}C = 13.003355, F = 18.9984, O = 15.994915, ^{35}Cl = 34.968853, ^{37}Cl = 36.965903.
[b] (S) = Labeled Standard. QC = Ion selected for monitoring instrument stability during the HRGC/HRMS analysis.

TABLE 23–5—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH-RESOLUTION MASS SPECTROMETRY FOR PAHS

Aromatic ring No.	Mass [a]	Ion type [b]	Elemental composition	Target analyte
2	128.0624	M	$C1_0H_8$	Naphthalene.
	130.9920	LOCK		PFK/FC43.
2	134.0828	M	$^{13}C_6{}^{12}C_4H_8$	$^{13}C_6$-Naphthalene.
2	142.078	M	$C_{11}H_{10}$	2-Methylnaphthalene.
2	148.0984	M	$^{13}C_6{}^{12}C_5H_{10}$	$^{13}C_6$-2-Methylnaphthalene.
2	152.0624	M	$C_{12}H_8$	Acenaphthylene.
2	158.0828	M	$^{13}C_6{}^{12}C_6H_8$	$^{13}C_6$-Acenaphthylene.
2	154.078	M	$C_{12}H_{10}$	Acenaphthene.
2	160.078	M	$^{13}C_6{}^{12}C_6H_{10}$	$^{13}C_6$-Acenaphthene.
2	166.078	M	$C_{13}H_{10}$	Fluorene.
	169.988	QC		PFK/FC43.
2	172.0984	M	$^{13}C_6{}^{12}C_7H$	$^{13}C_6$-Fluorene.
3	178.078	M	$C_{14}H_{10}$	Phenanthrene.
3	184.0984	M	$^{13}C_6$ $^{12}C_8H_{10}$	$^{13}C_6$-Phenanthrene.
3	178.078	M	$C_{14}H_{10}$	Anthracene.
3	184.078	M	$^{13}C_6{}^{12}C_8H_{10}$	$^{13}C_6$-Anthracene.
3	202.078	M	$C_{16}H_{10}$	Fluoranthene.
	204.9888	QC		PFK.
3	208.0984	M	$^{13}C_6{}^{12}C_{10}H_{10}$	$^{13}C_6$-Fluoranthene.
4	202.078	M	$C_{16}H_{10}$	Pyrene.
4	205.078	M	$^{13}C_3{}^{12}C_{13}H_{10}$	$^{13}C_3$-Pyrene.
	213.9898	QC		FC43.
	218.9856	LOCK		FC43.
4	228.0936	M	$C_{18}H_{12}$	Benzo[*a*]anthracene.
	230.9856	LOCK		PFK.
4	234.114	M	$^{13}C_6C_{12}H_{12}$	$^{13}C_6$-Benzo[*a*]anthracene.
4	228.0936	M	$C_{18}H_{12}$	Chrysene.
4	234.114	M	$^{13}C_6{}^{12}C_{12}H_{12}$	$^{13}C_6$-Chrysene.
4	252.0936	M	$C_{20}H_{12}$	Benzo[*b*]fluoranthene.
4	258.114	M	$^{13}C_6{}^{12}C_{14}H_{12}$	$^{13}C_6$-Benzo[*b*]fluoranthene.
4	252.32	M	$C_{20}H_{12}$	Benzo[*k*]fluoranthene.
4	258.114	M	$^{13}C_6{}^{12}7C_{14}H_{12}$	$^{13}C_6$-Benzo[*k*]fluoranthene.
5	252.0936	M	$C_{20}H_{12}$	Benzo[*e*]pyrene.
5	256.1072	M	$^{13}C_4{}^{12}C_{16}H_{12}$	$^{13}C_4$-Benzo[*e*]pyrene.
5	256.1072	M	$^{13}C_4{}^{12}C_{16}H_{12}$	$^{13}C_4$-Benzo[*a*]pyrene.
5	252.0936	M	$C_{20}H_{12}$	Benzo[*a*]pyrene.
5	252.0936	M	$C_{20}H_{12}$	Perylene.
5	264.1692	M	$C_{20}D_{12}$	d_{12}-Perylene.
	268.9824	QC		PFK.
	263.9871	LOCK		FC43.
6	276.0936	M	$C_{22}H_{12}$	Indeno[*1,2,3-cd*]pyrene.
6	282.114	M	$^{13}C_6{}^{12}C_{16}H_{12}$	$^{13}C_6$-Indeno[*1,2,3,cd*]pyrene.
5	278.1092	M	$C_{22}H_{14}$	Dibenz[*a,h*]anthracene.
	280.9824	LOCK		PFK.
5	284.1296	M	$^{13}C_6{}^{12}C_{16}H_{14}$	$^{13}C_6$-Dibenz[*a,h*]anthracene.
6	276.0936	M	$C_{22}H_{12}$	Benzo[*g,h,i*]perylene.
6	288.1344	M	$^{13}C_{12}{}^{12}C_{10}H_{12}$	$^{13}C_{12}$-Benzo[*g,h,i*]perylene.
	313.9839	QC		FC43.

[a] Isotopic masses used for accurate mass calculation: ^1H = 1.0078, ^{12}C = 12.0000, ^{13}C = 13.0034, ^2H = 2.0141.
[b] LOCK = Lock-Mass Ion PFK or FC43. QC = Quality Control Check Ion.

TABLE 23–6—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH-RESOLUTION MASS SPECTROMETRY FOR PCBS

Chlorine substitution	Mass [a]	Ion type [b]	Elemental composition	Target analyte
Fn-1; Cl-1	188.0393	M	$^{12}C_{12}H_9{}^{35}Cl$	Cl-1 PCB
	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	$^{12}C_{12}H_9{}^{37}Cl$	$^{13}C_{12}$Cl-1 PCB
	218.9856	LOCK	C_4F_9	PFK
Fn-2; Cl-2,3	222.0003	M	$^{12}C_{12}H_8{}^{35}C_{l2}$	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	C4 F9	C_4 F_9	PFK
	255.9613	M	$^{12}C_{12}H_7{}^{35}C_{l3}$	Cl-3 PCB
	257.9584	M+2	$^{12}C_{12}H_7{}^{35}C_{l2}{}^{37}Cl$	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; Cl-3,4,5	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
	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	$^{13}C_{12}H_7{}^{35}Cl_2$	$^{13}C_{12}$ 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

TABLE 23–6—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH-RESOLUTION MASS SPECTROMETRY FOR PCBS—Continued

Chlorine substitution	Mass [a]	Ion type [b]	Elemental composition	Target analyte
	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	$^{12}C_{12}H_5{}^{35}Cl_5$	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; Cl-4,5,6	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+2	$^{13}C_{12}H_6{}^{35}Cl_3\ {}^{37}Cl$	$^{13}C_{12}$Cl-4 PCB
	303.9597	M+4	$^{13}C_{12}H_6{}^{35}C_{l2}\ {}^{37}Cl_2$	$^{13}C_{12}$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	$^{13}C_{12}H_4{}^{35}Cl_5$	^{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	$^{12}C_{12}H_4{}^{35}Cl_3\ {}^{37}Cl_3$	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; Cl-5,6,7	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
	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
Fn-6; Cl-7,8,9,10	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
	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	$C_{10}F_{17}$	PFK
	454.9728	LOCK	$C_{11}F_{17}$	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

[a] 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. An interference with PFK m/z 223.9872 may preclude meeting 10:1 S/N for the DiCB congeners at optional Calibration Level 1 (Table 23–12). If this interference occurs, 10:1 S/N must be met at the Calibration Level 2.

[b] LOCK = Lock-Mass Ion PFK or FC43. QC = Quality Control Check Ion.

