6560-50

ENVIRONMENTAL PROTECTION AGENCY
40 CFR Part 60

[AD-FRL-]
STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES
Appendix A , Test Method 23

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed Rule.

SUMMARY: This rule amends Method 23, entitled "Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources," to correct existing errors in the method, to eliminate the methylene chloride rinse of the sampling train, and to clarify the quality assurance requirements of the method.

DATES: Comments. Comments must be received on or before _____ (90 days after publication in the FEDERAL REGISTER].

Public Hearing. If anyone contacts EPA requesting to speak at a public hearing by _____ (two weeks after publication in the FEDERAL REGISTER), a public hearing will be held on _____ (four weeks after publication in the FEDERAL REGISTER), beginning at 10:00 a.m. Persons interested in attending the hearing should call Ms. Lala Cheek at (919) 541-5545 to verify that a hearing will be held.

Request to Speak at Hearing. Persons wishing to present oral testimony must contact EPA by _____ (two weeks after publication in the FEDERAL REGISTER).

ADDRESSES: Comments. Comments should be submitted (in duplicate if possible) to Public Docket No. A-94-2 at the following address: U. S. Environmental Protection Agency , Air and Radiation Docket and Information Center, Mail Code: 6102, 401 M Street, SW, Washington, DC 20460. The Agency requests that a separate copy also be sent to the contact person listed below. The docket is located at the above address in Room M-1500 Waterside Mall (ground floor), and may be inspected from 8:30 a.m. to Noon and 1:00 to 3:00 PM, Monday through Friday. The proposed regulatory text and other materials related to this rulemaking are available for review in the docket or copies may be mailed on request from the Air Docket by calling 202-260-7548. A reasonable fee may be charged for copying docket materials.

Public Hearing. If anyone contacts EPA requesting a public hearing, it will be held at EPA's Emission Measurement Laboratory, Research Triangle Park, North Carolina. Persons interested in attending the hearing or wishing to present oral testimony should notify Ms. Lala Cheek (MD-19), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-5545.

Docket: A Docket, A-94-22, containing materials relevant to this rulemaking, is available for public inspection and copying between 8:30 a.m. and Noon and 1:00 and 3:00 p.m., Monday through Friday, in at EPA's Air Docket Section (LE-131), Room M-1500 Waterside Mall (ground floor) 401 M Street, S.W., Washington,

D.C. 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Gary McAlister, Emission Measurement Branch (MD-19), Emissions, Monitoring, and Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone (919) 541-1062.

SUPPLEMENTARY INFORMATION:

The proposed regulatory text of the proposed rule is not included in this Federal Register notice, but is available in Docket No. A-94-22 or by written or telephone request from the Air Docket (see ADDRESSES). If necessary, a limited number of copies of the Regulatory Text are available from the EPA contact persons designated earlier in this notice. This Notice with the proposed regulatory language is also available on the Technology Transfer Network (TTN), one of EPA's electronic bulletin boards. TTN provides information and technology exchange in various areas of air pollution control. The service is free except for the cost of the phone call. Dial (919) 541-5742 for up to a 14400 bps modem. If more information on TTN is needed, call the HELP line at (919) 541-5384.

I. SUMMARY

Method 23 was promulgated along with the New Source Performance Standard for municipal waste combustors (Subpart Ea). As promulgated, the method contained some errors. This action would correct those errors and would clarify some of the existing quality assurance requirements. In addition, the current

procedure requires rinsing of the sampling train with two separate solvents which must be analyzed separately. Based on data the Agency has collected since promulgation of Method 23, we believe that one of these rinse steps and the resulting sample fraction can be eliminated. This could save as much as $2000 per test run in analytical costs.

II. THE RULEMAKING

This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations nor does it change any emission standard. Rather, the rulemaking would simply amend an existing test method associated with emission measurement requirements in the current regulations that would apply irrespective of this rulemaking.

III. ADMINISTRATIVE REQUIREMENTS

A. Public Hearing

A public hearing will be held, if requested, to discuss the proposed amendment in accordance with section 307(d)(5)of the Clean Air Act. Persons wishing to make oral presentations should contact EPA at the address given in the ADDRESSES section of this preamble. Oral presentations will be limited to 15 minutes each. Any member of the public may file a written statement with EPA before, during, or within 30 days after the hearing. Written statements should be addressed to the Air Docket Section address given in the ADDRESSES section of this preamble.

A verbatim transcript of the hearing and written statements

will be available for public inspection and copying during normal working hours at EPA's Air Docket Section in Washington, DC (see ADDRESSES section of this preamble).

B. Docket

The docket is an organized and complete file of all the information considered by EPA in the development of this rulemaking. The docket is a dynamic file, since material is added throughout the rulemaking development. The docketing system is intended to allow members of the public and industries involved to identify and locate documents readily so that they may effectively participate in the rulemaking process. Along with the statement of basis and purpose of the proposed and promulgated test method revisions and EPA responses to significant comments, the contents of the docket, except for interagency review materials, will serve as the record in case of judicial review [Section 307(d)(7)(A)].

C. Executive Order 12291 Review

Under Executive Order 12291, EPA is required to judge whether a regulation is a "major rule" and, therefore, subject to the requirements of a regulatory impact analysis. This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations, nor does it change any emission standard. The Agency has determined that this regulation would result in none of the adverse economic effects set forth in Section 1 of the Order as grounds for

finding the regulation to be a "major rule." The Agency has, therefore, concluded that this regulation is not a "major rule" under Executive Order 12291.

D. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) of 1980 requires the identification of potentially adverse impacts of Federal regulations upon small business entities. The RFA specifically requires the completion of an analysis in those instances where small business impacts are possible. This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations, nor does it change any emission standard. Because this rulemaking imposes no adverse economic impacts, an analysis has not been conducted.

Pursuant to the provision of 5 U.S.C. 605(b), I hereby certify that the promulgated rule will not have an impact on small entities because no additional costs will be incurred.

E. Paperwork Reduction Act

This rule does not change any information collection requirements subject to Office of Management and Budget review under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 et seq.

F. Statutory Authority

The statutory authority for this proposal is provided by sections 111 and 301(a) of the Clean Air Act, as amended: 42 U.S.C., 7411 and 7601(a).

LIST OF SUBJECTS

Air pollution control, municipal waste combustors, polychorinated dibenzo-p-dioxins, sources.

Date The Administrator

It is proposed that 40 CFR Part 60 be amended as follows:

1. The authority citation for Part 60 continues to read as follows: Authority: Clean Air Act (42 U.S.C. 7401 [et seq.], as amended by Pub. L 101-549).

2. Replace test Method 23 of Appendix A, with the following:

Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method is applicable to the determination of emissions of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from municipal waste combustors. Calibration standards are selected for regulated emission levels for municipal waste combustors.

1.2 Principle. A sample is withdrawn isokinetically from the gas stream and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle and vapor fraction. The

PCDD's and PCDF's are extracted from the sample, separated by high resolution gas chromatography (HRGC), and measured by high resolution mass spectrometry (HRMS).

2. APPARATUS

2.1 Sampling. A schematic of the sampling train is shown in Figure 23-1. Sealing greases shall not be used in assembling the train. The train is identical to that described in Section 2.1 of Method 5 of this appendix with the following additions:

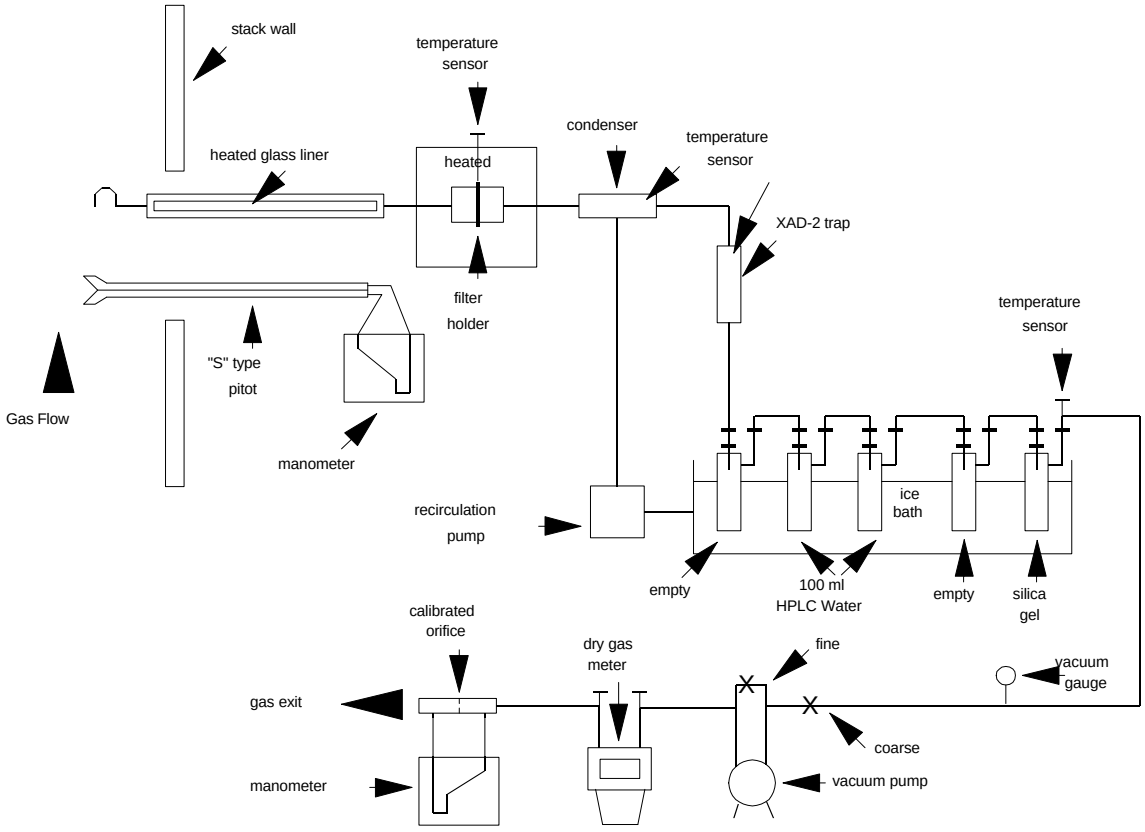

Figure 23.1 Sampling Train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (1/2 in. OD with 1/8 in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at $\geq$120°C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23-2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at $\leq$20°C (68°F).

