ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 60, 63, and 266

[EPA–HQ–OAR–2016–0677; FRL–5937–02–OAR]

RIN 2060–AT09

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

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action finalizes editorial and technical revisions to the Environmental Protection Agency's (EPA's) Method 23 (Determination of Polychlorinated Dibenzo-*p*-Dioxins, Polychlorinated Dibenzofurans, and Polycyclic Aromatic Hydrocarbons from Stationary Sources). Final revisions include incorporating true, comprehensive, and stable isotope dilution for quantifying target compounds using corresponding carbon-13 labeled compounds for each target compound including most of the polycyclic aromatic hydrocarbons (PAH) 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 finalizing revisions that expand the list of target compounds of Method 23 to include PAH and polychlorinated biphenyls (PCB). The final revisions allow facilities and their test teams flexibility when sampling and measuring polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), PAH, and PCB from stationary sources with a comprehensive isotope dilution method while ensuring that the stack testing community can consistently implement the method across emissions sources and facilities.

DATES: This final rule is effective on March 20, 2023. The incorporation by reference (IBR) of certain publications listed in the rule is approved by the Director of the Federal Register as of March 20, 2023.

ADDRESSES: The U.S. Environmental Protection Agency (EPA) has established a docket for this action under Docket ID No. EPA–HQ–OAR–2016–0677. All documents in the docket are listed on the *https://www.regulations.gov* website. Although listed, some information is not publicly available, *e.g.,* Confidential Business Information or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, is not placed on the internet and will be publicly available only in hard copy form. Publicly available docket materials are available either electronically through *https://www.regulations.gov* or in hard copy at the EPA Docket Center, WJC West Building, Room 3334, 1301 Constitution Avenue NW, Washington, DC 20004. Out of an abundance of caution for members of the public and our staff, the EPA Docket Center and Reading Room are closed to the public, with limited exceptions, to reduce the risk of transmitting Coronavirus 2019 (COVID–19). Our Docket Center staff will continue to provide remote customer service via email, phone, and webform.

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

SUPPLEMENTARY INFORMATION:

Preamble acronyms and abbreviations. We use multiple acronyms in this preamble. While this list may not be exhaustive, to ease the reading of this preamble and for reference purposes, the EPA defines the following terms and acronyms here:

AQAD Air Quality Assessment Division
ASTM American Society for Testing and Materials International
CAA Clean Air Act
CARB California Environmental Protection Agency Air Resources Board
CCV continuing calibration verification
CFR Code of Federal Regulations
EDL estimated detection limit
EPA U.S. Environmental Protection Agency
FR Federal Register
GC gas chromatograph
HRGC high-resolution gas chromatography
HRMS high-resolution mass spectrometry
IBR incorporation by reference
IDC initial demonstration of capability
MDL method detection limit
MS mass spectrometer
NTTAA National Technology Transfer and Advancement Act
OAQPS Office of Air Quality Planning and Standards
OLEM Office of Land and Emergency Management
OMB Office of Management and Budget
OW Office of Water
PAH polycyclic aromatic hydrocarbons
PCB polychlorinated biphenyls
PCDD polychlorinated dibenzo-*p*-dioxins
PCDPE polychlorinated diphenyl ethers
PCDPF polychlorinated dibenzofurans
PRA Paperwork Reduction Act
QCS Quality Control Sample
RFA Regulatory Flexibility Act
RRF relative response factor
SVOC semivolatile organic compounds
SW solid waste
TTN Technology Transfer Network
UMRA Unfunded Mandates Reform Act

Organization of this document. The information in this preamble is organized as follows:

I. General Information

A. Does this final action apply to me?

The final amendments to Method 23 apply to stationary sources that are subject to certain provisions of 40 CFR parts 60, 62, 63, 79, and 266. The source categories and entities potentially affected are listed in Table 1 of this preamble. This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be affected 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 affected.

TABLE 1—POTENTIALLY AFFECTED SOURCE CATEGORIES

Category	NAICS [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 final 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 final method revisions is available on the Technology Transfer Network (TTN) website at *https://www.epa.gov/ttn/emc/methods/*. The TTN provides information and technology exchange in various areas of air pollution control.

C. Judicial Review

Under Clean Air Act (CAA) section 307(b)(1), judicial review of this final rule is available only by filing a petition for review in the U.S. Court of Appeals for the District of Columbia Circuit by May 19, 2023. Moreover, under section 307(b)(2) of the CAA, the requirements established by this final rule may not be challenged separately in any civil or criminal proceedings brought by the EPA to enforce these requirements. Section 307(d)(7)(B) of the CAA further provides that ''[o]nly an objection to a rule or procedure which was raised with reasonable specificity during the period for public comment (including any public hearing) may be raised during judicial review.'' This section also provides a mechanism for the EPA to convene a proceeding for reconsideration, ''[i]f the person raising an objection can demonstrate to the EPA that it was impracticable to raise such objection within [the period for public comment] or if the grounds for such objection arose after the period for public comment, (but within the time specified for judicial review) and if such objection is of central relevance to the outcome of the rule.'' Any person seeking to make such a demonstration should submit a Petition for Reconsideration to the Office of the Administrator, U.S. EPA, Room 3000, WJC South Building, 1200 Pennsylvania Ave. NW, Washington, DC 20460, with a copy to both the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section, and the Associate General Counsel for the Air and Radiation Law Office, Office of General Counsel (Mail Code 2344A), U.S. EPA, 1200 Pennsylvania Ave. NW, Washington, DC 20460.

II. Background

The EPA's Method 23 (Determination of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources) is EPA's current reference test method used to determine the amount of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) emitted from stationary sources.

The EPA promulgated Method 23 (Appendix A of 40 Code of Federal Regulations (CFR) Part 60, Test Methods) on February 13, 1991 (56 FR 5758). Since promulgation, the ability to measure PCDD and PCDF 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 (PCDF) 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.
- 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 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, regulated sources, 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 PAH and PCB emitted from

stationary sources. The docket contains summaries of the stakeholder discussions. EPA proposed editorial and technical revisions to Method 23 on January 14, 2020 (85 FR 2234). EPA received comments on the proposed revisions to the method and has addressed these in a separate response to comments document, the *Summary of Public Comments and Responses for the Proposed EPA Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources.* This final action summarizes the changes made in response to comments.

III. Incorporation by Reference

The EPA is incorporating by reference American Society for Testing and Materials (ASTM) D6911–15 and ASTM D4840–99(2018)e1 in Method 23. 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 ASTM International and may be obtained from *https://www.astm.org* or from the American Society for Testing and Materials 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428–2959.

IV. Summary of Revisions to Method 23

In this action, we are finalizing technical revisions and editorial changes to clarify and update the requirements and procedures specified in Method 23 and reformatting the method to conform with the current EPA method format (see *https://www.epa.gov/measurements-modeling/method-development#format*). We are also expanding the applicability of Method 23 to include procedures for sampling and analyzing PAH and PCB. In addition, we are finalizing revisions to various sections of the CFR that either require Method 23 or require the analysis of PCDD/PCDF, PAH, or PCB.

Our intent for the final revisions is to ensure that Method 23 is implemented consistently. EPA has updated the method procedures to include many current best practices. We have added flexibility to the method based on meeting quality control requirements.

The primary focus of the final revisions to Method 23 is to change the method from a prescriptive method to a method which allows 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 final revisions also address concerns over recovery of target compounds from particulate matter by requiring a pre-extraction filter recovery standard procedure and acceptance criteria for the pre-extraction filter recovery standard recovery as a tool to evaluate filter extraction. 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 PCDD/PCDF.

The EPA's second focus for the final revisions is to modify the method to allow isotope dilution with isotopically labeled compounds for each target compound. Quantitation is based on isotope dilution, moving from nine to 17 labeled compounds for 17 target toxic 2,3,7,8-substituted PCDD/PCDF. 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 final revisions eliminate biases with recovery correction based on individual corresponding labeled compounds.

The third major focus for the EPA's final revisions to Method 23 is to include options for combining sampling and analysis of PCDD/PCDF with sampling and analysis of PAH and PCB to allow the measurement of these toxic semivolatile organic compounds (SVOC). Therefore, PCB and PAH were added to the list of target compounds measured by Method 23.

The EPA's final amendments to Method 23 in response to public comments are presented below for each section of Method 23. The proposed revisions to sections of Method 23 that EPA is not changing based on public comments are finalized as proposed. A summary of public comments and our responses are provided in a separate response to comments document in the docket for this action.

A. Section 1.0 Scope and Application

In this action, EPA is renaming Section 1.0 from ''Applicability and Principle'' to ''Scope and Application,'' and revising the text to expand the target compounds for Method 23 to include PCB and PAH. We are also adding 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, isotope dilution, and the use of high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) when applying Method 23. We are also adding language to specify that Method 23 is performance-based and allows 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 Summary of Method

The EPA is renaming Section 2.0 from ''Apparatus'' to ''Summary of Method,'' and revising Section 2.0 to provide an overview of the method's sampling and analytical procedures. We are also moving the current language in Section 2.0, which describes the materials needed to conduct Method 23, to a new Section 6.0 (Equipment and Supplies).

C. Section 3.0 Definitions

The current version of Method 23 does not include definitions of key terms and variables used in Method 23. In this action, we are adding a new Section 3.0 titled ''Definitions.'' We are defining acronyms and technical terms to improve the clarity of the method principles and procedures. We are also moving language from the current Section 3.0 to a new Section 7.0 (Reagents, Media, and Standards).

D. Section 4.0 Interferences

The current version of Method 23 does not discuss the conditions that can potentially interfere with measurements obtained using the method. In this action, we are adding a new Section 4.0 titled ''Interferences,'' that presents the potential causes and recommendations for avoiding or mitigating interferences or sample contamination. We are stating that enhanced selectivity, or confidence in the data, is based on the fractionation, GC separation, HRMS sensitivity, and monitoring for polychlorinated diphenyl ether (PCDPE) interferences. We are also moving language from the current Section 4.0 to a new Section 8.0 (Sample Collection, Preservation, and Storage).

E. Section 5 Safety

Currently, Method 23 does not provide procedures for safety. In this action, we are adding a new Section 5.0 titled ''Safety,'' that presents the health hazards and procedures for minimizing risks to field and laboratory personnel when conducting Method 23. We are also moving language from the current Section 5.0 to a new Section 11.0 (Analysis Procedure).

F. Section 6.0 Equipment and Supplies

In this action, we are renumbering and moving the current language in Section 2.0 (Apparatus) to a new

Section 6.0 titled ''Equipment and Supplies,'' and making clarifying edits and technical revisions to the specifications in Section 6.0. Table 2 of this preamble identifies the 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 including in Section 6.0.

TABLE 2—CROSSWALK FOR REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Revised 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
Adsorbent module	2.1.4	6.1.9
Fitting caps	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 container	2.2.9	6.2.8
Extraction thimble	2.3.4	6.3.3.3
Pasteur pipettes	2.3.5	6.4.1
GC oven	2.3.10.1	6.5.1.1
GC Temperature monitor	2.3.10.2	6.5.1.2
GC Flow system	2.3.10.3	6.5.1.3
Capillary GC column	2.3.10.4	6.5.2
Mass spectrometer (MS)	2.3.11	6.5.3
MS data system	2.3.12	6.5.4

TABLE 3—ADDITIONAL SPECIFICATIONS FOR SECTION 6.0

Description	Revised 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
Heating mantle	6.3.3.4
Kuderna-Danish concentrator	6.3.4
Liquid chromatography columns	6.4.2
GC Injection port	6.5.1.4
PCDD/PCDF GC column	6.5.2.1
PAH GC column	6.5.2.2
PCB GC column	6.5.2.3

In Section 6, we are also finalizing changes to:

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

We are also moving language from Method 23's current Section 6.0 to new Section 10.0 (Calibration and Standardization).

G. Section 7.0 Reagents, Media, and Standards

In this action, the EPA is renumbering and moving the current language in Section 3.0 (Reagents) to a new Section 7.0 titled ''Reagents, Media, and Standards,'' and making clarifying edits and technical revisions to the specifications. Table 4 of this preamble identifies the 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 including in Section 7.0.

TABLE 4—CROSSWALK FOR REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Revised 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

TABLE 4—CROSSWALK FOR REVISIONS TO CURRENT METHOD SECTIONS—Continued

Description	Current section	Revised section
Silica gel	3.1.5	7.5
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—ADDITIONAL SPECIFICATIONS FOR SECTION 7.0

Description	Revised 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 adsorbent standard	7.9.3
Pre-extraction filter recovery standard	7.9.4
Pre-extraction standard	7.9.5
Pre-analysis standard	7.9.6

We are replacing the filter precleaning procedures of the current method with specifications for conducting a filter quality control check. We are also deleting unnecessary specifications (presented in Table 6 of this preamble) to reflect modern methods. We are renaming the isotopic spiking standard mixtures to better relate the standards to their use in the final method. We are ensuring that the isotopically labeled spiking standards are named consistently throughout the final method.

TABLE 6—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
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 moving the current Section 7.0 to a new Section 9.0 (Quality Control).

H. Section 8.0 Sample Collection, Preservation, and Storage

In this action, the EPA is renumbering and moving the current language in Section 4.0 (Procedure) to a new Section 8.0 titled ''Sample Collection, Preservation, and Storage,'' and making clarifying edits and technical revisions to the current procedures for sampling and field sample recovery. The new Section 8.0 also includes added requirements for sample storage conditions and holding times.

Under the sampling procedures of Method 23, we are finalizing 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 REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Revised 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
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 adding to the new Section 8.0. This action finalizes a minimum sample volume and sampling time requirements at each traverse point for continuous industrial processes that 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 final 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 final adsorbent module orientation requirements clarify the configuration of the adsorbent module to ensure that condensed moisture flows through the module into the water collection impinger. We are adding sampling filter temperature monitoring requirements to align Method 23 with other isokinetic stationary source methods. Also, we are adding 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—ADDITIONAL SPECIFICATIONS FOR SECTION 8.1

Description	Revised 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 finalizing technical revisions as shown in Table 9 of this preamble. In this action, we are also adding specifications as shown in Table 10 of this preamble.

TABLE 9—CROSSWALK FOR REVISIONS TO CURRENT METHOD SECTIONS

Description	Current section	Revised section
Adsorbent module sample preparation	4.2.2	8.2.5
Preparation of Container No. 2	4.2.3	8.2.6
Rinsing of the filter holder and condenser	4.2.3	8.2.7
Weighing impinger water	4.2.5	8.2.8
Preparation of Container No. 3	4.2.4	8.2.9
Silica gel	4. 2.7	8.2.10

TABLE 10—ADDITIONAL SPECIFICATIONS FOR SECTION 8.2

Description	Revised 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 the new Section 8.2.6, acetone and toluene rinses are collected in one bottle rather than separately. New Section 8.2.8 measures moisture by weight rather than by volume.

I. Section 9.0 Quality Control

In this action, the EPA is moving and renumbering the current Section 7.0 (Quality Control) to a new Section 9.0 titled "Quality Control," and making clarifying and technical revisions to the new Section 9.0. We are adding an introductory note that addresses maintaining, and documenting quality control compliance required in Method 23. We are adding a new subsection that clarifies the recordkeeping and reporting necessary to demonstrate compliance with quality control requirements of this method. We are also adding specifications for conducting pre-sampling, pre-extraction, and pre-analysis standard recoveries of isotopically-labeled standards and adding specifications for:

- Initial demonstration of capability (IDC).
- Quality Control Sample (QCS).
- Method detection limits (MDL).
- Laboratory method blank (LMB).
- Estimated detection limits (EDL).
- Field train proof blank.

It should be noted that the EDLs as proposed remain in the method and are sample specific. It should also be noted that the second source QCS also serves as an initial calibration verification. We are also moving language from the current Section 9.0 to new Section 12.0 (Data Analysis and Calculations).

J. Section 10.0 Calibration and Standardization

In this action, the EPA is renumbering and moving the text in Section 6.0 (Calibration) of the current method to a new Section 10.0 titled "Calibration and Standardization," and making clarifying and technical revisions to the specifications for calibrating the sampling and the HRGC/HRMS systems. We are adding specifications for tuning the HRMS system, moving the specification for HRMS resolution (currently in Section 5) to this new section, and adding text on the procedures for assessing the relative standard deviation for the mean instrument response factors to bring Method 23 up to date with current laboratory practice. We are also

updating the requirements for ion abundance ratio limits, and resolution checks under the continuing calibration verification to serve as performance indicators for analysis quality. We are adding a specification to prepare the continuing calibration verification (CCV) standard at the same time as the batch of field samples using the same labeled standards. We are also moving language in the current Section 10.0 to a new Section 16.0 (Bibliography).