TABLE 23–7—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARD SOLUTIONS FOR PCDDS AND PCDFS [a]

Compound	Amount (pg/μL of final extract) [b]	Spike recovery (percent)
Pre-sampling Adsorbent Standards		
$^{13}C_{12}$-1,2,3,4-TeCDD	50	70–130
$^{13}C_{12}$-1,2,3,4,7-PeCDD	50	70–130
$^{13}C_{12}$-1,2,3,4,6-PeCDF	50	70–130
$^{13}C_{12}$-1,2,3,4,6,9-HxCDF	50	70–130
$^{13}C_{12}$-1,2,3,4,6,8,9-HpCDF	50	70–130
Pre-extraction Filter Recovery Spike Standards		
$^{13}C_{12}$-1,2,7,8-TeCDF	100	70–130
$^{13}C_{12}$-1,2,3,4,6,8-HxCDD	100	70–130
Pre-extraction Standards		
$^{13}C_{12}$-2,3,7,8-TeCDD	100	20–130
$^{13}C_{12}$-2,3,7,8-TeCDF	100	20–130
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	20–130
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	20–130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	20–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	20–130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	20–130
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	20–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	20–130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	20–130
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	20–130
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	20–130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	20–130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	20–130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	20–130
$^{13}C_{12}$-OCDD	200	20–130
$^{13}C_{12}$-OCDF	200	20–130
Pre-analysis Standards		
$^{13}C_{12}$-1,3,6,8-TeCDD	100	S/N≥10
$^{13}C_{12}$-1,2,3,4-TeCDF	100	S/N≥10
$^{13}C_{12}$-1,2,3,4,6,7-HxCDD	100	S/N≥10
$^{13}C_{12}$-1,2,3,4,6,7,9-HpCDD	100	S/N≥10
Alternate Recovery Standards		
$^{13}C_{12}$-1,3,7,8-TeCDD	100	20–130
$^{13}C_{12}$-1,2,4,7,8-PeCDD	100	20–130

[a] Changes in the amounts of spike standards added to the sample or its representative extract will necessitate an adjustment of the calibration solutions to prevent the introduction of inconsistencies. Spike concentration assumes 1μL sample injection volume for analysis.
[b] Spike levels assume half of the extract will be archived before cleanup. Spike levels may be adjusted for different split levels.

TABLE 23–8—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARD SOLUTIONS FOR PAHS [a]

Compound	Amount (pg/μL of final extract) [b]	Spike recovery (percent)
Pre-sampling Adsorbent Standards		
$^{13}C_6$-Benzo[*c*]fluorene	100	70–130
$^{13}C_{12}$-Benzo[*j*]fluoranthene	100	70–130
Pre-extraction Filter Recovery Spike Standards		
d_{10}-Anthracene	100	70–130
Pre-extraction Standards		
$^{13}C_6$-Naphthalene	100	20–130
$^{13}C_6$-2-Methylnaphthalene	100	20–130
$^{13}C_6$-Acenaphthylene	100	20–130
$^{13}C_6$-Acenaphthene	100	20–130
$^{13}C_6$-Fluorene	100	20–130
$^{13}C_6$-Phenanthrene	100	20–130
$^{13}C_6$-Anthracene	100	20–130
$^{13}C_6$-Fluoranthene	100	20–130
$^{13}C_3$-Pyrene	100	20–130
$^{13}C_6$-Benzo[*a*]anthracene	100	20–130
$^{13}C_6$-^{13}Chrysene	100	20–130
$^{13}C_6$-Benzo[*b*]fluoranthene	100	20–130

TABLE 23–8—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARD SOLUTIONS FOR PAHS [a]—Continued

Compound	Amount (pg/μL of final extract) [b]	Spike recovery (percent)
$^{13}C_6$-Benzo[*k*]fluoranthene	100	20–130
$^{13}C_4$-Benzo[*e*]pyrene	100	20–130
$^{13}C_4$-Benzo[*a*]pyrene	100	20–130
d_{12}-Perylene	100	20–130
$^{13}C_6$-Indeno[*1,2,3-cd*]pyrene	100	20–130
$^{13}C_6$-Dibenz[*a,h*]anthracene	100	20–130
$^{13}C_{12}$-Benzo[*g,h,i*]perylene	100	20–150
Pre-analysis Standards		
d_{10}-Acenaphthene	100	S/N≥10
d_{10}-Pyrene	100	S/N≥10
d_{12}-Benzo[*e*]pyrene	100	S/N≥10

[a] Changes in the amounts of spike standards added to the sample or its representative extract will necessitate an adjustment of the calibration solutions to prevent the introduction of inconsistencies.
[b] Spike levels assume half of the extract will be archived before cleanup. You may adjust spike levels for different split levels.

TABLE 23–9—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARD SOLUTIONS FOR PCBS [a]

Compound	BZ No. [b]	Amount (pg/μL of final extract) [c]	Spike recovery (percent)
Pre-sampling Adsorbent Standards			
$^{13}C_{12}$-3,3′-DiCB	11L	100	70–130
$^{13}C_{12}$-2,4′,5-TrCB	31L	100	70–130
$^{13}C_{12}$-2,2′,3,5′,6-PeCB	95L	100	70–130
$^{13}C_{12}$-2,2′,4,4′,5,5′-HxCB	153L	100	70–130
Pre-extraction Filter Recovery Spike Standards			
$^{13}C_{12}$-2,3,3′,4,5,5′-HxCB	159L	100	70–130
Pre-extraction Standards			
$^{13}C_{12}$-2-MoCB (WDC)	1L	100	20–145
$^{13}C_{12}$-4-MoCB (WDC)	3L	100	20–145
$^{13}C_{12}$-2,2′-DiCB (WDC)	4L	100	20–145
$^{13}C_{12}$-4,4′-DiCB (WDC)	15L	100	20–145
$^{13}C_{12}$-2,2′,6-TrCB (WDC)	19L	100	20–145
$^{13}C_{12}$-3,4′,4′-TrCB (WDC)	37L	100	20–145
$^{13}C_{12}$-2,2′,6,6′-TeCB (WDC)	54L	100	20–145
$^{13}C_{12}$-3,3′,4,4′-TeCB (WDC) (WHOT) (NOAAT)	77L	100	20–145
$^{13}C_{12}$-3,4,4′,5-TeCB (WHOT)	81L	100	20–145
$^{13}C_{12}$-2,2′,4,6,6′-PeCB (WDC)	104L	100	20–145
$^{13}C_{12}$-2,3,3′,4,4′-PeCB (WHOT)	105L	100	20–145
$^{13}C_{12}$-2,3,4,4′,5-PeCB (WHO)	114L	100	20–145
$^{13}C_{12}$-2,3′,4,4′,5-PeCB (WHOT)	118L	100	20–145
$^{13}C_{12}$-2′,3,4,4′,5-PeCB (WHOT)	123L	100	20–145
$^{13}C_{12}$-3,3′,4,4′,5-PeCB (WDC) (WHOT)	126L	100	20–145
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB (WDC)	155L	100	20–145
$^{13}C_{12}$-2,3,3′,4,4′,5-HxCB (WHOT)	156L	100	20–145
$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB (WHOT)	157L	100	20–145
$^{13}C_{12}$-2,3′,4,4′,5,5′-HxCB (WHOT)	167L	100	20–145
$^{13}C_{12}$-3,3′,4,4′,5,5′-HxCB (WDC) (WHOT) (NOAAT)	169L	100	20–145
$^{13}C_{12}$-2,2′,3,3′,4,4′,5′-HpCB (NOAAT)	170L	100	20–145
$^{13}C_{12}$-2,2′,3,4,4′,5,5′-HpCB (NOAAT)	180L	100	20–145
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB (WDC)	188L	100	20–145
$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB (WDC) (WHOT)	189L	100	20–145
$^{13}C_{12}$-2,2′,3′,3′,5,5′,6,6′-OcCB (WDC)	202L	100	20–145
$^{13}C_{12}$-2,3′,3′,4,4′,5,5′,6-OcCB (WDC)	205L	100	20–145
$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′,6-NoCB (WDC)	206L	100	20–145
$^{13}C_{12}$-2,2′,3,3′,4,5,5′,6,6′-NoCB (WDC)	208L	100	20–145
$^{13}C_{12}$-DeCB (WDC)	209L	100	20–145
Pre-analysis Standards			
$^{13}C_{12}$-2,5-DiCB	9L	100	S/N≥10
$^{13}C_{12}$-2,2′,5,5′-TeCB (NOAAT)	52L	100	S/N≥10

TABLE 23–9—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARD SOLUTIONS FOR PCBS [a]—Continued

Compound	BZ No.[b]	Amount (pg/μL of final extract) [c]	Spike recovery (percent)
$^{13}C_{12}$-2,2′,4,5,5′-PeCBl (NOAAT)	101L	100	S/N≥10
$^{13}C_{12}$-2,2′,3,4,4′,5′-HxCB (NOAAT)	138L	100	S/N≥10
$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′-OcCB	194L	100	S/N≥10
Optional Cleanup Spiking Standards			
$^{13}C_{12}$-2-MoCB (NOAAT)	28L	100	20–130
$^{13}C_{12}$-2,2′,4,5,5′-PeCB	111L	100	20–130
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB	178L	100	20–130
Alternate Recovery Standards			
$^{13}C_{12}$-2,3′,4′,5-TeCB	70L	100	20–130
$^{13}C_{12}$-2,3,4,4′-TeCB	60L	100	20–130
$^{13}C_{12}$-3,3′,4,5,5′-PeCB	127L	100	20–130

[a] Changes in the amounts of spike standards added to the sample or its representative extract will necessitate an adjustment of the calibration solutions to prevent the introduction of inconsistencies.
[b] BZ No.: Ballschmiter and Zell 1980, or IUPAC number.
[c] Spike levels assume half of the extract will be archived before cleanup. Spike levels may be adjusted for different split levels.