2.1.4 Adsorbent Module. Glass container to hold up to 40 grams of resin adsorbent. A schematic diagram is shown in Figure 23-2. Other physical configurations of the water-jacketed resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. A coarse glass frit is included to retain the adsorbent in the water-jacketed sorbent module.

2.1.5 Probe Liner. The probe liner shall be made of glass and a Teflon ferrule or Teflon coated O-ring shall be used to make the seal at the nozzle end of the probe.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum

foil (Section 2.2.6) to cap off the sample exposed sections of the train and sorbent module.

2.2.2 Wash Bottles. Teflon, 500-mL.

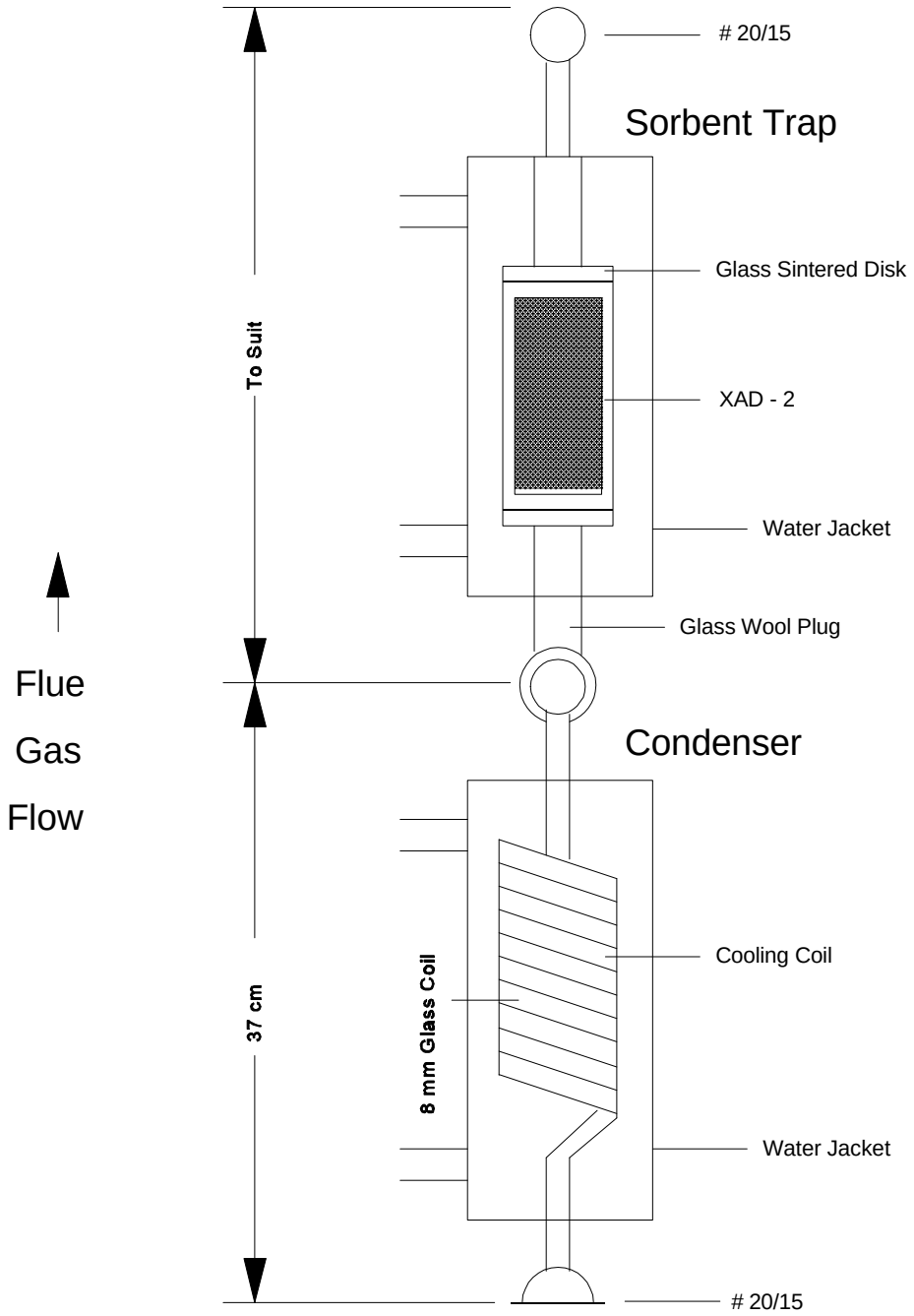

Figure 23.2 Condenser and Adsorbent Trap

2.2.3 Probe Liner, Probe Nozzle, and Filter Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, glass petri dish, or Teflon baggie.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed (Do not use to wrap or ship filter samples, because it may react with particulate matter).

2.2.7 Metal Storage Container. Air tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-mL with 2-mL graduations.

2.2.9 Glass Sample Storage Containers. Amber glass bottles for sample glassware washes, 500- or 1000-mL, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Containers. 125- and 250-mL flint glass bottles with Teflon-lined caps.

2.3.2 Test Tubes. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 x

123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-mL.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.

2.3.8 Kuderna-Danish Concentrator Apparatus.

2.3.9 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.10 Separatory Funnels. Glass, 2-liter.

2.3.11 Gas Chromatograph. Consisting of the following components:

2.3.11.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±10°C and performing programmed increases in temperature at rates of at least 40°C/min.

