

SAMPLING METHOD FOR POLYCHLORINATED DIBENZO-*p*-DIOXINS
AND POLYCHLORINATED DIBENZOFURAN EMISSIONS
FROM STATIONARY SOURCES

1.0 SCOPE AND APPLICATION

1.1 This method describes the sampling procedure to be used for determining stack emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources. The air sample is collected and analyzed by the determinative portion of Methods 8280 or 8290. This method describes the procedures for sampling and calculating results. This method may be modified to allow simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), or semivolatile organic compounds (SVOCs). However, specific approval is required for this modification, and detailed modification of the methodology is required.

1.1.1 This method is a revision of Method 23 (see Ref. 10).

1.1.2 The surrogates and recovery standards include the standards listed in Methods 8280 and 8290.

1.1.3 The method refers to specific techniques described in Methods 1, 2 and 5 (see Ref. 10). Analysts should obtain copies of those methods prior to sampling.

1.2 This method is restricted to use by or under the supervision of analysts experienced in the use of air sampling methods and the analysis of PCDDs, PCDFs, PCBs, PAHs, and SVOCs from the components of Method 0010 trains. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.3 Safety - The laboratory should develop a strict safety program for the handling of PCDDs and/or PCDFs.

1.3.1 2,3,7,8-TCDD has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst must be aware of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Personnel handling these types of samples should wear masks fitted with charcoal filters to prevent the inhalation of airborne particulates.

1.3.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined. However, each chemical should be treated as a potential health hazard, and exposure to these chemicals kept to a minimum. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be made available to all personnel involved in the sampling and chemical analysis of samples suspected to contain PCDDs/PCDFs. Method 8290 and References 7, 8, and 9 give additional information on laboratory safety.

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate PCDDs/PCDFs are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. The collection components consist of the front half glassware surfaces (nozzle, probe, and front half filter holder), the glass fiber filter, the back half glassware surfaces (back half filter holder and condenser coil) and the solid sorbent (XAD-2®) module.

2.2 Following sampling the glass collection components are rinsed. The PCDD/PCDF are then extracted from the front half rinses and filter and another separate extraction is performed on the XAD-2® and back half rinses.

2.3 The filter and XAD-2® extracts are then analyzed separately. Surrogate recoveries are determined for both fractions. The analysis is performed using high resolution gas chromatography (HRGC) and high resolution mass spectrometry (HRMS), using the procedures of Method 8290.

3.0 INTERFERENCES

3.1 The use, in this method, of high resolution mass spectrometry with high resolution capillary gas chromatography avoids the interference from polychlorinated biphenyls and polychlorinated diphenyl ethers which could be serious with lower resolution techniques.

3.2 Very high amounts of other organic compounds in the matrix will interfere with the analysis. Extensive column-chromatographic cleanup has been introduced into typical HRGC/HRMS analytical methodology to minimize matrix effects due to high concentrations of organic compounds.

3.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by preparing and analyzing laboratory method blanks.

Glassware must be cleaned thoroughly before using. A procedure which has been found to be effective is given in Sec. 6.1.4, but any protocol which consistently results in contamination-free glassware is acceptable.

3.3.1 The use of high purity reagents and solvents helps to minimize interference problems in sample analysis.

4.0 APPARATUS AND MATERIALS

The following section describes all the sampling equipment and the associated performance specifications necessary to collect a gas sample from a stationary source according to Method 0023.

4.1 Sampling train - A schematic diagram of the sampling train is shown in Figure 1. This train configuration has been adapted from Method 5 (Reference 10) with the addition of condenser, XAD-2® trap and filtration-coil connecting glassware. Sealing greases must not be used in assembling the train. Complete sampling systems are commercially available that have been developed to meet all the EPA equipment design specifications. The following equipment is required.

4.1.1 Nozzle - The nozzle should be made of quartz or borosilicate glass. Stainless steel nozzles should not be used. The taper angle should be $\leq 30^\circ$, with taper on the outside to preserve a constant inside diameter (ID). The nozzle ID should be determined in order to sample isokinetically at a rate that allows collection of an adequate sample volume. The minimum sample volume should be determined to allow appropriate detection limits to be achieved (see Sec. 6.2.3).

4.1.2 Probe liner - The sampling probe liner should be constructed of borosilicate or quartz glass tubing. The typical outside diameter (OD) used by sampling equipment manufacturers is about 16 mm, encased in a stainless steel sheath with an OD of 25.4 mm. Either borosilicate or quartz glass liners may be used for stack temperatures up to about 480°C, but quartz glass liners should be used at higher stack temperature [480 to 900°C].

4.1.3 Probe sheath and heating system - A stainless steel or equivalent probe sheath should be used to house the probe liner and heating system. The probe heating system should be capable of maintaining probe gas temperatures at the probe exit of $120^\circ\text{C} \pm 14^\circ\text{C}$ during sampling. This temperature should be verified by placing a thermocouple temperature sensor against the outer surface of the probe liner at least 2 feet upstream of the filter oven. Temperature readings should be recorded during sampling.

4.1.4 Glass cyclone - A glass cyclone may be used between the probe and filter holder for high particulate concentrations. A cyclone, if used, should be rinsed and recovered with the front half of the train.

4.1.5 Filter holder - A filter holder of borosilicate glass with a Teflon® frit filter support should be used. 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 is positioned immediately following the probe (or cyclone, if used) with the filter placed toward the flow.

4.1.6 Filter heating system - Any heating system may be used which is capable of maintaining the filter holder at $120^\circ\text{C} \pm 14^\circ\text{C}$ during sampling. Other temperatures may be specified by a subpart of the regulations or approved for a particular application. A gauge capable of measuring temperatures to within 3°C should be provided to monitor the temperature around the filter during sampling.

4.1.7 Sample transfer lines - A sample transfer line may be used if needed to direct sample flow from the probe to the filter or from the filter to the condenser. The probe-to-filter line should be insulated and heated so that gas exit temperatures are $120^\circ\text{C} \pm 14^\circ\text{C}$. The filter-to-condenser line should be insulated and oriented with the downstream end lower than the upstream end so that any condensate will flow away from the filter and into the condenser. These lines should be constructed of Teflon® or glass and should be recovered with their respective rinse fractions (front half or back half).

4.1.8 Condenser - A multi-coil water-cooled glass condenser should be used to cool the sample gas prior to entry into the sorbent module. The orientation of the condenser should be vertical.

4.1.9 Sorbent module - The glass water-cooled container configured to hold the solid sorbent (XAD-2®) should contain a minimum of 20 g of XAD-2® and may contain as much as 40 g. A schematic diagram is shown in Figure 2. A single piece condenser-trap can be used if desired. The sorbent trap configuration should be vertical so that condensate drains from

the condenser through the sorbent and so that channeling of the gas flow does not occur. The connecting fittings should form leak-free, vacuum tight seals. Sealant greases should not be used in the sampling train. A coarse glass or Teflon® frit along with glass wool plugs is included to retain the sorbent. The tester may engrave a unique identification number for inventory and sample tracking.

4.1.10 Impinger trains - Four impingers should be connected in series with leak-free ground-glass fittings or any similar noncontaminating fittings. The first impinger should be a short stem (knock out) version. The second impinger should be a Greenburg-Smith impinger with the standard tip and plate. The third and fourth impingers should be the Greenburg-Smith design modified so that the glass tube has an unobstructed 13 mm ID and extends to within 13 mm of the flask bottom. The fourth impinger outlet connection should allow insertion of a thermometer capable of measuring $\pm 1^{\circ}\text{C}$ of true value in the range of 0 to 25°C .

4.1.11 Water circulating bath - A bath and pump circulating system which is capable of providing chilled water flow to the condenser and sorbent trap water jackets should be used. Typically a submersible pump is placed in the impinger ice water bath so that the ice water contained there can be used. The function of this system should be verified by measuring sorbent trap gas entrance temperature $\leq 20^{\circ}\text{C}$.

4.1.12 Pitot tube - The pitot tube, preferably of Type S design, shall meet the requirements of Method 2. The pitot tube is attached to the probe as shown in Figure 1. The proper pitot tube-sampling nozzle configuration for prevention of aerodynamic interference is shown in Figures 2.6 and 2.7 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Sec. 4 of Method 2.

4.1.13 Differential pressure gauge - The differential pressure gauge should be an inclined manometer or the equivalent as described in Method 2. Two gauges are required: one gauge to monitor the stack velocity pressure (ΔP), and the other to measure the orifice pressure differential (ΔH).