TABLE 23–10—SAMPLE STORAGE CONDITIONS [a] AND LABORATORY HOLD TIMES [b]

Sample type	PCDD/PCDF	PAH	PCB
Field Storage and Shipping Conditions			
All Field Samples	≤20 ± 5 °C, (68 ± 9 °F)	≤20 ± 5 °C, (68 ± 9 °F)	≤20 ± 5 °C, (68 ± 9 °F).
Laboratory Storage Conditions			
Sampling Train Rinses and Filters	≤6 °C (43 °F)	≤6 °C (43 °F)	≤6 °C (43 °F).
Adsorbent	≤6 °C (43 °F)	≤6 °C (43 °F)	≤6 °C (43 °F).
Extract and Archive	< − 10 °C (14 °F)	< − 10 °C (14 °F)	< − 10 °C (14 °F).
Laboratory Hold Times			
Extract and Archive	One year	45 Days	One year.

[a] All samples must be stored in the dark.
[b] Hold times begin from the time the laboratory receives the samples.

TABLE 23–11—COMPOSITION OF THE INITIAL CALIBRATION STANDARD SOLUTIONS FOR PCDDS AND PCDFS [a]

[pg/μL]

Standard compound	Cal 1 (optional)	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7 (optional)
Target (Unlabeled) Analytes	0.50	1.0	5.0	10.0	25	50	100
Pre-sampling Adsorbent Standards	50	50	50	50	50	50	50
Pre-extraction Filter Recovery Standards	50	50	50	50	50	50	50
Pre-extraction Standards	50	50	50	50	50	50	50
Pre-analysis Standards	50	50	50	50	50	50	50
Alternate Recovery Standards	50	50	50	50	50	50	50

[a] Assumes 1 μL injection volume.

TABLE 23–12—COMPOSITION OF THE INITIAL CALIBRATION STANDARD SOLUTIONS FOR PAHS [a]

[pg/μL]

Standard compound	Cal 1 (optional)	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7 (optional)
Target (Unlabeled) Analytes	1	2	4	20	80	400	1,000
Pre-sampling Adsorbent Standards	100	100	100	100	100	100	100
Pre-extraction Filter Recovery Standards	100	100	100	100	100	100	100
Pre-extraction Standards	100	100	100	100	100	100	100
Pre-analysis Standards	100	100	100	100	100	100	100

[a] Assumes 1 μL injection volume.

TABLE 23–13—COMPOSITION OF THE INITIAL CALIBRATION STANDARD SOLUTIONS FOR PCBS [a]

[pg/μL]

Standard compound	Cal 1 (optional)	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7 (optional)
Target (Unlabeled) Analytes	0.50	1	5	10	50	400	2,000
Pre-sampling Adsorbent Standard(s)	100	100	100	100	100	100	100
Pre-extraction Filter Recovery Standards	100	100	100	100	100	100	100
Pre-extraction Standards	100	100	100	100	100	100	100
Pre-analysis Standards	100	100	100	100	100	100	100
Alternate Standards	100	100	100	100	100	100	100

[a] Assumes 1 μL injection volume.

TABLE 23–14—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS FOR ISOTOPICALLY LABELED AND NATIVE COMPOUNDS

Analyte group	Relative response factors	
	Initial calibration RSD	Daily and continuing calibration (percent difference)
Native (Unlabeled) Analytes	10	25
Pre-sampling Adsorbent Standard(s)	20	25
Pre-extraction Filter Recovery Standards	20	25
Pre-extraction Standards	20	30
Pre-analysis Standards	20	30
Alternative Recovery Standards	20	30

TABLE 23–15—RECOMMENDED ION TYPE AND ACCEPTABLE ION ABUNDANCE RATIOS

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
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
6 [a]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.05	0.89	1.21
7 [b]	M/M+2	0.44	0.37	0.51
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

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 23–16—TYPICAL DB5–MS COLUMN CONDITIONS

Column parameter	Analyte		
	PCDD/PCDF	PAH	PCB
Injector temperature	250 °C	320 °C	270 °C.
Initial oven temperature.	100 °C	100 °C	100 °C.
Initial hold time (minutes).	2	2	2.
Temperature program.	100 to 190 °C at 40 °C/min, then 190 to 300 °C at 3°C/min.	100 to 300 °C at 8°C/min	100 to 150 °C at 15 °C/min, then 150 to 290 °C at 2.5 °C/min.

TABLE 23–17—ASSIGNMENT OF PRE-EXTRACTION STANDARDS FOR QUANTITATION OF TARGET PCBS [b]

PCB congener	BZ No. [a]	Labeled analog	BZ No.
2,4′-DiCB (NOAAT)	8	$^{13}C_{12}$-2,2′-DiCB	4L
2,2′,5-TrCB (NOAAT)	18	$^{13}C_{12}$-2,2′,6-TrCB	19L
2,4,4′-TrCB (NOAAT)	28	$^{13}C_{12}$-2,2′,6-TrCB	19L
2,2′,3,5′-TeCB (NOAAT)	52	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L

TABLE 23–17—ASSIGNMENT OF PRE-EXTRACTION STANDARDS FOR QUANTITATION OF TARGET PCBS [b]—Continued

PCB congener	BZ No. [a]	Labeled analog	BZ No.
2,2′,5,5′-TeCB (NOAAT)	52	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L
2,3′,4,4′-TeCB (NOAAT)	66	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L
3,3′,4,4′-TeCB (NOAAT) (WHOT)	77	$^{13}C_{12}$-3,3′,4,4′-TeCB	77L
3,4,4′,5-TeCB (WHOT)	81	$^{13}C_{12}$-3,4,4'',5-TeCB	81L
2,2′,4,5,5′-PeCB (NOAAT)	101	$^{13}C_{12}$-2,2′,4,5,5′-PeCB	104L
2,3,3′,4,4′-PeCB (NOAAT) (WHOT)	105	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L
2,3,4,4′,5-PeCB (WHOT)	114	$^{13}C_{12}$-2,3,4,4′,5-PeCB	114L
2,3′,4,4′,5-PeCB (WHOT)	118	$^{13}C_{12}$-2,3′,4,4′,5-PeCB	118L
2′,3,4,4′,5-PeCB (WHOT)	123	$^{13}C_{12}$-2′,3,4,4′,5-PeCB	123L
3,3′,4,4′,5-PeCB (NOAAT) (WHOT)	126	$^{13}C_{12}$-3,3′,4,4′,5-PeCB	126L
2,2′,3,3′,4,4′-HxCB (NOAAT)	128	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L
2,2′,3,4,4′,5′-HxCB (NOAAT)	138	$^{13}C_{12}$-2,2′, 4,4′,6,6′-HxCB	155L
2,2′,4,4′,5,5′-HxCB (NOAAT)	153	$^{13}C_{12}$-2,2′, 4,4′,6,6′-HxCB	155L
2,3,3′,4,4′,5-HxCB (WHOT)	156	$^{13}C_{12}$-2,3,3′,4,4′,5-HxCB	156L
2,3,3′,4,4′,5′-HxCB (WHOT)	157	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L
2,3′,4,4′,5,5′-HxCB (WHOT)	167	$^{13}C_{12}$-2,3′,4,4′,5,5′-HxCB	167L
3,3′,4,4′,5,5′-HxCB (NOAAT) (WHOT)	169	$^{13}C_{12}$-3,3′,4,4′,5,5′-HxCB	169L
2,2′,3,3′,4,4′,5-HpCB (NOAA)	170	$^{13}C_{12}$-2,2′,3,3′,4,4′,5′-HpCB	170L
2,2′,3,4,4′,5,5′-HpCB (NOAAT)	180	$^{13}C_{12}$-2,2′,3,4,4′,5,5′-HpCB	180L
2,2′,3,4′,5,5′,6-HpCB (NOAAT)	187	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L
2,3,3′,4,4′,5,5′-HpCB (WHOT)	189	$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB	189L
2,2′,3,3′,4,4′,5,6-OcCB (NOAAT)	195	$^{13}C_{12}$-2,2′ 3,3′,5,5′,6,6′-OcCB	202L
2,2′,3,3′,4,4′,5,5′,6-NoCB (NOAAT)	206	$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′,6-NoCB	206L
2,2′,3,3′,4,4′,5,5′,6,6′-DeCB (NOAAT)	209	$^{13}C_{12}$-DeCB	209L

[a] BZ No.: Ballschmiter and Zell 1980, or IUPAC number.
[b] Assignments assume the use of the SPB-Octyl column. In the event you choose another column, you may select the labeled standard having the same number of chlorine substituents and the closest retention time to the target analyte in question as the labeled standard to use for quantitation.

