

7.9 Toxicity Equivalency Factor GC Mixture -- This tridecane solution contains four native (1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, and 2,3,4,6,7,8-HxCDF) and three carbon-labeled ($^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF, and $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD) 2,3,7,8-substituted PCDD/PCDF congeners. The concentration for each congener must not exceed 100 pg/uL. The mixture is used for confirming the presence of certain PCDD/PCDF congeners during the TEF determinations.

8. System Performance Criteria

System performance criteria are presented below. The laboratory may use the recommended GC column described in Section 6.2 (Exhibit D). It must be documented that all applicable system performance criteria specified in Section 8.1 (Exhibit D) were met before analysis of any sample is performed. Table 7 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 4 provides a typical 12-hour analysis sequence whereby the GC column performance and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hour period of operation. A routine calibration verification is only required at the beginning of each 12-

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hour period during which samples are analyzed. An HRGC/HRMS solvent blank run (this exhibit, Section 3.21) is required between a calibration run and the first sample run.

8.1 GC Column Performance

8.1.1 Inject 2 uL (this exhibit, Section 6.1.1) of the column performance check solution (this exhibit, Section 7.6) and acquire selected ion monitoring (SIM) data as described in Section 6.1.3 (Exhibit D) within a total cycle time of ≤ 1 second (this exhibit, Section 9.1.4.1).

8.1.2 The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of ≤ 25 percent (Figure 5), where

$$\text{Valley Percent} = (x/y) (100)$$

x = measured as in Figure 5 from the 2,3,7,8-closest TCDD eluting isomer, and

y = the peak height of 2,3,7,8-TCDD.

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It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used to determine the eight homologue retention times windows that are used for qualitative (this exhibit, Section 13.4.1) and quantitative purposes. All the peaks (that includes $^{13}\text{C}_{12}$ -2,3,7,8-TCDD) must be labeled and identified as such on the chromatograms. Furthermore, all homologous first eluters must be labeled with the letter F and all homologous last eluters must be labeled with the letter L (Figure 5). Any individual selected ion current profile (SICP) (for the tetras, this would be the SICP for m/z 322 and m/z 304) or the reconstructed homologue ion current (for the tetras, this would correspond to m/z 320 + m/z 322 + m/z 304 + m/z 306) constitutes an acceptable form of data presentation. An SICP for m/z 334 (labeled TCDD) is also required.

- 8.1.3 The retention times for the switching of SIM ions characteristic of one homologue to the next higher homologue must be indicated in the SICP. Accurate

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switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds. Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF) as those two compounds elute within 15 seconds of each other on the 60-m DB-5 column. Carbon-labeled ($^{13}\text{C}_{12}$) analogues of these two compounds will be, at a later time, incorporated within the recovery standard solution (used to prepare the final extract for HRGC/HRMS) as an additional QC check. (Section 2.4 note; Exhibit D.)

8.2 Mass Spectrometer Performance

8.2.1 The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed (this exhibit, Section 13). Static

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resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation. However, it is recommended that a visual check (i.e., documentation is not required) of the static resolution be made by using the peak matching unit before and after each analysis. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

8.2.2 Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on the instrument performances. Therefore, a mass-drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered inside

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the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in "downtime" for source cleaning by using the lock-mass ion SICP.

8.2.3 By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using the peak matching unit and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).

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8.2.4 Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 6) must allow manual determination of the resolution; i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

[OFF-THE-RECORD NOTE: Some magnetic sector instruments (in particular old models) are not capable of achieving a constant mass resolution across the mass range that is under consideration here. This is due to a lack of control or tracking of the magnet focal point at different masses. Ideally, one should require here that

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the 100 ppm resolution be demonstrated for a characteristic ion for each mass descriptor in use. A minimum resolving power of 10,000 is needed for both tetra- and hexa-chlorinated dioxins and furans. Until a solution to this problem can be found, the requirement of 100 ppm resolution must be demonstrated at least for tetrachlorinated homologues masses as described above. However, one may add "Laboratories that are capable of maintaining a constant resolving power through-out the mass range are encouraged to demonstrate at least 10,000 resolving power across the mass range; i.e., for a reference ion from each of the five descriptors described in Table 6].

9. Calibration

9.1 Initial Calibration

Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (this exhibit, Section 9.3) does not meet the required criteria listed in Section 9.4 (Exhibit D).

9.1.1 All seven high-resolution concentration calibration solutions listed in Table 5 must be used for the ini-

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tial calibration.

- 9.1.2 Tune the instrument with PFK as described in Section 8.2.3 (Exhibit D).
- 9.1.3 Inject 2 uL of the GC column performance check solution (this exhibit, Section 7.6) and acquire SIM mass spectral data as described earlier in Section 8.1 (Exhibit D). The total cycle time must be \leq 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criterion listed in Section 8.1.2 (Exhibit D) was met.
- 9.1.4 By using the same GC (this exhibit, Section 6.2) and mass spectrometer (this exhibit, Section 6.1.3) conditions that produced acceptable results with the column performance check solution, analyze a 2-uL aliquot of each of the seven concentration calibration solutions once with the following mass spectrometer operating parameters.
- 9.1.4.1 The total cycle time for data acquisition must be \leq 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

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9.1.4.2 Acquire SIM data for all the ions listed in the five descriptors of Table 6.

9.1.4.3 The ratio of integrated ion current for the ions appearing in Table 9 (homologue quantitation ions) must be within the indicated control limits (set for each homologue).

9.1.4.4 The ratio of integrated ion current for the ions belonging to the carbon-labeled internal and recovery standards must be within the control limits stipulated in Table 9.

NOTE: Sections 9.1.4.3 and 9.1.4.4 (this exhibit) require that 17 ion ratios from Section 9.1.4.3 and 11 ion ratios from Section 9.1.4.4 be within the specified control limits simultaneously in one run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

9.1.4.5 For each SIM trace and for each GC signal corresponding to the elution of a target analyte and of their labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Appendix C describes the procedure to be followed for the measurement of the S/N

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from conspicuously weak signals. This measurement is required for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SIM trace above the GC peak in question.

9.1.4.6 Referring to Table 10, calculate the 17 relative response factors (RRF) for unlabeled target analytes [RRF(n); n=1 to 17] relative to their appropriate internal standards (Table 5) and the nine RRFs for the labeled $^{13}\text{C}_{12}$ internal standards [RRF(m); m=18 to 26)] relative to the two recovery standards according to the following formula:

$$\text{RRF}(n) = \frac{A_x \cdot Q_{is}}{Q_x \cdot A_{is}}$$

$$\text{RRF}(m) = \frac{A_{is} \cdot Q_{rs}}{Q_{is} \cdot A_{rs}}$$

where

A_x is the sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for unlabeled PCDD/PCDFs,

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A_{is} is the sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled internal standards,

A_{rs} is the sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled recovery standards,

Q_{is} is the quantity of the internal standard injected (pg),

Q_{rs} is the quantity of the recovery standard injected (pg), and

Q_x is the quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RRF(n) and RRF(m) are dimensionless quantities; the units used to express Q_{is} , Q_{rs} and Q_x must be the same.

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9.1.4.7 Calculate the $\overline{RRF}(n)$'s and their respective percent relative standard deviations (%RSD) for each of the seven calibration solutions.

$$\overline{RRF}(n) = 1/7 \sum_{j=1}^7 RRF_j(n) ,$$

where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n=1-17; Table 10), and j is the injection number (or calibration solution number; j=1-7).

9.1.4.8 The relative response factors to be used for the determination of the concentration of total isomers in homologue (Table 10) are calculated as follows:

9.1.4.8.1 For congeners that belong to homologues containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean \overline{RRF} used will be the same as the mean \overline{RRF} determined in Section 9.1.4.7 (this exhibit).

NOTE: The calibration solutions do not contain $^{13}C_{12}$ -OCDF as an internal standard. This is because a mini-

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mum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}\text{C}_{12}$ -OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}\text{C}_{12}$ -OCDF with $[M]^+$ of OCDD). Therefore, the RRF for OCDF is calculated relatively to $^{13}\text{C}_{12}$ -OCDD.

[OFF-THE-RECORD NOTE: The presence of $^{13}\text{C}_{12}$ -OCDF would necessitate an additional GC resolution requirement to assure complete chromatographic separation between OCDD and OCDF.]

9.1.4.8.2 For congeners that belong to homologues containing more than one 2,3,7,8-substituted isomer (Table 4), the mean $\overline{\text{RRF}}$ used for the homologue will be the mean of the RRFs calculated for all the individual 2,3,7,8-substituted congeners using the equation below:

$$\overline{\text{RRF}} (k) = \frac{1}{t} \sum_{n=1}^t \text{RRF}_n ,$$

where $k = 27 - 30$ (Table 10)

with 27 = PeCDF; 28 = HxCDF; 29 = HxCDD; and
30 = HpCDF,

t = the total number of 2,3,7,8-substituted isomers present in the calibration solutions

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(Table 5) for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologue are different. However, this analytical protocol will make the assumption that the HRGC/HRMS response of all isomers in an homologue that do not have the 2,3,7,8-substitution pattern is the same as the response of one or more of the 2,3,7,8-substituted isomer(s) in that homologue.

9.1.4.9 Relative response factors [$\overline{\text{RRF}}$ (m)] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$\text{RRF (m)} = \frac{A_{\text{IS}}^{\text{m}} \times Q_{\text{RS}}}{Q_{\text{IS}}^{\text{m}} \times A_{\text{RS}}}$$

$$\overline{\text{RRF}} \text{ (m)} = \frac{1}{7} \sum_{j=1}^7 \text{RRF}_j \text{ (m)},$$

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where:

$m = 18-26$ (congener type) and $j = 1-7$ (injection number),

A_{IS}^m = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for a given internal standard ($m = 18-26$),

A_{RS} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the appropriate recovery standard (see Table 5 footnotes),

Q_{RS} and Q_{IS}^m = quantities of respectively, the recovery standard (RS) and a particular internal standard ($IS=m$) injected (pg),

RRF (m) = relative response factor of a particular internal standard (m) relative to an appropriate recovery standard as determined from one injection, and

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$\overline{\text{RRF}}$ (m) = calculated mean relative response factor of a particular internal standard (m) relative to an appropriate recovery standard as determined from the seven initial calibration injections (j).

9.2 Criteria for Acceptable Calibration

The criteria listed below for acceptable calibration must be met before the analysis is performed.

9.2.1 The percent relative standard deviations for the mean response factors [$\overline{\text{RRF}}$ (n) and $\overline{\text{RRF}}$ (m)] from each of the 26 determinations (17 for the unlabeled standards and 9 for the labeled reference compounds) must be less than 20 percent.

9.2.2 The S/N for the GC signals present in every SIM trace (including the ones for the labeled standards) must be ≥ 2.5 .

9.2.3 Isotopic ratios (Table 9) must be within the specified control limits.

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NOTE: If the criterion for acceptable calibration listed in Section 9.2.1 (Exhibit D) is met, the analyte-specific \overline{RRF} can then be considered independent of the analyte quantity for the calibration concentration range. The mean \overline{RRFs} will be used for all calculations until the routine calibration criteria (this exhibit, Section 9.4) are no longer met. At such time, new mean \overline{RRFs} will be calculated from a new set of injections of the calibration solutions.

9.3 Routine Calibration

Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks.

- 9.3.1 Inject 2 uL of the concentration calibration solution HRCC-2 containing 5 pg/uL of tetra- and penta-chlorinated congeners, 12.5 pg/uL of hexa- and hepta-chlorinated congeners, 25 pg/uL of octachlorinated congeners, and the respective internal and recovery standards (Table 5). By using the same HRGC/HRMS conditions as used in Sections 6.1.3 and 6.2 (Exhibit D), determine and document an acceptable calibration as provided in Section 9.4 (Exhibit D).

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9.4 Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken and the instrument must be recalibrated.

9.4.1 The measured RRFs [RRF (n) for the unlabeled standards] obtained during the routine calibration runs must be within 20 percent of the mean values established during the initial calibration (this exhibit, Section 9.1.4.7).

9.4.2 The measured RRFs [RRF (m) for the labeled standards] obtained during the routine calibration runs must be within 20 percent of the mean values established during the initial calibration (this exhibit, Section 9.1.4.9).

9.4.3 The ion-abundance ratios (Table 9) must be within the allowed control limits.

9.4.4 If either one of the criteria above (this exhibit, Sections 9.4.1 and 9.4.2) is not satisfied, a second

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attempt can be made before repeating the entire initialization process (this exhibit, Section 9.1).

NOTE: An initial calibration must be carried out whenever the HRCC-2 solution is replaced by a new solution from a different lot.

10. Quality Assessment/Quality Control Procedures

See Exhibit E for QA/QC requirements.