2.3.11.2 Temperature Gauges. To monitor column oven, detector, and exhaust temperatures ±1°C.

2.3.11.3 Flow Systems. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.11.4 Capillary Columns. A fused silica column, 60 x 0.25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m x 0.25 mm ID coated with DB-225. Other column systems may be substituted provided that the user is able

to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of Section 6.1.2.2.

2.3.12 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.13 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.14 Analytical Balance. To measure within 0.1 mg.

3. REAGENTS

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference - see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean nitrogen (N_2) stream. Store the filters in a glass petri

dishes and seal with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD-2 resin. Thoroughly cleaned before initial use. Do not reuse resin. If precleaned XAD-2 resin is purchased from the manufacturer, the cleaning procedure described in Section 3.1.2.1 is not required.

3.1.2.1 Cleaning. Procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial Rinse: Place resin in a beaker, rinse once with HPLC water, and discard water. Refill beaker with water, let stand overnight, and discard water.
Water	Extract with HPLC water for 8 hours.
Methanol	Extract with methanol for 22 hours.
Methylene Chloride	Extract with methylene chloride for 22 hours.
Methylene Chloride	Extract with methylene chloride for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source for large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 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. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles, but not so excessive as to cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual methylene chloride ($MeCl_2$) as well as PCDDs and PCDFs prior to use. The analyst may opt to omit this check for precleaned XAD-2.

3.1.2.3.1 $MeCl_2$ Residue Extraction. Weigh a 1.0 g sample of dried resin into a small vial, add 3 mL of toluene, cap the vial, and shake it well.

3.1.2.3.2 $MeCl_2$ Residue Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft x 1/8 in stainless steel containing 10 percent OV-101™ on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 mL/min.

Detector: Flame ionization detector operated at a sensitivity of 4 x 10^{-11} A/mV.

Injection Port Temperature: 250°C.

Detector Temperature: 305°C.

Oven Temperature: 30°C for 4 min; programmed to rise at 40°C/min until it reaches 250°C; return to 30°C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injecting 4.0 µl of methylene chloride into 100 mL of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.3.3 PCDD and PCDF Check. Extract the adsorbent sample as described in Section 5.1. Analyze the extract as described in Section 5.3. If any of the PCDDs or PCDFs (tetra through hexa) are present at concentrations above the target detection limits (TDLs), the adsorbent must be recleaned by repeating the last step of the cleaning procedure. The TDLs for the various PCDD/PCDF congeners are listed in Table 1.

3.1.2.4 Storage. After cleaning, the adsorbent may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in glass adsorbent modules tightly sealed with glass stoppers. It must be used within 4 weeks of cleaning. If

precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110°C oven, and stored in a methylene chloride-washed glass container with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175° C (350°F) for two hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 mL of water, and then carefully add 400 mL of concentrated sulfuric acid.

3.1.7 HPLC Water.

3.2 Sample Recovery.

3.2.1 Acetone. Pesticide quality.

3.2.2 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying.

Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

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

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide grade.

3.3.10 Toluene. Pesticide grade.

3.3.11 Nonane. Pesticide grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130°C. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180°C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50°C for 10 minutes, then increase the temperature gradually to 180°C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-mL glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 2 under the heading "Internal Standards" in 10 mL of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 2 under the heading "Surrogate Standards" in 10 mL of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 2 under the heading "Recovery Standards" in 10 mL of nonane.

4. PROCEDURE

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers and analysts should be trained and experienced with the procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps shall be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 40 µl of the surrogate standard solution (Section 3.3.21) to each trap for a sample that will be split prior to analysis or 20 μl of the surrogate standard solution (Section 3.3.21) to each trap for samples that will not be split for analysis (Section 5.1). After

addition of the surrogate standard solution, the trap must be used within 14 days. Keep the spiked sorbent under refrigeration until use.

4.1.1.3 Sampling Train. It is suggested that all components be maintained according to the procedure described in APTD-0576.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in air tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in the fifth impinger just prior to sampling.

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

4.1.2 Preliminary Determinations. Same as Section 4.1.2 Method 5.

4.1.3 Preparation of Sampling Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until sampling is about to begin. Wrap sorbent module with aluminum foil to shield from radiant heat of sun light. (NOTE: Do not use sealant grease in assembling the train.)

4.1.3.2 Place approximately 100 mL of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus the fifth impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the sampling train as shown in Figure 23-1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50°C because thermal decomposition and breakthrough of surrogate standards will occur. During testing, the XAD-2 temperature must not exceed 20°C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, Section 4.1.4.

4.1.5 Sampling Train Operation. Same as Method 5, Section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins 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 Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area. Cleanup personnel shall wash their hands prior to sample recovery.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Do not place the filter in aluminum foil. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container with Teflon tape.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, and store it on ice for transport to the laboratory.

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

Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of toluene for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Impinger Water. Measure the liquid in the first four impingers to within 1 mL by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight.

4.2.5 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

5. ANALYSIS

All glassware shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction. The analyst may choose to split the

sample extract after the completion of sample extraction procedures. One half of the sample can then be archived. Sample preparation procedures are given for using the entire sample and for splitting the sample.

5.1.1 Extraction System. Place an extraction thimble (Section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See Section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug to the thimble.

5.1.4 Container No. 2 (Acetone and Toluene). Concentrate the sample to a volume of about 1-2 mL using a Kuderna-Danish

concentrator apparatus, followed by N_2 blow down at a temperature of less than 37°C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the sampling train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in Section 5.1.1.