4.1.14 Metering system - The metering system should consist of a dry gas meter with 2% accuracy, a vacuum pump, a vacuum gauge, orifice meter, thermometers or thermocouples capable of measuring $\pm 3^{\circ}\text{C}$ of true value in the range of 0 to 90°C ; and related equipment as shown in Figure 1. Thermocouples should be used to monitor the temperature at the following sampling train locations:

- stack gas
- probe liner
- filter holder
- sorbent trap entrance
- silica gel impinger exit
- dry gas meter inlet and
- dry gas meter outlet.

Other metering systems capable of maintaining isokinetic sampling rates within 10% and determining sample volumes to within 2% may be used if approved. Sampling trains with metering systems designed for sampling rates higher than those described in APTD-0581 and APTD-0576 (Air Pollution Technical Document, see references) may be used if the above specifications can be met. When the metering system is used with a pitot tube, the system should permit verification of an isokinetic sampling rate through the use of a nomograph or by calculation.

4.1.15 Barometer - A mercury (Hg), aneroid, or other barometer capable of measuring atmospheric pressure to within ± 2.5 mm Hg is needed. A preliminary check of a new barometer should be made against a mercury-in-glass barometer or the equivalent. The absolute barometric pressure may be obtained from a nearby weather service station and adjusted for elevation difference between the station and the sampling point. Either subtract 2.5 mm Hg from the station value for every 30 m elevation increase or add the same for an elevation decrease. If the barometer cannot be adjusted to agree within 0.1 in. Hg of the reference barometric pressure, it should be repaired or discarded.

4.1.16 Gas density determination equipment - The equipment necessary for conducting Methods 2 - 4 for determining stack gas flow, molecular weight and moisture content, respectively, should be used. Required measurements include stack gas velocity and static pressure; gas temperature; concentrations of O₂, CO₂, and N₂ (by difference), metered gas volumes and meter temperatures and pressure; and condensate weight gain collected by the impinger train. All equipment should meet Methods 2 through 4 requirements.

4.2 Sample recovery equipment

4.2.1 Fitting caps - Ground glass or cleaned aluminum foil to cap the exposed sections of the train.

4.2.2 Wash bottles -Teflon® .

4.2.3 Probe-liner, probe-nozzle, and filter-holder brushes - These should be constructed with nylon or Teflon® bristles with precleaned stainless steel or Teflon® handles. The probe brush should have extensions of stainless steel or Teflon® at least as long as the probe. The brushes should be properly sized and shaped to brush out the nozzle, probe liner, and front half filter holder.

4.2.4 Filter storage container - Typically a glass petri dish sealed with Teflon® tape is used. Petri dishes should be cleaned according to glassware cleaning procedures listed in this method (Sec. 6.1.4).

4.2.5 Balance - This balance is used for measuring weight gain of the impingers and sample bottle weights as well. Typically a 0 to 2000-g balance is used. The balance should be accurate to within 0.5 g, verified with ASTM Class 1 (Class S) weights.

4.2.6 Aluminum foil - Heavy duty cleaned by rinsing three times with methylene chloride and once with toluene, stored in pre-cleaned glass petri dish or glass jar.

4.2.7 Graduated cylinder - Glass, 250-mL, with ± 1 mL resolution (this cylinder can be used for impinger volume determinations in place of the balance).

4.2.8 Glass sample storage container - Amber glass bottle for sample glassware washes, 500- or 1000-mL, with leak-free Teflon® -lined caps. The bottles should be either purchased as precleaned or cleaned according to glassware cleaning procedures listed in this method (Sec. 6.1.4).

5.0 REAGENTS

5.1 Filters - Glass fiber filters, without organic binder, exhibiting at least 99.95% efficiency (< 0.05% penetration) on 0.3 μm dioctyl phthalate smoke particles. One filter from each batch is tested for contamination using the procedure in Sec. 5.1.2. If the filter fails the test, then all filters must be cleaned and retested before their initial use according to the following procedures.

5.1.1 Precleaning - Place no more than 50 filters in a Soxhlet extraction apparatus. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool. Remove the filters and dry under a clean nitrogen (N_2) stream. Store the filters in cleaned glass petri dishes or amber glass bottles sealed with Teflon[®] tape or Teflon[®]-lined caps prior to using them.

5.1.2 As a quality control check prior to the field test, take one precleaned filter and perform Soxhlet extraction with toluene for 16 hours. Remove the toluene extract and analyze according to Method 8290. No analytes may be observed above the detection limit.

5.1.3 Filter surrogate spike solution - As stated in Sec. 7.3.3, this method calls for both the filter and the XAD-2[®] sorbent to be spiked with the same set of isotopically labeled PCDD/PCDF standards. Surrogate spikes are added to the sorbent prior to sampling and to the filter immediately before the sample extraction. The filter and XAD-2[®] fractions (including the associated glassware rinses) are extracted separately and analyzed separately. The surrogate standards listed in Table 1 should be used for both the filter spike and sorbent spike.

5.1.4 To ensure proper filter spiking, the isotopically-labeled standard solution, which is normally at a concentration of 0.1 ng/ μL , is diluted to 0.004 ng/ μL with nonane, for a dilution factor of 25. This spiking solution will be used to spike the surface of the filter as discussed in Sec. 7.3.1.

5.2 Sorbent resin - Amberlite XAD-2[®] resin. XAD-2[®] may be purchased precleaned or cleaned by the laboratory. If the sorbent has not been precleaned, a cleaning procedure capable of producing resin meeting the quality control check in Sec. 5.2.1.8 shall be implemented. The procedure given below has been found to produce excellent results.

5.2.1 Sorbent resin cleaning procedure

5.2.1.1 Place the sorbent resin in a clean beaker and rinse with reagent water. Discard the rinse. Fill the beaker a second time with reagent water and allow the resin to stand overnight. Discard this second rinse.

5.2.1.2 Place the sorbent resin in an all-glass thimble of a large Soxhlet extractor. The sorbent resin will float when in contact with methylene chloride. Therefore, add a glass wool plug on top of the resin in the thimble, and weight the glass wool plug down with a stainless steel ring that fits inside the thimble.

5.2.1.3 Place the thimble filled with resin into the Soxhlet extractor, add organic-free reagent water to the distilling flask, apply heat, and extract the resin for 8 hours.

5.2.1.4 Allow the Soxhlet extractor to cool, discard the water, and add methanol to the extractor. Apply heat and extract for 22 hours.

5.2.1.5 Again allowing the extractor to cool, drain off the methanol, replace it with methylene chloride. Make sure that the stainless steel ring and glass wool plug are still in place and extract for 22 hours.

5.2.1.6 Extract the resin a fourth time, using toluene as the extraction solvent, for 22 hours.

5.2.1.7 Following the toluene extraction, the sorbent resin must be dried under a stream of clean dry nitrogen or other inert gas. This may be accomplished by transferring the resin to a large diameter glass column and flowing the gas through the column. The gas may be heated to less than 40°C, using a steam bath or other appropriate heat source. Continue the inert gas flow through the resin until all the residual solvent is removed. The flow rate should be sufficient to agitate the resin particles, but not so excessive as to cause the particles to fracture.

5.2.1.8 A quality control check should be conducted on the cleaned sorbent using HRGC/HRMS techniques (Method 8290). Typically, a method blank conducted previously on the same lot of sorbent can serve this purpose.

5.2.2 Sorbent resin surrogate spike solution - The-XAD-2® sorbent is spiked with isotopically labeled PCDD/PCDF standards prior to sampling (surrogate spikes).

5.3 Glass wool - Cleaned by sequential immersion in three aliquots of methylene chloride and one aliquot of toluene, dried in a 110°C oven, and stored in a toluene-washed glass jar with a Teflon® -lined screw cap.

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.5 Silica gel - Indicating type, 6 to 16 mesh. If previously used, dry at 175°C for two hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, provided that appropriate performance has been demonstrated.

5.6 Recovery solvents - Solvents must be pesticide quality or equivalent.

5.6.1 Acetone, CH₃COCH₃

5.6.2 Methylene chloride, CH₂Cl₂

5.6.3 Toluene, C₆H₅CH₃

6.0 SAMPLING COLLECTION, PRESERVATION, AND PREPARATION

This section addresses preparation and collection procedures for sampling.