TABLE 23–18—ESTIMATED METHOD DETECTION LIMITS FOR PCDDS AND PCDFS

Target	MDL [a] (ng/sample)	TEQ–DL (ng/sample)
Total OCDD	1.75E–01	5.00E–05
Total OCDF	5.38E–02	1.51E–05
1,2,3,4,6,7,8-HpCDD	2.36E–02	2.16E–04
1,2,3,4,6,7,8-HpCDF	4.88E–02	4.82E–04
1,2,3,4,7,8-HxCDD	9.26E–03	8.50E–04
1,2,3,4,7,8-HxCDF	6.60E–02	6.48E–03
1,2,3,4,7,8,9-HpCDF	2.46E–02	2.40E–04
1,2,3,6,7,8-HxCDD	1.06E–02	9.86E–04
1,2,3,6,7,8-HxCDF	7.72E–03	7.06E–04
1,2,3,7,8-PeCDD	3.52E–02	3.46E–02
1,2,3,7,8-PeCDF	1.46E–02	4.20E–04
1,2,3,7,8,9-HxCDD	2.70E–02	2.60E–03
1,2,3,7,8,9-HxCDF	6.24E–03	5.54E–04
2,3,4,6,7,8-HxCDF	1.88E–02	1.82E–03
2,3,4,7,8-PeCDF	1.29E–02	3.70E–03
2,3,7,8-TeCDD	2.70E–02	2.68E–02
2,3,7,8-TeCDF	1.80E–02	1.75E–03
Mean DL	2.34E–02	5.48E–03
Sum of DL	2.90E–01	4.11E–02

[a] Detection Limits are based on a survey of laboratories MDL data from Information Collection Requests from the Industrial Boiler and Utility MACT rulemaking process. MDL assumes half of the sample was archived before concentration.

TABLE 23–19—TARGET DETECTION LIMITS FOR PAHS [a]

Target	MDL (ng/sample)
Naphthalene	110.5
2-Methylnaphthalene	36.3
Acenaphthylene	31.4
Acenaphthene	11.3
Fluorene	12.8
Phenanthrene	19.9
Anthracene	11.8
Fluoranthene	9.0
Pyrene	7.6
Benzo[*a*]anthracene	6.2

TABLE 23–19—TARGET DETECTION LIMITS FOR PAHS [a]—Continued

Target	MDL (ng/sample)
Chrysene	6.2
Benzo[*b*]fluoranthene	7.8
Benzo[*k*]fluoranthene	6.4
Benzo[*e*]pyrene	3.3
Benzo[*a*]pyrene	15.9
Perylene	28.3
Indeno[*1,2,3-cd*]pyrene	7.2
Dibenz[*a,h*]anthracene	6.8
Benzo[*g,h,i*]perylene	6.8
Mean DL	23
Sum of DL	435

[a] Detection limits are based on a survey of laboratories MDL data from Information Collection Requests form the Coke Oven and Electric Power Generating unit MACT rulemaking process.

TABLE 23–20—ESTIMATED METHOD DETECTION LIMITS FOR PCBS [a]

Target	BZ No.	Target detection limit (pg/sample)
2,4′-DiCB	8	30
2,2′,5-TrCB	18	32
2,4,4′-TrCB	28	44
2,2′,3,5′-TeCB	44	80
2,2′,5,5′-TeCB	52	30
2,3′,4,4′-TeCB	66	34
3,3′,4,4′-TeCB	77	28
3,4,4′,5-TeCB	81	36
2,2′,4,5,5′-PeCB	101	94
2,3,3′,4,4′-PeCB	105	34
2,3,4,4′,5-PeCB	114	30
2,3′,4,4′,5-PeCB	118	60
2′,3,4,4′,5-PeCB	123	34
3,3′,4,4′,5-PeCB	126	32
2,2′,3,3′,4,4′-HxCB	128	58
2,2′,3,4,4′,5′-HxCB	138	72
2,2′,4,4′,5,5′-HxCB	153	60
2,3,3′,4,4′,5-HxCB	156	46
2,3,3′,4,4′,5′-HxCB	157	46
2,3′,4,4′,5,5′-HxCB	167	26
3,3′,4,4′,5,5′-HxCB	169	30
2,2′,3,3′,4,4′,5-HpCB	170	24
2,2′,3,4,4′,5,5′-HpCB	180	60
2,2′,3,4′,5,5′,6-HpCB	187	34
2,3,3′,4,4′,5,5′-HpCB	189	26
2,2′,3,3′,4,4′,5,6-OcCB	195	44
2,2′,3,3′,4,4′,5,5′,6-NoCB	206	32
2,2′,3,3′,4,4′,5,5′,6,6′-DeCB	209	32
Mean DL	.....	42
Sum of DL	.....	1,188

[a] Detection Limits are based on information from EPA Method 1668C, assuming half of the sample extract is archived before concentration.