11. Sample Preservation

11.1 The sample collection, shipping, handling, and chain-of-custody procedures are not described in this document. Sample collection personnel will, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the lab. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly inhomogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula before removal of an aliquot.

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11.2 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Sampling equipment must be free of potential sources of contamination.

11.3 Grinding or Blending of Fish Samples.

If not otherwise specified by the EPA, the whole fish (frozen) should be blended or ground to provide an homogeneous sample. The use of a stainless steel meat-grinder with a 3- to 5-mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the EPA. If so requested by EPA, the above whole fish requirement is superseded.

11.4 With the exception of the fish and adipose tissues, which must be stored at -20° C, all samples must be stored at 4° C, extracted within 30 days and completely analyzed within 45 days of collection.

11.5 Phase Separation - This is a guideline for phase separation on very wet (>25 percent) soil and sediment samples.

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Place a 50-g aliquot in a suitable centrifuge bottle. Then place sample and counter-balance in centrifuge. Run for 30 minutes at 2,000 rpm. Stop. Remove. Mark interface levels on bottle. Estimate relative volume of each phase. By using disposable pipets, transfer the liquid layer into clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent moisture determination, extraction). Return the remaining solid portion to the original sample bottle (empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil and sediment method. Take note of and report the estimated volume of liquid before disposing of the liquid as a liquid waste.

CAUTION: Finely divided soils and sediments contaminated with PCDD/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing 2,3,7,8-substituted PCDD/PCDFs (including 2,3,7,8-TCDD). Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

11.6 Soil or Sediment Percent Moisture Determination.

The percent moisture of soil or sediment samples showing detectable levels (see note below) of at least one

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2,3,7,8-substituted PCDD/PCDF congener is determined according to the following recommended procedure.

Weigh between 9.5 and 10.5 g of the soil or sediment sample (± 0.5 g) to three significant figures. Dry it to constant weight at 100° C. Allow the sample to cool in a desiccator. Weigh the dried solid to three significant figures. Calculate and report the percent moisture on Form (to be determined). Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste.

NOTE: Until detection limits are determined (Section 1.2, Exhibit D), the lower MCLs (Table 1) may be used to estimate the minimum detectable levels.

$$\text{Percent moisture} = \frac{\text{Weight wet soil} - \text{Weight dry soil}}{\text{Weight wet soil}} \times 100$$

11.7 Fish Tissue Lipid Content Determination.

The percent lipid of fish samples showing detectable levels (see Section 11.6 note; Exhibit D) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined as follows:

Use a separate aliquot (2 g) of the ground frozen fish

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sample. Blend it with 6 g of anhydrous sodium sulfate, pour the mixture inside a 1-cm i.d. glass column and extract the lipids by passing two 25-mL portions of methylene chloride through the column and collecting the solvent inside a tared 100-mL round-bottom flask. Concentrate the extract using a rotary evaporator until constant weight is attained. The percent lipid is calculated using the following expression:

$$\text{Percent lipid} = \frac{\text{Weight of residue from extraction (in g)}}{\text{Weight of aliquot (in g)}} \times 100$$

11.8 Adipose Tissue Lipid Content Determination.

Details for the determination of the adipose tissue lipid content are provided in Section 12.11.3 (Exhibit D).

12. Extraction and Cleanup Procedures

12.1 Internal standard addition. Use a sample aliquot of 1 g to 1000 g (typical sample size requirements for each type of matrix are given in Section 12.2 of this exhibit and in Table 1) of sample to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Except for adipose tissue, add an appropriate quantity of the sample fortification mixture (this exhibit, Section

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3.8) to the sample. All samples should be spiked with 100 uL of the sample fortification mixture to give internal standard concentrations as indicated in Table 1. As an example, for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, a 10-g soil sample requires the addition of 1000 pg of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD to give the requisite 100 ppt fortification level. For the fortification of soil, sediment, fly-ash, water and fish samples, mix the 100 uL with 1.5 mL of acetone. Do not dilute the isooctane solution for the other matrices. The fortification of adipose tissue is carried at time of homogeneization (this exhibit, Section 12.11.2.3).

12.2 Extraction.

The extraction and purification procedures for biological tissue samples are described in Sections 12.10 (fish tissue) and 12.11 (adipose tissue) of this exhibit.

12.2.1 **Sludge/Fuel Oil.** Extract aqueous sludge samples by refluxing a sample (e.g., 2 g) with 50 mL of toluene (or benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water is removed. Cool the sample, filter the toluene (or benzene) extract through a glass-fiber filter, or equivalent, into a 100-mL round-bottom flask. Rinse the filter with 10 mL of

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toluene (or benzene), combine the extract and rinsate. Concentrate the combined solutions to near dryness by using a rotary evaporator at 50° C (toluene) or a Kuderna-Danish (KD) apparatus (benzene). Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 12.2.4 below.

12.2.2 **Still-Bottom.** Extract still-bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (or benzene) in a small beaker and filtering the solution through a glass-fiber filter (or equivalent) into a 50-mL round-bottom flask. Rinse the beaker and filter with 10 mL of toluene (or benzene). Concentrate the combined toluene (or benzene) solutions to near dryness using a rotary evaporator at 50° C. A KD apparatus can be used if benzene is the extraction solvent. Proceed with Section 12.2.4 below.

12.2.3 **Fly-Ash.** Extract fly ash samples by placing a sample (e.g., 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with 100 mL of toluene (or benzene) and extract for 16 hours by using a three cycle/hour schedule. Cool and filter the toluene (or benzene)

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extract through a glass-fiber filter into a 500-mL round-bottom flask. Rinse the filter with 5 mL of toluene (or benzene). Concentrate the combined toluene (or benzene) solutions to near dryness by using a rotary evaporator (toluene) at 50° C or a KD apparatus (benzene). Proceed with Section 12.2.4 below.

12.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5-mL portions of hexane and add the rinses to the funnel. Shake two minutes with 50 mL of 5 percent sodium chloride solution, discard the aqueous layer and proceed with Section 12.3 (Exhibit D).

12.2.5 Soil. Add 10 g anhydrous sodium sulfate and mix thoroughly by using a stainless steel spoon spatula. After breaking up any lumps, place the soil and sodium sulfate mixture in the Soxhlet apparatus by using a glass-wool plug (the use of an extraction timble is optional). Add 200 to 250 mL of benzene (or toluene) to the Soxhlet apparatus and reflux for 24 hours. The solvent must cycle completely through the system at least three times per hour.

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- 12.2.5.1 Transfer the extract from Section 12.2.5 to a KD apparatus mounted with a Snyder column (or to a 500-mL round-bottom flask for evaporating the toluene by using a rotary evaporator).
- 12.2.5.2 Add a TeflonTM or an equivalent boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70° C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 minutes.
- 12.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.
- 12.2.5.4 Remove and invert the Snyder column, and rinse it down into the KD apparatus with two 1-mL portions of hexane. Decant the contents of the KD apparatus and concentrator tube into a 125-mL separatory funnel. Rinse the KD apparatus with two additional 5-mL portions of hexane, and combine. Proceed with Section 12.3 (Exhibit D).

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12.2.6 **Aqueous Samples.** Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1 L) into a 2-L separatory funnel. Proceed with Section 12.2.6.1 (Exhibit D).

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered by using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Sections 12.2.6.1 and 12.2.6.2 (Exhibit D). Proceed with Section 12.2.6.3 (Exhibit D).

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12.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride into a KD apparatus (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass-wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

12.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the KD apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the KD apparatus before

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proceeding with the second concentration step. Rinse the flask and the lower joint with two 5-mL portions of hexane and combine rinses with extract to give a final volume of about 15 mL.

12.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Section 12.3 (Exhibit D).

12.3 Partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide (KOH). Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times). Strong base (KOH) is known to degrade certain PCDD/PCDFs, so contact time must be minimized.

12.4 Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

12.5 Partition the extract against 40 mL of concentrated sulfuric acid. Shake for two minutes. Remove and discard

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the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

12.6 Partition the extract against 40 mL of five percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate into a 50-mL round-bottom flask, wash with two 15-mL portions of hexane, and concentrate the hexane solution to near dryness with a rotary evaporator (35° C water bath), making sure all traces of toluene are removed. (Use of blow-down with an inert gas to concentrate the extract is also permitted.)

12.7 Pack a gravity column (glass 300 mm x 10.5 mm), fitted with a TeflonTM stopcock, in the following manner: Insert a glass-wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4-g layer of Woelm^R Super 1 neutral alumina. Tap the top of the column gently. Woelm^R Super 1 neutral alumina need not be activated or cleaned before use, but it should be stored in a sealed desiccator. Add a 4-g layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just before exposure of the sodium sulfate

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layer to air. Discard the eluant. Check the column for channeling. If channeling is present, discard the column. Do not tap a wetted column.

12.8 Dissolve the residue from Section 12.6 (Exhibit D) in 2 mL of hexane and apply the hexane solution to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

12.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane.

12.8.2 Elute the PCDDs and PCDFs from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15 mL) concentrator tube.

12.9 Carbon Column Cleanup.

Prepare a carbon column as described in Section 7.1.2 (Exhibit D).

12.9.1 By using a carefully regulated stream of nitrogen, concentrate the 60 percent fraction (this exhibit,

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Section 12.8.2) to about 2 mL. Rinse the carbon column with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, pre-elute the column with 4 mL of toluene, 2 mL of methylene chloride/methanol/benzene (75:20:5, v/v), and 4 mL of toluene, 2 mL of methylene chloride/methanol/benzene (75:20:5, v/v), and 4 mL of cyclohexane/methylene chloride (50:50, v/v). Discard all column rinsates. While remaining in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of cyclohexane/methylene chloride (50:50, v/v) and 5 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine them. This combined fraction may be used as a check on column efficiency. Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 mL toluene. [Note: Be sure no carbon fines are present in the eluant.]

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[OFF-THE-RECORD NOTE: The single laboratory evaluation of this protocol will consider loading the 15-mL alumina column eluate directly into the carbon column without concentrating the eluate.]

12.9.2 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50° C. Carefully transfer the concentrate into a 1-mL mini-vial and, again at elevated temperature (50° C), reduce the volume to about 100 uL using a stream of nitrogen and a sand bath. Rinse the rotary evaporator flask with three washings by using 300 uL of 1 percent toluene in methylene chloride. Add N uL (N = 10 for soil, sediment, and water and 50 for sludge, still-bottom and fly-ash) of the tridecane recovery standard solution. Store the sample in a refrigerator until HRGC/HRMS analysis is performed.

12.10 Extraction and Purification Procedures for Fish Samples.

12.10.1 Weigh 10 g of an homogeneous fish sample (Section 11.3, Exhibit D) into a 100-mL round-bottom boiling flask. Add directly to the sample 100 uL of the fortification solution diluted in 1.5 mL acetone.

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12.10.2 Fish Tissue Extraction Procedure

12.10.2.1 To the 100-mL round-bottom flask (Section 12.10.1, Exhibit D), add 20 mL of ethanol, 40 mL of a 45 percent potassium hydroxide solution, a TeflonTM-coated stir bar and stir at room temperature for 16 hours. Transfer the alcoholic-base solution to a 250-mL separatory funnel. Rinse the boiling flask with 10 mL of ethanol and add the rinse to the separatory funnel. Rinse the boiling flask with 25 mL of hexane and transfer the hexane wash to the separatory funnel. Shake the separatory funnel vigorously for one minute. Allow the hexane layer to separate and drain the aqueous layer (bottom layer) into a second 250-mL separatory funnel. Drain the hexane extract from the first separatory funnel into a 125-mL Erlenmeyer flask and save. Add 25 mL of hexane to the second separatory funnel and shake vigorously for one minute. Allow the layers to separate and drain the bottom layer into the first separatory funnel. Drain the hexane into the 125-mL Erlenmeyer flask. Repeat

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the extraction step with two more 25-mL portions of hexane. Combine the four 25-mL hexane extracts into one of the separatory funnels. Proceed with the acid and base cleanup in Section 12.10.3 (Exhibit D).

12.10.3 Fish Tissue Extract Cleanup Procedures

12.10.3.1 Wash the combined hexane extracts with 30 mL of potassium hydroxide (2 Normal). Allow layers to separate and discard the aqueous layer. Carefully add 50 mL of concentrated sulfuric acid. Shake vigorously for one minute, allow layers to separate and discard the acid layer. Repeat the acid wash with two more 50-mL portions of concentrated sulfuric acid. Carefully add 25 mL of distilled water, shake, allow layers to separate and discard the water. Transfer the hexane through a 42-mm x 160-mm filter funnel containing a glass-wool plug and 3 cm of sodium carbonate into a 250-mL Kuderna-Danish concentrator fitted with a 15-mL concentrator tube. Rinse the filter funnel with two 25-mL portions of hexane. Place a three-ball Snyder column on the KD apparatus and concentrate on a steam bath to approximately 5 mL. Complete the concentration to approximately 100 uL by using a gentle stream of

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nitrogen. The extract is ready for the alumina and carbon cleanups (this exhibit, Sections 12.7 through 12.9.2).