6.1 Laboratory preparation

6.1.1 Filters. (See Sec. 5.1.)

6.1.2 Sorbent trap. (See Sec. 5.2.)

6.1.3 Glass wool - Precleaning and storage. (See Sec. 5.3.)

6.1.4 Glassware - All glass components of the train should be cleaned thoroughly. The following procedure has been found to be effective, but any protocol which consistently results in contamination-free glassware is acceptable.

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

Rinse with tap water to remove soap.

Rinse with distilled/deionized H₂O (three times).

Bake at 400°C for 2 hours.

Rinse with methylene chloride (pesticide grade) (three times).

Rinse with toluene (pesticide grade) (three times).

Cap glassware with clean glass caps or cleaned aluminum foil.

Mark cleaned glassware with color-coded identification stickers.

Rinse glassware immediately before using with acetone and methylene chloride.

6.1.5 Because probe liners do not usually fit in glassware baths or ovens, they may be rinsed three times with methylene chloride followed by three rinses with toluene, and sealed during transport.

6.2 Preliminary field determinations

6.2.1 Sample site - The sampling site and the minimum number of sampling points should be selected according to Method 1 or as specified by the Agency. The stack static pressure, temperature, and range of velocity pressures (ΔP s) should be determined using Method 2. The stack gas moisture content should be determined using Method 4, its alternatives, previous data, or an engineering estimate. Stack gas O₂ and CO₂ concentrations should be estimated and dry molecular weight should be calculated. These parameters are used to estimate the isokinetic sampling rate settings.

6.2.2 Nozzle size - The nozzle size should be based on the range of velocity pressures so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates.

6.2.3 Sampling duration - The total length of sampling time needed to obtain the identified minimum sample gas volume is determined by comparing the anticipated average sampling rate with the volume requirement. (Average sampling rate should be within 0.5 to 0.75 cfm.) The same time should be allocated to all traverse points defined by Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half minute.

6.2.3.1 Calculation of length of the sampling duration - The minimum sampling time required to achieve a minimum sample volume and the corresponding detection limit (DL) are given below.

$$\text{Minimum sample time} = \frac{\text{analytical DL}}{(\text{Sample Rate}) \times (\text{desired gas conc. DL})}$$

6.2.3.2 The following calculation is for a single isomer (i.e., 2,3,7,8-TCDF). Detection limits for other isomers may need to be calculated as well. For this example, it will be assumed that the analytical detection limit is 0.5 ng (actual analytical detection limit will need to be specified for each test program).

6.2.3.3 At a sampling rate of 0.014 m³/min (0.5 cfm), the sample volume per hour will be 0.85 m³/h. Assuming a desired stack gas concentration detection limit to be 0.1 ng/m³, the minimum sample time required to collect 0.5 ng at concentration in the stack of 0.1 ng/m³ would be:

$$\text{Minimum sample time} = \frac{0.5 \text{ ng}}{0.85 \text{ m}^3/\text{h} \times 0.1 \text{ ng/m}^3} = 6.25 \text{ h}$$

6.2.3.4 The total sampling time should be greater than or equal to the minimum total sampling time required to achieve the necessary detection limit. In addition, the sampling time per point should be greater than 2 min (greater minimum time interval may be specified by the Agency), and the sample volume corrected to standard conditions shall exceed the required minimum total gas sample volume.

6.3 Calibration

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures for the sampling apparatus listed in this section can be found in Method 5 and Method 0010. Table 4 summarizes the quality assurance functions for the calibrations.

6.3.1 Metering system

6.3.1.1 Full dry gas meter calibration - The dry gas meter (DGM) in the meter console of the sampling system should be fully calibrated against a primary standard meter (wet test meter or spirometer) or alternatively against a second reference meter (dry gas meter or critical orifice) that has been calibrated against a primary standard meter. The procedure can be found in Method 5.

6.3.1.2 Post-test DGM calibration check - Following the test program, the full calibration factor or meter Y should be checked by performing a post-test DGM calibration check. Any secondary reference meters can be used. Three calibration runs are conducted at the maximum vacuum reached during the testing. The average post-test calibration factor should not deviate from the full DGM calibration factor by more than 5%. Additional details on these procedures can be found in Method 5.

6.3.2 Temperature gauges - Each thermocouple should be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers should conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, should be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5 percent.

6.3.2.1 Impinger, organic module, and dry gas meter thermocouples - For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2® resin bed, three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. The thermocouples should be accepted only if the readings at all three temperatures agree to ± 2°C with those of the absolute value of the reference thermometer.

6.3.2.2 Probe and stack thermocouple - For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures should be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

6.3.3 Probe heater - The probe heating system should be calibrated prior to field use according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the curves of APTD-0576 are used.

6.3.4 Barometer - The field barometer should be adjusted initially and before each test series to agree within 2.5 mm Hg of the mercury-in-glass barometer or with the station pressure value reported by a nearby National Weather Service station, corrected for elevation. The correction for elevation difference between the station and the sampling point should be applied at a rate of -2.4 mm Hg/30 m of elevation increase. The results should be recorded on the pretest sampling check form.

6.3.5 Probe nozzle - Probe nozzles should be calibrated before initial use in the field. The ID of the nozzle should be measured with a micrometer to the nearest 0.025 mm. Three measurements should be made using different diameters each time and the average obtained. The difference between the high and the low numbers should not exceed 0.1 mm. When nozzles become damaged they should not be used again. Each nozzle should be permanently and uniquely identified.

6.3.6 Pitot tube - The Type S pitot tube assembly should be calibrated using the procedure outlined in EPA Method 2.

6.3.7 Balance - The balance should be calibrated initially by using ASTM Class 1 (Class S) standard weights and should be within 0.5 g of the standard weight.

6.4 Sampling train preparation - Care should be taken to ensure a clean sampling train preparation area free of excessive dust and organic compounds for preparing the sampling train.

6.4.1 Preparation of impingers - During preparation and assembly of the sampling train, all train openings where contamination can enter should be sealed until just prior to assembly or until sampling is about to begin.

6.4.1.1 The first impinger should be left empty (used as a water knock-out impinger due to long run times).

6.4.1.2 Approximately 100 mL of reagent water should be placed in the second and third impingers. This method does not require that organic analyses be conducted on the impinger contents. However, if analyses of semivolatile organic compounds are to be conducted, then the proper specifications on cleaning the impingers and water quality (i.e., HPLC-grade water) should be observed.

6.4.1.3 Approximately 200 to 300 g of silica gel should be placed in the fourth impinger. All impingers should be weighed separately to the nearest 0.5 g and the weights recorded. Impingers should be connected with glass U-tube connectors.

6.4.2 Filter loading - A filter should be placed in a properly-cleaned filter holder using cleaned tweezers or clean disposable surgical gloves. The filter should be properly centered and the gasket (if used) properly placed to prevent the sample gas stream from circumventing the filter. The filter should be checked for tears after the assembly is completed.

6.4.3 Sorbent loading - The XAD-2® should be loaded and sealed in the analytical (preparation) laboratory.

6.4.4 Final assembly - The final assembly of the filter holder, condenser, and sorbent module can be performed at the stack location. All components should be sealed with either precleaned foil or socket joints.

6.5 Sampling train leak check procedures - Leak checks are necessary to assure that the sample has not been biased low by dilution air. Both pre-test and post-test leak checks are necessary.

6.5.1 Pre-test - After the sampling train has been assembled, the train should be leak checked at the sampling site by plugging the nozzle and pulling a 380 mm Hg vacuum. Leakage rates greater than 4% of the average sampling rate or 0.00057 m³/min, whichever is less, are unacceptable. Leak checks should be conducted according to Method 5 criteria.

6.5.2 During the sampling - If a component (e.g., filter assembly, sorbent module, or impinger) change is necessary during the sampling run, a leak check should be conducted before the change. The leak check should be done according to the procedure outlined above, except that it should be at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage is less than 0.00057 m³/min or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester should record the leakage rate and either void the sampling run or perform sample volume leak corrections (if approved by the Agency). After replacing the train component, an initial leak check should be completed before sampling.

6.5.3 Post-test - The leak check should be completed at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is less than 0.00057 m³/min or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained the tester shall either void the sample run or perform sample volume leak corrections (if approved by the Agency).

6.6 Sampling train operation

6.6.1 Final pre-test sampling checks - After conducting the initial leak check, the following checks should be made:

- Meter box examination
- Manometers leveled and zeroed
- Pump checked for proper operation
- Pitot lines leak checked
- Probe markings verified
- Thermocouples reading correctly
- Size and orientation of the nozzle verified
- Method 3 equipment for CO₂/O₂ checked for proper assembly and leak checked and
- Isokinetic K-factor checked to ensure that it is correct.