K. Section 11.0 Analysis Procedure

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

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

TABLE 11—ADDITIONAL SPECIFICATIONS FOR SECTION 11.0

Description	Revised section
Preparing and operating the extraction apparatus	11.1.7 through 11.1.9.
Allow the extraction apparatus to cool	11.2.1.
Initial extract concentration	11.2.2.
Allow the sample extract to cool	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 PAH and PCDPE	11.3.1.
Sample cleanup and fractionation for PCDD/PCDF and PCB	11.3.2.
Addressing unresolved compounds	11.4.1.2.1.
Relative retention time for PCB	11.4.3.4.5.
Chlorodiphenyl ether interference	11.4.3.4.8.
MS lock-mass ions	11.4.3.4.9.
Identification criteria for PAH	11.4.3.4.10.
Calculations of target mass and mass per dry standard cubic meter	11.4.3.5.1 and 11.4.3.5.2.
Quantifying native PCDD/PCDF	11.4.3.5.3.
Reporting options	11.4.3.5.4 through 11.4.3.5.6.

L. Section 12.0 Data Analysis and Calculations

In this action, the EPA is renumbering and moving the current language in Section 9.0 (Calculations) to a new Section 12.0 titled ''Data Analysis and Calculations,'' and revising the equation variable list. We are revising the equations shown in Table 12 of this preamble.

TABLE 12—EQUATION REVISIONS FOR SECTION 12.0

Current equation	Description	Revised section
23–1	Individual relative response factor (RRF) for each compound	12.2
23–2	Amount of individual target compound i in the extract using the RRF of the CCV	12.7
23–4	Recovery of Labeled Compound Standards	12.9
23–7	Estimated detection limit	12.10
23–8	Total concentration	12.11

This section specifies that the CCV RRFs are used to quantify the target compounds rather than the initial calibration RRFs. We are also removing and replacing the current equations in Method 23 with the equations shown in Table 13 of this preamble to accommodate the final changes to the method procedures.

TABLE 13—ADDITIONAL EQUATIONS FOR SECTION 12.0

New equation	Description	Revised section
23–1	Individual compound RRF for each calibration level	12.2
23–2	Individual compound RRF for pre-extraction standard	12.2
23–4	Percent relative standard deviation of the RRFs for a compound over the calibration levels.	12.4
23–5	Standard deviation of the RRFs for a compound over the calibration levels	12.5
23–6	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
23–9	Concentration of the Individual Target Compound or Group i in the Emission Gas.	12.8
23–13	Half range for the prediction interval of results	12.12
23–14	Upper limit for the prediction interval of results	12.12
23–15	Lower limit for the prediction interval of results	12.12

M. Section 13.0 Method Performance

In this action, the EPA is adding a new Section 13.0 titled ''Method Performance,'' that includes the specifications shown in Table 14 of this preamble. The new Section 13 provides the basis for assessing accuracy with LMBs, increases labeled standards, and establishes performance criteria to monitor method performance.

TABLE 14—METHOD PERFORMANCE SPECIFICATIONS FOR SECTION 13.0

Description	Revised section
Background assessment of field train proof blank, LMB, and Materials (filters, adsorbent resin, glass wool, etc.).	13.1.
GC column systems used to measure PCDD/PCDF, PAH, and PCB target compounds	13.2 through 13.5.
Detection limits (Method detection limits and Estimated detection limits)	13.6.
Tuning HRGC/HRMS system	13.7.
MS lock-mass ions	13.8.
Initial calibration and continuing calibration verification	13.9 and 13.10.
QCS analysis	13.11.
Identification of target compounds	13.12 and 13.13.
Pre-sampling and pre-extraction standard recovery requirements	13.14 and 13.15.
Pre-analysis standard sensitivity requirements	13.16.
IDC-Lowest calibration concentration, Demonstration of precision, Demonstration of accuracy	13.17.
Modifications of the method	13.18 and 13.19.

N. Section 14.0 Pollution Prevention

In this action, the EPA is adding 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 Waste Management

In this action, the EPA is adding 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 Bibliography

In this action, the EPA is renumbering and moving the current language in Section 10.0 (Bibliography) to a new Section 16.0 titled ''Bibliography.'' We are deleting previous reference number 3 which is no longer relevant and adding 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.
- U.S. Environmental Protection Agency. Method 8290A—Polychlorinated Dibenzo-p-dioxin (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1. February 2007. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW–846.
- 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.
- U.S. Environmental Protection Agency. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. EPA 821–R–16–006. December 2016.
- Tondeur Y, Niederhut WJ, Missler SR. A hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorodibenzo-p-Dioxins in Environmental Samples; Bio. Med. and Environ. Mass Spectr. 14, pages 449–456, 1987.
- Gianluca R., Mosca S., Guerriero E., Rotatori M. Development of a new automated clean-up system for the simultaneous analysis of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and 'dioxin-like' polychlorinated biphenyls (dl-PCB) in flue gas emissions by GPC–SPE. J. Environ. Monit. 14, pages 1082–1090, 2012.
- U.S. Environmental Protection Agency. The National Dioxin Air Monitoring Network (NDAMN) Report of the Results of Atmospheric Measurements of Polychlorinated Dibenzo-p-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), and Dioxin-like Polychlorinated Biphenyl (PCBs) in Rural and Remote Areas of the United States from June 1998 through November 2004. EPA/600/R–13/183F. August 2013.
- Guo, Y., Kannan, K. Analytical Methods for the Measurement of Legacy and Emerging Persistent Organic Pollutants in Complex Sample Matrices. Comprehensive Analytical Chemistry. Vol. 67. January 2015.
- U.S. Environmental Protection Agency. USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review. EPA–540–R–11–016. September 2011.

Q. Section 17.0 Tables, Diagrams, Flow Charts, and Validation Data

In this action, the EPA is adding a new Section 17 titled ''Tables, Diagrams, Flow Charts, and Validation Data,'' that contains all tables, diagrams, flow charts, and validation data referenced in Method 23. We are revising Figures 23–1 and 23–2 and renaming and/or renumbering the current Method 23 tables as shown in Table 15 of this preamble.

TABLE 15—REVISIONS TO METHOD 23 TABLES

Current method	Final method
Table 1—Composition of the Sample Fortification and Recovery Standards Solutions.	Table 23–7. Concentration of the Sample Fortification for PCDD and PCDF.
Table 2—Composition of the Initial Calibration Solutions	Table 23–11. Concentration of the Initial Calibration Standard Solutions for PCDD and PCDF.
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 PCDD and PCDF.
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 Continuing Calibration Response Factors for Isotopically Labeled and Native Compounds.

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

TABLE 16—ADDITIONAL TABLES TO METHOD 23

Revised 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 PAH.
23–6	Elemental Compositions and Exact Masses of the Ions Monitored by High-Resolution Mass Spectrometry for PCB.
23–8	Concentration of the Sample Fortification for PAH.
23–9	Concentration of the Sample Fortification for PCB.
23–10	Sample Storage Conditions and Laboratory Hold Times.
23–12	Concentration of the Initial Calibration Standard Solutions for PAH.
23–13	Concentration of the Initial Calibration Standard Solutions for PCB.
23–16	Typical DB5–MS Column Conditions.
23–17	Assignment of Pre-extraction Standards for Quantitation of Target PCB.
23–18	Initial Demonstration of Capability Quality Control (QC) Requirements.

V. Summary of Final 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 are incorporating by reference ASTM D4840–99(2018)e1, Standard Guide for Sample Chain-of-Custody Procedures, and amending the reference to ASTM D6911–15, Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis, to include for use in Method 23.

In 40 CFR part 60, subpart CCCC, we are revising 40 CFR 60.2125(g)(2) and (j)(2) to realign the requirement for quantifying isomers to the reorganized Section 11.4.2.4 in the revisions of Method 23.

In 40 CFR part 60, subpart DDDD, we are revising 40 CFR 60.2690(g)(2) and (j)(2) to realign the requirement for identifying isomers to the reorganized Section 11.4.2.4 in the revisions 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) and (a)(14), we are replacing CARB Method 428 with EPA Method 23 for the measurement of PCB emissions from roof monitors not employing wet roof scrubbers.

In 40 CFR 63.1208(b)(1), we are removing 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 are replacing CARB Method 429 with EPA Method 23 for measuring the emissions of PAH from ferromanganese electric arc furnaces.

In Table 3 to Subpart AAAAAAA, we are replacing the requirement for analysis of PAH by SW–846 Method 8270 with a requirement to use EPA Method 23. Specifically, we are deleting "with analysis by SW–846 Method 8270D" in row 6 of Table 3 to Subpart AAAAAAA. Because revisions to Method 23 eliminate the use of methylene chloride in field sampling activities, we are also removing footnote "b" in Table 3 to Subpart AAAAAAA.

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 are adding EPA Method 23 as an alternative to SW–846 Method 0023A. We proposed to make this change to 40 CFR 266.104. In addition to this specific change, we are making a conforming change in 40 CFR part 266 Appendix IX. EPA considers this conforming change a logical outgrowth of the proposed revisions to Method 23.

VI. Statutory and Executive Order Reviews

Additional information about these statutes and Executive Orders can be found at *https://www.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. Paperwork Reduction Act (PRA)

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

C. Regulatory Flexibility Act (RFA)

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

D. Unfunded Mandates Reform Act (UMRA)

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

E. Executive Order 13132: Federalism

This 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.

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

This 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. Thus, Executive Order 13175 does not apply to this action.

G. 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 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.

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

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

I. National Technology Transfer and Advancement Act (NTTAA)

This action involves technical standards. The EPA will 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 ASTM International. 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.

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

Executive Order 12898 (59 FR 7629, February 16, 1994) directs federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations (people of color) and low-income populations.

The EPA believes that this type of action does not concern human health or environmental conditions and, therefore, cannot be evaluated with respect to potentially disproportionate and adverse effects on people of color, low-income populations and/or Indigenous peoples. This action updates Method 23, which will improve the quality of the results when required by other rules to use Method 23.

K. Congressional Review Act (CRA)

This action is subject to the CRA and the EPA will submit a rule report to each House of the Congress and to the Comptroller General of the United States. This action is not a ''major rule'' as defined by 5 U.S.C. 804(2).

L. Determination Under Clean Air Act Section 307(d)

This final rule is not subject to the provisions of CAA section 307(d). This final rule does not promulgate any of the actions listed in CAA section 307(d)(1).

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 hydrocarbons, 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 hydrocarbons, Test methods, Waste management.

Michael S. Regan,

Administrator.

For the reasons stated in the preamble, the Environmental Protection Agency amends 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.*

Subpart A—General Provisions

■ 2. In § 60.17:

■ a. Redesignate paragraphs (h)(168) through (h)(213) as (h)(169) through (h)(214);

■ b. Add new paragraph (h)(168); and

■ c. Revise newly redesignated paragraph (h)(194).

The addition and revision read as follows:

§ 60.17 Incorporations by reference.

* * * * *

(h) * * *

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

* * * * *

(194) 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; Appendix A–8: Method 30B.

* * * * *

Subpart CCCC—Standards of Performance for Commercial and Industrial Solid Waste Incineration Units

■ 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 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 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.)

* * * * *

Subpart DDDD—Emissions Guidelines and Compliance Times for Commercial and Industrial Solid Waste Incineration Units

■ 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 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 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 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 the measurement of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), polychlorinated biphenyls (PCB), and/or polycyclic aromatic hydrocarbons (PAH) in emissions from stationary sources. Using this method, you can measure these analyte groups individually or in any combination using a single sample acquisition unless otherwise specified in a rule, regulation, or permit. Tables 23–1 through 23–3 of this method list the applicable target analytes for Method 23. If all 209 PCB are analyzed, the 17 toxic PCB congeners should be resolved and reported while the other PCB can be reported as totals by homolog, for example, total trichlorobiphenyl (TrCB).

1.2 Scope. This method describes the sampling and analytical procedures used to measure selected PCDD and PCDF in stationary sources when required in an applicable subpart. This method also describes how the same sampling and analysis technology can be used to measure selected PCB and PAH from stationary source in combination or as each individual compound class when required in an applicable subpart. 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 and have a working knowledge of isotope dilution and the use of high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

1.3 The HRGC/HRMS portions of this method are for use by laboratory analysts experienced with HRGC/HRMS analysis of PCDD, PCDF, PCB, and PAH 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, PCB, and PAH 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 particulate 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 through isotope dilution quantitation.

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 (QC) purposes. Alternate recovery standards can be used to assess the recovery of a compound class relative to any step in the sampling and analysis procedure that is not already assessed as a mandatory part of this method, such as the cleanup step.

3.2 Benzo[a]pyrene Toxic Equivalency Quotient (B[a]P–TEQ). 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.

3.3 Continuing Calibration Verification (CCV) Standard. A standard prepared at the mid-point concentration of the calibration used to verify the initial calibration. Prepare the CCV standard at the same time as the batch of field samples using the same labeled standards.

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

3.5 Estimated Detection Limit (EDL). The minimum qualitatively recognizable signal above background for a target compound. The EDL is a detection limit specific to each sample analysis based on the noise signal measured near the retention time of a target compound or target isomer group. Being sample specific, the EDL is affected by sample size, dilution, recoveries of pre-extraction standard, chemical noise from sample extract, electronic noise from instrument, extract aliquot, relative response of instrument, etc.

3.6 Estimated Maximum Possible Concentration (EMPC). An EMPC is a worst-case estimate of the target compound concentration. Report the results as EMPC when the ion abundance ratio for a target analyte is outside the performance criteria. Calculate the EMPC using both quantitation ions.

3.7 Field Train Proof Blank. A field train proof blank train is a QC sample to evaluate equipment preparation and potential contamination during sample recovery and consists of a fully assembled train at the sampling site, without actual sampling. The field train proof blank train uses glassware from the same preparation batch as the field samples.

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 of chlorine.

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 Isotope Dilution. A means of determining a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched.

3.11 Laboratory Method Blank (LMB). A quality control sample to assess background contamination or interference from media, reagents, equipment, etc. An LMB is prepared in the laboratory, composed of clean sampling media (filter and XAD–2), using same labeled standards, media, reagents, and materials (sodium sulfate, glass wool, etc.) and processed (extraction, fractionations, cleanup) and analyzed using the same procedures as a field sample.

3.12 Polychlorinated Biphenyl (PCB) congeners. Any or all 209 chlorinated biphenyl congeners. 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.

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

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

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

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

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

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

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

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

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

3.12.10 Decachlorobiphenyl (DeCB). Biphenyl fully chlorinated with 10 chlorine atom substituents replacing hydrogen in the parent compound.

3.13 Polychlorinated dibenzo-p-dioxin (PCDD) congeners. Any or all 75 chlorinated dibenzo-*p*-dioxin congeners. There are seven 2,3,7,8 substituted PCDD congeners and four PCDD homolog groups listed in Table 23–1 of this method. This method does not measure mono- through tri-PCDD and includes non-2,3,7,8 substituted congeners in the total homolog categories.

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

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

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

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

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

3.14 Polychlorinated dibenzofuran (PCDF) congeners. Any or all chlorinated dibenzofuran congeners. There are ten 2,3,7,8 substituted PCDF congeners and four PCDF homolog groups listed in Table 23–1 of this method. This method does not measure mono- through tri-PCDF and includes non-2,3,7,8 substituted congeners in the total homolog categories.

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

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

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

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

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

3.15 Polychlorinated diphenyl ethers (PCDPE). Any or all chlorinated substituted diphenyl ethers.

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

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

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

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

3.15.5 Decachlorodiphenyl ether (DCDPE).

3.16 Polycyclic Aromatic Hydrocarbons (PAH). 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 standard mixture and by following the other requirements for target PAH compounds in this method.

3.17 Pre-analysis Standard. A group of isotopically labeled compounds added at a known amount immediately prior to analysis and used to monitor instrument response, injection errors, instrument drift and to determine the recovery of the pre-extraction standard compounds. Add pre-analysis standard to every sample (including blank, QC samples, and calibration solutions) at a known amount.

3.18 Pre-extraction Filter Recovery Standard. 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 to the filter samples just prior extraction. The pre-extraction filter recovery standard is not used for quantitating or recovery correction.

3.19 Pre-extraction Standard. A group of isotopically labeled compounds added in a known amount to the XAD–2 adsorbent resin of each sample immediately before extraction and used for quantitation of target and other labeled compounds to correct for extraction, cleanup, and concentration recovery. These isotopically labeled compounds constitute a matrix spike of the resin. Add pre-extraction standard to every sample at the same level (including blank, QC samples, and calibration solutions).

3.20 Pre-sampling Adsorbent Standard. A group of isotopically labeled compounds added in a known amount to the XAD–2 adsorbent prior to sampling used to monitor sampling aspects of the method.

3.21 Pre-transport Standard. Spiking compound 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 prior to sampling. 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.