12.11 Extraction and Purification Procedures for Human Adipose Tissue.

12.11.1 The human adipose tissue samples must be stored at -20° C from the time of collection until the time for analysis. The use of chlorinated materials during the collection of the sample must be avoided. Samples are handled using stainless steel forceps, spatulas, or scissors. All sample bottles (glass) are cleaned as specified in the note appearing in Section 6.3 (Exhibit D). TeflonTM-lined caps should be used. As with any biological sample, the analyst should avoid any undue exposure.

12.11.2 Adipose Tissue Extraction Procedure

12.11.2.1 Accurately weigh to the nearest 0.01 g a 10-g portion of a frozen adipose tissue sample into a culture tube (2.2 x 15 cm).

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NOTE: The sample size may be smaller, depending on availability. In such a situation, the analyst is required to adjust the volume of the internal standard solution added to the sample to meet the fortification level stipulated in Table 1.

12.11.2.2 Allow the adipose tissue specimen to reach room temperature (up to 2 hours).

12.11.2.3 Add 10 mL of methylene chloride, 100 uL of the sample fortification solution, and homogenize the mixture for approximately 1 minute with a tissue homogenizer.

12.11.2.4 Allow the mixture to separate and decant the methylene chloride extract from the residual solid material by using a disposable pipet. The methylene chloride is percolated through a filter funnel containing a clean glass-wool plug and 10 g of anhydrous sodium sulfate. The dried extract is collected in a graduated 100-mL volumetric flask.

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12.11.2.5 A second 10-mL portion of methylene chloride is added to the sample and homogenized for 1 minute. The solvent is decanted, dried, and transferred to the 100-mL volumetric flask (this exhibit, Section 12.11.2.4).

12.11.2.6 The culture tube is rinsed with at least two additional portions of methylene chloride (10 mL each), and the entire contents are transferred to the filter funnel containing the anhydrous sodium sulfate. The filter funnel and contents are rinsed with additional methylene chloride (20 to 40 mL); collect the solvent into the 100-mL flask. Discard the sodium sulfate.

12.11.2.7 Adjust the volume to the 100-mL mark with methylene chloride.

12.11.3 Adipose Tissue Lipid Content Determination

12.11.3.1 Preweigh a clean 1-dram glass-vial to the nearest 0.0001 g using an analytical balance tared to zero.

12.11.3.2 Accurately transfer 1.0 mL of the final extract (100 mL) from Section 12.11.2.6 (Exhibit D) to the 1-dram vial. Reduce the volume of methylene chloride from the extract by using a water bath (50-60° C) and

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a gentle stream of purified nitrogen until an oil residue remains.

12.11.3.3 Accurately weigh the 1-dram vial and residue to the nearest 0.0001 g and calculate the weigh of lipid present in the vial based on the difference of the weights. (Nitrogen blow-down is continued until a constant weight is achieved.)

12.11.3.4 Calculate the percent lipid content of the original sample to the nearest 0.1 percent as shown below:

$$\text{Lipid Content, LC (\%)} = \frac{W_{LR} \times V_{EXT}}{W_{AT} \times V_{AL}} \times 100$$

where: W_{LR} = weight of the lipid residue to the nearest 0.0001 g calculated from Section 12.11.3.3 (Exhibit D),

V_{EXT} = total volume (100 mL) of the extract in mL from Section 12.11.2.6 (Exhibit D),

W_{AT} = weight of the original adipose tissue sample to the nearest 0.01 g from Section 12.11.2.1 (Exhibit D), and

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V_{AL} = volume of the aliquot of the final extract in mL used for the quantitative measure of the lipid residue (1.0 mL).

12.11.3.5 Record the lipid residue measured in Section 12.11.3.3 (Exhibit D) and the percent lipid content from Section 12.11.3.4 (Exhibit D).

12.11.4 Adipose Tissue Extract Concentration

12.11.4.1 Quantitatively transfer the remaining extract volume (99.0 mL) to a 500-mL Erlenmeyer flask. Rinse the volumetric flask with 20-to-30 mL of additional methylene chloride to ensure quantitative transfer. Add a magnetic stirring bar.

12.11.4.2 Place the Erlenmeyer flask on a hot plate (40° C) to remove the solvent until an oily residue remains (stirring is recommended at this stage).

12.11.5 Adipose Tissue Extract Cleanup Procedures

12.11.5.1 Add a total of 200 mL of hexane to the lipid residue in the 500-mL Erlenmeyer flask.

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12.11.5.2 Slowly add, with stirring, 100 g of 40 percent w/w sulfuric acid impregnated silica gel. Stir with a magnetic stir-plate for two hours at room temperature.

12.11.5.3 Allow the solid phase to settle and decant the liquid through a powder funnel containing 20 g anhydrous sodium sulfate and collect in another 500-mL Erlenmeyer flask.

12.11.5.4 Rinse the solid phase with two 50-mL portions of hexane. Stir each rinse for 15 minutes, decant, and dry by percolation through the sodium sulfate filter combining the hexane extracts from Section 12.11.5.3 (Exhibit D).

12.11.5.5 After the rinses have gone through the sodium sulfate, rinse the sodium sulfate with an additional 25 mL of hexane and combine with the hexane extracts from Section 12.11.5.4 (Exhibit D).

12.11.5.6 Prepare an acidic silica column as follows. Pack a 1-cm x 10-cm chromatographic column with a glass-wool plug, add approximately 25 mL of hexane, add 1 g of silica gel and allow to settle, then add 4 g of 40

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percent w/w sulfuric impregnated silica gel and allow to settle. Elute the excess hexane solvent through the column until the solvent level reaches the top of the chromatographic packing. Inspect the column for the presence of air bubbles and channels.

12.11.5.7 Quantitatively transfer the hexane extract from the Erlenmeyer flask (this exhibit, Sections 12.11.5.3 through 12.11.5.5) to the silica gel column reservoir. Allow the hexane extract to percolate through the column and collect in a 500-mL KD apparatus.

12.11.5.8 Complete the elution of the extract from the silica gel column with 50 mL of hexane in the KD apparatus. Concentrate on a steam bath the eluate to approximately 5 mL. Use nitrogen blow-down to bring the final volume to about 100 uL.

NOTE: If the 40 percent sulfuric acid on silica gel is highly discolored throughout the length of the adsorbent bed, it is necessary to repeat the cleaning procedure beginning with Section 12.11.5.1 (Exhibit D).

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12.11.5.9 The extract is ready for alumina and carbon cleanups described in Sections 12.7 through 12.9.2 (Exhibit D).

13. Analytical Procedures.

13.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature. With a stream of dry, purified nitrogen, reduce the extract volume to 10 uL or 50 uL as stipulated above (this exhibit, Section 12.9.2).

13.2 Inject a 2-uL aliquot of the extract into the GC, operated under the conditions previously used (this exhibit, Section 6.2) to produce acceptable results with the performance check solution.

13.3 Acquire SIM data according to Section 6.1.3 (Exhibit D). Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (this exhibit, Sections 9.1.4.6 through 9.1.4.9).

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously deter-

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mined (Section 8.1, Exhibit D). A selected ion current profile (SICP) for the lock-mass ion must also be recorded and included in the data package as a deliverable. This trace must be a true representation of the evolution of the lock-mass ion amplitude during the HRGC/HRMS run. (See this exhibit, Section 8.2.2 for proper level of reference compound to be metered inside the ion chamber.) It is recommended to examine the lock-mass ion SICP for departure of the instrument's basic sensitivity and stability that could affect the measurements.

13.4 Identification Criteria.

For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

13.4.1 Relative Retention Times.

13.4.1.1 For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard (this represents a total of 10 congeners including OCDD; Tables 2 and 3) present in the sample extract, the relative retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 6)

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must be within -1 and +3 seconds of the retention time of the peak for the isotopically labeled internal or recovery standard at m/z corresponding to the first characteristic ion (of the set of two; Table 6) to obtain a positive identification of these nine 2,3,7,8-substituted PCDD/PCDFs and OCDD.

13.4.1.2 For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard (this represents a total of six congeners; Table 3) present in the sample extract, the relative retention time must fall within the established homologous retention time windows by analyzing the column performance check solution (this exhibit, Section 8.1.3). Identification of OCDF is based on its retention time (0.006 units) relative to $^{13}\text{C}_{12}$ -OCDD as determined from the daily routine calibration results.

13.4.1.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologue retention time windows established by analyzing the column performance check solution (this exhibit, Section 8.1.3).

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13.4.1.4 The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8465 and 321.8936) must reach maximum simultaneously (± 1 second).

13.4.1.5 The ion current responses for both ions used for the labeled standards (e.g., for ^{13}C -TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously (± 1 second).

NOTE: The analyst is required to verify the presence of $^{13}\text{C}_{12}$ -1,2,8,9-TCDD and $^{13}\text{C}_{12}$ -1,3,4,6,8-PeCDF (this exhibit, Section 8.1.3) in the SICPs. Should anyone or both compounds be missing, the analyst is required to report that observation with the results associated with the sample as it may indicate a potential problem with the ability to detect all the PCDD/PCDFs.

13.4.2 Ion Abundance Ratios

13.4.2.1 The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologues, to which the peak is assigned. See Sec-

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tions 9.1.4.3 and 9.1.4.4 (Exhibit D) and Table 9 for details.

13.4.3 Signal-to-Noise Ratio

13.4.3.1 All ion current intensities must be ≥ 2.5 times noise level for positive identification of a PCDD/PCDF compound or group of coeluting isomers. Appendix C describes the procedure to be followed for the determination of the S/N.

NOTE: It is recommended that the percent recovery of each internal standard be greater than 40 percent and does not exceed 120 percent. Matrix-specific Contractual windows for percent recoveries will be established when sufficient data are obtained from the use of this analytical protocol.

14. Calculations

14.1 For gas chromatographic peaks that have met the criteria outlined in Sections 13.4.1.1 through 13.4.3.1 (Exhibit D), calculate the concentration of the PCDD or PCDF compounds using the formula:

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$$C_x = \frac{A_x \times Q_{IS}}{A_{IS} \times W \times \overline{RRF} (n)}$$

where

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologue) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 6) for unlabeled PCDD/PCDFs,

A_{IS} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standards,

Q_{IS} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight, in g, of sample (solid or liquid), and

$\overline{RRF} (n)$ = calculated mean relative response factor for the analyte [$\overline{RRF} (n)$ with $n = 1-17$; Section 9.1.4.7, Exhibit D].

If the analyte is identified as one of the 2,3,7,8-

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substituted PCDDs or PCDFs, \overline{RRF} (n) is the value calculated using the equation in Section 9.1.4.7 (Exhibit D). However, if it is a non-2,3,7,8-substituted congener, the \overline{RRF} (k) value is the one calculated using the equation in Section 9.1.4.8.2 (Exhibit D). [\overline{RRF} (k) with k = 27-30.]

14.2 Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\begin{array}{l} \text{Internal standard} \\ \text{percent recovery} \end{array} = \frac{A_{IS} \times Q_{RS}}{Q_{IS} \times A_{RS} \times \overline{RRF}_{(m)}} \times 100$$

where

A_{IS} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standard,

A_{RS} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled recovery standard; the selection of the recovery standard depends on the type of homologues (see Table 5 footnotes),

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Q_{IS} = quantity, in pg, of the internal standard added to the sample before extraction, and

Q_{RS} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}_{(m)}$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5 footnotes) recovery standard. This represents the mean obtained in Section 9.1.4.9.

- 14.3 If the concentration in the 10 uL or 50 uL final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limits (MCL) listed in Table 1 (e.g., 200 pg/uL for TCDD in soil), the linear range of response versus concentration may have been exceeded, and a reanalysis of the sample (using one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation (this exhibit, Sections 12.1 to 12.9.3). For the other congeners (including OCDD) however, report the measured concentration and indicate that the value exceeds the MCL.

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14.4 The total concentration for each homologue of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers in each homologue. Therefore, the total should also include the 2,3,7,8-substituted congeners.

14.5 Sample Specific Estimated Detection Limit.

The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each homologue that is found deficient in 2,3,7,8-substituted isomers regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation are available depending on the type of response produced during the analysis of a particular sample.