Immediately prior to sampling:

- Portholes should be cleaned to minimize the chance of sampling deposited material
- Probe and filter heating system temperatures should be checked
- Condenser/sorbent cooling system temperatures should be checked and
- Proper nozzle location should be verified.

6.6.2 The sampling procedure below should be followed.

6.6.2.1 Sampling - Initial dry gas meter readings, barometric pressure, and temperatures should be recorded. The tip of the probe should be positioned at the first sampling point with the nozzle tip pointing directly into the gas stream. When the probe is in position, the open area around the probe and the porthole should be blocked off to prevent flow disturbances and non-representative dilution of the gas stream. The pump should be turned on and the sample flow adjusted immediately to attain isokinetic conditions. The Method 3 sampling system should be turned on. Velocity pressures should be recorded and the sampling rate adjusted to isokinetic. Other readings of velocity pressure (ΔP), orifice pressure (ΔH), stack gas temperature (T_s), probe temperature (T_p), filter temperature (T_f), sorbent trap temperature (T_t), silica gel impinger temperature (T_{sg}), dry gas meter inlet and outlet temperatures (T_m), dry gas meter volume, and sample vacuum should be made.

6.6.2.2 The stack should be traversed as directed in Method 5 procedures. At each sample point, the above readings should be taken and sample flow rates adjusted to isokinetic. Following the traverses, the pump is turned off, the probe removed from the stack, and the final DGM readings recorded. Care should be taken not to bump the nozzle against stack walls in order to minimize the chance of breakage or extracting deposited material. Following each port traverse, a leak check is recommended in order to ensure a leak tight system. An additional leak check may also be performed after the train is moved to the next port, prior to sampling. The necessary post-test leak check should be conducted and the leak rate recorded.

6.6.2.3 Periodically during the test run, the connecting glassware from the probe, through the filter, and to the condenser should be checked for water condensation. If any condensation is evident, verify that the temperature sensors and heater systems are functioning properly. Ice should be maintained around the impingers to keep both the sorbent trap entrance and silica gel exit temperature at 20°C. Filter vacuum should be checked for sudden increases. The filter should be changed if the vacuum exceeds 15 in. Hg. The manometer level and zero should also be checked periodically during each traverse, because vibrations and temperature fluctuations can cause the manometer zero to shift.

6.6.2.4 Following the post-test leak check, the probe should be disconnected, and the nozzle and the end of the probe capped with precleaned aluminum foil, or equivalent caps. The inlet to the filter holder should be capped according to one of the methods previously mentioned. It may be necessary to loosen the seal between the sorbent module outlet and the inlet to the first impinger to prevent water from being drawn back into the module when the sample train cools. Alternatively, the filter holder, condenser and sorbent module may be disassembled and immediately capped at the stack location and removed to the sample recovery area.

6.7 Collection of blanks - Four different sampling blanks should be collected: field blanks, reagent blanks, proof blanks, and method blanks (laboratory only). Only two sampling blanks should be analyzed initially: the field blank and the laboratory method blank. If the field blank has high levels of contamination and the laboratory blank does not show high background levels of PCDD/PCDF, the other blanks should be analyzed to help determine the source of the contamination. Blanks are further discussed in Sec. 8.0.

7.0 PROCEDURE

7.1 Recovery preparation - Proper recovery procedure begins as soon as the probe is removed from the stack at the end of the sampling period. The nozzle end of the sampling probe should be sealed with precleaned aluminum foil and disconnected from the filter holder. When the probe is cool enough to be handled safely, all external particulate matter near the tip of the probe should be wiped off and both ends of the probe closed off with aluminum foil. Both openings to the filter holder, transfer line (if used), condenser, sorbent trap, and impinger train should be disconnected and sealed. Care should be taken not to lose any condensed water upstream of the impingers (if present) during this process.

Train components should be transferred to the cleanup area. This area should be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, is not allowed in the cleanup area. Cleanup personnel should wash their hands prior to sample recovery. The train should be inspected prior to and during disassembly and any abnormal conditions, e.g., broken filter, colored impinger liquid, etc., noted.

7.2 Sample recovery procedure - As shown in Figure 3, the sampling train should be recovered into four containers. The procedures applicable to each sample container are briefly discussed in the following section.

7.2.1 Filter (Container 1) - The filter should be removed carefully from the filter holder and placed in its identified container. Cleaned tweezers should be used to handle the filter. Fold the filter, if necessary, with the particulate cake inside the fold. Any particulate matter and filter fibers which adhere to the filter holder gasket should be transferred to the container by using a dry inert bristle brush and a sharp-edged blade. The container should be sealed with Teflon® tape.

7.2.2 Front half rinse (Container 2) - Quantitatively recover material deposited in the nozzle, probe liner, probe transfer line, cyclone (if used), and the front half of the filter holder. Brush while rinsing three times each with acetone and then rinse three times with methylene chloride. All rinses should be put into Container 2. The outside of the probe, the pitot tube, and the nozzle should be cleaned to prevent particulates from being brushed into the sample bottle. The probe liner should be tilted and rotated while squirting acetone into the upper end to assure complete wetting of the inside surface. Acetone is then squirted into the upper end while pushing the probe brush through the liner with a twisting motion, with the drainage caught in the sample bottle (Container 2). The brushing procedure should be repeated two more times or until no particles are visible in the drainage and a visual inspection of the liner reveals no particles remaining inside. The brush should be rinsed into the sample bottle to collect any particulates that may be retained within the bristles. The three acetone rinses are followed with methylene chloride and two rinses with toluene allowing the rinsate to collect into the same sample container.

After all the rinsings have been collected, the lid on the sample container should be tightened securely. As a precaution in case of leakage, the liquid level should be marked on the sample container and the cap sealed with Teflon® tape. The sample recovery should be recorded on the sample recovery form.

7.2.3 Sorbent module (Container 3) - The sorbent module should be removed from the train, tightly capped at both ends with aluminum foil or glass caps, labeled and stored on ice for transport to the laboratory. Care should be taken to ensure that no ice water can leak into the stored traps or any other train component.

7.2.4 Back half rinse (Container 4) - Rinse the back half of the filter holder, the connecting line between the filter holder and the condenser, and the condenser itself (if separate from the trap) three times with acetone, followed by two rinses with methylene chloride and two rinses with toluene. The sample container (Container 4) is then identified and sealed as discussed above.

7.2.5 Impinger water - Any color or film in the impinger water should be noted on the sample recovery form. The entrained moisture in the first three impingers should be measured to within ± 1 mL by using a graduated cylinder or by weighing to within 0.5 g by using a balance, and the data recorded appropriately. This information is needed to calculate the moisture content of the effluent gas. If the sampling train catch is to be analyzed exclusively for dioxins and furans, then the impinger liquid may be discarded after the volume or weight is recorded.

7.2.6 Silica gel - The color of the indicating silica gel should be noted on the recovery form to determine if it has been completely spent and the impinger weighed to determine entrained moisture weight gain. Analysis is not required.

7.3 Analysis summary - The following section summarizes the analytical procedures for quantitating PCDD/PCDF collected by the sampling train. Sample preparation procedures and the basic analytical techniques are listed. The detailed analytical protocol can be found in Method 8290.

7.3.1 As shown in Figure 4, the analytical procedure requires the sampling train to be analyzed in two fractions. Containers 1 and 2 (filter and front half rinse) are combined and analyzed. Containers 3 and 4 (sorbent trap and back half rinse) are also combined and analyzed. In this way filter surrogate standard recoveries and XAD-2® surrogate standard recoveries are both determined separately.

7.3.2 Acceptance criteria and corrective actions for surrogate recoveries are as follows:

7.3.2.1 All PCDD/PCDF surrogate recoveries should be within 70 to 130 percent.

7.3.2.2 If all isomer recoveries are greater than 130 percent, the sampling runs should be repeated,

7.3.2.3 If all isomer recoveries are less than 70 percent, the sampling runs should either be repeated or the final results should be divided by the fraction of surrogate recovery.

7.3.2.4 If some of the isomer recoveries are within the acceptance range and some are not, then the final results for the isomers outside the range should be divided

by the fraction of the surrogate recovery, the resulting corrected results should be flagged in the data tables, and a discussion should be included in the final report.