5.1.5 Extraction. For samples that are to be split prior to analysis add 40 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from Section 5.1.4. Alternatively, 20 µl of the internal standard solution (Section 3.3.20) for samples that are <u>not</u> to be split prior to analysis. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Add additional toluene to fill the reservoir approximately 2/3 full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-mL rinses to the rotary evaporator. Concentrate the extract to approximately 10 mL. If

decided to split the sample, store one half for future use, and analyze the other half according to the procedures in Sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 mL of hexane.

5.2 Sample Cleanup and Fractionation.

The following sample cleanup and fractionation procedures are recommended. Alternative procedures may be utilized providing acceptable identification criteria (Section 5.3.2.5) and quantification criteria (Section 5.3.2.6) are met.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 mL of hexane and discard. Add the sample extract, dissolved in 5 mL of hexane to the column with two additional 5-mL rinses. 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 (Section 2.3.9).

5.2.2 Basic Alumina Column. Shorten a 25-mL disposable Pasteur pipette to about 16 mL. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 mL of 0.5 percent methylene chloride in hexane followed by 120 mL of 35

percent methylene chloride in hexane. Discard the first 120 mL of eluate. Collect the second 120 mL of eluate and concentrate it to about 0.5 mL using the nitrogen evaporative concentrator. Transfer this extract with hexane to "13 mL tubes".

5.2.3 AX-21 Carbon/Celite 545 Column. Remove the bottom 0.5 in. from the tip of a 2-mL disposable Pasteur pipette. Insert a glass fiber filter disk or glass wool plug in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/Celite™ mixture to form a 2 cm column (the 0.6 mL mark column. Top with a glass wool plug. In some cases AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Pre-elute the column with 5 mL toluene, followed by 1 mL of a 50:50 methylene chloride/cyclohexane mixture, followed by 5 mL of hexane. Load in sequence, the sample extract in 1 mL hexane, 2x0.5 mL rinses in hexane, 2 mL of 50 percent methylene chloride in hexane and 2 mL of 50 percent benzene in ethyl acetate and discard the eluates. Invert the column and elute in the reverse direction with 13 mL of toluene. Collect this eluate. Concentrate the eluate in a nitrogen evaporator at 45°C to about 1 mL. Transfer the concentrate to a Reacti-vial using a toluene rinses and concentrate to near dryness (less than 20 μl) using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental

parameters in Sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the recovery standard solution from Table 2 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If 2,3,7,8-TCDF is detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that it can be demonstrated using calibration and performance checks that the column system is able to meet the specifications of Section 6.1.2.

5.3.1 Gas Chromatograph Operating Conditions. The recommended conditions are shown in Table 4.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10,000 resolving power or 100 ppm mass/mass.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250°C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is presented in Table 5.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable

ion-abundance ratio ranges (±15%) for the identification of chlorine-containing compounds are given in Table 6. If the ion-abundance ratio ranges are the outside those in Table 6, the source has the option of using the results if the concentration is determined using procedures in Section 9.3 or redoing the analysis to eliminate the unacceptable ion-abundance ratio.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard or surrogate standard.

3. The monitored ions, shown in Table 5 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8-TCDF shall satisfy all of the above identification criteria.

7. Any PCDF coeluting (±2 s) with a peak in the corresponding PCDPE channel, of intensity 10% or greater compared to the analyte peak is evidence of a positive interference, the source may opt keep the value to calculate CDD/CDF concentration or conduct a complete reanalysis in an effort to remove or shift the

interference. If a reanalysis is conducted, all values from the reanalyzed sample will be used for CDD/CDF concentration calculations.

8. Set the mass spectrometer lock channels as specified in Table 5. Monitor the quality control check channels specified in Table 5 to verify instrument stability during the analysis. If the signal varies by more than 25 percent from the average response, results for all isomers at corresponding residence time shall be invalid. The source has the options of conducting additional cleanup procedures on the other portion of the sample for split samples or diluting the original sample or following other procedures recommended by the Administrator. When a complete reanalysis is conducted, all concentration calculations shall be based on the reanalyzed sample.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$-2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$-1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard. When no peak is detected, the noise level, as measured

by the intensity of the noise in a clear zone of the chromatogram, is used to calculate the detection limit. Tables 7, 8, and 9 summarize the quantification relationships for the unlabeled analytes, internal standards and surrogate standards, respectively.

6. CALIBRATION

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 3. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 3) and of the internal and surrogate standards shall be less than or equal to the values in Table 6. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 10. The ion abundance ratios shall be within the control limits in Table 5.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject 2 µl of solution Number 3 from Table 3. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 10. In addition, the ion-abundance ratios shall be within the allowable control limits

shown in Table 6.

6.1.2.2 Column Separation Check. Inject 2 μl of a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series. Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 5. Monitor the quality control check channels specified in Table 5 to verify instrument stability during the analysis.

7. QUALITY CONTROL

7.1 Sampling Train Collection Efficiency Check. Add 40 µl of the surrogate standards in Table 2 for samples split for analysis or 20 μl of the surrogate standards for sample <u>not</u> split for analysis to the adsorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon-labeled PCDDs and PCDFs representing the tetra- through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards shall be between 40 to 130 percent for the

tetra- through hexachlorinated compounds while the range is 25 to 130 percent for the hepta- and octachlorinated homologues.