3.22 Quality Control Sample (QCS). A mid-level standard prepared from a second source standard or prepared from a source of standards different from the source of calibration standards. The purpose of the QCS is to verify the integrity of the primary calibration standards. A QCS is analyzed during the initial demonstration of capability (IDC) and following each initial calibration (at a minimum quarterly) thereafter.

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

3.24 2,3,7,8-Tetrachlorodibenzo-p-dioxin Toxic Equivalency Quotient (2,3,7,8-TeCDD TEQ). A procedure that expresses the toxicity of PCDD, PCDF, and PCB in terms of the most toxic dioxin, as specified in applicable regulations, permits, or other requirements.

4.0 Interferences

Despite interferences, confidence of the data is based on the enhanced selectivity of fractionation, gas chromatograph (GC) separation and detector resolving power, the QC check ions, and monitoring PCDPE.

4.1 PCB and PCDPE have similar molecular weight and chromatographic properties to PCDD and PCDF. PCB may produce fragment ions at interfering mass-to-charge ratios (m/z) when losing chlorine (Cl_2) or 2 Cl_2 during ionization processes. With HRMS, GC separation, and fractionation, PCB should not pose a problem for PCDD/PCDF identification and quantitation. PCDPE, when losing Cl_2, also produce interfering m/z values in the PCDF homolog group with two fewer chlorine atoms (*i.e.,* an octachlorinated PCDPE can interfere with a hexachlorinated PCDF). The latter interferences are potentially detected by monitoring an m/z corresponding to the potentially interfering PCDPE; however, the fragmentation patterns of all PCDPE may not be known, complicating any attempt to quantify the extent of ether interference.

Note: Consider monitoring 328 m/z if high levels of PCB are expected.

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 an LMB. Use high purity reagents, solvents, and standards to minimize interferences in sample analysis.

4.4 PAH 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 PCDD, PCDF, PCB, and/or PAH.

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 PCDD and PCDF containing chlorine atoms in positions 2,3,7,8 have toxicities comparable to that of 2,3,7,8-TeCDD.

5.2 PCB and benzo[a]pyrene 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 PCDD, PCDF, PCB, and PAH.

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. Do not use silicon tubing in direct contact with flue gases. 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, 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 (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 (½ in.) inside diameter (ID) glass tube extending to approximately 1.3 cm (½ 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 0.5 g.

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 Silica Adsorbent Storage Container. Use an air-tight container to store silica gel.

6.2.8 Glass Sample Storage Container. 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 Container. 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 thimble holder 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. The use of cellulose thimbles for sample extraction in this method is prohibited.

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

6.3.4 Kuderna-Danish (KD) 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.

Note: Rotary evaporation has only been demonstrated when analyzing PCDD/PCDF. The KD with Snyder column is recommended when analyzing for PAH and/or PCB to avoid evaporation loss resulting in failed performance criteria for pre-extraction spike recovery.

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 Liquid 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 GC 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 40 °C/min with isothermal hold.

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

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

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

6.5.2 Capillary GC Column. Use different columns for the analysis of the different target compound classes in this method, if needed. Perform the resolution checks in Sections 10.2.3.5 and 10.2.3.6 of this method to document the required resolution. Compound separation must meet the resolution specifications in Section 10.2.3.5 of this method and the identification specifications found in Section 11.4.3.4 of this method.

6.5.2.1 PCDD/PCDF Column. Gas chromatographic columns used to measure PCDD/PCDF should be capable of achieving separation of the 17 PCDD/PCDF target compounds from the nearest eluting target compound(s). The valley height resolution between 2,3,7,8-substituted TeCDD and TeCDF and the nearest eluting isomers must not exceed 25% of the taller of the two peaks. The valley height resolution between all other target PCDD/PCDF compounds and the nearest eluting targets (or interference) must not exceed 40% of the taller of the two peaks.

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% phenyl methylpolysiloxane (DB–5, HP–5MS, Rtx-5MS, Equity-5) and 50% cyanopropylmethyl, 50% phenylmethylsiloxane (DB–225, SP 2331) GC columns and the other set consisted of 5% phenyl, 94% methyl, 1% vinyl silicone bonded-phase (DB–5MS, ZB–5MS, VF–5MS, CP-Sil 8 CB LowBleed/MS) with 50% cyanopropylmethyl, 50% phenylmethylsiloxane (SP–2331).

6.5.2.2 PAH Column. Use column systems for measuring PAH that can achieve separation of anthracene and phenanthrene at m/z 178 such that the valley between the peaks does not exceed 50% 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% of the height of the taller peak. These requirements are achievable using a 30-m narrow bore (0.25 mm ID) 5% phenyl polysilphenylene-siloxane (BPX5 or equivalent) bonded-phase, fused-silica capillary column.

6.5.2.3 PCB Column. Use column systems for measuring PCB that can achieve unique resolution and identification of the toxics for determination of a TEQ_{PCB} using toxic equivalency factors (TEF). Resolution is shown by a valley between the peaks not exceeding 40% of the taller of the two peaks. Isomers may be unresolved if they have the same TEF and RRF 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% phenyl polycarborane-siloxane (HT8), DB–XLB, and poly (50% n-octyl/50% methyl siloxane) (SPB-Octyl). Quantification of unresolved isomers should use the nearest eluting target PCB pre-extraction standard in Appendix A of this method, unless otherwise specified in applicable rule, regulation, or permit.

Note: If all 209 PCB are analyzed the 17 toxic PCB congeners should be resolved and reported while the other PCB can be reported as totals by homolog, for example, total TrCB.

6.5.3 Mass Spectrometer. Instrument employing 28 to 70 electron volt ionization. The instrument and data system must be capable of repetitive monitoring of at least 12 exact m/z values with a mass resolution defined in Section 10.2.1 within the measurement mass range. The recommended lock-mass ions to be used for mass drift correction are presented in Tables 23–4, 23–5, and 23–6 of this method for PCDD/PCDF, PAH, and PCB, respectively, as applicable to target analytes. Mass drifts of 5 parts per million (ppm) or more can have serious effects on instrument performance.

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

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

7.1.1 Conduct a QC check on the filter lot prior to the field test to demonstrate that filters are free from contamination or interference by extracting and analyzing a minimum of three filters from each lot as follows. Spike with pre-extraction and pre-extraction filter recovery standards for target compounds to be measured and extract each filter separately with toluene as described in Section 11 of this method. After extraction, remove the filters and the solvent from the filters under clean conditions (*e.g.,* a clean nitrogen stream). Analyze the extracts according to the procedures in Section 11 of this method, including adding pre-analysis standard. This filter check analysis must meet the performance requirements in Section 13.1 of this method. Ongoing analysis of LMB can be used to fulfill this check. If criteria are not met for target compounds, repeat with additional filters from the lot or evaluate another lot.

7.2 Adsorbent Resin. Amberlite® XAD–2 resin. All adsorbent resin must meet the cleanliness criteria described for LMB in Section 13.1 of this method 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 described for LMB in Section 13.1 of this method.

7.2.1 Conduct a QC check on the cleaned adsorbent lot or batch following the extraction and analyses procedures in Section 11 of this method, including adding applicable labeled standards. The cleaned adsorbent must meet the criteria described for LMB in Section 13.1 of this method. An LMB conducted with an adsorbent lot or batch can serve this purpose.

7.2.2 Storage. Store adsorbent in a solvent-rinsed nonporous clean container and secure lid.

7.3 Glass Wool. Clean the glass wool to meet the specifications in Section 13.1 of this method. Glass wool is dried of the solvent and stored in a clean glass container with a PTFE-lined screw cap.

7.4 Water. Use deionized or distilled water meeting requirements in Section 13.1 of this method and store in its original container or in a clean glass container with a PTFE-lined screw cap.

7.5 Silica Gel. Indicating type for sampling, 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% (weight/volume) in water.

7.8.2 Sodium Sulfate. Granulated or powdered, reagent grade. Evaluate for cleanliness prior to use with an LMB. The LMB must meet the requirements in Section 13.1 of this method for target compounds. Store in a clean 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 MoCB 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 by fractionation and removal of interferences. Commercially prepacked cleaning columns may be available for this purpose. The liquid column chromatography packing materials must be adequate to clean the samples to be fit for purpose and meet the performance criteria of this method. 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 LMB 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 target compounds. Store at 130 °C (266 °F) in a covered flask. Recommended storage time for acidic alumina is up to five days from 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. Allow to cool and store activated Florisil® silica in a desiccator.

7.8.9.3 Silica Gel. Use either activated, acid- or base-coated 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 LMB performance.

7.8.9.3.1 Activated Silica Gel. Supelco® 1–3651, Bio-Sil® A, 100–200 mesh (or equivalent). Prior to use, silica gel should be activated by solvent rinsing and heat activation. It is recommended to rinse with methylene chloride and activate the silica gel by heating for at least 1 hour at 180 °C (356 °F). After allowing to cool, 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. Allow to cool in a desiccator to room temperature and store in a glass container with a PTFE-lined screw cap. Alternative conditioning procedure may be used if the performance criteria in Section 13.1 are met for target compounds.

7.8.9.3.2 Acidic Silica Gel (30% 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 of acid-coated silica gel. 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 of base-coated silica gel. Store the mixture in glass container with a PTFE-lined screw cap.

7.8.9.4 Carbon/Celite® 545 (or equivalent solid support). Use of a carbon-based column

cleanup material (*e.g.,* one of the many including for example Carbopack® B or C) to further remove non-planar impurities from the samples prior to analysis may be necessary. You must evaluate alternative carbon-based sorbents for this purpose prior to their use. An 18% weight/weight mixture of Carbopack® C and Celite® 545 has been used for this purpose and should be activated at 130 °C (266 °F) for a minimum of 6 hours. Allow to cool and store this mixture in a desiccator.

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

7.9 Sample Analysis.

7.9.1 Helium. 99.999% (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 and extract preparation. You may adjust the sample fortification 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.

Note: When adjusting the fortification concentrations in the final sample extract, consider variables such as the aliquot of extract used and injection volume of samples and calibration.

7.9.3 Pre-Sampling Adsorbent Standard. Prepare stock standard solutions in nonane to enable spiking so that the isotopically labeled compounds in the final sample extract are at the concentration shown under the heading ''Pre-sampling Adsorbent Standard'' in Tables 23–7, 23–8, and 23–9 of this method, for applicable target compound classes.

7.9.4 Pre-extraction Filter Recovery Standard. Prepare stock standard solutions in nonane to enable spiking so that the isotopically labeled compounds in the final sample extract are at the concentration shown under the heading ''Pre-extraction Filter Recovery Standard'' in Tables 23–7, 23–8, and 23–9 of this method, for applicable target compound classes.

7.9.5 Pre-extraction Standard. Prepare stock standard solutions in nonane to enable spiking so that the isotopically labeled compounds in the final sample extract are at the concentration shown under the heading ''Pre-extraction Standard'' in Tables 23–7, 23–8, and 23–9 of this method, for applicable target compound classes.

7.9.6 Pre-analysis Standard. Prepare stock standard solutions in nonane to enable spiking so that the isotopically labeled compounds in the final sample extract are at the concentration shown under the heading ''Pre-analysis Standard'' in Tables 23–7, 23–8, and 23–9 of this method, for applicable target compound classes.

8.0 Sample Collection, Preservation, and Storage

8.1 Sampling. This method involves collection and recovery of trace concentrations of target semivolatile organic compounds. Therefore, field sampling and recovery staff should be trained and experienced 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 LMB criteria in Section 13.1 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 up to 400 °C (752 °F) for a minimum of 2 hours may be necessary to remove contaminants or interferents from particularly dirty samples. Allow glassware to cool after baking.

Note: Repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb 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. Fill a module with 20 to 40 g of XAD–2. Spike modules before the sampling event, but do not spike the modules in the field. Add the pre-sampling adsorbent standard to the top quarter of the adsorbent bed rather than onto the top or bottom of the adsorbent bed. Add sufficient spike (picograms (pg)/module) to result in the final sample theoretical concentrations specified in Tables 23–7, 23–8, and 23–9 of this method for PCDD/PCDF, PAH, and PCB, respectively, and to be above the lowest calibration concentration to ensure the standard recovery is quantitative. For samples with known or anticipated target compound concentration significantly higher or lower than the specified concentration in these tables, adjust the pre-sampling adsorbent standard concentration to the expected native compound concentration, but no less than 10 times the method detection limit (MDL). Follow the XAD–2 with cleaned glass wool and tightly cap both ends of the module. For analysis that includes 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, regulation, or permit, 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 a tool to evaluate equipment preparation and potential contamination during sample recovery 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, using the 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 with a 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.

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 °C, 68 °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 sampling 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 PAH and/or PCB are the target compounds. Quantitatively recover impinger water samples for analysis if PAH and/or PCB 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 °C, 68 °F) and dark conditions prior to transport to the laboratory. Ship samples cool (≤20 °C, 68 °F), shielded from ultraviolet light. In addition, follow the procedures in American Society for Testing and Materials (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 the storage conditions in Table 23–10 from the time the laboratory receives the samples until analysis.

8.3.3 You may store adsorbent samples for PCDD/PCDF or PCB analysis 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.

Note: The hold times listed in this method for adsorbent samples for PCDD/PCDF and PCB are recommendations as these compounds are very stable under the conditions listed in this section.

8.3.4 Protect adsorbent samples destined for PAH analysis from ultraviolet light. You may store adsorbent samples for PAH analysis in the dark 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 40 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. Sample extracts must not be stored with pierced septa.

Note: The hold times listed in this method for sample aliquots for PCDD/PCDF and PCB are recommendations as these compounds are very stable under the conditions listed in this section.

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. The minimum requirements of this method consist of the initial demonstration of capability (IDC) and ongoing QC requirements. The analysis team shall perform an IDC to demonstrate acceptable accuracy and precision with this method as described in Section 9.3. The ongoing QC includes performing CCVs and LMBs to evaluate an individual laboratory's performance against the criteria in this method. The method includes analysis of samples spiked with labeled compounds to evaluate and document data quality. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics and requirements of the method.

9.1 Record and report data and information that will allow an independent reviewer to validate the determination of each target compound concentration. Record and report the data as described in Sections 9.1.1 through 9.1.7 of this method and performance criteria results required in Section 13 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 EMPC-flagged data to be zero concentrations. Calculate and report the EMPC concentrations.

9.1.7.2 In determining compliance with any PCDD and PCDF standard developed using zero for values that are below the EDL of the method, including federal emission standards using Method 23 promulgated under 40 CFR parts 60 and 63 prior to March 20, 2023, 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 For each sample you must report EDLs, MDLs, LMBs and Field Train Proof Blank results and target compound analysis results.

9.2 Isotopically Labeled Standard Recovery.

9.2.1 Pre-sampling Adsorbent Standard and Pre-extraction Filter Recovery Standard Recoveries. Pre-sampling adsorbent standard and pre-extraction filter recovery standard 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 adsorbent standard may be an indication of breakthrough in the sampling train.

9.2.1.1 If the pre-sampling adsorbent standard average percent recovery is below 70%, the sampling run is not valid, and the stack test must be repeated. As an alternative, you do not have to repeat the stack test for invalid analyses if the pre-sampling adsorbent standard average percent recovery is 25% or more and you divide the final results by the fraction of the pre-sampling adsorbent standard average percent recovery.

9.2.1.2 If the percent recovery of all the pre-extraction filter recovery standard compounds is below 70%, you may reanalyze the sample. If the recovery is still below the limit, the filter sampling extraction is not valid, and you must repeat the stack or vent sampling and subsequent analysis.

9.2.2 Pre-extraction Standard Recoveries. Pre-extraction standard recoveries must demonstrate on a per sample basis that recovery of the labeled standard achieved the requirements in Section 13.15 of this method. If the recovery criteria are not met, you may reanalyze the sample. If the recovery criteria are still not met, the sampling run is not valid, and the stack test must be repeated. Recoveries outside the acceptable range for pre-extraction standard 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 Standard Response. Pre-analysis standard recoveries must demonstrate on a per sample basis that adequate labeled standard signal meets the requirements in Section 13.16 of this method. Add pre-analysis standard to every sample (including blanks, QC samples, and calibration solutions) in a known concentration. If the prepared samples do not meet the pre-analysis standard response criteria, you may reanalyze and/or prepare and analyze archive samples to attempt meeting requirements for the compounds that do not meet the pre-analysis standard response criteria. Poor sensitivity compared to initial calibration response may indicate injection errors or instrument drift.

9.3 Initial Demonstration of Capability (IDC). The IDC must be successfully performed prior to analyzing field samples by meeting the QC requirements in Table 23–18. The IDC must be repeated if changes are made to analytical parameters not previously validated during the IDC. This may include, for example, changing the sample volume, selecting alternate quantitation ions, extending the calibration range, adding additional pre-analysis standard, or adding additional pre-extraction standard. The same calibration range used during the IDC must be used for the analysis of field samples.