BILLING CODE 6560–50–P

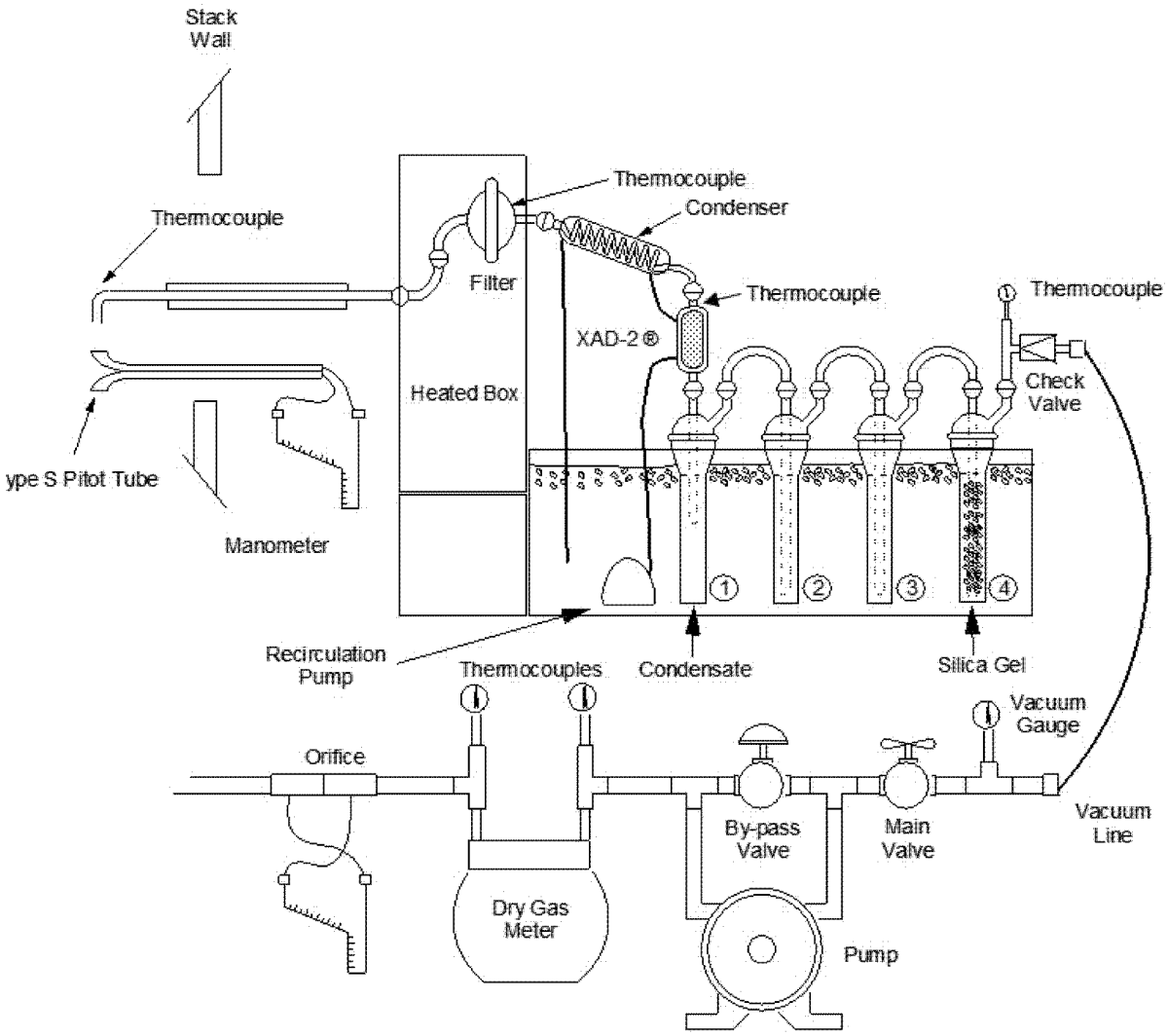

Figure 23-1. Method 23 Sampling Train

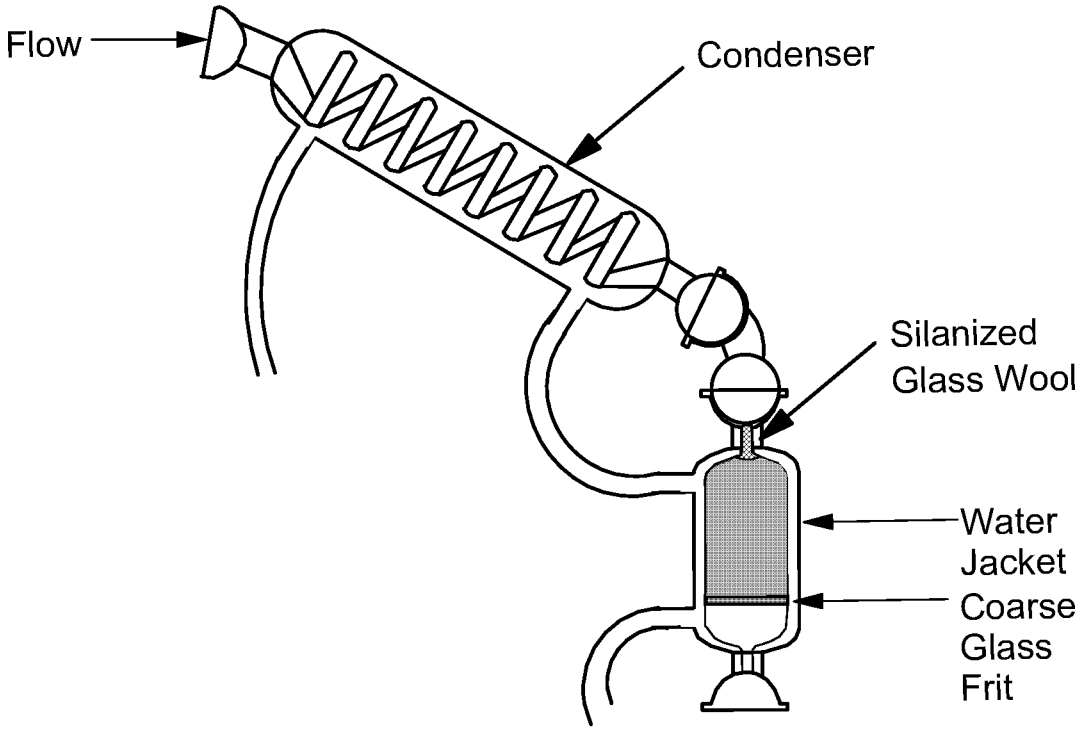

Figure 23–2. Condenser and Adsorbent Module

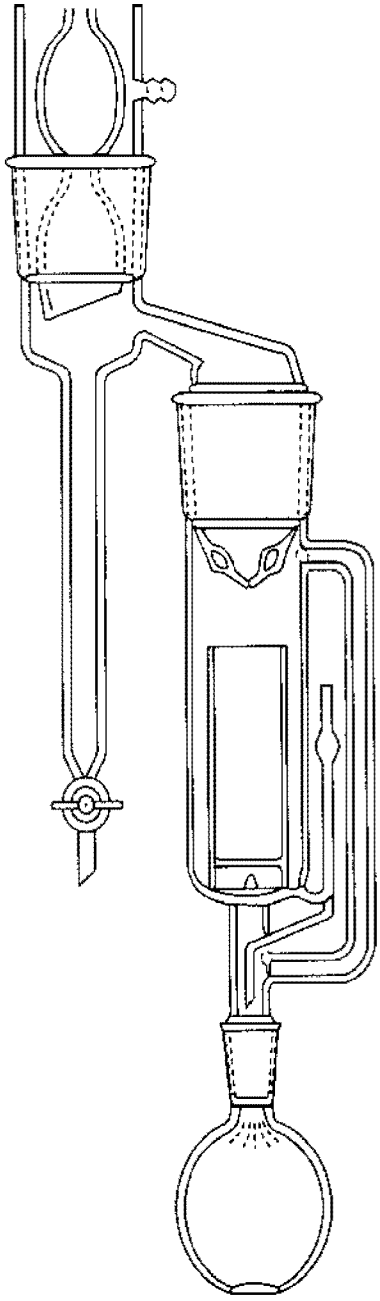

Figure 23–3. Soxhlet/Dean-Stark Extractor

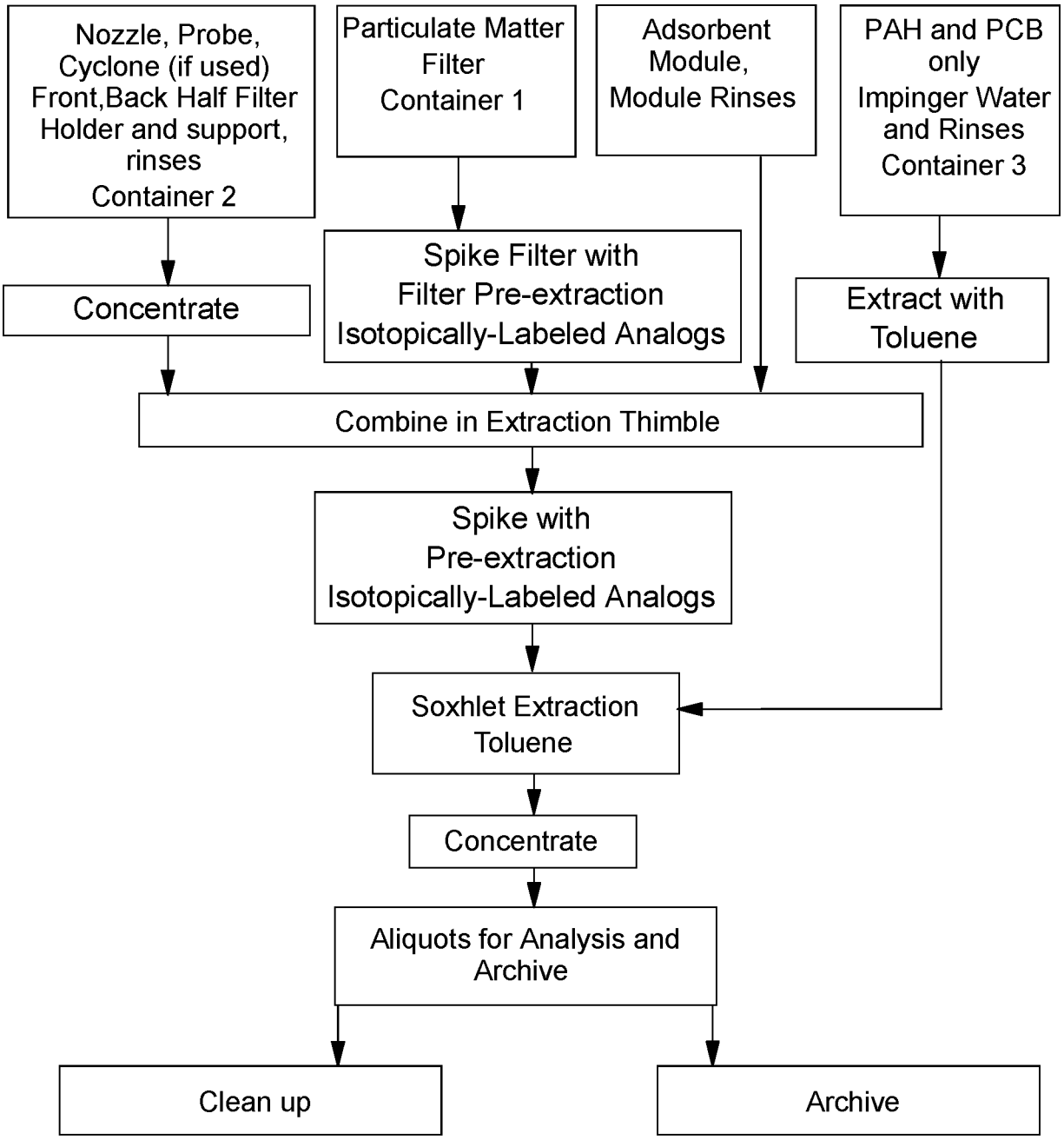

Figure 23–4. Sample Preparation Flow Chart

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Appendix A to Method 23

COMPLETE LIST OF 209 PCB CONGENERS AND THEIR ISOMERS WITH CORRESPONDING ISOTOPE DILUTION QUANTITATION STANDARDS [a]