14.5.1 Samples presenting a response that is less than 2.5 times the background level.

14.5.1.1 By using the expression of EDL (homologue) below, calculate an EDL for each homologue characterized by the absence (i.e., $S/N < 2.5$) of all homologous 2,3,7,8-substituted isomers. The background level is determined by measuring the range of the noise (peak-

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to-peak) for the first quantitation ion (Table 6) of a particular 2,3,7,8-substituted isomer within an homologue, in the region of the SICP trace corresponding to the elution of the homologue internal standard, multiplying that noise height by 2.5, and relating the product height to an estimated concentration that would produce that product height. For the homologues that have more than one 2,3,7,8-substituted isomer (e.g., HxCDD), use the retention time region corresponding to the elution of the carbon-labeled internal standard (e.g., $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD) and over a time window identical to the one determined for the carbon-labeled analogue.

Use the formula:

$$\text{EDL}(\text{homologue}) = \frac{2.5 \times A_x \times Q_{IS}}{A_{IS} \times W \times \overline{\text{RRF}}(n)}$$

where

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDD/PCDFs.

A_x , A_{IS} , W , $\overline{\text{RRF}}(n)$, and Q_{IS} retain the same meanings as defined in Section 14.1.

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14.5.2 Samples characterized by a response above the background level with a S/N of at least 2.5.

14.5.2.1 When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5:1 and does not meet any of the other qualitative identification criteria listed in Section 13.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section 14.1.

14.6 The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{| S_1 - S_2 |}{(S_1 + S_2) / 2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

14.7 The 2,3,7,8-TCDD toxic equivalents (TE) of PCDDs and PCDFs present in the sample are calculated according to the method recommended by the EPA's Chlorinated Dioxins Workgroup (CDWG) and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency

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factor (TEF) for each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs (Table 3) and the homologues of the non-2,3,7,8-substituted compounds as shown in Table 11. The 2,3,7,8-TCDD equivalent of the PCDD and PCDF present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 11. The exclusion of other homologues such as mono-, di-, tri- and octa-chlorinated dibenzodioxins and dibenzofurans does not mean that they are non-toxic. Their toxicity, as known at this time, is much less than the toxicity of the compounds listed in Table 11. The above procedure for calculating the 2,3,7,8-TCDD toxic equivalents is not claimed by CDWG to be based on a thoroughly established scientific foundation. The procedure, rather, represents a "Consensus recommendation on science policy". Since the procedure may be changed in the future, reporting requirements for PCDD and PCDF data would still include the reporting of the analyte concentration of the toxic congeners and the various homologues (toxic or not) of PCDD and PCDF as calculated in Sections 14.1 and 14.4.

14.7.1. Two-GC Column TEF Determination

Isomer specificity for all 2,3,7,8-substituted

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PCDD/PCDFs cannot be achieved on the 60-m DB-5 GC column alone. In order to determine the proper concentrations of the individual 2,3,7,8-substituted congeners, the sample extract must be reanalyzed on a 60-m SP-2330 (or SP-2331) GC column.

14.7.1.1. The concentrations of 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,7,8,9-HpCDF are calculated from the analysis of the sample extract on the 60-m DB-5 fused-silica column. The experimental conditions remain the same as the conditions described previously in Section 13 (Exhibit D), and the calculations are performed as outlined in Section 14 (Exhibit D).

14.7.1.2. The concentrations of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD and -PeCDF, 1,2,3,4,7,8-HxCDD and -HxCDF, 1,2,3,6,7,8-HxCDD and -HxCDF, 1,2,3,7,8,9-HxCDD and -HxCDF, and 2,3,4,6,7,8-HxCDF are obtained from the analysis of the sample extract on the second fused-silica capillary column (60 m SP-2330). However, the GC/MS conditions should be altered so that: (1) only the first three descriptors (i.e., tetra-, penta-, and hexa-chlorinated congeners) of Table 6 are used; and (2) the switching time between descriptor 2

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(pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD. The concentration calculations are performed as outlined in Section 14 (Exhibit D).

14.7.1.3. For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratios criteria listed respectively in Sections 13.4.2 and 13.4.3 (Exhibit D). In addition, the retention time identification criterion described in Section 13.4.1.1 (Exhibit D) applies here for congeners for which a carbon-labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions and the TEF GC Mixture (Sections 3.22 and 7.9, Exhibit D) described in Table 12.

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APPENDICES

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Appendix A

Procedure for the Collection, Handling, Analysis, and Reporting

Requirements of Wipe Tests Performed within the Laboratory.

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This procedure is designed for the periodic evaluation of potential contamination by 2,3,7,8-substituted PCDD/PCDF congeners of the working areas inside the laboratory.

WIPE TESTS COLLECTION

The wipe tests will be performed on surfaces covering two inches by one foot using laboratory wipers saturated with distilled-in-glass acetone and a pair of clean stainless steel forceps. One wiper will be used for each of the designated areas. The wipers are then combined into one composite sample in an extraction jar containing 200 mL distilled-in-glass acetone. Place six unused wipers in 200-mL acetone to be used as a control.

COMPOSITE SAMPLE PREPARATION

- * Close the jar containing the six wipers and 200 mL acetone.
- * Extract wipers for 20 minutes using a wrist-action shaker.
- * Transfer the solvent into a KD apparatus fitted with a concentration tube and a three-ball Snyder column.

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- * Add two tetrafluoroethylene (TFE) or CarborundumTM boiling chips.
- * Concentrate to an apparent volume of 1.0 mL.
- * Rinse the Synder column and the KD assembly with 2- x 1-mL portions of hexane.
- * To the concentrator tube, add 100 uL of the sample fortification solution (Section 3.8, Exhibit D).
- * Concentrate the contents of the concentrator tube to nearly dryness using a gentle stream of nitrogen.
- * Add 1.0 mL hexane to the concentrator tube.
- * Swirl the solvent on the walls.
- * Prepare a neutral alumina column as described in Section 12.7 (Exhibit D) and follow the steps outlined in Sections 12.8 thru 12.8.2 (Exhibit D).
- * Add the recovery standards as described in Section 12.9.2 (Exhibit D).

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ANALYSIS

- * Concentrate the contents of the vial to a final volume of 10 uL (either in a minivial or in a capillary tube).
- * Submit extracts to the high-resolution mass spectrometry laboratory (HRMS) for analysis.
- * Inject two uL of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDD/PCDFs as specified in the analytical method Section 13 (Exhibit D).
- * Calculations are to be performed according to Section 14 (Exhibit D).

REPORTING FORMAT

The presence of 2,3,7,8-substituted PCDDs and PCDFs are reported as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 25 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 8 pg of

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2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is $25 \times 5 = 125$ pg/WTE and the positive response for the blank would be $8 \times 5 = 40$ pg). Recoveries of the internal standards during the simplified clean-up procedure are also reported.

FREQUENCY OF WIPE TESTS

At a minimum, wipe tests should be performed when there is evidence of contamination in the method blanks.

CORRECTIVE ACTION

An upper limit of 25 pg per TCDD isomer and per wipe test experiment is allowed. (Use multiplication factors listed in footnote (a) from Table 1 for other congeners.) This value corresponds to the analytical method lower calibration limit. Procedures to correct the contamination should be taken whenever the above levels are exceeded. To that effect, vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high-efficiency particulate absorbant (HEPA) filter followed by a detergent wash. A new set of wipes should be analyzed before anyone is allowed to work in the dioxin-working area of the laboratory.

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APPENDIX B

Standards Traceability Procedure

NOTE: The content of this appendix is based on the assumption that EPA will have within its repository a mixture (named S2) containing known concentrations (e.g., 100 pg/uL) of the eight ¹³C-labeled 2,3,7,8-substituted PCDD/PCDF asterisked congeners listed in Table 3 of Exhibit D and a second solution (named S1 with the same concentration as for S2) containing the eight corresponding native analogues.

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All contractors are expected to maintain traceability of their standard solutions by verifying that all standard solutions used for direct quantitation of samples agree in chemical identity and concentration with the EPA primary standard solutions. The specific procedures are described below:

Each time a new laboratory working standard solution (W) is prepared, the identities and concentrations of the components of this solution must be verified. Verifications of the identities of the compounds are to be carried out by HRGC/HRMS. The EPA reference standard (S) and the laboratory's working standard (W) are to be analyzed under the instrumental conditions described in Exhibit D, which are appropriate for the analysis of PCDDs and PCDFs. Two criteria must be satisfied to verify the identifications:

- o Elution of the component(s) of the laboratory's working standard must be at the same retention time as the component(s) of the EPA reference standard solution

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- o Concentration(s) of the laboratory working standard's component(s) must be equal to or less than 20 percent difference relative to the EPA reference standard's component(s).

Qualitative Characterization

Due to the complexity brought by the large number of possible PCDD and PCDF congeners, the requirement for qualitative verification by comparison of the retention times only applies to the eight 2,3,7,8-substituted PCDD/PCDF asterisked congeners listed in Table 3 and for which a carbon-labeled analogue is available. Two situations need to be considered:

- a) The laboratory is required to trace back its native PCDD/PCDF standards to EPA standards. This is accomplished by adding an appropriate aliquot of the EPA ¹³C-labeled standard solution (S2) to an aliquot of the laboratory working solution (W1); the new mixture is then analyzed by HRGC/HRMS. The retention times of the eight native PCDD/PCDFs discussed above must fall within -1 to +3 seconds of the EPA carbon-labeled analogues.

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- b) In addition to a), the laboratory is required to trace back its carbon-labeled standards to EPA standards. Proceed as follows: Add an aliquot of the contract laboratory working standard solution (W2) containing the carbon-labeled compounds to an aliquot of the EPA standard solution (S1) containing the eight native 2,3,7,8-substituted PCDD/PCDF congeners discussed above, and analyze by HRGC/HRMS. The retention times for the eight laboratory carbon-labeled compounds must fall within -3 to +1 seconds of the EPA native analogues.

Quantitative Characterization

To establish that the concentration of the laboratory's working standard is correct with respect to the EPA reference standard, the relative response factors (RRF) for the eight 2,3,7,8-substituted PCDD/PCDF congeners (asterisked congeners in Table 3) must be determined as described in Exhibit D. The concentrations of the EPA reference and laboratory working standards should be approximately the same (e.g., 50 pg/uL/congener). Proceed as follows:

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- 1) Mix equal portions of the two EPA standard solutions (S1 and S2) and analyze by HRGC/HRMS. Calculate two RRFs for each of the eight analytes as shown below:

Response factor of native congener (i) relative to carbon-labeled analogue (j):

$$\text{RRF (S1,i)} = \frac{A_i \times Q_j}{Q_i \times A_j}$$

Response factor of carbon-labeled congener (j) relative to native analogue (i):

$$\text{RRF (S2,j)} = \frac{A_j \times Q_i}{Q_j \times A_i}$$

where A_i and A_j represent the integrated ion abundances of respectively the native congener and carbon-labeled congener,
and Q_i and Q_j the quantities of respectively the native congener and carbon-labeled congener,
with $i=1-8$, $j=1-8$.

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- 2) Add an appropriate aliquot of the laboratory working solution W1 (or W2) to an aliquot of the EPA solution S2 (or S1). Analyze the mixture by HRGC/HRMS and calculate the corresponding response factors as indicated below:

$$\text{RRF (W1,i)} = \frac{A_i \times Q_j}{Q_i \times A_j}$$

or

$$\text{RRF (W2,j)} = \frac{A_j \times Q_i}{Q_j \times A_i}$$

A and Q have the same meanings as in (1).

- 3) The percent difference between each congener relative response factors -- RRF (S1,i) and RRF (W1,i), and RRF (S2,j) and RRF (W2,j) -- must not exceed 20 percent in order to consider the concentration of the laboratory working standard correct. (RPD = relative percent difference.)

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$$\text{RPD} = \frac{|\text{RRF}(\text{S1}, \text{i}) - \text{RRF}(\text{W1}, \text{i})|}{\text{RRF}(\text{S1}, \text{i})} \times 100$$

and

$$\text{RPD} = \frac{|\text{RRF}(\text{S2}, \text{j}) - \text{RRF}(\text{W2}, \text{j})|}{\text{RRF}(\text{S2}, \text{j})} \times 100$$

Traceability Requirements

If any or all of the above conditions for qualitative and quantitative verifications for the laboratory working standard are not met, the standard is not traceable to the EPA reference standard and cannot therefore be used for the analysis of samples.

In addition to the above qualitative and quantitative requirements, records of all verifications, documentation of the preparation, and inventory must be kept for all contract laboratory primary, secondary, and working standards that are generated for the purpose of analyzing samples for EPA. These records should include the signed and dated logbooks containing the information pertaining to the preparation of the contract laboratory standards (weight of compound(s), volume and nature of the solvent, laboratory code name, EPA reference standard lot number) and of any modification brought to the EPA reference standard. All standards should be used on a first in, first out basis. The raw data, quantitation reports and calculations must be kept on file.