9.3.1 Perform initial calibration following the procedures in Section 10. The lowest calibration standard used to establish the initial calibration must not be less than three times the MDL. The initial calibration must meet performance criteria in Section 13.9.

9.3.2 Lowest Calibration Concentration Confirmation. Establish a target concentration for the lowest calibration standard based on the intended use of the method. The lowest calibration concentration may be established by a laboratory or programmatic lowest quantitative reporting requirement. The laboratory calibration curve must be set at or below this level. Perform seven replicate analyses of a calibration sample prepared at proposed lowest calibration concentration. The replicate analyses of the lowest calibration concentrations standards must meet the criteria in Sections 13.9 and 13.17.1.

Note: Consider that establishing the lowest calibration concentration too low may cause repeated failure of ongoing QC requirements.

9.3.3 Calculate Lowest Calibration Statistics. Calculate the mean and standard deviation for each analyte in these replicates (those used in Section 9.3.2). Determine the Half Range for the Prediction Interval of Results (HRPIR) using Equation 23–13. Calculate the Upper and Lower Limits for the Prediction Interval of Results (PIR) with Equations 23–14 and 23–15.

9.3.4 Lowest Calibration Point Acceptance Criteria. The laboratory's ability to measure analyte concentrations down to the lowest calibration point is confirmed if the criteria presented in Section 13.17.1 are met. If these criteria are not met, the lowest calibration point as been set too low and must be confirmed at a higher concentration.

9.3.5 Demonstration of Low System Background. Analyze an LMB after the highest standard in the calibration range. If an automated extraction system is used, an LMB must be extracted on each port. Performance criteria are presented in Section 13.1. Note: When using automated systems, the same systems must be used for samples and QC samples, such as blanks and resin checks.

9.3.6 Initial Calibration Verification. A QCS must be analyzed during the IDC, and then following each initial calibration thereafter (at a minimum quarterly). A QCS is a mid-level standard prepared from a second source standard or prepared from a source of standards different from the source of calibration standards. The purpose of the QCS is to verify the integrity of the primary calibration standards. The acceptance criterion is presented in Section 13.11.

9.3.7 MDL. Perform an MDL determination using a minimum of seven spiked combined filter/sorbent media samples, spiked within 2 to 10 times of the expected MDL, and seven LMBs (combined filter/sorbent media) through all the steps of the method following the requirements in 40 CFR part 136 Appendix B. Confirm target compounds meet the qualitative identification criteria in Sections 13.12 and 13.13. The criteria for the MDL determination are presented in Section 13.6.1 of this method.

9.3.8 MDL Confirmation. Confirm newly determined MDLs by preparing a low-level spiked combined filter/sorbent media sample by spiking the sorbent with native target compounds at 1 to 5 times the MDL and pre-extraction standard at the concentration used to analyze field samples and analyze. The criterion for the MDL confirmation is presented in Section 13.6.1 of this method.

9.3.9 Demonstration of Precision. Prepare, extract, and analyze seven replicate spiked samples in a valid Extraction Batch. Fortify the spiked samples near the midpoint of the initial calibration curve. The criterion is presented in Section 13.17.2 and Table 23–18. Demonstration is repeated for failed compounds only.

9.3.10 Demonstration of Accuracy. Using the same set of replicate data generated for

Section 9.3.9 of this method, calculate the average % recovery. The criterion is presented in Section 13.17.3 and Table 23–18. Demonstration is repeated for failed compounds only.

9.4 LMBs. Evaluate background contamination from glassware, equipment, solvents, standards, and media used for sample batches using an LMB prepared and analyzed identically to the field samples, including the same labeled standards, media, sodium sulfate, glass wool, glassware, solvents, etc. An LMB must be extracted with every batch of samples. Analyze an LMB at least once during each analytical sequence or every 12 hours, whichever period is shorter. If multiple LMB are required for an analytical sequence, report the initial LMB associated with each 12 hour analysis period.

9.5 EDL. Calculate the EDL using Equation 23–11 of this method.

Note: If the applicable compliance limit is total dioxin or total furan, report the sum of the EDLs for all the target compounds. If the applicable rule limit is a TEQ value, report the sum of the EDLs for all target compounds multiplied by their corresponding compound specific TEF.

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 is used to evaluate equipment preparation and potential contamination during sample recovery and consists of a fully assembled train at the sampling site. Prepare and assemble the field train proof blank train in a manner identical to that described in Sections 8.1.3 and 8.1.4 of this method using glassware from the same preparation batch as the field samples. The field train proof blank train must remain assembled for the same average amount of time samples are collected. Recover the field train proof blank train as described in Section 8.2 of this method. Follow all subsequent steps for field train proof blank train sample preparation and analysis used for field samples including data reporting. Section 13.1 of this method describes the criteria for the field train proof blank.

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 resolving power of at least 10,000 at 10% percent of the peak height or 25,000 at 50% percent of the peak height. The resolving power for PAH and PCB analysis may be 8,000 at 10% of the peak height or 15,000 at 50% of the peak height. Assess the resolution at three exact m/z's representing the low-, mid-, and high-m/z range of the masses used to measure the target compound class. 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.

10.2.2 Initial Calibration. Calibrate the HRGC/HRMS system using a minimum of five concentrations over a range that brackets expected 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 show the calibration concentrations recommended by this method, as applicable to the target compound classes. Determine the initial relative response factors for the target compounds and isotopically labeled standards using the initial calibration. Criteria for the initial calibration is in Section 13.9 of this method.

10.2.2.1 Lock-Mass Ions. Tables 23–4, 23–5, and 23–6 of this method present the recommended mass spectrometer lock-mass ions for PCDD/PCDF, PAH, and PCB, respectively. The reference compounds PFK or FC43 have ions that may be selected as your lock-mass and QC check ions. Monitor the QC check ions specified in these tables to verify instrument stability during the analysis (see Section 13.8 for performance criteria). Additional cleanup of the sample extract (or archive extract) and reanalysis is necessary for failure to maintain the lock-mass during analysis.

10.2.2.2 The relative standard deviation (RSD) for the mean calibration relative 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 GC/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.

Note: An interference with PFK m/z 223.9872 may preclude meeting 10:1 S/N for the DiCB congeners at the optional Cal 1 level (Table 23–11). If this interference occurs, 10:1 S/N must be met at the Cal 2 level.

10.2.3 Continuing Calibration Verification.

10.2.3.1 Prepare the CCV standard at the same time as the batch of field samples using the same labeled standards. Prepare CCV standards at mid-level of the calibration (C3 level from Tables 23–11, 23–12, or 23–13 of this method). Inject a CCV standard, for the target compound class, at least once every 12 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 RRF for each native compound measured in a CCV must not deviate from the initial calibration RRF by more than the limits shown in Table 23–14.

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 The S/N ratio for the GC/MS signal present in every selected ion current profile must be greater than or equal to 10.

10.2.3.4 Repeat the initial calibration when there is a failure to meet the requirements for acceptable CCV standard analysis.

10.2.3.5 Column Separation Check. Use the results from a CCV to verify and document the resolution required in Section 13.2, 13.3, or 13.4 of this method for the target compound classes analyzed with this method. If target compounds are not sufficiently resolved to meet the requirement, an analysis on a confirmation column is recommended (see Section 13.5 of this method).

10.2.3.6 If you use a confirmation column, perform the resolution check in Section 10.2.3.5 of this method to document the required resolution on the confirmation column. See Section 13.5 of this method on confirmation columns, if needed.

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 PAH and the mono- through tri-chlorobiphenyls may be totally or partially lost. Note: Rotary evaporation is applicable when analyzing for PCDD/PCDF only. Snyder column apparatus is recommended when analyzing for PAH and PCB.

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 LMB for associated reagents, materials, and media meets the performance requirements in Section 13.1 of this method.

11.1.2 Container No. 1 (Filter) Preparation. Spike the filter with the appropriate pre-extraction filter recovery standard to result in the final sample extract concentrations 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 dry enough to prevent overspill, 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. Spike the adsorbent with the appropriate pre-extraction standard to result in the final sample extract concentrations shown in Tables 23–7, 23–8, and 23–9 of this method, as applicable, spiked into the adsorbent, not on top of the adsorbent. 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 glass solvent rinse catch 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 add 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 sodium sulfate.

11.1.7 Add the appropriate pre-extraction standard for the target compound classes (to result in the final sample extract concentrations shown in 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 solvent reservoir to 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 standard recovery performance criteria in Section 13.15 of this method. The solvent should cycle completely through the system a minimum of 48 times.

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 the pre-extraction standard sufficient to meet the performance criteria in Section 13.15 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 LMB samples in the same manner as samples.

Note: To meet isotopically labeled standard recoveries for low molecular weight PCB and PAH, do not evaporate samples to dryness and do not use a rotary evaporator to concentrate extracts.

11.2.3 Allow the sample extract 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 sample extract for PCB and/or PAH analysis and archive.

Note: If using amount other than half the sample extract, adjust the spiking amount of the labeled standards accordingly.

11.2.4 If necessary, further concentrate the sample extract for cleanup and analysis using concentration techniques (*e.g.,* Kuderna Danish, rotary evaporation, nitrogen blowdown) found to recover the pre-extraction standard 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, Gel Permeation Chromatography, 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 PCDPE 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 PCDPE Fractionation and Cleanup. You may use a Florisil® column to remove PAH and PCDPE from the sample extract. You may also fractionate sample extracts using Florisil® as the first cleanup step to separate PAH for analysis.

Note: High concentrations of PAH may interfere, 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% dichloromethane in hexane. This fraction (Fraction 1) should contain target PCB, and selected hydrocarbons and chlorinated monoaromatic compounds.

11.3.1.3 Elute the column with 35 mL of 15% 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% dichloromethane in hexane. The fraction (Fraction 3) should contain target PAH.

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

11.3.2 PCDD/PCDF and PCB Fractionation and Cleanup. You may remove PAH from the original aliquot of sample extract used for PCDD/PCDF analysis as described in Section 11.3.1 of this method. Design the column cleanup chromatography for PCDD/PCDF and PCB such that two consecutive fractions are collected (one with PCDD/PCDF and one with PCB) without impacting the detection limits. Depending on the source and sample matrix of the original sample, one or more of the following column cleanup approaches may be necessary to further 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 LMB 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 × 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% 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 transfer the concentrated sample (about 5 mL). Rinse the container 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 PCDD/PCDF.

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% potassium hydroxide silica gel, 0.9 g of silica gel, 4.5 g of 44% sulfuric acid silica gel, 6.0 g of 22% sulfuric acid silica gel, 0.9 g of silica gel, 3.0 g of 10% 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. Rinse the container 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 PCDD/PCDF.

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 PCDD/PCDF from the column with 20 to 40 mL of 50% 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 volume/volume (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 PCDD/PCDF 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 extract 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 to result in the final sample extract concentrations in Tables 23–7, 23–8, and 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, typically 1 µl. You may perform separate analyses using different GC columns for each of the target compound classes. Perform calibration and sample analysis for each target compound class using the same instrument operating conditions including injection volume.

11.4.1.2.1 If target compounds are not resolved sufficiently from other target compounds or interferences in the sample to meet the requirements in Section 10.2.3.5 or 10.2.3.6 of this method, as applicable to the compound class being analyzed, or as otherwise specified in an applicable regulation, permit, or other requirement, analyze sample (or 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 CCVs, that the alternative column system is able to meet the applicable specifications of Section 10.2.3.5 or 10.2.3.6 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/PCDF, PAH, and PCB, 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 analyzed 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/PCDF and PCB, Table 23–15 of this method provides acceptance limits for the integrated ion abundance ratio of primary and secondary target compound ions. 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 further cleanup an archived sample to remove the interference(s). Report analysis results as an EMPC when a response meets identification criteria except the ion abundance ratio criteria or when a peak representing a PCDPE has been detected at the retention time. This method does not consider EMPC-flagged data to be zero concentrations.

Note: Some EMPCs may be caused by poor ion statistics when the concentration of the target compound is at or near the DL.

11.4.3.4.2 The retention time for the analytes must be within 3 seconds of the corresponding 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/PCDF and PCB, 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 pre-extraction standard compounds by comparing to the pre-extraction 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 congeners, the retention time of the native congener must be within 0.006 relative retention time (RRT) units of the pre-extraction 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.

11.4.3.4.7 The separation of target compounds, including 2,3,7,8–TeCDD and 2,3,7,8–TeCDF, must satisfy the separation criteria in Section 10.2.3.5 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. See Section 13.5 of this method on confirmation columns, if needed.

11.4.3.4.8 Chlorodiphenyl Ether Interference. If chromatographic peaks are detected at the retention time of any PCDF in any of the m/z channels used to monitor PCDPE, there is evidence of a positive interference and you may opt to flag data noting the interference and keep the value to calculate PCDF concentration as EMPC or reanalyze 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 PCDPE during sample cleanup.

11.4.3.4.9 The recommended MS lock-mass ions are specified in Tables 23–4, 23–5, and 23–6 of this method for PCDD/PCDF, PAH, and PCB, respectively. Monitor the QC check ions to verify instrument stability during the analysis. If the QC check ion signal varies by more than 25% from the average response across the run, flag results for all isomers at corresponding retention time as the lock-mass ions or QC check ions. You have the option to reanalyze after additional cleanup on the sample (or an archived portion of the sample if the archive is available), or after dilution of the sample. Alternately, determine through additional quality review whether the target analyte and its corresponding isotopically labeled standard are equally affected by the change in lock-mass ions and/or QC check ions. When you reanalyze a sample, ensure all concentration calculations are reported from the reanalyzed sample.

11.4.3.4.10 For the identification of PAH, the RRT of each native to its labeled compound must be within 0.006 RRT units compared to the corresponding RRTs in the continuing calibration. 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. Using the CCV RRF, calculate the mass of each target compound, using equations in Section 12.7 of this method. Use the pre-extraction standard to correct the native target compounds result for variations in performance of the extraction, cleanup, and concentration steps of the analysis. Recovery of pre-extraction standard must meet the 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 pre-extraction standard compounds for use in calculating the response factor and the concentrations of PCB. Recoveries of all labeled standard compounds must meet the minimum recovery specifications in Section 13 of this method. Note: Unacceptably low recoveries can be an indication of a sample processing step that caused the low recoveries, such as spiking errors.

11.4.3.5.1 Use Equation 23–7 to calculate the amount of each target compound or group in the sample.

11.4.3.5.2 Use Equation 23–8 to calculate the concentration per dscm of each target compound or group in the gas.

11.4.3.5.3 Quantify native 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-TeCDD 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 RRF of the nearest eluting native target PCB in the same homolog group and the pre-extraction standard 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, etc.) 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 PCB may be reported by summing all congeners identified at all window-defining 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.

$A1_n$ = Integrated ion current of the primary m/z values for the target native compound.
$A1_{pe}$ = Integrated ion current of the primary m/z values for the pre-extraction standard compound (assigned in Tables 23–4, 23–5, and 23–6 of this method).
$A1_{pa}$ = Integrated ion current of the primary m/z values for the pre-analysis standard compound.
$A2_n$ = Integrated ion current of the secondary m/z values for the target native compound. For PAH $A2_n = 0$.
$A2_{pe}$ = Integrated ion current of the secondary m/z's for the pre-extraction standard compound. For PAH $A2_l = 0$.
$A2_{pa}$ = Integrated ion current of the secondary m/z values for the pre-analysis standard compound.
C_i = Mass of compound i in the sample, pg.
C_{idscm} = Concentration of target native compound i in the emission gas, pg/dscm.
C_T = Total mass of target compounds in the sample, pg/sample.
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 for each quantitation ion for native target compounds.
H_{ci} = Summed heights of the noise at the primary and secondary m/z's of the pre-extraction standard i.
L_{PIR} = Lower limit for the prediction interval of results.
n = Number of values.
PD = Percent Difference in the RRF of the continuing calibration verification compared to the average RRF of the initial calibration, %.
Q_n = Quantity of the target native compound, pg.
Q_{pe} = Quantity of the pre-extraction standard, pg.
Q_{pa} = Quantity of the pre-analysis standard, pg.
R = Recovery of pre-sampling adsorbent standard and pre-extraction filter recovery standard, %.
R_{pe} = Recovery of pre-extraction standard, %.
RRF_i = Relative response factor of a native target compound or pre-sampling adsorbent standard and pre-extraction filter recovery standard at calibration level i.
RRF_{pe} = Relative response factor of a pre-extraction standard compound.
RRF_{ccv} = Relative response factor of a native target compound or pre-sampling adsorbent standard and pre-extraction filter recovery standard in the continuing calibration verification.
RSD = Relative standard deviation, in this case, of RRFs over the calibration levels, %.
SD = Standard deviation.
SD_{RRF} = Standard deviation of initial calibration RRFs.
U_{PIR} = Upper limit for the prediction interval of results.
WDC = Window-defining congener representing an isotopically labeled compound that defines the beginning or end of a retention time window bracketing a target homolog.