7.3.2.5 Acceptance criteria for other standard recoveries (i.e., internal) should conform to Method 8290 requirements.

7.3.3 As discussed in Secs. 5.1.2 and 5.2.1, surrogate spikes are added to the sorbent trap prior to sampling and to the filter immediately prior to extraction. The same set of isotopically-labeled compounds is used for these spikes. The analytical procedure for both fractions is given in the following sections. All samples should be extracted within 30 days of collection and analyzed within 45 days of extraction.

7.3.4 Sample preparation and internal standard addition - The following procedure should be performed for the filter/front half analysis and the sorbent trap/back half analysis. The only difference between the two procedures is that surrogate standards are added to the filter/front half fraction immediately prior to sample preparation whereas the surrogate standards have already been added to the sorbent trap/back half prior to sampling.

7.3.4.1 Filter/front half fraction procedures - Place a cellulose extraction thimble, 1 g of silica gel or sodium sulfate, 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.

7.3.4.2 Add exactly 1.0 mL of the surrogate spiking solution (Sec. 5.1.2) uniformly onto the surface of the filter while it is still in the petri dish in which it was returned from the field, using an adjustable pipet. Transfer the filter directly to the extraction thimble of the extraction system. Rinse the petri dish with 10 mL of toluene three times collecting the rinsate into the beaker.

7.3.4.3 Concentrate the sample in Container 2 (acetone/ methylene chloride rinses) to a volume of about 1-2 mL using a Kuderna-Danish concentrator apparatus, followed by nitrogen 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 train probe and nozzle. Add the concentrate to the filter in the Soxhlet apparatus described above.

7.3.4.4 Add 40 µL of the internal standard solution. Fortification is accomplished by using the sample fortification solutions described in Table 1. Cover the contents of the extraction thimble with the cleaned glass wool plug and proceed to the extraction procedure.

7.3.4.5 Sorbent trap/back half fraction procedures - Prepare another extraction thimble/silica gel system as described above. Suspend the adsorbent module directly over the extraction thimble in the beaker. 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, first with methanol, if needed, then with toluene into the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add glass wool plug from the XAD-2® sampling module to the thimble.

7.3.4.6 Concentrate the sample in Container 4 (acetone/methylene chloride rinses) to a volume of about 1 - 2 mL using a Kuderna-Danish concentrator apparatus, followed by nitrogen evaporation at a 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. Add the concentrate to the XAD-2® resin in the Soxhlet apparatus described above.

7.3.4.7 Add 40 µL of the internal standard solution. Fortification is accomplished by using the sample fortification solutions described in Table 1. Cover the contents of the extraction thimble with a cleaned glass wool plug to prevent the XAD-2® resin from floating into the solvent reservoir of the extractor and proceed with extraction (Sec. 7.3.2).

7.3.5 Sample extraction - Place the thimble in the extractor and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately two-thirds 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 between rinses to the rotary evaporator. Concentrate the extract to approximately 10 mL.

Use a nitrogen evaporative concentrator to reduce the volume of the extract to about 100 µL. Redissolve the residue in 5 mL of hexane.

7.3.6 Sample clean-up and fractionation - Sample extracts described above are spiked with 40 µL of the alternate standard fortification solution, then divided into two equal portions. One half of each sample extract is archived for future needs. The other portion is solvent-exchanged to hexane then subjected to three column chromatographic cleanup steps as described in Method 8290.

7.3.7 Analysis summary - The samples are analyzed with a high resolution gas chromatographic column coupled to a high resolution mass spectrometer (HRGC/HRMS) using the instrumental parameters described below. Prior to analysis, the Recovery Standard solution from Table 1 is added to each sample. Sample extracts are first analyzed using a capillary column to determine the concentration of each isomer of PCDDs and PCDFs (tetra-through octa-). If 2,3,7,8-TCDF is detected in this analysis, another aliquot of the sample is analyzed separately, using a second, dissimilar column to confirm and more accurately measure the 2,3,7,8-TCDF isomer. Other column systems may be used, provided that the user is able to demonstrate by means of calibration and performance checks that the column system is able to meet the specifications of Method 8290.

7.3.8 All other analytical specifications for determining the amounts of PCDD/PCDF isomers collected in the filter/front half and sorbent trap/back half fractions can be found in Method 8290.

7.4 Calculations

The mass of each isomer from the front half train fraction is added to that from the back half fraction to obtain a train total before further calculation. If a measurable amount of the isomer is found in one fraction, but the amount in the second fraction is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "nondetect" as zero if the detection limit is less than 10% of the total of the detected amount from the other fraction. In cases where the detection limit in the second fraction is greater than 10% of

the amount detected in the first fraction, then report the total as greater than the detected amount but less than the detected amount plus the second fraction detection limit.

The following section describes the calculations used to determine gas concentrations and emissions of PCDD and PCDF isomers. Toxic equivalent calculations are not included in this method. Each set of calculations should be repeated or spot-checked, as a QC measure. Calculations should be carried out to at least one extra decimal place beyond that of the acquired data and should be rounded off after final calculation to two significant digits for each run or sample. All rounding of numbers should be performed in accordance with the ASTM 380-76 procedures.

The nomenclature and sampling equations are presented in Sec. 7.4.1.

7.4.1 Sampling nomenclature

- A_n = Cross sectional area of nozzle, m^2 (ft^2).
- A_s = Cross sectional area of stack, m^2 (ft^2).
- B_{ws} = Water vapor in the gas stream, proportion by volume.
- C_i = Concentration of pollutant i , $\mu g/dscm$ ($lb/dscf$).
- E_i = Emission rate of pollutant i , g/sec (lb/hr).
- D_N = Diameter of nozzle, mm ($in.$)
- I = Percent of isokinetic sampling.
- M_w = Molecular weight of water, 18.0 $g/g\text{-mole}$ (18.0 $lb/lb\text{-mole}$).
- M_d = Molecular weight of dry stack gas, $g/g\text{-mole}$ ($lb/lb\text{-mole}$).
- M_s = Molecular weight of wet stack gas, $g/g\text{-mole}$ ($lb/lb\text{-mole}$).
- m_i = Mass of pollutant i collected by sampling train, μg (lb).
- P_{bar} = Barometric pressure at the sampling site, mm Hg ($in.$ Hg).
- P_{static} = Static gauge pressure of stack gas, mm H_2O ($in.$ H_2O).
- P_s = Absolute stack gas pressure, mm Hg ($in.$ Hg).
- P_{std} = Standard absolute pressure, 760 mm Hg (29.92 $in.$ Hg).
- Q_{sd} = Average stack gas volumetric flow, dry, standard conditions, $dscmm$ ($dscfm$).
- R = Ideal gas constant, 0.06236 [$(mm$ Hg) (m^3)] / [$(^\circ K)$ ($g\text{-mole}$)] { 21.85 [$(in.$ Hg) (ft^3)] / [$(^\circ R)$ ($lb\text{-mole}$)]}.
- T_m = Absolute average DGM temperature $^\circ K$ ($^\circ R$).

- T_s = Absolute average stack gas temperature °K (°R).
 T_{std} = Standard absolute temperature, 293°K (528°R).
 V_{lc} = Total volume liquid collected in impingers and silica gel (mL).
 V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
 $V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
 $V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
 V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
 Y = Dry gas meter calibration factor.
 ΔP = Average pressure differential across pitot tube, mm H₂O (in. H₂O).
 ΔH = Average pressure differential across the orifice meter, mm H₂O (in. H₂O).
 ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).
 θ = Total sampling time, min.
 K_p = $85.49 \frac{\text{ft}}{\text{sec}} \left[\frac{(\text{lb/lb-mole}) (\text{in. Hg})}{^\circ \text{R} (\text{in. H}_2\text{O})} \right]^{1/2}$
 13.6 = Specific gravity of mercury.

7.4.2 Dry gas volume - Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in. Hg) by using the following equation, where:

$$\begin{aligned}
 K_i &= 0.3858 \text{ } ^\circ\text{K/mm Hg for metric units, or} \\
 &= 17.64 \text{ } ^\circ\text{F/in. Hg for English units.}
 \end{aligned}$$

If the leak corrections to sample volume are necessary and have been approved by the test administrator, follow procedures listed in Method 0010.

7.4.3 Volume of water vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w R T_{std}}{M_w P_{std}} = K_2 V_{lc}$$

where:

$$K_2 = 0.001333 \text{ m}^3/\text{mL} \text{ for metric units, or} \\ = 0.04707 \text{ ft}^3/\text{mL} \text{ for English units.}$$

7.4.4 Moisture content

$$B_{ws} = \frac{V_{w(\text{std})}}{V_{m(\text{std})} + V_{w(\text{std})}}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas should be made, one from the impinger analysis (Sec. 7.4.3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} should be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in a "Note" in Sec. 1 of Method 4. For the purposes of this method, the average stack gas temperature may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm 2^\circ\text{C}$.