7.3 Surrogate Standard Recoveries. The five surrogate compounds in Table 3 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of the sampling train collection efficiency. They are not used to measure the native PCDD's and PCDF's. All surrogate standard recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery (on a homolog group basis). Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

7.5 Detection Limits. Calculate the detection limits using the equation in Section 9.8. If the detection limits meet the Target Detection Limits (TDLs) in Table 1, then they are considered acceptable. If the TDLs are not met, the impact of the detection limits shall be calculated using the procedures in Section 9.9. If the maximum potential value of the sum of the

summed detection limits is less then 50 percent of the emission standard, the detection limits are acceptable. If the value is greater than 50 percent of the emission standard, then the analysis and/or sampling and analysis must be repeated until acceptable detection limits are obtained.

8. QUALITY ASSURANCE

8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. Audit samples may be obtained by writing:

Source Test Audit Coordinator (MD-77B)
Quality Assurance Division
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The audit sample request must be made at least 30 days

prior to the scheduled compliance sample analysis.

8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure provided in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

9. CALCULATIONS

Same as Method 5, Section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of

internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.

DL = Detection limit, pg/sample.

DL_{hs} = Detection limit for each homologous series, pg/sample.

DL_{sum} = Sum of all isomers times the corresponding detection limit, ng/m^3.

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

m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.

m^*_{ci} = Mass of labeled compound i in the calibration standard injected into the analyzer, pg.

m^*_i = Mass of internal standard i added to the sample, pg.

m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.

m_s = Mass of surrogate compound in the sample to be analyzed, pg.

m_{si} = Mass of surrogate compound i in the calibration standard, pg.

RRF_i = Relative response factor for compound i.

RRF_{rs} = Recovery standard response factor.

RRF_s = Surrogate compound response factor.

$V_{m(std)}$= Metered volume of sample run, dscm.

1000 = pg per ng.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m^*_i\, A_i}{A^*_i\, RRF_i\, V_{m_{std}}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A^*_{ci}\, m_{rs}}{A_{rs}\, m^*_{ci}} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R^*).

$$R^* = \frac{A^*_i\, m_{rs}}{A_{rs}\, RF_{rs}\, m^*_i}\times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A^*_{ci}\, m_{si}}{A_{csi}\, m^*_{ci}} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_{si}\, m^*_i}{A^*_i\, RRF_s\, m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Detection Limit (DL). The detection limit can be calculated based on either the height of the noise or the area of the noise using one of the two equations.

Detection limit using height for the DB-225 column. Three and one half times the height has been empirically determined to give area.

$$DL = \frac{2.5\ (3.5\ x\ H_{ai})\ m^*_i}{A^*_{ci}\, RRF_i} \qquad \text{Eq. 23-7}$$

Detection limit using height for the DB-5 column. Five times the height has been empirically determined to give area.

$$DL = \frac{2.5\ (5\ x\ H_{ai})\ m_i^*}{A_{ci}^*\ RRF_i} \qquad \text{Eq. 23-8}$$

Detection limit using area of the noise.

$$DL = \frac{2.5\ A_{ai}\ m_i^*}{A_{ci}^*\ RRF_i} \qquad \text{Eq. 23-9}$$

9.9 Summed Detection Limits. Calculate the maximum potential value of the summed detection limits. If the isomer (group of unresolved isomers) was not detected, use the value calculated for the detection limit in Section 9.8 above. If the isomer (group of unresolved isomers) was detected, use the value (target detection limit) from Table 1.

$$DL_{sum} = (13\ DL_{TCDD} + 16\ DL_{TCDF} + 12\ DL_{PeCDD} + 14\ DL_{PeCDF} + 7\ DL_{HxCDD} + 12\ DL_{HxCDF} + 2\ DL_{HpCDD} + 4\ DL_{HpCDF} + DL_{OCDD} + DL_{OCDF})\ /\ 1000\ V_{m(std)} \qquad \text{Eq.23-10}$$

Note: The number of isomers used to calculate the summed detection limit represent the total number of isomers typically separated and not the actual number of isomers for each series.

9.10 Total Concentration of PCDD's and PCDF's in the Sample.

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

Any PCDDs or PCDFs that are reported as not detected (below the DL) shall be counted as zero for the purpose of calculating the total concentration of PCDDs and PCDFs in the sample.

10. BIBLIOGRAPHY

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6. Personnel communications with R. L. Harless of U.S. EPA and Triangle Laboratory staff.

TABLE 23-1. TARGET DETECTION LIMITS (TDLs)

ANALYTE	TDL (pg/Sample Train)
TCDD/TCDF	50
PeCDD/PeCDF	250
HxCDD/HxCDF	250
HpCDD/HpCDF	250
OCDD/OCDF	500

TABLE 23-2. COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS*

ANALYTE	CONCENTRATION(pg/µL)
Internal Standards	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards	
$^{13}C_{12}$-1,2,3,4-TCDD	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100

*Calibration levels are specific for samples at

the MWC compliance standard level.