12.2 Individual Compound RRF for Each Calibration Level i. Equation 23–1 for the response factor of each target native compound relative to its labeled pre-extraction standard analog includes the integrated ion current of both the primary and secondary m/z values for each compound in the calibration standard, excluding PAH, which use only primary m/z values. Use Equation 23–2 to calculate the RRF for pre-extraction standard.

$$RRF_i = \frac{(A1_n + A2_n)Q_{pe}}{(A1_{pe}+A2_{pe})Q_n} \quad \text{Eq. 23-1}$$

$$RRF_{pe} = \frac{(A1_{pe} + A2_{pe})Q_{pa}}{(A1_{pa}+A2_{pa})Q_{pe}} \quad \text{Eq. 23-2}$$

Note: the units for Q_{pe} and Q_n in Eq. 23–1 and the units for Q_{pa} and Q_{pe} in Equation 23–2 must be the same.

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

$$\overline{RRF} = \frac{1}{n}\sum_{i=1}^{n} RRF_i \quad \text{Eq. 23-3}$$

12.4 Percent RSD of the RRFs for a Compound Over the Calibration Levels. The requirement for the initial calibration RSD is in Section 13.9 and Table 23–14 of this method.

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} x\ 100\% \quad \text{Eq. 23-4}$$

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

$$SD_{RRF} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1}} \quad \text{Eq. 23-5}$$

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. Use Equation 23–1 to calculate the RRF for the continuing calibration verification for comparison to the average RRF from the initial calibration. The requirement for the continuing calibration verification % difference is in Section 13.10 and Table 23–14 of this method.

$$PD = \frac{RRF_{ccv} - \overline{RRF}}{\overline{RRF}} x\ 100\% \quad \text{Eq. 23-6}$$

12.7 Amount of Individual Target Compound i in the Sample by Isotope Dilution (pg). This equation corrects for the target native compound recovery based on its labeled pre-extraction standard analog. This equation is also used to calculate the amount of pre-sampling adsorbent standard and pre-extraction filter recovery standard recovered.

$$C_i = \left[\frac{Q_{pe}\,(A1_n + A2_n)}{(A1_{pe}+A2_{pe})RRF_{CCV}}\right] \quad \text{Eq. 23-7}$$

Note: For the quantitation of the pre-sampling adsorbent standard and the pre-extraction filter recovery standard, use a corresponding pre-extraction isomer (or homolog) with the closest retention time.

12.8 Concentration of the Individual Target Compound or Group i in the Emission Gas (pg/dscm). The total concentration of a target compound group in the sample can be calculated by substituting C_T from Eq. 23–12 for C_i in Equation 23–8.

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

12.9 Recovery of Labeled Compound Standards. Use Equation 23–9 to determine the recovery of pre-sampling adsorbent standard and the pre-extraction filter recovery standard. Use Equation 23–10 to determine the recovery of the pre-extraction standard. The recovery performance criteria for these standards are in Sections 13.14, 13.15, and 13.16 of this method.

$$R = \frac{conc.\ found}{conc.\ spiked}\ x\ 100\% \qquad \text{Eq. 23-9}$$

$$R_{pe} = \left[\frac{Q_{pa}\,(A1_{pe}+A2_{pe})}{(A1_{pa}+A2_{pa})(Q_{pe})(RRF_{pe})}\right] x\ 100\% \qquad \text{Eq. 23-10}$$

Note: Recovery may be calculated based on mass instead of concentration, as needed.

Note: R_{pe} must be corrected for the fraction of the original sample extract used for analysis. (*e.g.*, if half of the extract is used for analysis of the target class, R_{pe} must be multiplied by a factor of 2).

12.10 Estimated Detection Limit (EDL).

$$EDL = \frac{2.5\,(H_{ai})\,Q_{pe}}{H_{ci}\,x\,RRF_{CCV}} \qquad \text{Eq. 23-11}$$

12.11 Total Target Compound Mass.

$$C_T = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-12}$$

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.

12.12 Upper and Lower Limits for the Prediction Interval of Results (PIR)

Half Range (HR) for the Predication Interval of Results

$$HR_{PIR} = (3.963)(S) \qquad \text{Eq. 23-13}$$

Note: 3.963 is a constant value for seven replicates.

Upper and Lower Limits for the Prediction Interval of Results

$$U_{PIR} = \left[\frac{(Mean+HR_{PIR})}{Spike\ Concentration}\right] 100\% \qquad \text{Eq. 23-14}$$

$$L_{PIR} = \left[\frac{(Mean-HR_{PIR})}{Spike\ Concentration}\right] 100\% \qquad \text{Eq. 23-15}$$

13.0 Method Performance

Data generated with this method must be fit for purpose. Applicable results of method performance criteria in this section must be reported. Consequences of failed quality criteria are provided with the criteria in this section.

13.1 Background Assessment—Field Train Proof Blank, LMB and Materials. Determine the contribution to target compound concentration from reagents, media and glassware used to make target compound measurements. Conduct at least one field train proof blank for each test series at a single facility. Analyze at least one LMB sample during an analytical sequence or every 12 hours, whichever is shorter. Native target compound concentrations in the field train proof blank, LMB and materials assessment 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 (*e.g.*, compliance limit or other limits set by consent decree or permit), whichever is higher. The field train proof blank, LMB and materials assessment must also meet the performance specifications in Tables 23–7, 23–8, and 23–9, as applicable to the compound target list.

13.2 GC column or column systems used to measure PCDD/PCDF must meet the column separation requirements in Section 6.5.2.1 of this method and the applicable requirements in Sections 10.2.3.5 and 11.4.3.4 of this method using the continuing calibration verification. Failure to meet this chromatographic resolution criterion requires data from this analysis to be flagged explaining the potential bias of the results.

13.3 GC column or column systems used to measure PAH must meet the column separation requirements in Section 6.5.2.2 of this method and the applicable requirements in Sections 10.2.3.5 and 11.4.3.4 of this method using the continuing calibration check. Failure to meet this chromatographic resolution criterion requires data from this analysis to be flagged explaining the potential bias of the results.

13.4 GC column or column systems used to measure PCB must meet the column separation requirements in Section 6.5.2.3 of this method and the applicable requirements in Sections 10.2.3.5 and 11.4.3.4 of this method using the continuing calibration check and be able to achieve unique resolution and identification of the toxics for determination of a TEQ_{PCB}. The rule requiring the use of this method will establish which WHO TEF to use. Failure to meet this chromatographic resolution criterion requires data from this analysis to be flagged explaining the potential bias of the results.

13.5 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 13.2, 13.3, and/or 13.4 of this method, analyze sample (or 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. When using a confirmation column, document the required resolution.

13.6 Detection Limits.

13.6.1 MDL. The MDLs are determined following the procedures in Section 9.3.7 of this method. MDLs are confirmed by

preparing and analyzing a spiked sample (spiked at 1 to 5 times the determined MDL, see Section 9.3.8), then confirm that the target compounds meet the qualitative identification criteria in Section 11.4.3.4 of this method. If the MDL confirmation criteria are not met, the MDL determination is repeated with a higher spike concentration until criteria are met.

13.6.2 EDL. If the sample specific EDLs are less than 50% of the emission standard, the EDLs are acceptable.

13.7 Tune. The groups of monitored ions are listed in Tables 23–4, 23–5, and 23–6 of this method, as applicable for the target compound class. Tune the instrument to meet the required resolving power in Section 10.2.1 for the desired target compound class. Assess the resolution at three exact m/z's representing the low-, mid-, and high-m/z range of the masses used to measure the target compound class. You may use peak matching and the chosen PFK (or FC43) reference peak to verify that the exact mass is within 5 ppm of the required value.

13.8 Lock-Mass Ions. The MS lock-mass and QC check ions in Tables 23–4, 23–5, and 23–6 of this method are recommended for PCDD/PCDF, PCB, or PAH, respectively. The reference compounds PFK or FC43 have ions that may be selected as your lock-mass and QC check ions. Monitor the QC check ions specified in these tables to verify instrument stability during the analysis; these must not vary >25% from the average response. Additional cleanup on sample extract (or archive extract) and reanalysis is necessary for failure to maintain lock-mass during analysis.

13.9 Initial Calibration.

13.9.1 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.

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

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

13.10 Continuing Calibration Verification.

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

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

13.10.3 The S/N ratio for the GC/MS signal present in every selected ion current profile must be greater than or equal to 10.

13.10.4 Repeat the initial calibration when there is a failure to meet the requirements for an acceptable CCV analysis.

13.10.5 Column Separation Check. Use the results from a CCV to verify and document the resolution required in Sections 13.2, 13.3, or 13.4 of this method for the target compound classes analyzed with this method. The separation criteria are applicable to all the compounds in a target class whether analyzed by a single or multiple GC columns. If a confirmation column is used, document required resolution (see Section 13.5).

13.11 QCS. A QCS must be analyzed during the IDC and after initial calibrations (at a minimum quarterly). The acceptance criterion for the QCS is 70–130% of the true value. If the accuracy for any analyte fails the recovery criterion, prepare a fresh standard dilution and repeat. If the freshly prepared QCS fails, determine the cause, recalibrate the instrument if necessary and reanalyze the QCS.

13.12 Compound Identification for PCDD/PCDF and PCB.

13.12.1 Target compounds must have ion abundance ratios within the control limits in Table 23–15 of this method. PAH target compounds have single ion identifiers with no ion abundance ratio requirement. Report analysis results as an EMPC when a response meets identification criteria but fails the ion abundance ratio criteria or when a peak representing a PCDPE has been detected at the target compound retention time.

13.12.2 The retention time for the analytes must be within 3 seconds of the corresponding pre-extraction standard.

13.12.3 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.

13.12.4 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.

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

13.12.6 The S/N ratio for the monitored ions for native compounds must be greater than or equal to 2.5.

13.12.7 Identify and quantify isomers that do not have corresponding pre-extraction standard compounds by comparing to the pre-extraction standard of the same compound class with the nearest retention time to the target compound.

13.12.8 If chromatographic peaks are detected at the retention time of any PCDD/PCDF in any of the m/z channels used to monitor PCDPE, 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 PAH.

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 Pre-sampling Adsorbent Standard and Pre-extraction Filter Recovery Standard Recovery. Recoveries of pre-sampling adsorbent standard added to the sample and pre-extraction filter recovery standard added to the filter must be between 70 and 130% (see Tables 23–7, 23–8, and 23–9 of this method).

13.14.1 If the recovery of all the pre-sampling adsorbent standard compounds is below 70%, the sampling runs are not valid, and you must repeat the stack or vent sampling. As an alternative, you do not have to repeat the test if the average pre-sampling adsorbent standard recovery is 25% or more and you divide the final results by the average fraction of pre-sampling adsorbent standard recovery.

13.14.2 If the recovery of all the pre-extraction filter recovery standard compounds is below 70%, you may reanalyze the sample. If the recovery criteria are still not met, the sampling recovery is not valid, and you must repeat the stack or vent sampling.

13.15 Pre-extraction Standard Recovery. Recoveries of all pre-extraction standard compounds added to the sample must be between 20 to 130% for PCDD/PCDF and PAH (see Tables 23–7 and 23–8 of this method) and between 20 to 145% for PCB (see Table 23–9 of this method). If the recovery criteria are not met, you may reanalyze the sample and/or prepare and analyze the archive sample. If the recovery criteria are still not met, the sampling run is not valid, and the stack test must be repeated.

13.16 Pre-analysis Standard Response. Response of all pre-analysis standard compounds must show a S/N for every selected ion current profile of ≥ 10. If the minimum response is not met, you must reanalyze the sample. Poor sensitivity compared to initial calibration response may indicate injection errors or instrument drift.

13.17 IDC—Lowest calibration concentration, Demonstration of precision, Demonstration of accuracy.

13.17.1 Lowest calibration concentration. The Upper PIR Limit must be less than, or equal, to 150%; and the Lower PIR Limit must be greater than, or equal to, 50%. If these criteria are not met, the lowest calibration point has been set too low and must be confirmed at a higher concentration.

13.17.2 Demonstration of precision. The percent relative standard deviation (%RSD) of the concentrations from the replicate analyses must be less than 20% for all target analytes. Demonstration would be repeated for failed compounds only.

13.17.3 Demonstration of accuracy. The average % recovery for each target analyte must be within 70 to 130%. Demonstration would be repeated for failed compounds only.

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 modifications 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 handled and disposed in accordance with federal, state, and local regulations.

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

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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 No.	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	34465–46–8	1,2,3,4,7,8,9-HpCDF	55673–89–7
Total HpCDD	37871–00–4	Total TeCDF	55722–27–5
OCDD	3268–87–9	Total PeCDF	30402–15–4
		Total HxCDF	55684–94–1
		Total HpCDF	38998–75–3
		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-Methylnaphthalene	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	192–97–2
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
Benz[*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 PCDD AND PCDF

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	$C_{12}H_4{}^{35}Cl{}^{37}ClO$	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	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TeCDF (S)	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S).
317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_2{}^{37}ClO$	TeCDF (S)	425.9775	QC	$C_9F_{16}N$	FC43.
319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	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.
330.9792	QC	C_7F_{13}	PFK	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF (S).
331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TeCDD (S)	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF (S).
333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TeCDD (S)	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD.
339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD.
341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF	430.9729	QC	C_9F_{17}	PFK.
354.9792	LOCK	C_9F_{13}	PFK	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD (S).
351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S).
353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)	442.9728	LOCK	$C_{10}F_{17}$	PFK.
355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCPDE.
357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD	430.9729	LOCK	C_9F_{17}	PFK.
367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF.
369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF.
375.9807	QC	$C_8F_{14}N$	FC43	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD.
375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD.
409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE	463.9743	QC	$C_9F_{18}N$	FC43.
373.8208	M+2	$C_{12}H_235Cl_5{}^{37}ClO$	HxCDF	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S).
375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S).
375.9807	QC	$C_8F_{14}N$	FC43	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE.
				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. LOCK = Lock-Mass Ion PFK or FC43. QC = Quality Control Check Ion. Note: Consider monitoring 328 m/z if a high level of PCB is expected.

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

Aromatic ring No.	Mass [a]	Ion type [b]	Elemental composition	Target analyte
2	128.0624	M	$C_{10}H_8$	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	$^{13}C_6{}^{12}C_7H_{10}$	$^{13}C_6$-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	$C_{18}H_{12}$	Benz[*a*]anthracene.
	230.9856	LOCK		PFK.
4	234.114	M	$^{13}C_6C_{12}H_{12}$	$^{13}C_6$-Benz[*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	$^{13}C_6{}^{12}C_{14}H_{12}$	$^{13}C_6$-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 PCB

Chlorine substitution	Mass [a]	Ion type [b]	Elemental composition	Target analyte	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	Fn-5; Cl-5,6,7	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB.
	190.0363	M+2	$^{12}C_{12}H_9{}^{37}Cl$	Cl-1 PCB		325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB.
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	$^{13}C_{12}$ Cl-1 PCB		327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB.
	202.0766	M+2	$^{12}C_{12}H_9{}^{37}Cl$	$^{13}C_{12}$ Cl-1 PCB		337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB.
	218.9856	LOCK	C_4F_9	PFK		339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB.
Fn-2; Cl-2,3	222.0003	M	$^{12}C_{12}H_8{}^{35}Cl_2$	Cl-2 PCB		354.9792	LOCK	C_9F_{13}	PFK.
	223.9974	M+2	$^{12}C_{12}H_8{}^{35}Cl{}^{37}Cl$	Cl-2 PCB		359.8415	M+2	$^{12}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB.
	225.9944	M+4	$^{12}C_{12}H_8{}^{37}Cl_2$	Cl-2 PCB		361.8385	M+4	$^{12}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB.
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	$^{13}C_{12}$ Cl-2 PCB		363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB.
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl{}^{37}Cl$	$^{13}C_{12}$ Cl-2 PCB		371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB.
	242.9856	LOCK	C_4F_9	PFK		373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB.
	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB		393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB.