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Appendix C

Signal-to-Noise Determination Method.

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SIGNAL-TO-NOISE DETERMINATION METHOD

MANUAL DETERMINATION

This method corresponds to a manual determination of the S/N from a GC/MS signal, based on the measurement of its peak height relative to the baseline noise. The procedure is composed of four steps as outlined below. (Refer to Figure 7 for the following discussion.)

1. Estimate the peak-to-peak noise (N) by tracing the two lines (E_1 and E_2) defining the noise envelope. The lines should pass through the estimated statistical mean of the positive and the negative peak excursions as shown on Figure 7. In addition, the signal offset (O) should be set high enough such that negative-going noise (except for spurious negative spikes) is recorded.
2. Draw the line (C) corresponding to the mean noise between the segments defining the noise envelope.

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3. Measure the height of the GC/MS signal (S) at the apex of the peak relative to the mean noise C. For noisy GC/MS signals, the average peak height should be measured from the estimated mean apex signal D between E_3 and E_4 .

4. Compute the S/N.

This method of S/N measurement is a conventional, accepted method of noise measurement in analytical chemistry.

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FIGURES CAPTIONS

1. Method flow chart for sample extraction and cleanup as used for the analysis of PCDDs and PCDFs in complex waste and biological samples.
2. General structures of dibenzodioxin and dibenzofuran.
3. Peak profile displays demonstrating the effect of the detector zero on the measured resolving power. In this example, the true resolving power is 5,600.
 - A) The zero was set too high; No effect is observed upon the measurement of the resolving power. (Not aesthetic.)
 - B) The zero was adjusted properly.
 - C) The zero was set too low; This results in overestimating the actual resolving power because the peak-to-peak noise cannot be measured accurately.
4. Typical 12-hour analysis sequence of events.
5. Selected Ion Current Profile for m/z 322 (TCDDs) produced by MS analysis of the GC performance check solution by

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using a 60-m DB-5 fused-silica capillary column and conditions listed in Table 8.

6. Peak profiles representing two PFK reference ions at m/z 305 and 387. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power $m/\Delta m$ of 10,500 (10 percent valley definition).

7. Manual determination of S/N.

The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E_1 and E_2 , and between the apex average noise extremes, E_3 and E_4 , at the apex of the signal. Note, it is imperative that the instrument's interface amplifier electronic's zero offset be set high enough such that negative-going baseline noise is recorded.

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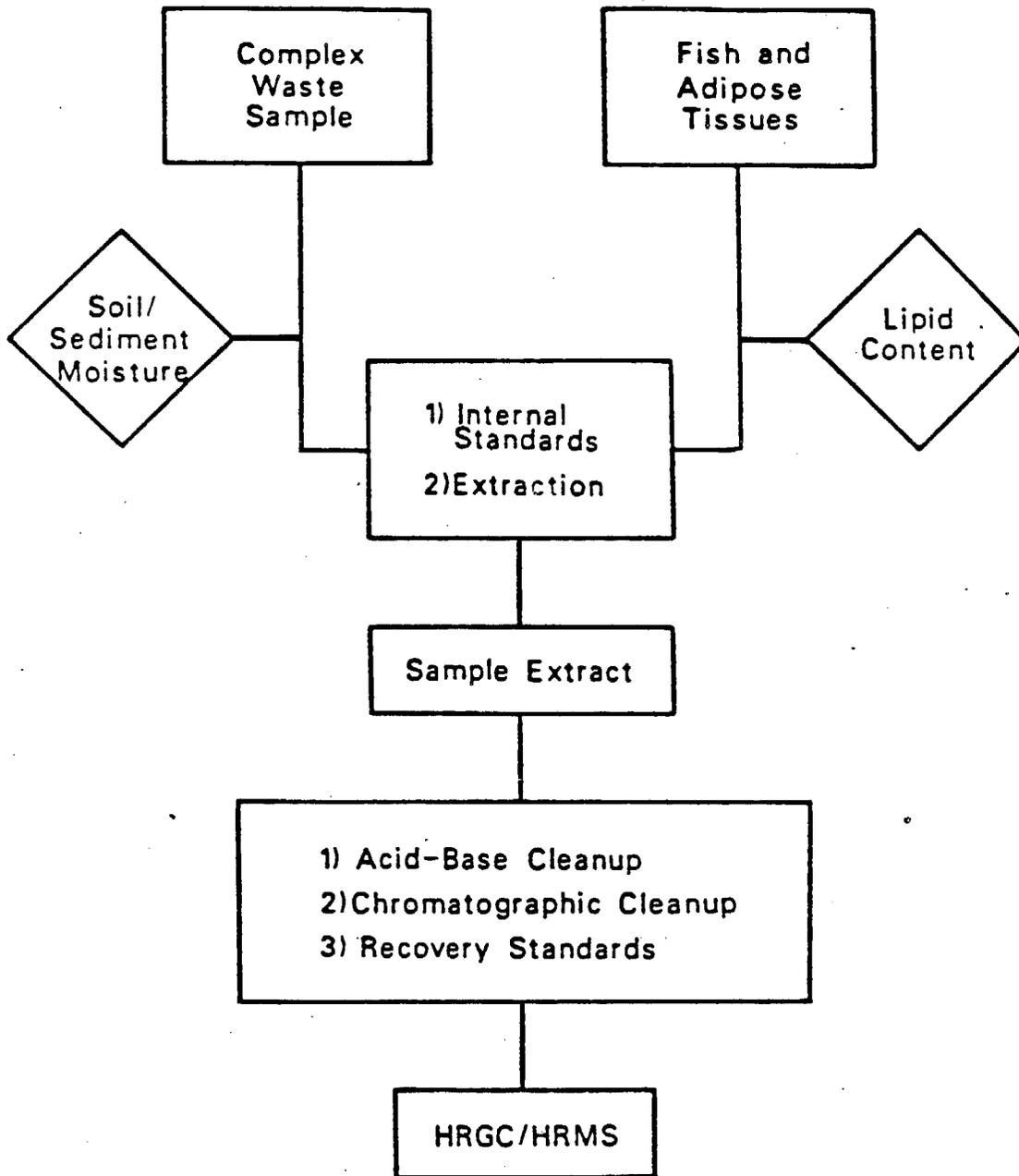
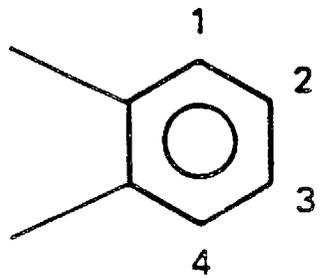
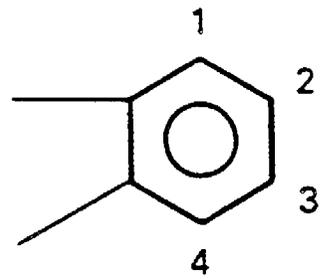


Figure 1

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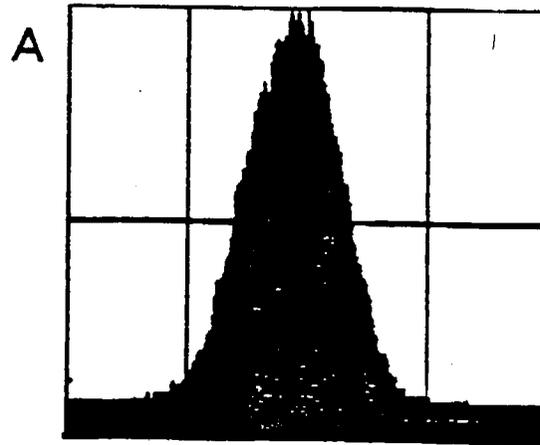