TABLE 23-3. COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

COMPOUND	CONCENTRATIONS (pg/µl)				
SOLUTION NO.	1	2	3	4	5
UNLABELED ANALYTES					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5	10	50	500	1000
OCDF	5	10	50	500	1000
INTERNAL STANDARDS					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100

$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100

TABLE 23-3. (Continued)

COMPOUND	CONCENTRATION (pg/µl)				
SOLUTION NO.	1	2	3	4	5
SURROGATE STANDARDS					
$^{37}Cl_4$-2,3,7,8-TCDD	60	80	100	120	140
$^{13}C_{12}$-2,3,4,7,8-PeCDF	60	80	100	120	140
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	60	80	100	120	140
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	60	80	100	120	140
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	60	80	100	120	140
RECOVERY STANDARDS					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 23-4. RECOMMENDED GC OPERATING CONDITIONS

Column Type	DB-5	DB-225
Length (m)	60	30
i.d. (mm)	0.25	0.25
Film Thickness (μm)	0.25	0.25
Carrier Gas	Helium	Helium
Carrier Gas Flow (mL/min)	1-2	1-2
Injection Mode	<-- splitless -->	
Valve Time (min)	2.5	2.5
Initial Temperature (◦ C)	150	130
Initial Time (min)	0.5	2.5
Rate 1 (deg. C/min)	60	50
Temperature 2 (deg. C)	170	170
Rate 2 (deg. C/min)	3	4
Final Temperature (deg. C)	300	250

TABLE 23-5. ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD's AND PCDF's

DESCRIPTOR NUMBER	ACCURATE MASS	ION TYPE	ELEMENTAL COMPOSITION	ANALYTE
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF(S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF(S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD(S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD(S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD(S)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF(S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF(S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_3{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD(S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD(S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M+2	$C_{12}H_235Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF(S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF(S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD(S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD(S)

	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK

TABLE 23-5. (Continued)

DESCRIPTOR NUMBER	ACCURATE MASS	ION TYPE	ELEMENTAL DESCRIPTION	ANALYTE
	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF(S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD(S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD(S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF(S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF(S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD(S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD(S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD(S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD(S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

The following nuclidic masses were used:
H = 1.007825 O = 15.994914 C = 12.000000 ^{35}Cl = 34.968853
^{13}C = 13.003355 ^{37}Cl = 36.965903 F = 18.9984
S = Labeled Standard

QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 23-6. ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD's AND PCDF's

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
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[b]	M?M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

TABLE 23-7. UNLABELED ANALYTES QUANTIFICATION RELATIONSHIPS

ANALYTE	INTERNAL STANDARD USED
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
Other TCDD's	$^{13}C_{12}$-2,3,7,8-TCDD
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
Other PeCDD's	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Other HxCDD's	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
Other HpCDD's	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD	$^{13}C_{12}$-OCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
Other TCDF's	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Other PeCDF's	$^{13}C_{12}$-1,2,3,7,8-PeCDF
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
Other HxCDF's	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF

TABLE 23-8. INTERNAL STANDARDS QUANTIFICATION RELATIONSHIPS

INTERNAL STANDARD	STANDARD USED DURING PERCENT RECOVERY DETERMINATION
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

TABLE 23-9. SURROGATE STANDARDS QUANTIFICATION RELATIONSHIPS

SURROGATE STANDARD	STANDARD USED DURING PERCENT RECOVERY DETERMINATION
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF

TABLE 23-10. MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

COMPOUND	RELATIVE RESPONSE FACTORS	
	INITIAL CALIBRATION (RSD)	DAILY CALIBRATION (% DIFFERENCE)
UNLABELED ANALYTES		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
SURROGATE STANDARDS		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF		
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD		
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF		
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF		

(Figure 1)