Pre-extraction standard	BZ [b] No.	Unlabeled target analyte	BZ [b] No.	Pre-extraction standard	BZ [b] No.	Unlabeled target analyte	BZ [b] No.
MoCBs				**DiCBs**			
$^{13}C_{12}$-2-MoCB	1L	2-MoCB	1	$^{13}C_{12}$-2,2′-DiCB	4L	2,2′-DiCB	4
$^{13}C_{12}$-2-MoCB	1L	3-MoCB	2	$^{13}C_{12}$-2,2′-DiCB	4L	2,3-DiCB	5
$^{13}C_{12}$-4-MoCB	3L	4-MoCB	3	$^{13}C_{12}$-2,2′-DiCB	4L	2,3′-DiCB	6
				$^{13}C_{12}$-2,2′-DiCB	4L	2,4-DiCB	7
				$^{13}C_{12}$-2,2′-DiCB	4L	2,4′-DiCB	8
				$^{13}C_{12}$-2,2′-DiCB	4L	2,5-DiCB	9
				$^{13}C_{12}$-2,2′-DiCB	4L	2,6-DiCB	10
				$^{13}C_{12}$-2,2′-DiCB	4L	3,3′-DiCB	11
				$^{13}C_{12}$-2,2′-DiCB	4L	3,4-DiCB	12
				$^{13}C_{12}$-2,2′-DiCB	4L	3,4′-DiCB	13
				$^{13}C_{12}$-2,2′-DiCB	4L	3,5-DiCB	14
				$^{13}C_{12}$-4,4′-DiCB	15L	4,4′-DiCB	15
TrCBs							
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,2′,3-TrCBTrCB	16	$^{13}C_{12}$-3,4,4′-TrCB	19L	2,4,4′-TrCB	28
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,2′,4-TrCB	17	$^{13}C_{12}$-3,4,4′-TrCB	19L	2,4,5-TrCB	29
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,2′,5-TrCB	18	$^{13}C_{12}$-3,4,4′-TrCB	19L	2,4,6-TrCB	30
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,2′,6-TrCB	19	$^{13}C_{12}$-3,4,4′-TrCB	19L	2,4′,5-TrCB	31
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3,3′-TrCB	20	$^{13}C_{12}$-3,4,4′-TrCB	19L	2,4′,6-TrCB	32
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3,4-TrCB	21	$^{13}C_{12}$-3,4,4′-TrCB	19L	2′,3,4-TrCB	33
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3,4′-TrCB	22	$^{13}C_{12}$-3,4,4′-TrCB	19L	2′,3,5-TrCB	34
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3,5- TrCB	23	$^{13}C_{12}$-3,4,4′-TrCB	19L	3,3′,4-TrCB	35
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3,6- TrCB	23	$^{13}C_{12}$-3,4,4′-TrCB	19L	3,3′,5-TrCB	36
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3′,4-TrCB	25	$^{13}C_{12}$-3,4′,4′-TrCB	37L	3,4,4′-TrCB	37
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3′,5-TrCB	26	$^{13}C_{12}$-3,4′,4′-TrCB	37L	3,4,5-TrCB	38
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,3′,6-TrCB	27	$^{13}C_{12}$-3,4′,4′-TrCB	37L	3,4′,5-TrCB	39
TeCBs							
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,3′-TeCB	40	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,4,5-TeCB	61
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,4-TeCB	41	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,4,6-TeCB	62
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,4′-TeCB	42	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,4′,5-TeCB	63
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,5-TeCB	43	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,4′,6-TeCB	64
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,5′-TeCB	44	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,5,6-TeCB	65
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,6-TeCB	45	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,4,4′-TeCB	66
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,3,6′-TeCB	46	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,4,5-TeCB	67
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,4,4′-TeCB	47	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,4,5′-TeCB	68
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,4,5-TeCB	48	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,4,6-TeCB	69
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,4,5′-TeCB	49	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,4′,5-TeCB	70
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,4,6-TeCB	50	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,4′,6-TeCB	71
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,4,6′-TeCB	51	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,5,5′-TeCB	72
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,5,5′-TeCB	52	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3′,5′,6-TeCB	73
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,5,6′-TeCB	53	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,4,4′,5-TeCB	74
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,2′,6,6′-TeCB	54	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,4,4′,6-TeCB	75
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,3′,4′-TeCB	55	$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2′,3,4,5-TeCB	76
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,3′,4′-TeCB	56	$^{13}C_{12}$-3,3′,4,4′-TeCB	77L	3,3′,4,4′-TeCB	77
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,3′,5-TeCB	57	$^{13}C_{12}$-3,3′,4,4′-TeCB	77L	3,3′,4,5-TeCB	78
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,3′,5′-TeCB	58	$^{13}C_{12}$-3,3′,4,4′-TeCB	77L	3,3′,4,5′-TeCB	79
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,3′,6-TeCB	59	$^{13}C_{12}$-3,3′,4,4′-TeCB	77L	3,3′,5,5′-TeCB	80
$^{13}C_{12}$-2,2′,6,6′-TeCB	54L	2,3,4,4′-TeCB	60	$^{13}C_{12}$-3,4,4′,5-TeCB	81L	3,4,4′,5-TeCB	81
PeCBs							
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,3′,4-PeCB	82	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,4,4′-PeCB	105
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,3′,5-PeCB	83	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,4,5-PeCB	106
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,3′,6-PeCB	84	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,4′,5-PeCB	107
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4,4′-PeCB	85	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,4,5′-PeCB	108
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4,5-PeCB	86	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,4,6-PeCB	109
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4,5′-PeCB	87	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,4′,6-PeCB	110
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4,6-PeCB	88	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,5,5′-PeCB	111
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4,6′-PeCB	89	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,5,6-PeCB	112
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4′,5-PeCB	90	$^{13}C_{12}$-2,3,3′,4,4′-PeCB	105L	2,3,3′,5′,6-PeCB	113
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,4′,6-PeCB	91	$^{13}C_{12}$-2,3,4,4′,5-PeCB	114L	2,3,4,4′,5-PeCB	114
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,5,5′-PeCB	92	$^{13}C_{12}$-2,3,4,4′,5-PeCB	114L	2,3,4,4′,6-PeCB	115
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,5,6-PeCB	93	$^{13}C_{12}$-2,3,4,4′,5-PeCB	114L	2,3,4,5,6-PeCB	116
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,5,6′-PeCB	94	$^{13}C_{12}$-2,3,4,4′,5-PeCB	114L	2,3,4′,5,6-PeCB	117
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,5′,6-PeCB	95	$^{13}C_{12}$-2,3′,4,4′,5-PeCB	118L	2,3′,4,4′,5-PeCB	118
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3,6,6′-PeCB	96	$^{13}C_{12}$-2,3′,4,4′,5-PeCB	118L	2,3′,4,4′,6-PeCB	119
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3′,4,5-PeCB	97	$^{13}C_{12}$-2,3′,4,4′,5-PeCB	118L	2,3′,4,5,5′-PeCB	120
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,3′,4,6-PeCB	98	$^{13}C_{12}$-2,3′,4,4′,5-PeCB	118L	2,3′,4,5,′6-PeCB	121
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,4,4′,5-PeCB	99	$^{13}C_{12}$-2,3′,4,4′,5-PeCB	118L	2′,3,3′,4,5-PeCB	122
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,4,4′,6-PeCB	100	$^{13}C_{12}$-2′,3,4,4′,5-PeCB	123L	2′,3,4,4′,5-PeCB	123
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,4,5,5′-PeCB	101	$^{13}C_{12}$-2′,3,4,4′,5-PeCB	123L	2′,3,4,5,5′-PeCB	124
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,4,5,6′-PeCB	102	$^{13}C_{12}$-2′,3,4,4′,5-PeCB	123L	2′,3,4,5,6′-PeCB	125
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,4,5,′6-PeCB	103	$^{13}C_{12}$-3,3′,4,4′,5-PeCB	126L	3,3′,4,4′,5-PeCB	126
$^{13}C_{12}$-2,2′,4,6,6′-PeCB	104L	2,2′,4,6,6′-PeCB	104	$^{13}C_{12}$-3,3′,4,4′,5-PeCB	126L	3,3′,4,5,5′-PeCB	127