ioxin

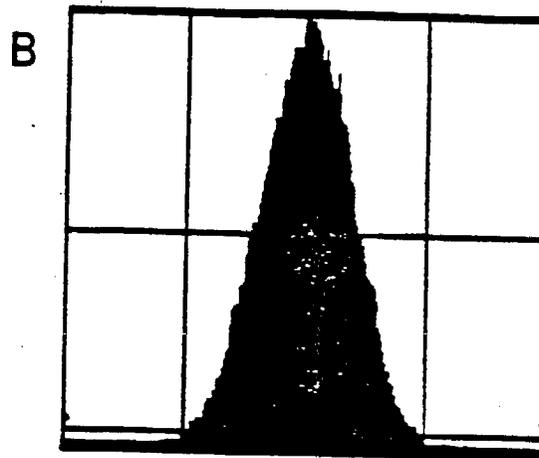


uran

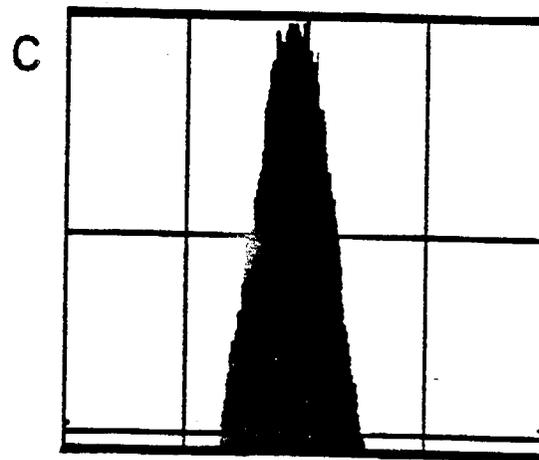
M/ Δ M



5,600



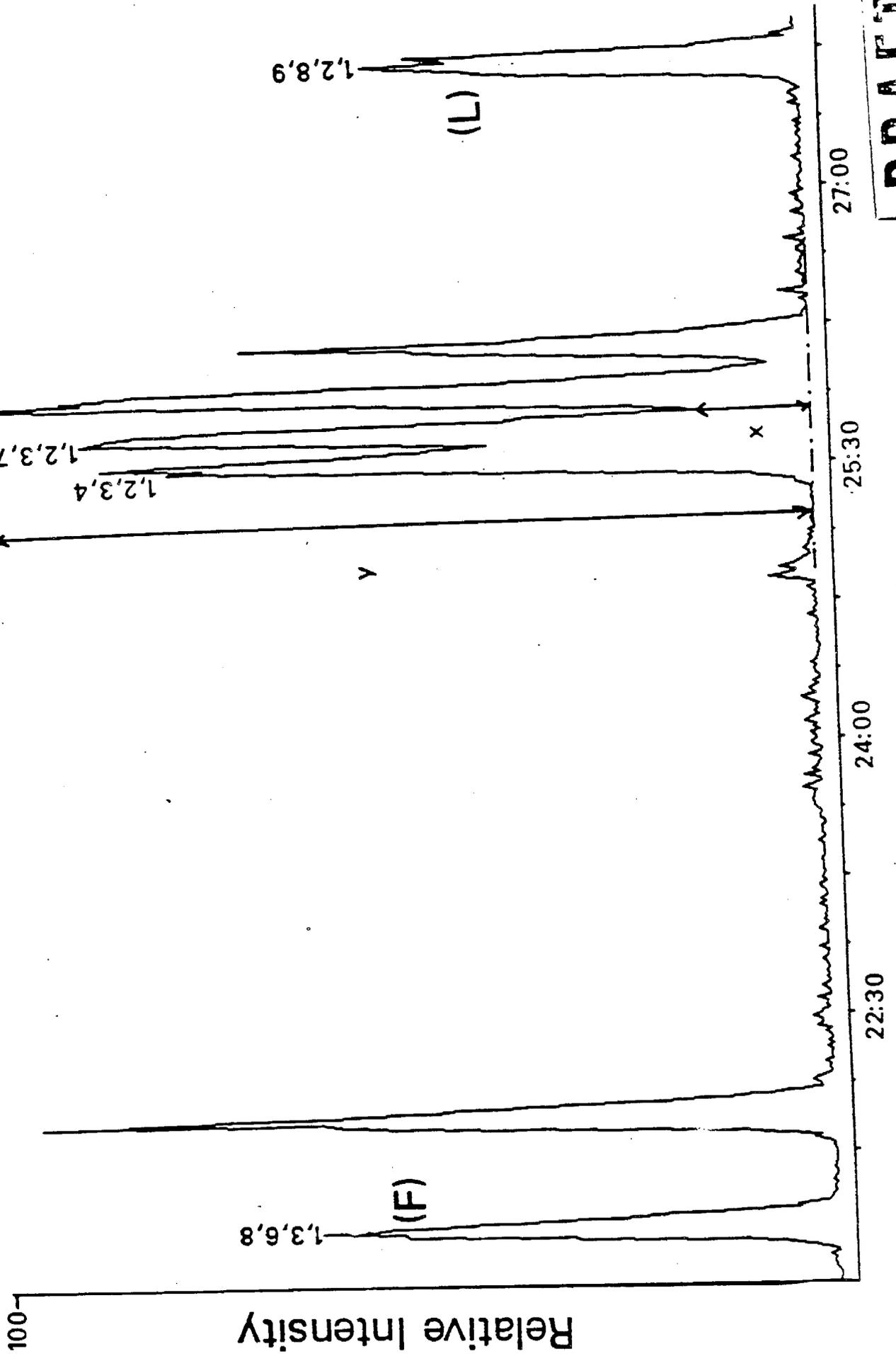
5,600



8,550

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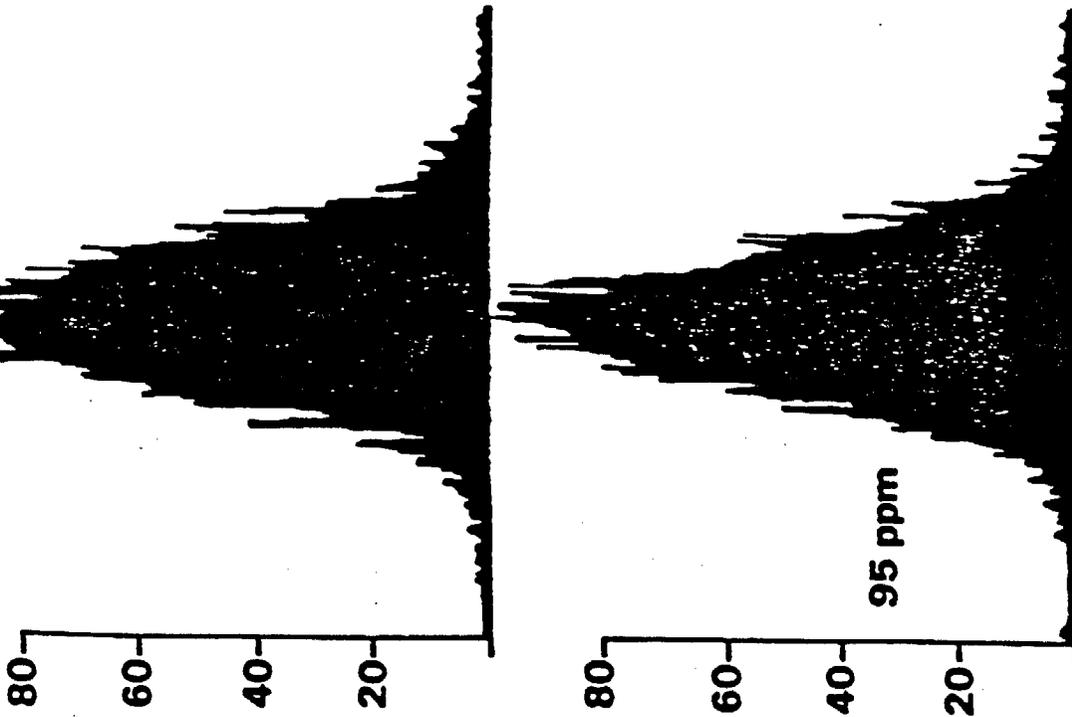
Figure 3



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ne

Figure 4



Ref. mass 304.9824 Peak top
Span 200 ppm

System file name YVES150

Data file name A:85Z567

Resolution 10000

Group number 1

Ionization mode EI+

Switching VOLTAGE

Ref. masses 304.9824

380.9260

M/ΔM ~ 10,500

Channel B 380.9260 Lock mass
Span 200 ppm

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Figure 5

Table 1. Type of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (part per trillion).

	soil sediment	ash	water	sludges fuel oil	still bottom	fish	human adipose
Lower MCL ^a	2.5	2.5	0.025	12.5	25	2.5	2.5
Upper MCL ^a	200	200	2	1000	2000	200	200
Weight (g)	10	10	1000	2	1	10	10
IS Spiking Levels (ppt)	100	100	1	500	1000	100	100
Final Extr. Vol. (uL)	10	50	10	50	50	10	10

(a) For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

NOTE: Reactor residues are treated as still-bottom if their appearance suggest so.

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Table 2. Composition of the Sample Fortification and Recovery Standard Solutions.

Analyte	Sample fortification Solution Concentration (pg/uL; solvent: Isooctane)	Recovery Standard Solution Concentration (pg/uL; solvent: Tridecane)
$^{13}\text{C}_{12}$ -2,3,7,8-TCDD	10	--
$^{13}\text{C}_{12}$ -2,3,7,8-TCDF	10	--
$^{13}\text{C}_{12}$ -1,2,3,4-TCDD	--	50
$^{13}\text{C}_{12}$ -1,2,8,9-TCDD	--	10
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD	10	--
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF	10	--
$^{13}\text{C}_{12}$ -1,3,4,6,8-PeCDF	--	10
$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD	25	--
$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF	25	--
$^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD	--	50
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD	25	--
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF	25	--
$^{13}\text{C}_{12}$ -OCDD	50	--

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Table 3. The Most Toxic PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD (*)	2,3,7,8-TCDF (*)
1,2,3,7,8-PeCDD (*)	1,2,3,7,8-PeCDF (*)
1,2,3,6,7,8-HxCDD (*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD (*)	1,2,3,4,7,8-HxCDF (*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF (*)
	1,2,3,4,7,8,9-HpCDF

(*) The ^{13}C -labeled analogue is used as an internal standard.
 (+) The ^{13}C -labeled analogue is used as a recovery standard.

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Table 4. Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	---	4	---
2	10	---	16	---
3	14	---	28	---
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

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Table 5. High-Resolution Concentration Calibration Solutions

Compound	Concentration (pg/uL)							
	HRCC	7	6	5	4	3	2	1
Native								
2,3,7,8-TCDD	200	100	50	25	10	5	2.5	
2,3,7,8-TCDF	200	100	50	25	10	5	2.5	
1,2,3,7,8-PeCDD	200	100	50	25	10	5	2.5	
1,2,3,7,8-PeCDF	200	100	50	25	10	5	2.5	
2,3,4,7,8-PeCDF	200	100	50	25	10	5	2.5	
1,2,3,4,7,8-HxCDD	500	250	125	62.5	25	12.5	6.25	
1,2,3,6,7,8-HxCDD	500	250	125	62.5	25	12.5	6.25	
1,2,3,7,8,9-HxCDD	500	250	125	62.5	25	12.5	6.25	
1,2,3,4,7,8-HxCDF	500	250	125	62.5	25	12.5	6.25	
1,2,3,6,7,8-HxCDF	500	250	125	62.5	25	12.5	6.25	
1,2,3,7,8,9-HxCDF	500	250	125	62.5	25	12.5	6.25	
2,3,4,6,7,8-HxCDF	500	250	125	62.5	25	12.5	6.25	
1,2,3,4,6,7,8-HpCDD	500	250	125	62.5	25	12.5	6.25	
1,2,3,4,6,7,8-HpCDF	500	250	125	62.5	25	12.5	6.25	
1,2,3,4,7,8,9-HpCDF	500	250	125	62.5	25	12.5	6.25	
OCDD	1,000	500	250	125	50	25	12.5	
OCDF	1,000	500	250	125	50	25	12.5	

Internal Standards

¹³ C ₁₂ -2,3,7,8-TCDD	50	50	50	50	50	50	50	50
¹³ C ₁₂ -2,3,7,8-TCDF	50	50	50	50	50	50	50	50
¹³ C ₁₂ -1,2,3,7,8-PeCDD	50	50	50	50	50	50	50	50
¹³ C ₁₂ -1,2,3,7,8-PeCDF	50	50	50	50	50	50	50	50
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	125	125	125	125	125	125	125	125
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	125	125	125	125	125	125	125	125
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	125	125	125	125	125	125	125	125
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	125	125	125	125	125	125	125	125
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	125	125	125	125	125	125	125	125
¹³ C ₁₂ -OCDD	250	250	250	250	250	250	250	250

Recovery Standards

¹³ C ₁₂ -1,2,3,4-TCDD (a)	50	50	50	50	50	50	50	50
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD (b)	125	125	125	125	125	125	125	125

(a) Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.

(b) Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF, and OCDD internal standards.

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Table 6. Ions Monitored for HRGC/HRMS analysis of PCDD/PCDFs
(S= internal/recovery standard).

Descriptor	Accurate ^(a) Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	C ₁₂ H ₄ ³⁵ Cl ₄ O	TCDF
	305.8987	M+2	C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO	TCDF
	315.9419	M	¹³ C ₁₂ H ₄ ³⁵ Cl ₄ O	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 ₄ O ₂	TCDD
	321.8936	M+2	C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO ₂	TCDD
	331.9368	M	¹³ C ₁₂ H ₄ ³⁵ Cl ₄ O ₂	TCDD (S)
	333.9339	M+2	¹³ C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO ₂	TCDD (S)
	375.8364	M+2	C ₁₂ H ₄ ³⁵ Cl ₆ O	HxCDFE
	[354.9792]	LOCK	C ₉ F ₁₃	PFK
2	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 ₂ O	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 ₂ O	PeCDF (S)
	355.8546	M+2	C ₁₂ H ₃ ³⁵ Cl ₄ ³⁷ ClO ₂	PeCDD
	357.8516	M+4	C ₁₂ H ₃ ³⁵ Cl ₃ ³⁷ Cl ₂ O ₂	PeCDD
	367.8949	M+2	¹³ C ₁₂ H ₃ ³⁵ Cl ₄ ³⁷ ClO ₂	PeCDD (S)
	369.8919	M+4	¹³ C ₁₂ H ₃ ³⁵ Cl ₃ ³⁷ Cl ₂ O ₂	PeCDD (S)
	409.7974	M+2	C ₁₂ H ₃ ³⁵ Cl ₇ O	HpCDFE

(Continued)

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Table 6. Continued

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
	[354.9792]	LOCK	C ₉ F ₁₃	PFK
3	373.8208	M+2	C ₁₂ H ₂ ³⁵ Cl ₅ ³⁷ ClO	HxCDF
	375.8178	M+4	C ₁₂ H ₂ ³⁵ Cl ₄ ³⁷ Cl ₂ O	HxCDF
	383.8642	M	¹³ C ₁₂ H ₂ ³⁵ Cl ₆ O	HxCDF (S)
	385.8610	M+2	¹³ C ₁₂ H ₂ ³⁵ Cl ₅ ³⁷ ClO	HxCDF (S)
	389.8156	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 ₂ O ₂	HxCDD
	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 ₂ O ₂	HxCDD (S)
	445.7555	M+4	C ₁₂ H ₂ ³⁵ Cl ₆ ³⁷ Cl ₂ O	OCDFE
	[354.9792]	LOCK	C ₉ F ₁₃	PFK
4	407.7818	M+2	C ₁₂ H ³⁵ Cl ₆ ³⁷ ClO	HpCDF
	409.7789	M+4	C ₁₂ H ³⁵ Cl ₅ ³⁷ Cl ₂ O	HpCDF
	417.8253	M	¹³ C ₁₂ H ³⁵ Cl ₇ O	HpCDF (S)
	419.8220	M+2	¹³ C ₁₂ H ³⁵ Cl ₆ ³⁷ ClO	HpCDF (S)

(Continued)

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Table 6. Continued

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
	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	$C_{12}H^{35}Cl_7^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	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	$C_{12}^{35}Cl_8^{37}Cl_2O$	DCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK

(a) The following nuclidic masses were used.

H = 1.007825	O = 15.994915
C = 12.000000	$^{35}Cl = 34.968853$
$^{13}C = 13.003355$	$^{37}Cl = 36.965903$

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Table 7. Recommended GC Operating Conditions

Column coating	DB-5
Film thickness	0.25 μm
Column dimension	60 m x 0.32 mm
Helium linear velocity	
Injector temperature	270° C
Splitless valve time	45 s
Interface temperature	function of the final temperature

Temperature program

Stage	Init. Temp. (° C)	Init. Hold. Time (min)	Temp. Ramp (° C/min)	Fin. Temp. (° C)	Fin. Hol. Time
1	200	2	5	220	16
2			5	235	7
3			5	330	5
Total time: 60 -min					

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Table 8. PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and used for Defining the Homologous GC Retention Time Windows on a 60-m DB-5 Column.

No. of Chlorine	PCDD-Positional Isomer		PCDF-Positional Isomer	
	Early Eluter	Late Eluter	Early Eluter	Late Eluter
4 (a)	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/ 1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,3,4,6,8	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,8	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,9
8	1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9	

(a) In addition to these two isomers, 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, ¹³C₁₂-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present.