7.4.5 Absolute stack gas pressure

$$P_s = P_{\text{bar}} + \frac{P_{\text{static}}}{13.6}$$

7.4.6 Average molecular weight of dry stack gas

$$\text{Dry: } M_d = (0.32 \times \%O_2) \times (0.44 \times \%CO_2) + (0.28 \times (100 - (\%O_2 + \%CO_2)))$$

$$\text{Wet: } M_s = M_d \times (1 - B_{ws}) + (B_{ws} \times M_w)$$

7.4.7 Stack gas velocity at stack conditions

$$V_s = K_p \times C_p \times \sqrt{\Delta P} \times \sqrt{\frac{T_s + T_{\text{std}}}{P_s \times M_s}}$$

7.4.8 Average stack gas volumetric flow at dry, standard conditions

$$Q_{sd} = V_s \times A_s \times (1 - B_{ws}) \times \frac{T_{\text{std}} \times P_s}{T_s \times P_{\text{std}}} \times \frac{60 \text{ sec}}{\text{min}}$$

7.4.9 Concentration of pollutant

$$C_i = \frac{M_i}{V_{m(\text{std})}}$$

7.4.10 Emission of pollutant

$$E_i = \frac{C_i \times Q_{sd}}{\left(60 \frac{\text{sec}}{\text{min}}\right) \left(1 \times 10^6 \frac{\text{ug}}{\text{g}}\right)}$$

7.4.11 Isokinetic sampling rate

$$\%I = \frac{1039.5746 \times V_{m(\text{std})} \times (T_s + 460)}{V_s \times \theta \times P_s \times (1 - B_{ws}) \times (D_n)^2}$$

*English units

8.0 QUALITY CONTROL

The following quality control (QC) guidelines outline pertinent steps to be followed during the production of emission data to ensure and quantify the acceptability and reliability of the data generated.

8.1 Sampling QC procedures - Quality control procedures specific to manual source gas sampling procedures should follow EPA Method 5 and those listed in EPA Manual 600/4-77-0276 for Method 5. Sampling QC procedures are summarized in Table 2.

8.2 Blanks

8.2.1 Field blank - A field blank should be collected from a set of glassware that has not been used to collect any field samples. In the case of results exceeding regulatory limits, field blank data may be useful for convincing the regulatory official that contamination was the cause. This may result in retesting rather than a violation charge. Collection of the field blank is optional but recommended. Collect one field blank for every nine test runs at each test location.

8.2.2 Optional Glassware blank (proof blank) - A proof blank should be periodically recovered from sampling train glassware that is used to collect organic samples. The precleaned glassware, which consists of a probe liner, filter holder, condenser coil, and impinger set, is loaded as if for sampling and then quantitatively recovered exactly as the samples will be. Analysis of the generated fractions will ensure that laboratory contamination levels are under control.

8.2.3 Reagent blank - Reagent blanks should contain 500 mL of each reagent used at the test site. Reagent blanks are saved for potential analysis. Each reagent blank is part of the same lot used during the sampling program. If a field blank is unsatisfactory because of contamination, reagent blanks may be analyzed to determine the specific source of contamination. Collect one reagent blank per compliance test and archive for future analysis in the event that the field blank shows contamination.

8.2.4 Laboratory method blank - A method blank is a performance control sample that is prepared in the laboratory and processed in a manner identical to a field sample. The XAD-2® resin should be from the same batch used for preparation of the field traps. One laboratory method blank should be analyzed for every batch of samples analyzed.

9.0 METHOD PERFORMANCE

9.1 Method performance evaluation - Evaluation of analytical procedures for a selected series of compounds shall include the sample preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

9.2 Method detection limit - The overall method detection limits (lower and upper) should be calculated as shown in Sec. 6.2.3.1. Generally, analytical detection limit for tetra-CDD/CDF congeners are 50 pg. Penta-, hexa-, and hepta- congener detection limits are 250 pg and octa-congener detection limits are 500 pg.

9.3 Method precision and bias - The overall method precision and bias should be determined on a compound-by-compound basis at a given concentration level. The method precision value includes a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias is dependent upon the collection, retention, and extraction efficiency of the train components. Interlaboratory testing of Method 0023 and Method 8290 to establish method accuracy and precision for sampling a variety of stationary sources has not been performed.

10.0 REFERENCES

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TABLE 1

COMPOSITION OF THE SAMPLE FORTIFICATION
AND RECOVERY STANDARDS SOLUTIONS

Analyte	Method 0023 Concentration (pg/ μ L)	Method 8290 Concentration ¹ (pg/ μ L)
<u>Internal Standards</u>		
¹³ C ₁₂ -2,3,7,8-TCDD	100	10
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	10
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	25
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	25
¹³ C ₁₂ -OCDD	100	50
¹³ C ₁₂ -2,3,7,8-TCDF	100	10
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	10
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	25
<u>Surrogate Standards</u>		
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	25
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	
<u>Recovery Standards</u>		
¹³ C ₁₂ -1,2,3,4-TCDD	500	50
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	500	50
<u>Alternate Standard</u>		
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	--

¹ Provided as reference only; also see Method 8290.

TABLE 2

SAMPLING QC PROCEDURES SUMMARY

QC Procedure	Frequency	Criteria
Sample equipment calibrations	See Sec. 6.3.1	See Sec. 6.3.1
Dry gas meter sample leak check	Before and after each test run	0.00057 cmm (\leq 0.02 cfm) or 4% of sample rate whichever is less at highest vacuum
O ₂ and CO ₂ sampling system leak check	Once per test	See Method 3, or equivalent for Method 3A
Δ P meter leveling	Before and after each test run	Level
Pitot tube leak check	Before and after each test run	No visible leak observed at 75 mm (3 in.) H ₂ O for 15 seconds
Pitot tube orientation check	Every test	Pitot tube is level with no visible rotation from perpendicular to flow
Cyclonic flow check	Made at every location	< 20° average offset from perpendicular to flow
Probe, filter, trap, and silica gel impinger are maintained at specified temperature ranges	Every test	See Sec. 4.0
Overall isokinetic sampling rate	Every test	\pm 10% of 100%
Sampling blanks	See Sec. 8.2	See Sec. 8.2

TABLE 3

REQUIREMENTS FOR ANALYTICAL PREPARATION,
SURROGATE RECOVERIES AND SAMPLE BLANKS

Item	Description	Control Limit
Precogning filters	Soxhlet extraction	Detection limits listed in Sec. 9.2
Precogning sorbent	Soxhlet extraction	Detection limits listed in Sec. 9.2
Filter and sorbent surrogate spikes	Isotopically-labeled compounds	70 to 130% recovery
Field blank	Collect one for every 9 sample runs at each test location	< 5 times the detection limits
Method blank	Prepared at analytical laboratory (laboratory blank). One per analytical batch	Criteria decided by laboratory QA officer
Reagent blanks	One per lot of solvent used. Archive for possible analysis	Analyze only if requested by Agency to determine source of field blank confirmation
Proof Blank	One per set of glassware. Archive for possible analysis (collect only if requested by Agency)	Analyze only if requested by Agency to determine source of field blank contamination

TABLE 4

SAMPLE EQUIPMENT CALIBRATION SUMMARY

Equipment	Procedure	Frequency	Control Limits
Primary WTM ^a or DGM ^a	Primary calibration	Every 12 months	± 1% average
Sample DGM	Full calibration	Every 6 months	$Y_i \leq 2\%$ from Y_{avg}
Sample DGM	Post calibration	After each test program	$Y_{post} \leq 5\%$ from Y_{full}
Thermometers, Thermocouples	Calibration check	Initially	± 2°C (3.6°F) at 3 point calibration from reference thermometer
Nozzle	ID calibration	Before every test program	Repeated measurements ± 0.1 mm (0.004 in.)
Pitot tube	Wind tunnel calibration or construction specifications verification	Before every test program	Specifications listed in Method 2
ΔP gauge (if not an inclined manometer)	See Method 2	Once/test program	Within 5% of reference at three readings
Balance	Calibration check	Initially	Observed weight ≤ 0.5 g from Class S weight
Barometer	Calibration check	Initially	< 0.1 in. Hg from primary barometer

^aWTM = wet test meter; DGM = dry gas meter.