COMPLETE LIST OF 209 PCB CONGENERS AND THEIR ISOMERS WITH CORRESPONDING ISOTOPE DILUTION QUANTITATION STANDARDS [a]—Continued

Pre-extraction standard	BZ [b] No.	Unlabeled target analyte	BZ [b] No.	Pre-extraction standard	BZ [b] No.	Unlabeled target analyte	BZ [b] No.
HxCBs							
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,4,4′-HxCB	128	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4′,5′,6-HxCB	149
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,4,5-HxCB	129	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4′,6,6′-HxCB	150
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,4,5′-HxCB	130	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,5,5′,6-HxCB	151
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,4,6-HxCB	131	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,5,6,6′-HxCB	152
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,4,6′-HxCB	132	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,4,4′,5,5′-HxCB	153
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,5,5′-HxCB	133	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,4,4′,5′,6-HxCB	154
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,5,6-HxCB	134	$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,4,4′,6,6′-HxCB	155
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,5,6′-HxCB	135	$^{13}C_{12}$-2,3,3′,4,4′,5- HxCB	156L	2,3,3′,4,4′,5-HxCB	156
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,3′,6,6′-HxCB	136	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4,4′,5′-HxCB	157
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,4′,5-HxCB	137	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4,4′,6-HxCB	158
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,4′,5′-HxCB	138	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4,5,5′-HxCB	158
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,4′,6-HxCB	139	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4,5,6-HxCB	160
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,4′,6′-HxCB	140	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4,5′,6-HxCB	161
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,5,5′-HxCB	141	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4′,5,5′-HxCB	162
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,5,6-HxCB	142	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4′,5,6-HxCB	163
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,5,6′-HxCB	143	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,4′,5′,6-HxCB	164
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,5′,6-HxCB	144	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,3′,5,5′,6-HxCB	165
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4,6,6′-HxCB	145	$^{13}C_{12}$-2,3,3′,4,4′,5′-HxCB	157L	2,3,4,4′,5,6-HxCB	166
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4′,5,5′-HxCB	146	$^{13}C_{12}$-2,3′,4,4′,5,5′-HxCB	167L	2,3′,4,4′,5,5′-HxCB	167
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4′,5,6-HxCB	147	$^{13}C_{12}$-2,3′,4,4′,5,5′-HxCB	167L	2,3′,4,4′,5′,6-HxCB	168
$^{13}C_{12}$-2,2′,4,4′,6,6′-HxCB	155L	2,2′,3,4′,5,6′-HxCB	148	$^{13}C_{12}$-3,3′,4,4′,5,5′-HxCB	169L	3,3′,4,4′,5,5′-HxCB	169
HpCBs							
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,4′,5-HpCB	170	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,4′,5,6′-HpCB	182
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,4′,6-HpCB	171	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,4′,5′,6-HpCB	183
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,5,5′-HpCB	172	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,4′,5′,6-HpCB	184
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,5,6-HpCB	173	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,4′,6,6′-HpCB	185
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,5,6′-HpCB	174	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,5,5′,6-HpCB	186
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,5′,6-HpCB	175	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4′,5,5′,6-HpCB	187
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4,6,6′-HpCB	176	$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4′,5,6,6′-HpCB	188
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,4′,5,6-HpCB	177	$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB	189L	2,3,3′,4,4′,5,5′-HpCB	189
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,5,5′,6-HpCB	178	$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB	189L	2,3,3′,4,4′,5,6-HpCB	190
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,3′,5,6,6′-HpCB	179	$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB	189L	2,3,3′,4,4′,5′,6-HpCB	191
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,4′,5,5′-HpCB	180	$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB	189L	2,3,3′,4,5,5′,6-HpCB	192
$^{13}C_{12}$-2,2′,3,4′,5,6,6′-HpCB	188L	2,2′,3,4,4′,5,6-HpCB	181	$^{13}C_{12}$-2,3,3′,4,4′,5,5′-HpCB	189L	2,3,3′,4′,5,5′,6-HpCB	193
OcCBs				**NoCBs**			
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,4′,5,5′-OcCB	194	$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′,6-NoCB.	206L	2,2′,3,3′,4,4′,5,5′,6-NoCB	206
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,4′,5,6-OcCB	195	$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′,6-NoCB.	206L	2,2′,3,3′,4,4′,5,6,6′-NoCB	207
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,4′,5,6′-OcCB	196	$^{13}C_{12}$-2,2′,3,3′,4,5,5′,6,6′-NoCB.	208L	2,2′,3,3′,4,5,5′,6,6′- NoCB	208
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,4′,6,6′-OcCB	197	**DeCB**			
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,5,5′,6-OcCB	198	$^{13}C_{12}$-DeCB	209L	2,2′,3,3′,4,4′,5,5′,6,6′-DeCB	209
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,5,5′,6′-OcCB	199				
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,5,6,6′-OcCB	200				
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,4,5′,6,6′-OcCB	201				
$^{13}C_{12}$-2,2′,3,3′,5,5′,6,6′-OcCB.	202L	2,2′,3,3′,5,5′,6,6′-OcCB	202				
$^{13}C_{12}$-2,3′,3′,4,4′,5,5′,6-OcCB.	205L	2,2′,3,4,4′,5,5′,6-OcCB	203				
$^{13}C_{12}$-2,3′,3′,4,4′,5,5′,6-OcCB.	205L	2,2′,3,4,4′,5,6,6′-OcCB	204				
$^{13}C_{12}$-2,3′,3′,4,4′,5,5′,6-OcCB.	205L	2,3,3′,4,4′,5,5′,6-OcCB	205				

[a] Assignments assume the use of the SPB-Octyl column. In the event you choose another column, you may select the labeled standard having the same number of chlorine substituents and the closest retention time to the target analyte in question as the labeled standard to use for quantitation.

[b] BZ No.: Ballschmiter and Zell 1980, also referred to as IUPAC number.

Appendix B to Method 23

Preparation of XAD–2 Adsorbent Resin

1.0 Scope and Application

XAD–2® resin, as supplied by the original manufacturer, is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Remove both the salt solution and any residual extractable chemicals used in the polymerization process before use. Prepare the resin by a series of water and organic extractions, followed by careful drying.

2.0 Extraction

2.1 You may perform the extraction using a Soxhlet extractor or other apparatus that generates resin meeting the requirements in Section 13.14 of Method 23. Use an all-glass thimble containing an extra-coarse frit for extraction of the resin. The frit is recessed 10–15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. Because the resin floats on methylene chloride, carefully retain the resin in the extractor cup with a glass wool plug and stainless-steel screen. This process involves sequential extraction with the following recommended solvents in the listed order.

- Water initial rinse: Place resin in a suitable container, soak for approximately 5 min with Type II water, remove fine floating resin particles and discard the water. Fill with Type II water a second time, let stand overnight, remove fine floating resin particles and discard the water.
- Hot water: Extract with water for 8 hr.
- Methyl alcohol: Extract for 22 hr.
- Methylene chloride: Extract for 22 hr.
- Toluene: Extract for 22 hr.
- Toluene (fresh): Extract for 22 hr.

Note: You may store the resin in a sealed glass container filled with toluene prior to the final toluene extraction. It may be necessary to repeat the final toluene extractions to meet the requirements in Section 13.14 of Method 23.

2.2 You may use alternative extraction procedures to clean large batches of resin. Any size extractor may be constructed; the choice depends on the needs of the sampling programs. The resin is held in a glass or stainless-steel cylinder between a pair of coarse and fine screens. Spacers placed under the bottom screen allow for even distribution of clean solvent. Clean solvent is circulated through the resin for extraction. A flow rate is maintained upward through the resin to allow maximum solvent contact and prevent channeling.

2.2.1 Experience has shown that 1 mL/g of resin extracted is the minimum necessary to extract and clean the resin. The aqueous rinse is critical to the subsequent organic rinses and may be accomplished by simply flushing the canister with about 1 liter of distilled water for every 25 g of resin. A small pump may be useful for pumping the water through the canister. You should perform the water extraction at the rate of about 20 to 40 mL/min.

2.2.2 All materials of construction are glass, PTFE, or stainless steel. Pumps, if used, should not contain extractable materials.

3.0 Drying

3.1 Dry the adsorbent of extraction solvent before use. This section provides a recommended procedure to dry adsorbent that is wet with solvent. However, you may use other procedures if the cleanliness requirements in Sections 13.2 and 13.14 of Method 23 are met.

3.2 Drying Column. A simple column with suitable retainers, as shown in Figure A–2, will hold all the XAD–2 from the extractor shown in Figure A–1 or the Soxhlet extractor, with sufficient space for drying the bed while generating a minimum backpressure in the column.