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Table 10. Relative Response Factor Attributions

RRF Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and total HpCDDs)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	¹³ C ₁₂ -2,3,7,8-TCDD
19	¹³ C ₁₂ -2,3,7,8-TCDF
20	¹³ C ₁₂ -1,2,3,7,8-PeCDD
21	¹³ C ₁₂ -1,2,3,7,8-PeCDF
22	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD
23	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF
24	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD
25	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF
26	¹³ C ₁₂ -OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

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TABLE 11. 2,3,7,8-TCDD Equivalent Factors (TEF's) for the Polychlorinated-dibenzodioxins and -dibenzofurans

Number	Compound(s)	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.20
3	1,2,3,6,7,8-HxCDD	0.04
4	1,2,3,7,8,9-HxCDD	0.04
5	1,2,3,4,7,8-HxCDD	0.04
6	1,2,3,4,6,7,8-HpCDD	0.001
7	* Total - TCDD	0.01
8	* Total - PeCDD	0.002
9	* Total - HxCDD	0.0004
10	* Total - HpCDD	0.00001
11	2,3,7,8-TCDF	0.10
12	1,2,3,7,8-PeCDF	0.10
13	2,3,4,7,8-PeCDF	0.10
14	1,2,3,6,7,8-HxCDF	0.01
15	1,2,3,7,8,9-HxCDF	0.01
16	1,2,3,4,7,8-HpCDF	0.01
17	2,3,4,6,7,8-HxCDF	0.01
18	1,2,3,4,6,7,8-HpCDF	0.001
19	1,2,3,4,7,8,9-HpCDF	0.001
20	* Total - TCDF	0.001
21	* Total - PeCDF	0.001
22	* Total - HxCDF	0.0001
10	* Total - HpCDF	0.00001

* Excluding the 2,3,7,8-substituted congeners.

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Table 12. Toxicity Equivalency Factor GC Mixture Qualitative Composition and Analyte Relative Retention Time Reference Attributions.

Analyte (a)	Analyte RRT Reference (b)
1,2,3,4,7,8-HxCDD	$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF	$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF

- (a) The solution also contains $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD as a retention time marker for the SIM switching time on the SP-2330 GC column.
- (b) The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to $^{13}\text{C}_{12}$ -1,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF.

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QUALITY ASSURANCE REQUIREMENTS

(Quality Assessment and Quality Control)

(EXHIBIT E)

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1. SUMMARY OF QA/QC ANALYSES

- o Initial and periodic calibration and instrument performance checks.
- o HRGC/HRMS solvent blank run.
- o Field blank analyses (Section 2.4.2, Exhibit E); a minimum of one field blank shall be analyzed with each sample batch; an additional fortified field blank must be analyzed when a new lot of absorbent or solvent is used.
- o Analysis of a batch of samples with accompanying QA/QC analyses:
 - Sample Batch -- \leq 24 samples, including field blank and rinsate sample(s).

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Additional QA/QC analyses per batch:

Fortified field blank	1
Method blank	1
Duplicate sample	<u>1</u>
Total	3

- o "Blind" QC samples may be submitted to the contractor as ordinary (soil, sediment, water) samples included among the batch of samples. Blind samples include:

Uncontaminated soil, sediment, or water sample
Split samples,
Unidentified duplicates, and
Performance evaluation samples.

2. QUALITY ASSESSMENT/QUALITY CONTROL

- 2.1 Performance Evaluation Samples -- Included among the samples in all batches will be samples (blind or double blind) containing known amounts of unlabeled 2,3,7,8-substituted PCDD/PCDFs or other PCDD/PCDF congeners.

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2.2 Performance Check Solutions

2.2.1 At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 2 (HRGC-2) shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, mass range calibration and establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended).

These procedures are described in Section 8 of Exhibit D. If the required criteria are not met, remedial action must be taken before any samples are analyzed.

2.2.2 To validate positive sample data, the GC column performance check and the mass resolution check must be performed also at the end of each 12-hour period during which samples are analyzed. Furthermore, an HRGC/HRMS solvent blank run must be recorded following a calibration run and the first sample run.

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- 2.2.2.1 If the contractor laboratory operates only during one period (shift) each day of 12 hours or less, the GC performance check solution must be analyzed twice (at the beginning and end of the period) to validate data acquired during the interim period. This applies also to the mass resolution check.
- 2.2.2.2 If the contractor laboratory operates during consecutive 12-hour periods (shifts), analysis of the GC performance check solution at the beginning of each 12-hour period and at the end of the final 12-hour period is sufficient. This applies also to the mass resolution check.
- 2.2.3 Results of at least two analyses of the GC column performance check solution and the mass resolution check must be reported with the sample data collected during a 12-hour period.
- 2.2.4 Deviations from criteria specified for the GC performance check or for the mass resolution check (Section 8, Exhibit D) invalidate all positive sample data

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collected between analyses of the performance check solution, and the extract from those positive samples shall be reanalyzed (Exhibit C).

2.3 The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-LV. However, if not available from the EMSL-LV, standards can be obtained from other sources, and solutions can be prepared in the contractor laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDD/PCDFs, which are not obtained from the EMSL-LV, must be verified by comparison with the EPA standard solutions that are available from the EMSL-LV. (Refer to Appendix B for details on the recommended standards traceability procedure.)

2.4 Blanks

2.4.1 Method Blank

One Method blank is required per batch of samples. To that effect, perform all steps detailed in the analytical procedure (Section 12, Exhibit D) using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a

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sample analysis, but omit addition of the soil, aqueous or any other matrix sample portion.

2.4.1.1 The method blank must contain the same amount of $^{13}\text{C}_{12}$ -labeled internal standards that is added to samples before extraction.

2.4.1.2 An acceptable method blank exhibits no positive response as stated in Section 3.16, Exhibit D. If the method blank, which was extracted along with a batch of samples, is contaminated, all positive samples must be rerun (Exhibit C).

2.4.1.2.1 If the above criterion is not met, check solvents, reagents, fortification solutions, apparatus, and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed.

2.4.1.2.2 If new batches of reagents or solvents contain interfering contaminants, purify or discard them.

2.4.2 Field Blanks

Each batch of samples contains a field blank sample of uncontaminated soil, sediment or water that is to

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be fortified before analysis according to Section 2.4.2.1 (Exhibit E). In addition to this field blank, a batch of samples may include a rinsate, which is a portion of solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment.

2.4.2.1 Fortified Field Blank

2.4.2.1.1 Weigh a 10-g portion or use 1 L (for aqueous samples) of the specified field blank sample and add 100 uL of the solution containing the nine internal standards (Table 2, Exhibit D) diluted in 1.5 mL of acetone (Section 12.1, Exhibit D).

2.4.2.1.2 Extract by using the procedures beginning in Sections 12.2.5 or 12.2.6 of Exhibit D, as applicable, and add 10 uL of the recovery standard solution (Section 12.9.2, Exhibit D) and analyze a 2-uL aliquot of the concentrated extract.

2.4.2.1.3 Calculate the concentration (Section 14.1, Exhibit D) of 2,3,7,8-substituted PCDD/PCDFs and the percent

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recovery of the internal standards (Section 14.2, Exhibit D). If the percent recovery at the measured concentration of any 2,3,7,8-substituted PCDD/PCDF congener is <40 percent or >120 percent, report the results to SMO before proceeding with the samples.

2.4.2.1.4 Extract and analyze a new simulated fortified field blank whenever new lots of solvents or reagents are used for sample extraction or for column chromatographic procedures.

2.4.2.2 Rinsate Sample

2.4.2.2.1 The rinsate sample must be fortified as a regular sample.

2.4.2.2.2 Take a 100-mL (\pm 0.5 mL) aliquot of sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100 μ L of the solution containing the nine internal standards (Table 2, Exhibit D).

2.4.2.2.3 Using a Kuderna-Danish apparatus, concentrate to approximately 5 mL.

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2.4.2.2.4 Transfer the 5-mL concentrate in 1-mL portions to a 1-mL minivial, reducing the volume as necessary with a gentle stream of dry nitrogen.

2.4.2.2.5 Rinse the container with two 0.5-mL portions of hexane and transfer the rinses to the 1-mL minivial.

2.4.2.2.6 Just before analysis, add 10 uL tridecane recovery standards spiking solution (Table 2, Exhibit D), and reduce the volume to a final volume of 10 uL, or 50 uL as necessary (Section 12.9.2, Exhibit D). No column chromatography is required.

2.4.2.2.7 Analyze an aliquot following the same procedures used to analyze samples (Section 13, Exhibit D).

2.4.2.2.8 Report percent recovery of the internal standard and the level of contamination by any PCDD/PCDF compounds on Form (to be determined) in pg/mL of rinsate solvent.

2.5 Duplicate Analyses

2.5.1 In each batch of samples, locate the sample specified for duplicate analysis and analyze a second 10-g soil

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or sediment sample portion or 1-L water sample, or an appropriate amount of the type of matrix under consideration.

2.5.1.1 The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) must agree within 50 percent relative difference (difference expressed as percentage of the mean). If the relative difference is >50 percent for any one of the fifteen 2,3,7,8-substituted PCDD/PCDFs, the Contractor shall immediately contact the Sample Management Office for resolution of the problem. Report all results.

2.5.1.2 Recommended actions to help locate problems:

2.5.1.2.1 Verify satisfactory instrument performance (Section 8, Exhibit D).

2.5.1.2.2 If possible, verify that no error was made while weighing the sample portions.

2.5.1.2.3 Review the analytical procedures with the performing laboratory personnel.

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2.6 Percent Recovery of the Internal Standards $^{13}\text{C}_{12-2,3,7,8}$ -Substituted PCDD/PCDF Compounds

For each sample, method blank and rinsate, calculate the percent recovery (Section 14.2, Exhibit D). It is recommended that the percent recovery be >40 percent and <120 percent for all 2,3,7,8-substituted internal standards.

NOTE: A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data.

2.7 Identification Criteria

2.7.1 If either one of the identification criteria appearing in Sections 13.4.1.1 through 13.4.1.4, Exhibit D is not met for a homologue, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologue at the calculated detection limit (Section 14.5, Exhibit D).

2.7.2 If the first initial identification criteria (Sections 13.4.1.1 through 13.4.1.4) are met, but the criteria appearing in Sections 13.4.1.5 and 13.4.2.1, Exhibit D are not met, that sample is presumed to contain interfering contaminants. This

must be noted on the analytical report form and the sample must be rerun or the extract reanalyzed. Detailed sample rerun and extract reanalysis requirements are presented in Exhibit C.

2.8 Blind QA/QC Samples

Included among soil, sediment and aqueous samples may be QA/QC samples that are not specified as such to the performing laboratory. Types that may be included are:

2.8.1 Uncontaminated soil, sediment, or water.

2.8.1.1 If a false positive is reported for such a sample, the Contractor shall be required to rerun the entire associated batch of samples (Section to be determined, Exhibit C).

2.8.2 Split samples -- composited sample portions sent to more than one laboratory.

2.8.3 Unlabeled field duplicates -- two portions of a composited sample.

2.8.4 Performance evaluation sample -- soil/sediment or water sample containing a known amount of unlabeled

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2,3,7,8-substituted PCDD/PCDFs and/or other PCDD/PCDF compounds.

2.8.4.1 If the performance evaluation sample result falls outside the acceptance windows established by EPA, the Contractor shall be required to rerun the entire associated batch of samples (Exhibit C).

NOTE: EPA acceptance windows are based on previously generated data.

2.9 Quality Control Charts

The performance of the entire measurement system (i.e., from the extraction of the sample to the mass spectrometric determination) must be documented by using germane control charts. The selection and design of a specific measurement control chart must be accomplished in a rational manner so that the measurement process can be adequately surveyed. By using the standard deviations obtained from control samples or control runs, the laboratory must delineate control limits; i.e., statistically congruous extreme values, which should warn the operator of possible trouble. It is recommended to consider the values corresponding to two standard deviations as warning limits and the values from three standard

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deviations as control limits (i.e., corrective actions are required). For some particular applications, however, the control limits must not exceed the limits set forth by the EPA (e.g., ion-abundance ratios).

2.10 Standard Operation Procedures (SOPs)

As part of the quality control program, the laboratory must use in-house SOPs describing how the basic operations executed within the laboratory are done.

2.11 Internal Audits

Internal audits of records, instrumentation performances and calibration data are highly encouraged in order to identify defects that could compromise the quality of the results.

2.12 Records

At each contractor laboratory, records must be maintained on site for six months after contract completion to document the quality of all data generated during the contract period. Before any records are disposed, written concurrence from the Contracting Officer must be obtained.

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2.13 Unused portions of samples and sample extracts must be preserved for six months after sample receipt; appropriate samples may be selected by EPA personnel for further analyses.