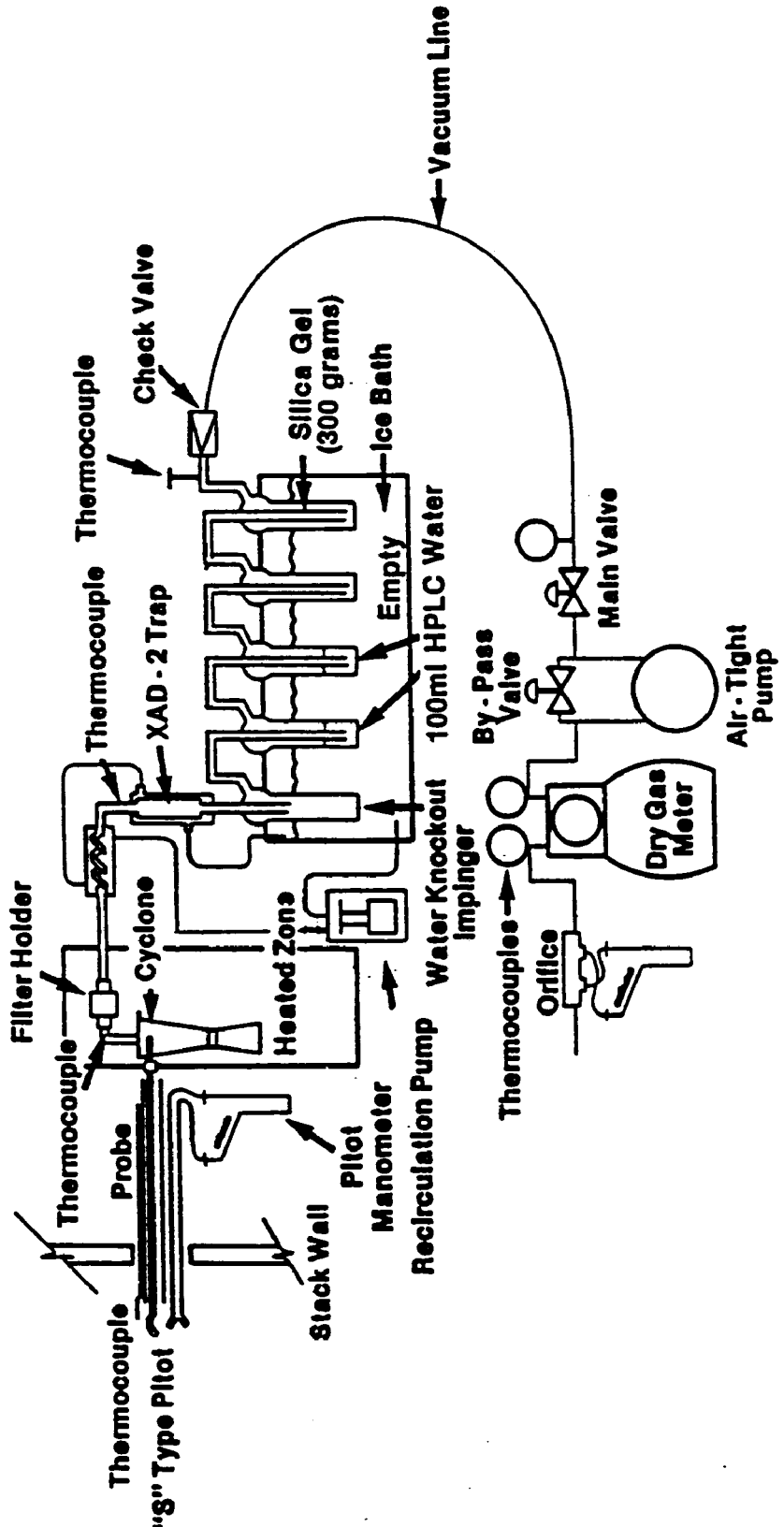

Figure 5-1. CDD/CDF Sampling Train Configuration

(Figure 2)

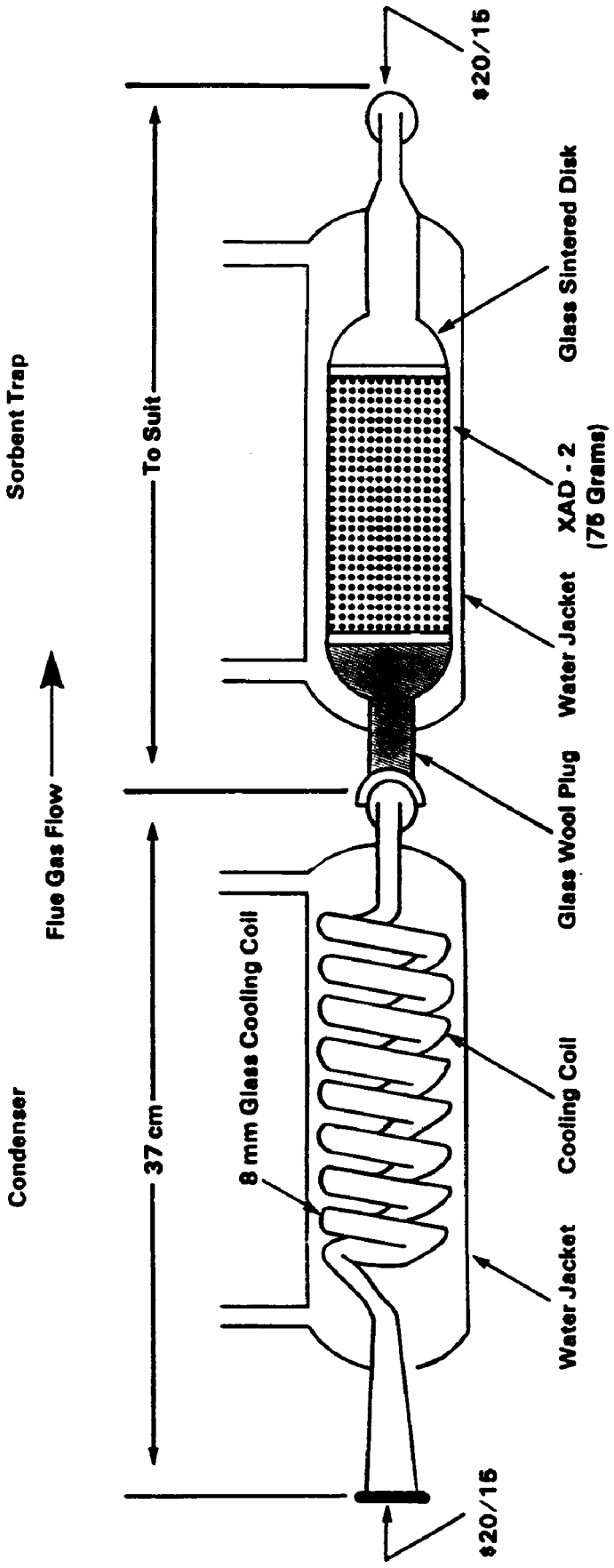

FIGURE 2. CONDENSER AND SORBENT TRAP FOR COLLECTION OF GASEOUS PCDDs AND PCDFs