3.3 Drying Procedure: Dry the adsorbent using clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. You may use high-purity tank nitrogen to dry the resin. However, you should pass the high-purity nitrogen through a bed of activated charcoal approximately 150 mL in volume prior to entering the drying apparatus.

3.3.1 Connect the gas vent of a liquid nitrogen cylinder or the exit of the activated carbon scrubber to the column by a length of precleaned copper tubing (*e.g.,* 0.95 cm ID) coiled to pass through a heat source. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C.

3.3.2 Allow the toluene to drain from the resin prior to placing the resin in the drying apparatus.

3.3.3 Flow nitrogen through the drying apparatus at a rate that does not fluidize or agitate the resin. Continue the nitrogen flow until the residual solvent is removed.

Note: Experience has shown that about 500 g of resin may be dried overnight by consuming a full 160–L cylinder of liquid nitrogen.

4.0 Quality Control Procedures

4.1 Report quality control results for the batch. Re-extract the batch if the residual extractable organics fail the criteria in Section 13.14 of Method 23.

4.2 Residual Toluene Quality Check. If adsorbent resin is cleaned or recleaned by the laboratory, perform a quality control check for residual toluene. The maximum acceptable concentration of toluene is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, continue drying until the excess toluene is removed.

4.2.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 mL of methylene chloride, cap the vial, and shake it well.

4.2.2 Analysis. Inject a 2-µl sample of the extract into a gas chromatograph operated to provide separation between the methylene chloride extraction solvent and toluene.

4.2.2.1 Typical GC conditions to accomplish this performance requirement include, but are not limited to:

- *Column:* Sufficient to separate extraction solvents used to verify adsorbent has been sufficiently dried (*i.e.,* gas chromatographic fused-silica capillary column coated with a slightly polar silicone).
- *Carrier Gas:* Typically, helium at a rate appropriate for the column selected. Other carrier gases are allowed if the performance criteria in Method 23 are met.
- *Injection Port Temperature:* 250 °C.
- *Detector:* Flame ionization detector or an MS installed on a GC able to separate methylene chloride and toluene.
- *Oven Temperature Profile:* Typically, 30 °C for 4 min; programmed to rise at 20 °C/min until the oven reaches 250 °C; return to 30 °C after 17 minutes. You may adjust the initial temperature, hold time, program rate, and final temperature to ensure separation of extraction solvent from toluene.

4.2.2.2 Compare the results of the analysis to the results from a toluene calibration standard at a concentration of 0.22 µl/mL (22 µl/100 mL) of methylene chloride. This concentration corresponds to maximum acceptable toluene concentration in the dry adsorbent of 1,000 µg/g of adsorbent. If the adsorbent exceeds this level, continue drying until the excess toluene is removed.

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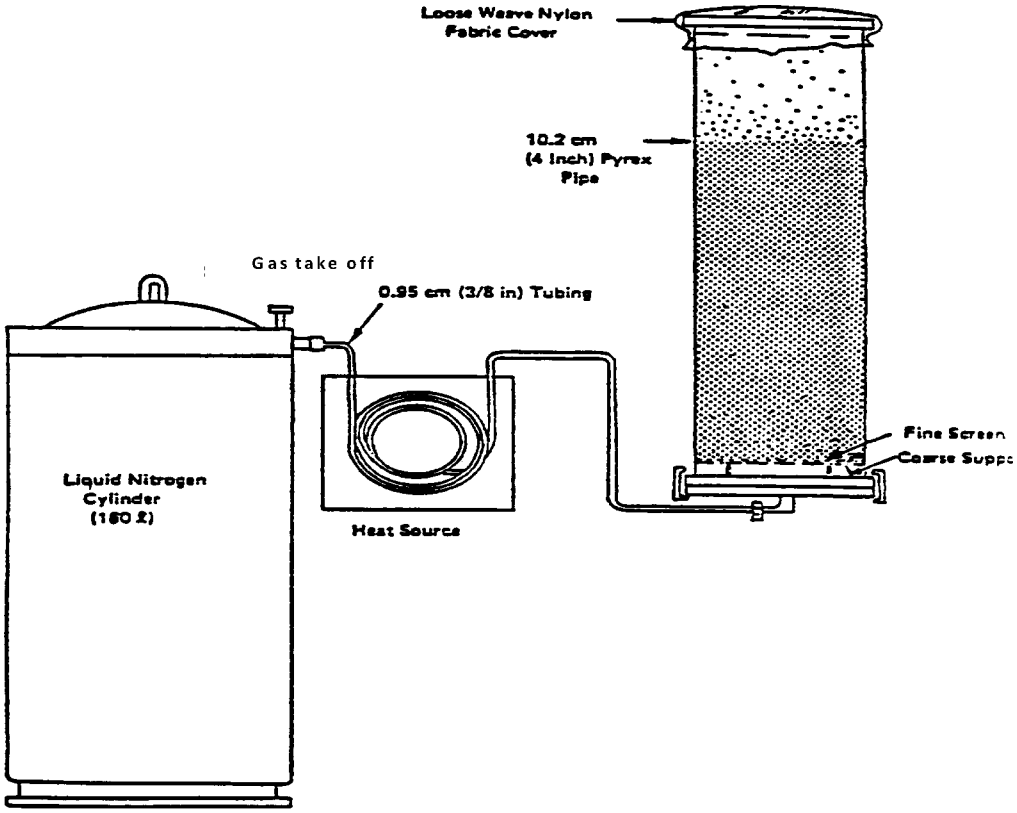

Figure A–1. XAD-2 fluidized-bed drying apparatus

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PART 63—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FOR SOURCE CATEGORIES

■ 6. The authority citation for part 63 continues to read as follows:

Authority: 42 U.S.C. 7401 *et seq.*

■ 7. In § 63.849, revise paragraphs (a)(13) and (a)(14) to read as follows:

§ 63.849 Test methods and procedures.

* * * * *

(a) * * *

(13) Method 23 of Appendix A–7 of 40 CFR part 60 for the measurement of Polychlorinated Biphenyls (PCBs) where stack or duct emissions are sampled; and

(14) Method 23 of appendix A–7 of 40 CFR part 60 and Method 14 or Method 14A in appendix A to part 60 of this chapter or an approved alternative method for the concentration of PCB where emissions are sampled from roof monitors not employing wet roof scrubbers.

* * * * *

■ 8. In § 63.1208, revise paragraph (b)(1) to read as follows:

§ 63.1208 What are the test methods?

* * * * *

(b) * * *

(1) *Dioxins and furans.* (i) To determine compliance with the emission standard for dioxins and furans, you must use:

(A) Method 0023A, Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans emissions from Stationary Sources, EPA Publication SW–846 (incorporated by reference—see § 63.14); or

(B) Method 23, provided in appendix A, part 60 of this chapter.

(ii) You must sample for a minimum of three hours, and you must collect a minimum sample volume of 2.5 dscm;

(iii) You may assume that nondetects are present at zero concentration.

* * * * *

■ 9. In § 63.1625, revise paragraph (b)(10) to read as follows:

§ 63.1625 What are the performance test and compliance requirements for new, reconstructed, and existing facilities?

* * * * *

(b) * * *

(10) Method 23 of appendix A–7 of 40 CFR part 60 to determine PAH.

* * * * *

■ 10. In table 3 to subpart AAAAAAA of part 63 revise the entry ''6. Measuring the PAH emissions'' to read as follows:

TABLE 3 TO SUBPART AAAAAAA OF PART 63—TEST METHODS

For * * *	You must use * * *
* * *	
6. Measuring the PAH emissions.	EPA test method 23.

* * * * *

PART 266—STANDARDS FOR THE MANAGEMENT OF SPECIFIC HAZARDOUS WASTES AND SPECIFIC TYPES OF HAZARDOUS WASTE MANAGEMENT FACILITIES

■ 11. The authority citation for part 266 continues to read as follows:

Authority: 42 U.S.C. 1006, 2002(a), 3001–3009, 3014, 3017, 6905, 6906, 6912, 6921, 6922, 6924–6927, 6934, and 6937.

■ 12. In § 266.104, revise paragraph (e)(1) to read as follows:

§ 266.104 Standards to control organic emissions.

* * * * *

(e) * * *

(1) During the trial burn (for new facilities or an interim status facility applying for a permit) or compliance test (for interim status facilities), determine emission rates of the tetra-octa congeners of chlorinated dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs) using Method 0023A, Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans Emissions from Stationary Sources, EPA Publication SW–826, as incorporated by reference in § 266.11 of this chapter or Method 23, provided in appendix A–7, part 60 of this chapter.

* * * * *

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