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

Chlorine substitution	Mass [a]	Ion type [b]	Elemental composition	Target analyte	Chlorine substitution	Mass [a]	Ion type [b]	Elemental composition	Target analyte
	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB		395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB.
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB		397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	$^{37}Cl_3$ Cl-7 PCB.
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	$^{13}C_{12}$ Cl-3 PCB		405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB.
Fn-3; Cl-3,4,5	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB		407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB.
	257.9584	M+2	$^{12}C_{12}$ $H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB		454.9728	QC	$C_{11}F_{17}$	PFK.
	259.9554	M+4	$^{12}C_{12}H_7{}^{35}Cl^{37}Cl_2$	Cl-3 PCB	Fn-6; Cl-7,8,9,10	393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB.
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB		395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB.
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	$^{13}C_{12}$ Cl-3 PCB		397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	Cl-7 PCB.
	280.9825	LOCK	C_6F_{11}	PFK		405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB.
	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB		407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB.
	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB		427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB.
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB		429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB.
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	$^{13}C_{12}$ Cl-4 PCB		431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB.
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB		439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB.
	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB		441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB.
	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB		454.9728	QC	$C_{11}F_{17}$	PFK.
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB		427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB.
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB		429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB.
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB		431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB.
Fn-4; Cl-4,5,6	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB		439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB.
	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB		441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB.
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB		442.9728	QC	$C_{10}F_{17}$	PFK.
	301.9626	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB		454.9728	LOCK	$C_{11}F_{17}$	PFK.
	303.9597	M+4	$^{13}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	$^{13}C_{12}$ Cl-4 PCB		461.7246	M+2	$^{12}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	Cl-9 PCB.
	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB		463.7216	M+4	$^{12}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	Cl-9 PCB.
	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB		465.7187	M+6	$^{12}C_{12}H_1{}^{35}Cl_6{}^{37}Cl_3$	Cl-9 PCB.
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB		473.7648	M+2	$^{13}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	$^{13}C_{12}$ Cl-9 PCB.
	330.9792	LOCK	C_7F_{15}	PFK		475.7619	M+4	$^{13}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	$^{13}C_{12}$ Cl-9 PCB.
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB		495.6856	M+2	$^{13}C_{12}H_4$ $^{5}Cl_9{}^{37}Cl$	Cl-10 PCB.
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$Cl-5 PCB		499.6797	M+6	$^{12}C_{12}H_4{}^{35}Cl_8{}^{37}Cl_2$	Cl-10 PCB.
	359.8415	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB		501.6767	M+8	$^{12}C_{12}H_4{}^{35}Cl_7{}^{37}Cl_3$	Cl-10 PCB.
	361.8385	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB		507.7258	M+2	$^{13}C_{12}H_4{}^{35}Cl_9{}^{37}Cl$	$^{13}C_{12}$ Cl-10 PCB.
	363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB		509.7229	M+4	$^{13}C_{12}H_4{}^{35}Cl_8{}^{37}Cl_2$	$^{13}C_{12}$ Cl-10 PCB.
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB		511.7199	M+6	$^{13}C_{12}H_4{}^{35}Cl_7{}^{37}Cl_3$	$^{13}C_{12}$ Cl-10 PCB.
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 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 Cal 1 level (Table 23–11). If this interference occurs, 10:1 S/N must be met at the Cal 2 level.

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

TABLE 23–7—CONCENTRATION OF THE SAMPLE FORTIFICATION FOR PCDD AND PCDF [a]

Compound	pg/μL in final extract [b]	Spike recovery
Pre-sampling Adsorbent Standard		
$^{13}C_{12}$-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 Standard		
$^{13}C_{12}$-1,2,7,8-TeCDF	50	70–130%
$^{13}C_{12}$-1,2,3,4,6,8-HxCDD	50	70–130%
Pre-extraction Standard		
$^{13}C_{12}$-2,3,7,8-TeCDD	50	20–130%
$^{13}C_{12}$-2,3,7,8-TeCDF	50	20–130%
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	20–130%
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	20–130%
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	20–130%
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	20–130%
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	20–130%
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	50	20–130%
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	20–130%

TABLE 23–7—CONCENTRATION OF THE SAMPLE FORTIFICATION FOR PCDD AND PCDF [a]—Continued

Compound	pg/µL in final extract [b]	Spike recovery
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	20–130%
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	20–130%
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20–130%
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	20–130%
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20–130%
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20–130%
$^{13}C_{12}$-OCDD	100	20–130%
$^{13}C_{12}$-OCDF	100	20–130%
Pre-analysis Standard		
$^{13}C_{12}$-1,3,6,8-TeCDD	50	S/N≥10
$^{13}C_{12}$-1,2,3,4-TeCDF	50	S/N≥10
$^{13}C_{12}$-1,2,3,4,6,7-HxCDD	50	S/N≥10
$^{13}C_{12}$-1,2,3,4,6,7,9-HpCDD	50	S/N≥10
Alternate Recovery Standard		
$^{13}C_{12}$-1,3,7,8-TeCDD	50	20–130%
$^{13}C_{12}$-1,2,4,7,8-PeCDD	50	20–130%

[a] Changes in the amounts of labeled 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 1 µL sample injection volume for analysis or the injection volume for calibration standards and samples is the same.

[b] Labeled standard concentrations are recommendations (equivalent mass per sample of 25 pg pre-extraction standard, as an example, based on a 200 µL extract volume split in half before cleanup with a 20 µL aliquot of a 500 pg/µL spiking solution). Recommendations are based on assumption that half of the extract will be archived before cleanup. Spike levels may be adjusted for different split levels.

Note: all standards used should be reported.

TABLE 23–8—CONCENTRATION OF THE SAMPLE FORTIFICATION FOR PAH [a]

Compound	pg/µL in final extract [b]	Spike recovery
Pre-sampling Adsorbent Standard		
$^{13}C_6$-Benzo[*c*]fluorene	100	70–130%
$^{13}C_{12}$-Benzo[*j*]fluoranthene	100	70–130%
Pre-extraction Filter Recovery Standard		
d_{10}-Anthracene	100	70–130%
Pre-extraction Standard		
$^{13}C_6$-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%
$^{13}C_6$-Benz[*a*]anthracene	100	20–130%
$^{13}C_6$-Chrysene	100	20–130%
$^{13}C_6$-Benzo[*b*]fluoranthene	100	20–130%
$^{13}C_6$-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	20–130%
Pre-analysis Standard		
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 labeled standards added to the sample or its representative extract will necessitate an adjustment of the calibration solutions to prevent the introduction of inconsistencies.

[b] Labeled standard concentrations are recommendations (equivalent mass per sample of 25 pg pre-extraction standard, as an example, based on a 200 µL extract volume split in half before cleanup with a 20 µL aliquot of a 1000 pg/µL spiking solution). Recommendations are based on assumption that half of the extract will be archived before cleanup. Spike levels may be adjusted for different split levels.

Note: all standards used should be reported.

TABLE 23–9—CONCENTRATION OF THE SAMPLE FORTIFICATION FOR PCB [a]

Compound	BZ No.[b]	pg/µL in final extract [c]	Spike recovery
Pre-sampling Adsorbent Standard			
$^{13}C_{12}$-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 Standard			
$^{13}C_{12}$-2,3,3′,4,5,5′-HxCB	159L	100	70–130%
Pre-extraction Standard			
$^{13}C_{12}$-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 Standard			
$^{13}C_{12}$-2,5-DiCB	9L	100	S/N≥10
$^{13}C_{12}$-2,2′,5,5′-TeCB (NOAAT)	52L	100	S/N≥10
$^{13}C_{12}$-2,2′,4,5,5′-PeCB (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 Standard			
$^{13}C_{12}$-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 Standard			
$^{13}C_{12}$-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] Labeled standard concentrations are recommendations (equivalent mass per sample of 25 pg pre-extraction standard, as an example, based on a 200 µL extract volume split in half before cleanup with a 20 µL aliquot of a 1000 pg/µL spiking solution). Recommendations are based on assumption that half of the extract will be archived before cleanup. Spike levels may be adjusted for different split levels.
NOAAT = PCB considered toxic by the National Oceanic and Atmospheric Administration.
WHOT = PCB considered toxic by the World Health Organization.
Note: all standards used should be reported.

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 °C, (68 °F)	≤20 °C, (68 °F)	≤20 °C, (68 °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	<26 °C (79 °F) [c]	< −10 °C (14 °F)	< −10 °C (14 °F).
Laboratory Hold Times			
Extract and Archive	One year	45 Days	One year.

[a] Samples and extracts must be stored in the dark.
[b] Hold times begin from the time the laboratory receives the sample.
[c] Room temperature is acceptable if PCDD/PCDF are the only target compounds.
Note: Hold times for PCDD/PCDF and PCB are recommendations.

TABLE 23–11—CONCENTRATION OF THE INITIAL CALIBRATION STANDARD SOLUTIONS FOR PCDD AND PCDF [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 Standard	50	50	50	50	50	50	50
Pre-extraction Filter Recovery Standard	50	50	50	50	50	50	50
Pre-extraction Standard ($^{13}C_{12}$-OCDD, $^{13}C_{12}$-OCDF − 100 pg/µL)	50	50	50	50	50	50	50
Pre-analysis Standard	50	50	50	50	50	50	50
Alternate Recovery Standard	50	50	50	50	50	50	50

[a] Assumes 1 µL injection volume or the injection volume for standards and samples is the same.

TABLE 23–12—CONCENTRATION OF THE INITIAL CALIBRATION STANDARD SOLUTIONS FOR PAH [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 Standard	100	100	100	100	100	100	100
Pre-extraction Filter Recovery Standard	100	100	100	100	100	100	100
Pre-extraction Standard	100	100	100	100	100	100	100
Pre-analysis Standard	100	100	100	100	100	100	100

[a] Assumes 1 µL injection volume.

TABLE 23–13—CONCENTRATION OF THE INITIAL CALIBRATION STANDARD SOLUTIONS FOR PCB [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	100	100	100	100	100	100	100
Pre-extraction Filter Recovery Standard	100	100	100	100	100	100	100
Pre-extraction Standard	100	100	100	100	100	100	100
Pre-analysis Standard	100	100	100	100	100	100	100
Alternate Standard	100	100	100	100	100	100	100

[a] Assumes 1 µL injection volume.

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

Analyte group	Initial calibration RRF RSD	Continuing calibration RRF compared to ICAL RRF (PD)
Native (Unlabeled) Analytes	10	25
Pre-sampling Adsorbent Standard	20	25
Pre-extraction Filter Recovery Standard	20	25
Pre-extraction Standard	20	30
Alternative Recovery Standard	20	30

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

Number of chlorine atoms	Ion type	Theoretical ratio	Lower control limit	Upper control limit
1	M/M+2	3.13	2.66	3.60
2	M/M+2	1.56	1.33	1.79
3	M/M+2	1.04	0.88	1.20
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
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	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 PCB [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
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 (NOAAT)	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

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

PCB Congener	BZ No.[a]	Labeled analog	BZ No.
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.
NOAAT = PCB considered toxic by the National Oceanic and Atmospheric Administration.
WHOT = PCB considered toxic by the World Health Organization.

TABLE 23–18—INITIAL DEMONSTRATION OF CAPABILITY QC REQUIREMENTS

Section	Requirement	Specification and frequency	Acceptance criteria
9.3.5	Demonstration of low system background	Analyze an LMB after the highest calibration standard. Note: If an automated extraction system is used, an LMB must be extracted on each port.	Confirm that the LMB is free from contamination as defined in Section 13.1.
9.3.7	Determination of MDL	Prepare, extract, and analyze 7 replicate spiked samples (spiked within 2 to 10 times of the expected MDL) and 7 LMBs. See 40 CFR Part 136 Appendix B	See MDL confirmation.
9.3.8	MDL confirmation	Prepare, extract, and analyze a spiked sample (spiked at the MDL).	Confirm that the target compounds meet the qualitative identification criteria in Section 11.4.3.4 of this method.
9.3.9	Demonstration of precision	Prepare, extract, and analyze 7 replicate spiked samples (spiked near mid-range).	Percent relative standard deviation must be ≤20%.
9.3.10	Demonstration of accuracy	Calculate mean recovery for replicate spiked samples in Section 9.3.9.	Mean recovery within 70–130% of true value.
9.3.2	Lowest Calibration Concentration Confirmation.	Establish a target concentration for the lowest calibration based on the intended use of the method.	Upper PIR ≤150%. Lower PIR ≥50%.
9.3.6	Calibration Verification	Analyze a mid-level QCS	Within limits in Section 13.11.