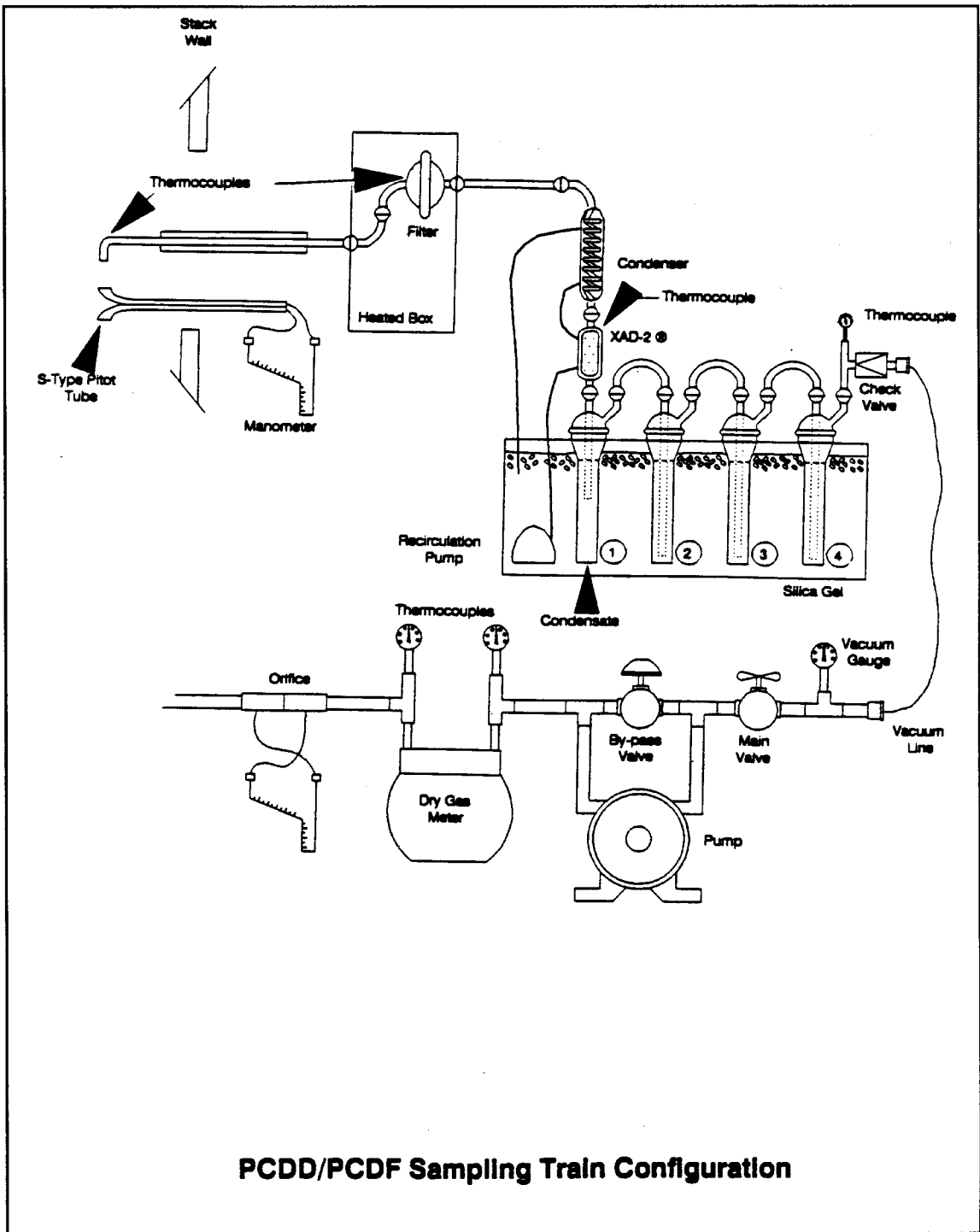


Figure 1

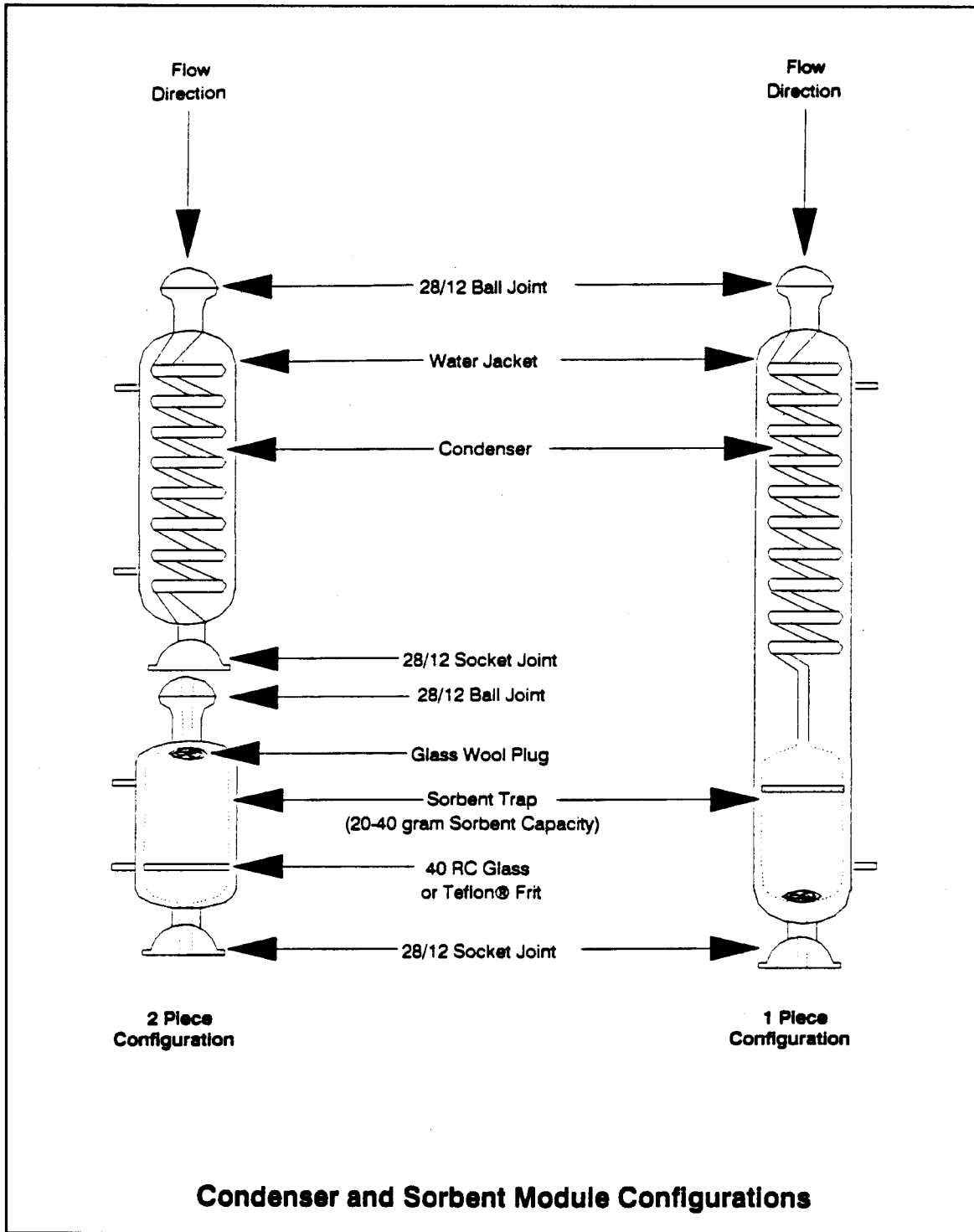
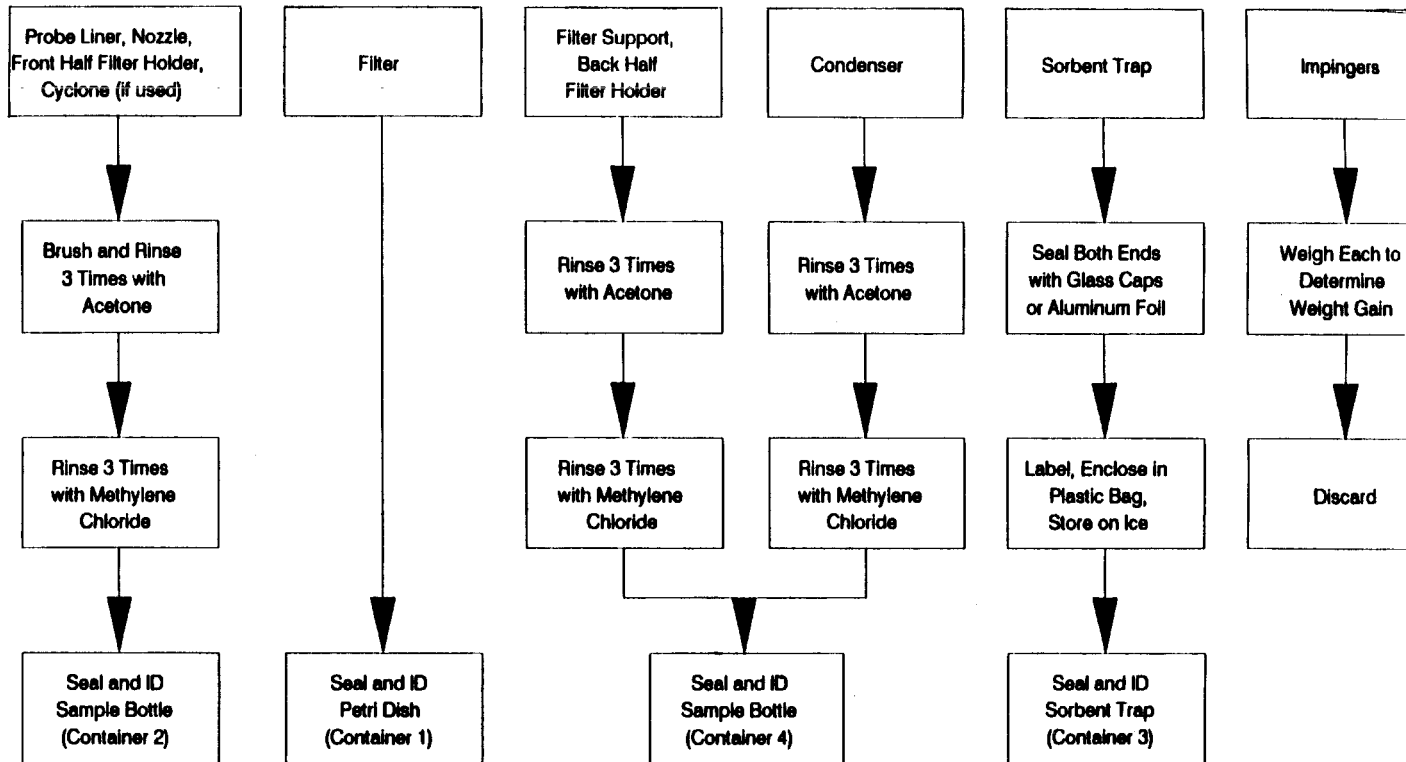