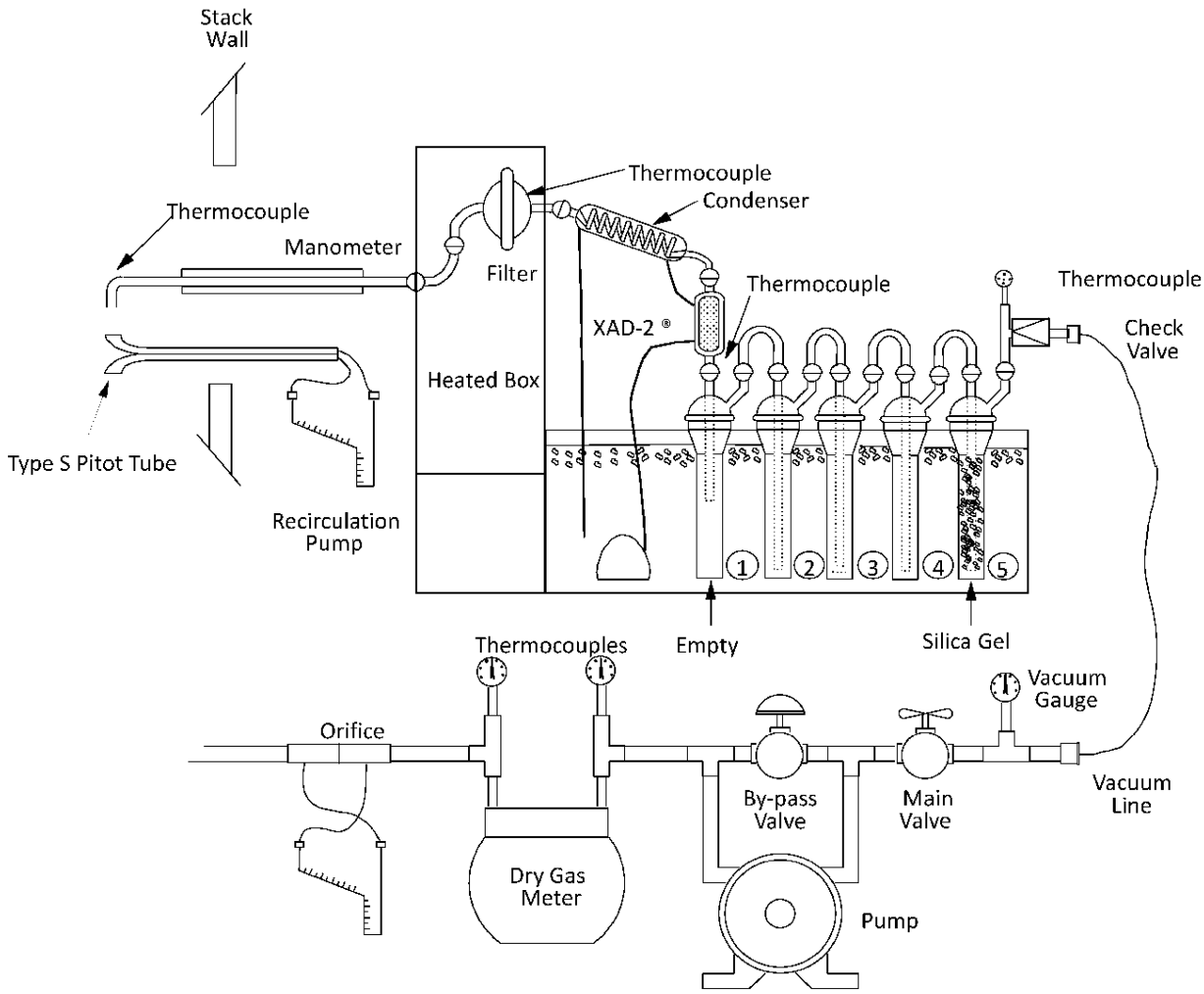

Figure 23–1. Method 23 Sampling Train

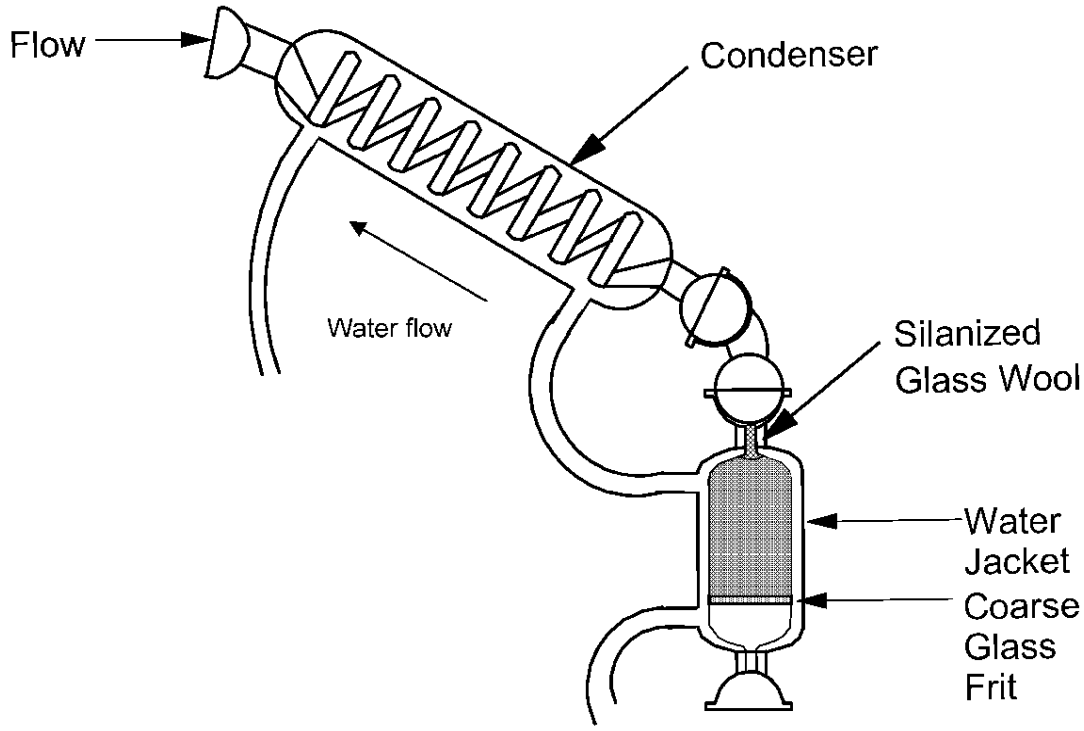

Figure 23–2. Condenser and Adsorbent Module

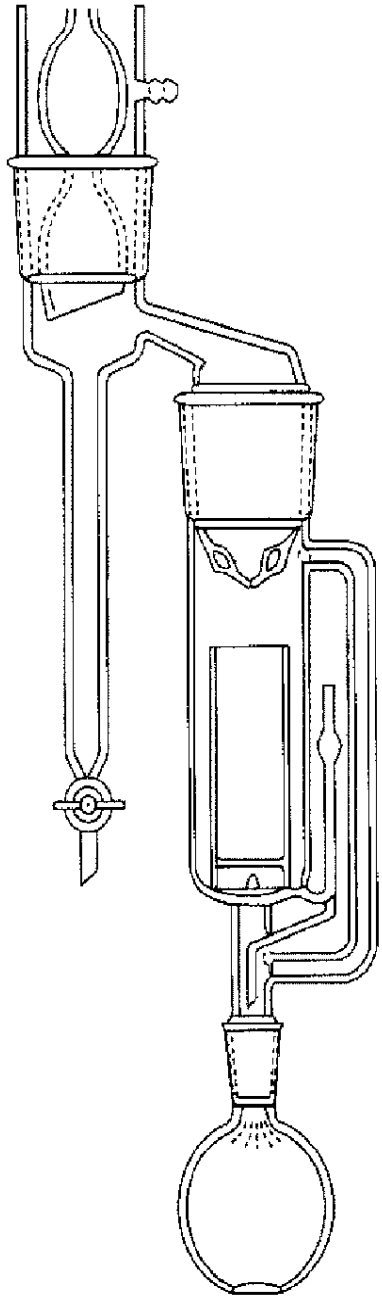

Figure 23–3. Soxhlet/Dean-Stark Extractor

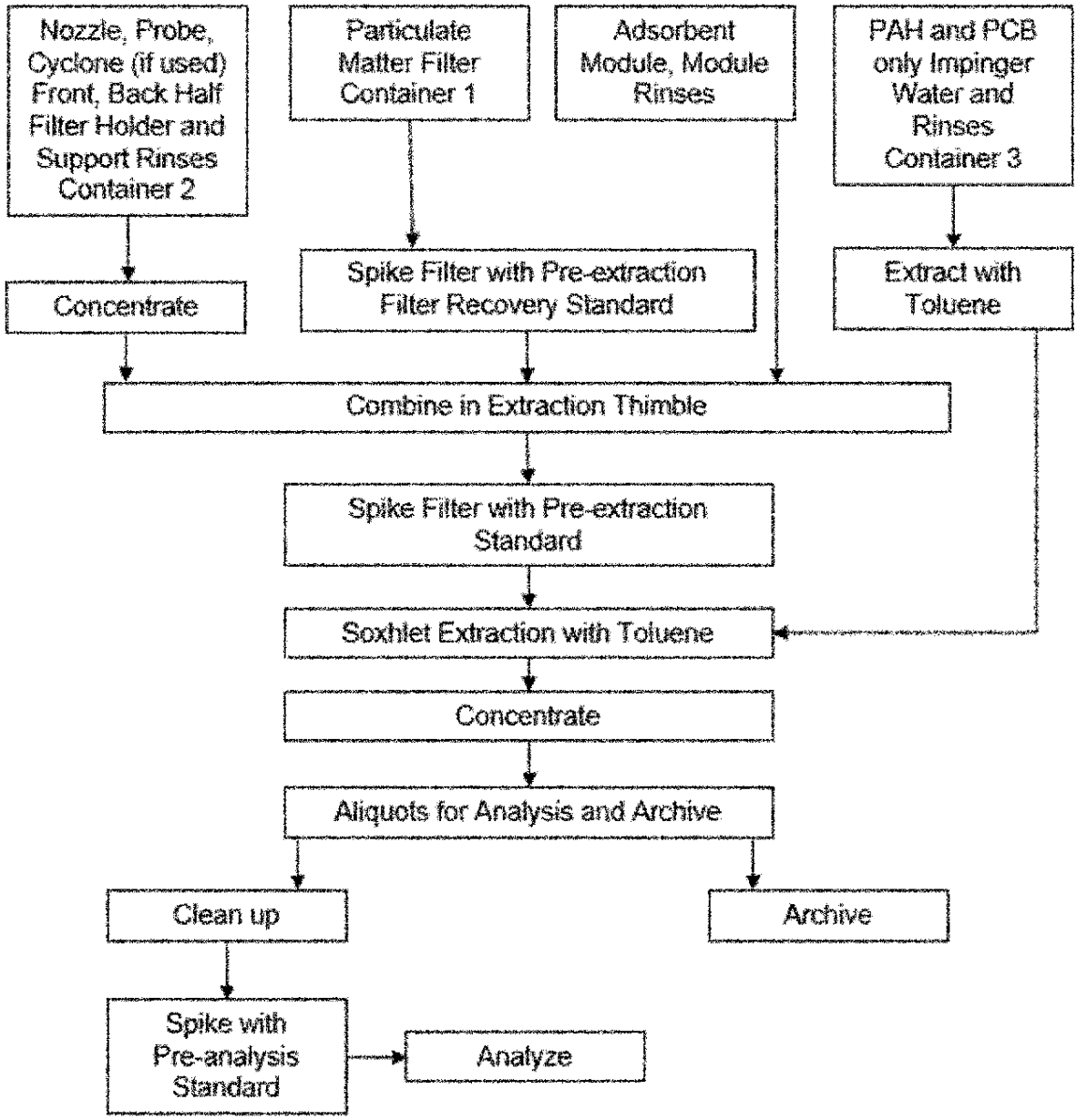

Figure 23–4. Sample Preparation Flow Chart

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.
MoCB				**DiCB**			
$^{13}C_{12}$-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
TrCB							
$^{13}C_{12}$-2,2′,6-TrCB	19L	2,2′,3-TrCB	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
TeCB							
$^{13}C_{12}$-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
PeCB							
$^{13}C_{12}$-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

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.
$^{13}C_{12}$-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
HxCB							
$^{13}C_{12}$-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
HpCB							
$^{13}C_{12}$-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
OcCB				**NoCB**			
$^{13}C_{12}$-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

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.
$^{13}C_{12}$-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 13.1 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.
- *Methylene chloride:* 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 methylene chloride extractions to meet the cleanliness requirements in Section 13.1 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 Section 13.1 of Method 23 are met.

3.2 Drying Column. A simple column with suitable retainers will hold all the XAD–2 from the extractor or the Soxhlet extractor, as shown in Figure B–1, 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 methylene chloride 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.

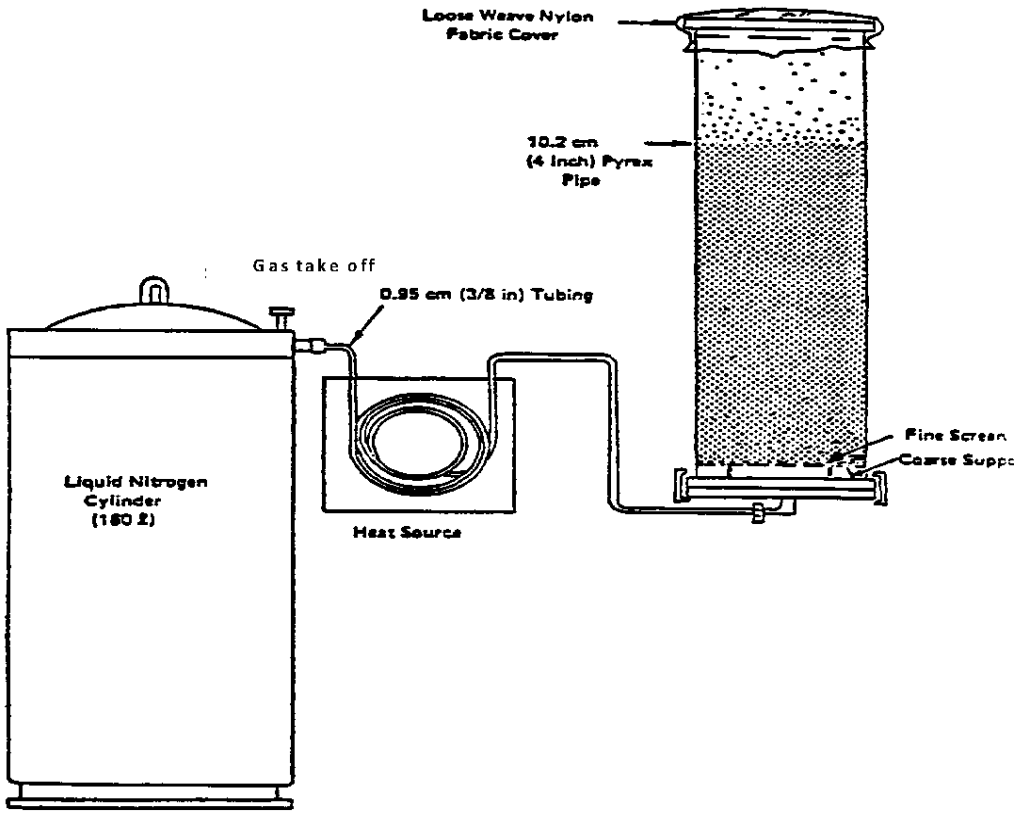

Figure B–1. XAD–2 fluidized-bed drying apparatus

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.*

Subpart LL—National Emission Standards for Hazardous Air Pollutants for Primary Aluminum Reduction Plants

■ 7. In § 63.849, revise paragraphs (a)(13) and (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.

* * * * *

Subpart EEE—National Emission Standards for Hazardous Air Pollutants from Hazardous Waste Combustors

■ 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.

* * * * *

Subpart XXX—National Emission Standards for Hazardous Air Pollutants for Ferroalloys Production: Ferromanganese and Silicomanganese

■ 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.

* * * * *

Subpart AAAAAAA—National Emission Standards for Hazardous Air Pollutants for Area Sources: Asphalt Processing and Asphalt Roofing Manufacturing

■ 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.

Subpart H—Hazardous Waste Burned in Boilers and Industrial Furnaces

■ 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–846, as incorporated by reference in § 260.11 of this chapter or Method 23, provided in Appendix A–7, Part 60 of this chapter.

* * * * *

[FR Doc. 2023–04958 Filed 3–17–23; 8:45 am]

BILLING CODE 6560–50–P

(b) In such circumstances, the authorized officer shall solicit applications competitively by issuing a prospectus for persons to apply for a visitor services authorization. Notwithstanding Forest Service outfitting and guiding policy in Forest Service Handbook 2709.14, Chapter 50, when authorizations, including priority use permits for activities other than sport hunting and fishing, expire in accordance with their terms, they shall not be reissued if there is a need to limit use and when there is competitive interest by preferred operators.

* * * * *

Homer Wilkes,

Under Secretary, Natural Resources and Environment.

[FR Doc. 2023–26666 Filed 12–5–23; 8:45 am]

BILLING CODE 3411–15–P

LIBRARY OF CONGRESS

Copyright Royalty Board

37 CFR Part 386

[Docket No. 23–CRB–0010–SA–COLA (2024)]

Cost of Living Adjustment to Satellite Carrier Compulsory License Royalty Rates; Correction

AGENCY: Copyright Royalty Board (CRB), Library of Congress.

ACTION: Final rule; correction.

SUMMARY: This document corrects a final rule published in the **Federal Register** of November 29, 2023, regarding the cost of living adjustment (COLA) to the royalty rates that satellite carriers pay for a compulsory license under the Copyright Act.

DATES: *Effective* January 1, 2024.

FOR FURTHER INFORMATION CONTACT: Anita Brown, (202) 707–7658, *crb@loc.gov.*

SUPPLEMENTARY INFORMATION: In FR Doc. 2023–26122, appearing on page 83354 in the **Federal Register** of Wednesday, November 29, 2023, the following corrections are made:

§ 386.2 [Corrected]

■ 1. On page 83354, in the second column, in part 386, in amendment 2, the instruction ''Section 386.2 is amended by adding paragraphs (b)(1)(xiv) and (b)(2)(xiv) to read as follows:'' is corrected to read ''Section 386.2 is amended by adding paragraphs (b)(1)(xv) and (b)(2)(xv) to read as follows:''.

Dated: November 30, 2023.

David P. Shaw,

Chief Copyright Royalty Judge.

[FR Doc. 2023–26741 Filed 12–5–23; 8:45 am]

BILLING CODE 1410–72–P

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 261, 262, and 266

[EPA–HQ–OLEM–2023–0081; FRL 8687–03–OLEM]

RIN 2050–AH23

Hazardous Waste Generator Improvements Rule, the Hazardous Waste Pharmaceuticals Rule, and the Definition of Solid Waste Rule; Technical Corrections

AGENCY: Environmental Protection Agency (EPA).

ACTION: Partial withdrawal of direct final rule.

SUMMARY: Because the EPA received adverse comment on eight amendments in the direct final rule published on August 9, 2023, we are withdrawing amendments to specific provisions through correction to the direct final rule.

DATES: This correction is effective December 7, 2023.

FOR FURTHER INFORMATION CONTACT: Brian Knieser, U.S. Environmental Protection Agency, Office of Resource Conservation and Recovery, (MC: 5304T), 1200 Pennsylvania Avenue NW, Washington, DC 20460, (202) 566–0516, (*knieser.brian@epa.gov*) or Kathy Lett, U.S. Environmental Protection Agency, Office of Resource Conservation and Recovery, (MC: 5304T), 1200 Pennsylvania Avenue NW, Washington, DC 20460, (202) 566–0517, (*lett.kathy@epa.gov*).

SUPPLEMENTARY INFORMATION: Because the EPA received adverse comment on specific amendments, through this correction, we are withdrawing only those specific amendments from the direct final rule, Hazardous Waste Generator Improvements Rule, the Hazardous Waste Pharmaceuticals Rule, and the Definition of Solid Waste Rule; Technical Corrections, published on August 9, 2023 (88 FR 54086). We stated in that direct final rule that if we received adverse comment by the close of the comment period on October 10, 2023, the specific amendments in the direct final rule that are the subject of adverse comment would not take effect, and we would publish a timely withdrawal in the **Federal Register**. Because the EPA subsequently received adverse comment on eight amendments in that direct final rule, we are withdrawing only the eight affected amendments. All other amendments in that direct final rule will go into effect on the effective date (December 7, 2023). The eight specific amendments that are being withdrawn are:

1. Section 261.4(e)(1) introductory text related to sample waste generated or collected for the purpose of conducting treatability studies.
2. Section 262.11(d) introductory text related to identifying hazardous characteristics for listed hazardous wastes when the characteristic is already addressed by the listing.
3. Section 262.11(g) related to identifying hazardous characteristics for listed hazardous wastes when the characteristic is already addressed by the listing.
4. Section 262.16(b)(1) related to the accumulation limit for small quantity generators generating acute hazardous waste.
5. Section 262.17(a)(8)(i) introductory text related to LQG closure notification when closing a waste accumulation unit but not the whole facility.
6. Section 262.17(a)(8)(i)(A) related to LQG closure notification when closing a waste accumulation unit but not the whole facility.
7. Section 262.232(b)(6)(iv) related to adding ''RCRA-'' to the term ''designated facility'' to match the language of parallel provisions in this section.
8. Section 266.508(a)(2)(ii) related to allowing applicable EPA hazardous waste numbers (also known as waste codes) in addition to the required PHARMS code in item 13 of the hazardous waste manifest for shipments of hazardous waste pharmaceuticals from a healthcare facility subject to 40 CFR part 266 subpart P. We are also withdrawing language from this provision that allows the use of PHRM in lieu of PHARMS in item 13 of the hazardous waste manifest.