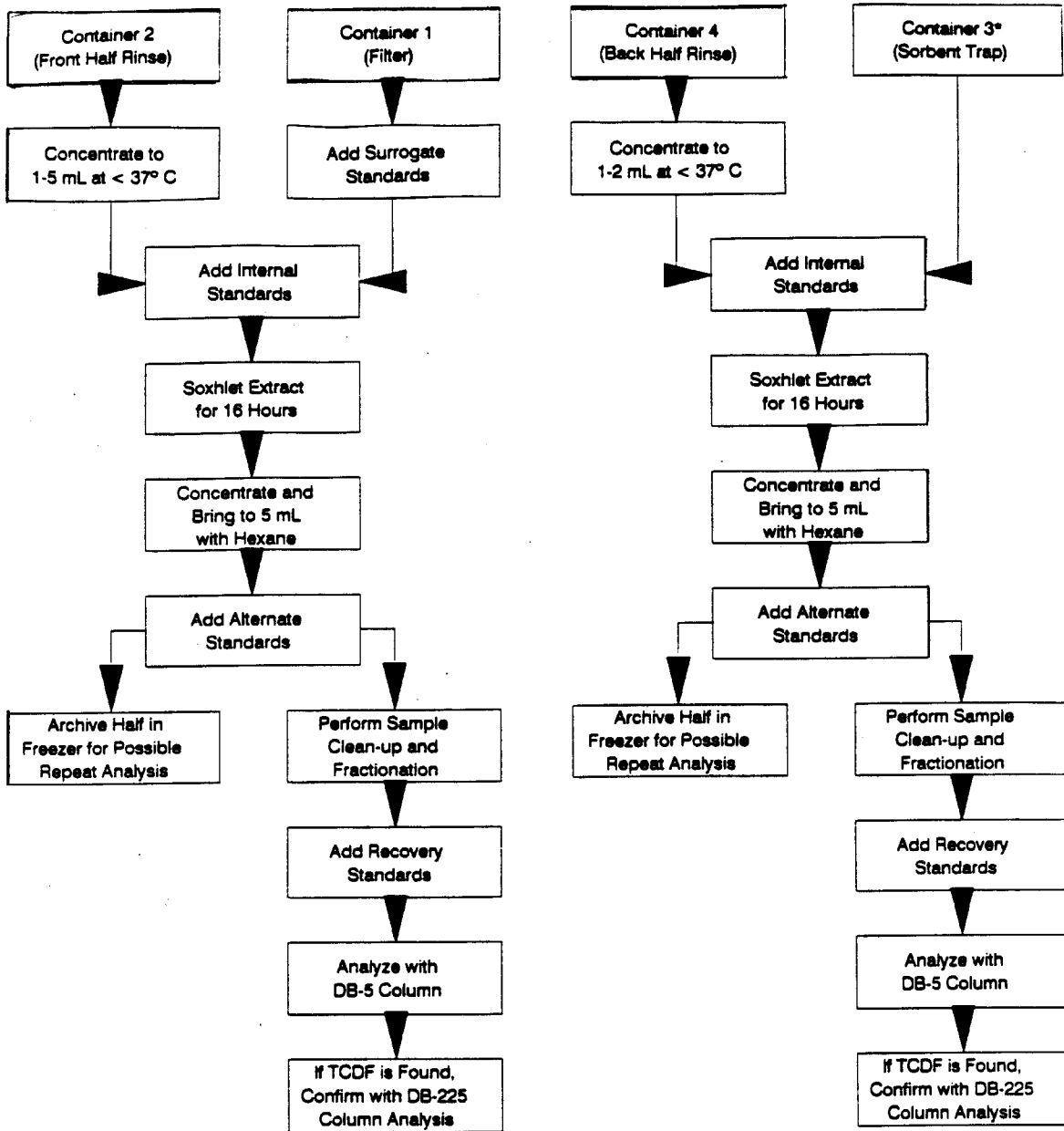
Figure 2

FIGURE 3



PCDD/PCDF Sample Recovery Scheme

FIGURE 4



* Surrogate Standards are added to the sorbent trap prior to sampling

PCDD/PCDF Analytical Summary Scheme

APPENDIX A
RECOMMENDED AUDITING PROCEDURES

An audit is an independent assessment of data quality. Both performance audits and system audits may be performed.

Performance Audit - A performance audit is conducted to evaluate quantitatively the quality of data produced by the sampling, analysis, or the total measurement system (sample collection, sample recovery, sample analysis, and data processing).

Audit Sample - A performance audit sample contains tetra- through octa-isomers of PCDD and PCDF. Audit samples are not normally required.

Performance Audit of the Field Test - A field test performance audit may be conducted by checking the dry gas meter for accuracy using procedures located in the Quality Assurance Handbook for Air Pollution Measurement Systems (EPA 600/4-77-027b). Performance audits on thermocouple readings, ΔP gauges, barometric pressure gauges and others, may also be conducted.

Performance Audit of Data Processing - The data processing procedures may be audited by requiring the testing laboratory to provide an example calculation for one sample run. This example calculation will include all the calculations used to determine the emissions based on the raw field and laboratory data.

System Audit - A system audit is an on-site, qualitative inspection and review of the total measurement system.

The functions of the auditor are:

- a) Observe procedures and techniques of the field team during sample collection and sample recovery; and
- b) Examine records of apparatus calibrations and other quality control procedures used in sampling and analytical activities

When on-site, the auditor observes the source test team's overall performance, including the following operations:

- a) Setting the sampling system and leak checking the sample train and pitot tube;
- b) Collecting the samples isokinetically;
- c) Conducting the final leak checks; and
- d) Sample documentation procedures, sample recovery, and preparation of the samples for shipment.