Except for the amendment to § 262.11 at instruction 25, which is withdrawn in full, because the provisions we are withdrawing appear in amendatory instructions affecting other provisions, we are correcting the corresponding amendments in full minus those provisions withdrawn.

The EPA published a parallel proposed rule on the same day as the direct final rule. The proposed rule invited comment on the substance of the direct final rule. We will address those comments in any subsequent final action, which will be based on the parallel proposed rule also published on

August 9, 2023. As stated in the direct final rule and the parallel proposed rule, we will not institute a second comment period on this action.

List of Subjects

40 CFR Part 261

Environmental protection, Administrative practice and procedure, Air pollution control, Confidential business information, Hazardous waste, Intergovernmental relations, Licensing and registration, Reporting and recordkeeping requirements.

40 CFR Part 262

Environmental protection, Exports, Hazardous materials transportation, Hazardous waste, Imports, Labeling, Packaging and containers, Reporting and recordkeeping requirements.

40 CFR Part 266

Environmental protection, Energy, Hazardous waste, Recycling, Reporting and recordkeeping requirements.

Michael S. Regan,

Administrator.

■ For the reasons stated above, EPA is withdrawing amendments in the direct final rule published August 9, 2023, at 88 FR 54086, by making the following corrections:

Correction

■ In FR Rule Doc. No. 2023–14731, published August 9, 2023, at 88 FR 54086, make the following corrections:

■ 1. On page 54109, in the first column, amendatory instruction 25 amending § 262.11 is removed.

■ 2. Beginning on page 54100 and ending on page 54114, correct amendatory instructions 5 (§ 261.4), 27 (§ 262.16), 28 (§ 262.17), 34 (§ 262.232), and 55 (§ 266.508) to read as follows:

■ 5. Section 261.4 is amended by revising paragraphs (a)(25)(i)(I), (a)(25)(vi) and (vii), and (a)(25)(xi)(D) to read as follows:

§ 261.4 Exclusions.

(a) * * *

(25) * * *

(i) * * *

(I) The name of any countries of transit through which the hazardous secondary material will be sent and a description of the approximate length of time it will remain in such countries and the nature of its handling while there (for purposes of this section, the terms ''EPA Acknowledgment of Consent'', ''country of import'' and ''country of transit'' are used as defined in 40 CFR 262.81 with the exception that the terms in this section refer to hazardous secondary materials, rather than hazardous waste):

* * * * *

(vi) The export of hazardous secondary material under this paragraph (a)(25) is prohibited unless the hazardous secondary material generator receives from EPA an EPA Acknowledgment of Consent documenting the consent of the country of import to the receipt of the hazardous secondary material. Where the country of import objects to receipt of the hazardous secondary material or withdraws a prior consent, EPA will notify the hazardous secondary material generator in writing. EPA will also notify the hazardous secondary material generator of any responses from countries of transit.

(vii) Prior to each shipment, the hazardous secondary material generator or a U.S. authorized agent must:

(A) Submit Electronic Export Information (EEI) for each shipment to the Automated Export System (AES) or its successor system, under the International Trade Data System (ITDS) platform, in accordance with 15 CFR 30.4(b).

(B) Include the following items in the EEI, along with the other information required under 15 CFR 30.6:

(*1*) EPA license code;

(*2*) Commodity classification code per 15 CFR 30.6(a)(12);

(*3*) EPA consent number;

(*4*) Country of ultimate destination per 15 CFR 30.6(a)(5);

(*5*) Date of export per 15 CFR 30.6(a)(2);

(*6*) Quantity of waste in shipment and units for reported quantity, if required reporting units established by value for the reported commodity classification number are in units of weight or volume per 15 CFR 30.6(a)(15); or

(*7*) EPA net quantity reported in units of kilograms, if required reporting units established by value for the reported commodity classification number are not in units of weight or volume.

* * * * *

(xi) * * *

(D) By reclaimer and intermediate facility, for each hazardous secondary material exported, a description of the hazardous secondary material and the EPA hazardous waste number that would apply if the hazardous secondary material was managed as hazardous waste, the DOT hazard class, the name and U.S. EPA ID number (where applicable) for each transporter used, the consent number(s) under which the hazardous secondary material was shipped and for each consent number, the total amount of hazardous secondary material shipped and the number of shipments exported during the calendar year covered by the report;

* * * * *

■ 27. Section 262.16 is amended by revising the introductory text and paragraphs (b) introductory text, (b)(5) introductory text, and (b)(8)(iv)(A) and (B) to read as follows:

§ 262.16 Conditions for exemption for a small quantity generator that accumulates hazardous waste.

A small quantity generator may accumulate hazardous waste on site without a permit or interim status, and without complying with the requirements of parts 124, 264 through 267, and 270 of this chapter, or the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, provided that all the conditions for exemption listed in this section are met:

* * * * *

(b) *Accumulation.* The generator accumulates hazardous waste on site for no more than 180 days, unless in compliance with the conditions for exemption for longer accumulation in paragraphs (c), (d), and (e) of this section. The following accumulation conditions also apply:

* * * * *

(5) *Accumulation of hazardous waste in containment buildings.* If the waste is placed in containment buildings, the small quantity generator must comply with 40 CFR part 265 subpart DD. The generator must label its containment buildings with the words ''Hazardous Waste'' in a conspicuous place easily visible to employees, visitors, emergency responders, waste handlers, or other persons on site and also in a conspicuous place provide an indication of the hazards of the contents (examples include, but are not limited to, the applicable hazardous waste characteristic(s) (*i.e.,* ignitable, corrosive, reactive, toxic); hazard communication consistent with the Department of Transportation requirements at 49 CFR part 172, subpart E (labeling) or subpart F (placarding); a hazard statement or pictogram consistent with the Occupational Safety and Health Administration Hazard Communication Standard at 29 CFR 1910.1200; or a chemical hazard label consistent with the National Fire Protection Association code 704). The generator must also maintain:

* * * * *

(8) * * *

(iv) * * *

(A) Whenever hazardous waste is being poured, mixed, spread, or

otherwise handled, all personnel involved in the operation must have immediate access (*e.g.,* direct or unimpeded access) to an internal alarm or emergency communication device, either directly or through visual or voice contact with another employee, unless such a device is not required under paragraph (b)(8)(ii) of this section.

(B) In the event there is just one employee on the premises while the facility is operating, the employee must have immediate access (*e.g.,* direct or unimpeded access) to a device, such as a telephone (immediately available at the scene of operation) or a hand-held two-way radio, capable of summoning external emergency assistance, unless such a device is not required under paragraph (b)(8)(ii) of this section.

* * * * *

■ 28. Section 262.17 is amended by revising the introductory text and paragraphs (a)(2), (a)(7)(i)(A), (a)(8)(iii)(A)(*4*), (b), (c) introductory text, (d), (e), and (f) introductory text to read as follows:

§ 262.17 Conditions for exemption for a large quantity generator that accumulates hazardous waste.

A large quantity generator may accumulate hazardous waste on site without a permit or interim status, and without complying with the requirements of parts 124, 264 through 267, and 270 of this chapter, or the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, provided that all of the following conditions for exemption are met:

* * * * *

(a) * * *

(2) *Accumulation of hazardous waste in tanks.* If the waste is placed in tanks, the large quantity generator must comply with the applicable requirements of subpart J (except §§ 265.197(c) and 265.200 of this subchapter) as well as the applicable requirements of 40 CFR part 265, subparts AA through CC.

* * * * *

(7) * * *

(i)(A) Facility personnel must successfully complete a program of classroom instruction, online training (*e.g.,* computer-based or electronic), or on-the-job training that teaches them to perform their duties in a way that ensures compliance with this part. The large quantity generator must ensure that this program includes all the elements described in the document required under paragraph (a)(7)(iv)(C) of this section.

* * * * *

(8) * * *

(iii) * * *

(A) * * *

(*4*) If the generator demonstrates that any contaminated soils and wastes cannot be practicably removed or decontaminated as required in paragraph (a)(8)(iii)(A)(*2*) of this section, then the waste accumulation unit is considered to be a landfill and the generator must close the waste accumulation unit and perform postclosure care in accordance with the closure and post-closure care requirements that apply to landfills (§ 265.310 of this subchapter). In addition, for the purposes of closure, post-closure, and financial responsibility, such a waste accumulation unit is then considered to be a landfill, and the generator must meet all of the requirements for landfills specified in 40 CFR part 265, subparts G and H.

* * * * *

(b) *Accumulation time limit extension.* A large quantity generator who accumulates hazardous waste for more than 90 days is subject to the requirements of 40 CFR parts 124, 264 through 268, and part 270 of this chapter, and the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, unless it has been granted an extension to the 90-day period. Such extension may be granted by EPA if hazardous wastes must remain on site for longer than 90 days due to unforeseen, temporary, and uncontrollable circumstances. An extension of up to 30 days may be granted at the discretion of the Regional Administrator on a case-by-case basis.

(c) *Accumulation of F006.* A large quantity generator who also generates wastewater treatment sludges from electroplating operations that meet the listing description for the EPA hazardous waste number F006, may accumulate F006 waste on site for more than 90 days, but not more than 180 days without being subject to parts 124, 264 through 267, and 270 of this chapter, and the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, provided that it complies with all of the following additional conditions for exemption:

* * * * *

(d) *F006 transported over 200 miles.* A large quantity generator who also generates wastewater treatment sludges from electroplating operations that meet the listing description for the EPA hazardous waste number F006, and who must transport this waste, or offer this waste for transportation, over a distance of 200 miles or more for off-site metals recovery, may accumulate F006 waste on site for more than 90 days, but not more than 270 days without being subject to parts 124, 264 through 267, and 270 of this chapter, and the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, if the large quantity generator complies with all of the conditions for exemption of paragraphs (c)(1) through (4) of this section.

(e) *F006 accumulation time extension.* A large quantity generator accumulating F006 in accordance with paragraphs (c) and (d) of this section who accumulates F006 waste on site for more than 180 days (or for more than 270 days if the generator must transport this waste, or offer this waste for transportation, over a distance of 200 miles or more), or who accumulates more than 20,000 kilograms of F006 waste on site is an operator of a storage facility and is subject to the requirements of 40 CFR parts 124, 264, 265, 267, and 270, and the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, unless the generator has been granted an extension to the 180-day (or 270-day if applicable) period or an exception to the 20,000 kilogram accumulation limit. Such extensions and exceptions may be granted by EPA if F006 waste must remain on site for longer than 180 days (or 270 days if applicable) or if more than 20,000 kilograms of F006 waste must remain on site due to unforeseen, temporary, and uncontrollable circumstances. An extension of up to 30 days or an exception to the accumulation limit may be granted at the discretion of the Regional Administrator on a case-by-case basis.

(f) *Consolidation of hazardous waste received from very small quantity generators.* Large quantity generators may accumulate on site hazardous waste received from very small quantity generators under control of the same person (as defined in § 260.10 of this subchapter), without a storage permit or interim status and without complying with the requirements of parts 124, 264 through 268, and 270 of this chapter, and the notification requirements of section 3010 of RCRA for treatment, storage, and disposal facilities, provided that they comply with the following conditions. "Control," for the purposes of this section, means the power to direct the policies of the generator, whether by the ownership of stock, voting rights, or otherwise, except that contractors who operate generator facilities on behalf of a different person

shall not be deemed to ''control'' such generators.

* * * * *

■ 34. Section 262.232 is amended by revising the paragraphs (a)(5), (b)(4) introductory text, and (b)(4)(ii)(C) to read as follows:

§ 262.232 Conditions for a generator managing hazardous waste from an episodic event.

(a) * * *

(5) The very small quantity generator must comply with the hazardous waste manifest provisions of subpart B of this part and the recordkeeping provisions for small quantity generators in § 262.44 when it sends its episodic event hazardous waste off site to a designated facility, as defined in § 260.10 of this subchapter.

* * * * *

(b) * * *

(4) *Accumulation by small quantity generators.* A small quantity generator is prohibited from accumulating hazardous wastes generated from an episodic event on drip pads and in containment buildings. When accumulating hazardous waste generated from an episodic event in containers and tanks, the following conditions apply:

* * * * *

(ii) * * *

(C) Use inventory logs, monitoring equipment or other records to identify the date upon which each episodic event begins; and

* * * * *

■ 55. Section 266.508 is amended by revising paragraphs (a)(1)(iii)(C) and (a)(2)(i) to read as follows:

§ 266.508 Shipping non-creditable hazardous waste pharmaceuticals from a healthcare facility of evaluated hazardous waste pharmaceuticals from a reverse distributor.

(a) * * *

(1) * * *

(iii) * * *

(C) Lab packs that will be incinerated in compliance with § 268.42(c) of this subchapter are not required to be marked with EPA hazardous waste numbers (*i.e.,* hazardous waste codes), except D004, D005, D006, D007, D008, D010, and D011, where applicable. A nationally recognized electronic system, such as bar coding or radio frequency identification tag, may be used to identify the applicable EPA hazardous waste numbers (*i.e.,* hazardous waste codes).

* * * * *

(2) * * *

(i) A healthcare facility shipping noncreditable hazardous waste pharmaceuticals is not required to list all applicable EPA hazardous waste numbers (*i.e.,* hazardous waste codes) in Item 13 of EPA Form 8700–22.

* * * * *

[FR Doc. 2023–26750 Filed 12–5–23; 8:45 am]

BILLING CODE 6560–50–P

DEPARTMENT OF HEALTH AND HUMAN SERVICES

Centers for Medicare & Medicaid Services

42 CFR Parts 430 and 435

Office of the Secretary

45 CFR Part 16

[CMS–2447–IFC]

RIN 0938–AV26

Medicaid; CMS Enforcement of State Compliance With Reporting and Federal Medicaid Renewal Requirements Under Section 1902(tt) of the Social Security Act

AGENCY: Centers for Medicare & Medicaid Services (CMS), HHS.

ACTION: Interim final rule with comment period.

SUMMARY: This interim final rule with request for comments (IFC) implements reporting requirements and enforcement authorities in the Social Security Act (the Act) that were added by the Consolidated Appropriations Act, 2023 (CAA, 2023). CMS will use these new enforcement authorities as described in this rule if States fail to comply with the new reporting requirements added by the CAA, 2023 or with Federal Medicaid eligibility redetermination requirements during a timeframe that is generally aligned with the period when States are restoring eligibility and enrollment operations following the end of the Medicaid continuous enrollment condition under the Families First Coronavirus Response Act (FFCRA). The new enforcement authorities include requiring States to submit a corrective action plan, suspending disenrollments from Medicaid for procedural reasons, and imposing civil money penalties (CMPs). They also include applying a reduction to the State-specific Federal Medical Assistance Percentage (FMAP) for failure to meet reporting requirements.

DATES: These regulations are effective on December 6, 2023.

Comment date: To be assured consideration, comments must be received at one of the addresses provided below, by February 2, 2024.

ADDRESSES: In commenting, please refer to file code CMS–2447–IFC.

Comments, including mass comment submissions, must be submitted in *one* of the following three ways (please choose only *one* of the ways listed):

1. *Electronically.* You may submit electronic comments on this regulation to *http://www.regulations.gov.* Follow the ''Submit a comment'' instructions.

2. *By regular mail.* You may mail written comments to the following address ONLY: Centers for Medicare & Medicaid Services, Department of Health and Human Services, Attention: CMS–2447–IFC, P.O. Box 8016, Baltimore, MD 21244–8016.

Please allow sufficient time for mailed comments to be received before the close of the comment period.

3. *By express or overnight mail.* You may send written comments to the following address ONLY: Centers for Medicare & Medicaid Services, Department of Health and Human Services, Attention: CMS–2447–IFC, Mail Stop C4–26–05, 7500 Security Boulevard, Baltimore, MD 21244–1850.

For information on viewing public comments, see the beginning of the **SUPPLEMENTARY INFORMATION** section.

FOR FURTHER INFORMATION CONTACT: Abby Kahn, (410) 786–4321, *Abigail.Kahn@cms.hhs.gov,* or Anna Bonelli, (443) 615–1268, *Anna.Bonelli@cms.hhs.gov.*

SUPPLEMENTARY INFORMATION:

Inspection of Public Comments: All comments received before the close of the comment period are available for viewing by the public, including any personally identifiable or confidential business information that is included in a comment. We post all comments received before the close of the comment period on the following website as soon as possible after they have been received: *http://www.regulations.gov.* Follow the search instructions on that website to view public comments. CMS will not post on *Regulations.gov* public comments that make threats to individuals or institutions or suggest that the commenter will take actions to harm an individual. CMS continues to encourage individuals not to submit duplicative comments. We will post acceptable comments from multiple unique commenters even if the content is identical or nearly identical to other comments.