2.14 Reuse of glassware is to be minimized to avoid the risk of contamination.

3. Laboratory Evaluation Procedures

3.1 On a quarterly basis, the EPA Project Officer or his/her designated representatives may conduct an evaluation of the laboratory to ascertain that the laboratory is meeting contract requirements. This section outlines the procedures which may be used by the Project Officer or his/her authorized representative in order to conduct a successful evaluation of laboratories conducting dioxin analyses according to this protocol. The evaluation process consists of the following steps: 1) analysis of a performance evaluation (PE) sample, and 2) on-site evaluation of the laboratory to verify continuity of personnel, instrumentation, and quality assessment/quality control functions. The following is a description of these two steps.

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3.2 Performance Evaluation (PE) Sample Analysis

3.2.1 The PE sample set will be sent to a participating laboratory to verify the laboratory's continuing ability to produce acceptable analytical results. The PE sample will be representative of the types of samples that will be subject to analysis under this contract.

3.2.2 When the PE sample results are received, they are scored using the PE Sample Score Sheet shown in Figure (to be determined). If a false positive (e.g., a PE sample not containing 2,3,7,8-TCDD or other PCDD/PCDF but reported by the laboratory to contain it or them) is reported, the laboratory has failed the PE analysis requirement. The Project Officer will notify the laboratory immediately if such an event occurs.

3.2.3 As a general rule, a laboratory should achieve 75 percent or more of the total possible points for all three categories, and 75 percent or more of the maximum pos

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3.3.2 The sequence of events for the on-site evaluations is shown in Figure (to be determined). A Site Evaluation Sheet (SES) is used to document the results of the evaluation.

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sible points in each category to be considered acceptable for this program. However, the Government reserves the right to accept scores of less than 75 percent.

3.2.4 If unanticipated difficulties with the PE samples are encountered, the total points may be adjusted by the Government evaluator in an impartial and equitable manner for all participating laboratories.

3.3 On-site Laboratory Evaluation

3.3.1 An on-site laboratory evaluation is performed to verify that (1) the laboratory is maintaining the necessary minimum level in instrumentation and levels of experience in personnel committed to the contract and (2) that the necessary quality assurance activities are being carried out. It also serves as a mechanism for discussing laboratory weaknesses identified through routine data audits, PE sample analyses results, and prior on-site evaluation. Photographs may be taken during the on-site laboratory evaluation tour.

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(REVISED 3/87 SKV)

KMnO₄/NaOH COLUMN CLEAN-UP
(ANAL. CHEM. 1982,54,2292-2299 NESTRICK, LAMPARSKI)

1.) PREPARATION OF KMnO₄/NaOH COLUMN PACKING MATERIAL

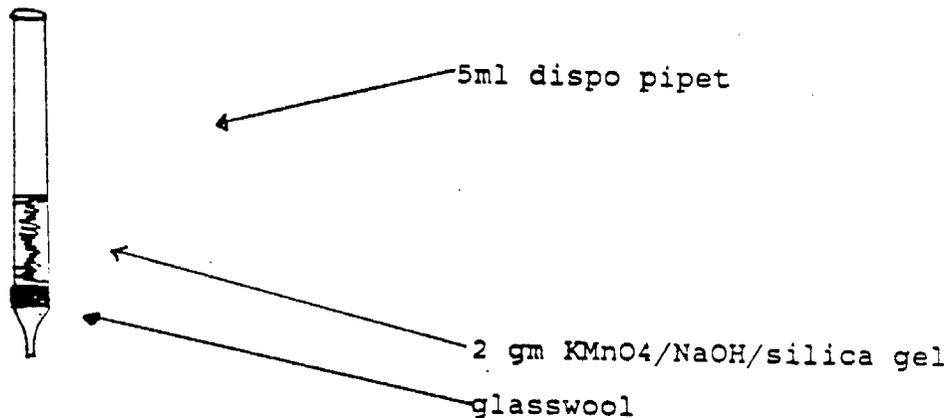
- a.) Mix in an amber 8 oz bottle:
250ml distilled water
7.9 KMnO₄
1.0 g NaOH

Store in refrigerator.

- b.) Immediately prior to use, combine:
67 parts silica gel
33 parts KMnO₄/NaOH solution

Shake until free flowing and homogenous.

2.) KMnO₄/NaOH clean-up column



- Plug 5ml dispo pipet with glasswool.
- Add 2gm KMnO₄/NaOH/Silica gel.
- Pre-wash with 5ml hexane, discard eluate.
- Transfer extract to column with 3x 1.0ml hexane portions.
- Elute with 15ml hexane, collect in a vov vial.
- N₂ as appropriate.

APPENDIX H
METHOD FOR THE DETERMINATION OF POLYCHLORINATED
DIBENZO-p-DIOXINS IN AMBIENT AIR USING HIGH
RESOLUTION GAS CHROMATOGRAPHY/HIGH DENSITY
RESOLUTION MASS SPECTROMETRY

METHOD T09

METHOD FOR THE DETERMINATION OF POLYCHLORINATED DIBENZO-
p-DIOXINS (PCDDs) IN AMBIENT AIR USING HIGH RESOLUTION GAS
CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

1. Scope

1.1 This document describes a method for the determination of polychlorinated dibenzo-p-dioxins (PCDDs) in ambient air. In particular, the following PCDD's have been evaluated in the laboratory utilizing this method:

- ° 1,2,3,4 - tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD);
- ° 1,2,3,4,7,8 - hexachlorodibenzo-p-dioxin (1,2,3,4,7,8-H_xCDD)
- ° Octachlorodibenzo-p-dioxin (OCDD); and
- ° 2,3,7,8 - Tetrachlorodibenzo-p-dioxin (2,3,7,8 - TCDD)

The method consists of sampling ambient air using a sampler equipped with an inlet filter followed by a cartridge (filled with polyurethane foam) and the analysis of the sample using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Original laboratory studies have indicated that the use of polyurethane foam (PUF) or silica gel in the sampler will give equal efficiencies for retaining PCDD/PCDF isomers; i.e., the median retention efficiencies for the PCDD isomers when using PUF ranged from 67 to 124 percent and from 47 to 133 percent when using silica gel. The silica gel, however, produced lower levels of background interferences than did the PUF. The detection limits were, therefore, approximately four times lower for tetrachlorinated isomers and ten times lower for hexachlorinated isomers when using silica gel as the adsorbent. The difference in detection limit was approximately a factor of two for the octachlorinated isomers. However, due to variable recovery and extensive cleanup required with the silica gel, the method has been written using PUF as the adsorbent rather than the silica gel.

- 1.2 With careful attention to reagent purity and other factors, the method can detect these compounds in filtered air at levels below 15 pg/m³.
- 1.3 Average percentage recoveries varied between 68 percent and 140 percent in laboratory evaluations of the method sampling ultra pure filtered air. Percentage recoveries and sensitivities obtainable for ambient air samples have not been determined.

2. Applicable Documents

2.1 ASTM Standards

- 2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.
- 2.1.2 Method E 260 - Recommended Practice for General Gas Chromatography Procedures.
- 2.1.3 Method E 355 - Practice for Gas Chromatography Terms and Relationships.

2.2 EPA Documents

- 2.2.1 Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - "Ambient Air Specific Methods," Section 2.2 - "Reference Method for the Determination of Suspended Particulates in the Atmosphere," Revision 1, July 1979, EPA-600/4-77-027A.
- 2.2.2. Protocol For the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin By High Resolution Gas Chromatography-High Resolution Mass Spectrometry, U.S. Environmental Protection Agency, January 1986, EPA-600/4-86-004.
- 2.2.3 Evaluation of an EPA High Volume Air Sampler for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-furans, undated report by Battelle under Contract 68-02-4127, Project Officers Robert G. Lewis and Nancy K. Wilson, U.S. Environmental Protection Agency, EMSL, Research Triangle Park, North Carolina.
- 2.2.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, April 1984, 600/4-84-041.
- 2.2.5 Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, 1983, U.S. Environmental Protection Agency, June 1983, EPA-600/4-83-027.

2.3 Other Documents

- 2.3.1 General Metals Works Operating Procedures for Model 1 Sampler.

2.3.2 Chicago Air Quality: PCB Air Monitoring Plan, Phase 2, Illinois Environmental Protection Agency, Division of Air Pollution Control, April 1986, IEPA/APC/86-011.

3. Summary of Method

- 3.1 Filters and adsorbent cartridges (with PUF) are cleaned in solvents and vacuum dried. The filters and adsorbent cartridges are stored in screw cap jars wrapped in aluminum foil (or otherwise protected from light) prior to careful installation on a modified high volume sampler.
- 3.2 Approximately 325 m³ of ambient air are drawn through the cartridge on a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not been shown to be a problem with sampling volumes of 325 m³).
- 3.3 The amount of air sampled through the adsorbent cartridge is recorded, and the cartridge is placed in an appropriately labeled container and shipped along with blank adsorbent cartridges to the analytical laboratory for analysis.
- 3.4 The filters and PUF adsorbent cartridge are extracted together with benzene. The extract is concentrated, diluted with hexane, and cleaned up using column chromatography.
- 3.5 The High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) is verified to be operating properly and is calibrated with five concentration calibration solutions, each analyzed in triplicate.
- 3.6 A preliminary analysis of a sample of the extract is performed to check the system performance and to assure that the samples are within the calibration range of the instrument. If necessary recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

3.7 The samples and the blanks are analyzed by HRGC/HRMS and the results are used (along with the amount of air sampled) to calculate the concentrations of polychlorinated dioxins in ambient air.

4. Significance

- 4.1 Polychlorinated dibenzo-p-dioxins (PCDDs) are extremely toxic. They are carcinogenic and are of major environmental concern. Certain isomers, for example 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), have LD50 values in the part-per-trillion range for some animal species. Major sources of these compounds have been commercial processes involving polychlorinated phenols and polychlorinated biphenyls (PCBs). Recently, however, combustion sources have been shown to emit polychlorinated dibenzo-p-dioxin (PCDD), including the open flame combustion of wood containing chlorophenol wood preservatives and emissions from burning transformers and/or capacitors that contain PCBs and chlorobenzenes.
- 4.2 Several documents have been published describing sampling and analytical approaches for PCDDs, as outlined in the Bibliography (Section 2.2). The attractive features of these methods have been combined in this procedure. This method has not been validated in its final form, and therefore, one must use caution when employing it for specific applications.
- 4.3 The relatively low levels of such compounds in the environment requires the use of high volume sampling techniques to acquire sufficient sample for analysis. However, the volatility of these compounds prevents efficient collection on filter media. Consequently, this method utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most PCDD's.

5. Definitions

Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356 and E 355. All abbreviations and symbols within this document are defined the first time they are used.

6. Interferences

- 6.1 Chemicals which elute from the gas chromatograph (GC) column within + 10 scans of the standards or compounds of interest and which produce, within the retention time windows, ions with any mass to charge (m/e) ratios close enough to those of the ion fragments used to detect or quantify the analyte compounds are potential interferences. Most frequently encountered potential interferences are other sample components that are extracted along with PCDDs, e.g. polychlorinated biphenyls, PCBs, methoxybiphenyls, chlorinated hydroxydiphenylethers, chlorinated naphthalenes, DDE, DDT, etc. The actual incidence of interference by these compounds depends also upon relative concentrations, mass spectrometric resolution, and chromatographic conditions. Because very low levels of PCDDs must be measured, the elimination of interferences is essential. High-purity reagents and solvents must be used and all equipment must be scrupulously cleaned. Laboratory reagent blanks must be analyzed to demonstrate absence of contamination that would interfere with the measurements. Column chromatographic procedures are used to remove some coextracted sample components; these procedures must be performed carefully to minimize loss of analyte compounds during attempts to increase their concentration relative to other sample components.
- 6.2 In addition to chemical interferences, inaccurate measurements could occur if PCDDs are retained on particulate matter, the filter, or PUF adsorbent cartridge, or are chemically changed during sampling and storage in ways that are not accurately measured by adding isotopically labeled spikes to the samples.

- 6.3 The system cannot separately quantify gaseous PCDDs versus particulate PCDDs because the material may be lost from the filter (and particulates on the filter) by volatilization after collection and transferred to the absorbent cartridge. Gaseous PCDDs may also be adsorbed on particulate matter on the filter.

7. Apparatus

- 7.1 General Metal Works (GMW) Model PS-1 Sampler.
- 7.2 At least two Model PS-1 sample cartridges and filters per PS-1 Sampler.
- 7.3 Calibrated GMW Model 40 calibrator.
- 7.4 High-Resolution Gas Chromatograph/High Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS)
- 7.4.1 The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but this may severely reduce column lifetime for non-chemically bonded columns. When using the method in this protocol, a 2- μ L injection volume is used consistently. With some GC injection ports, however, 1- μ L injections may produce some improved precision and chromatographic separation. A 1- μ L injection volume may be used if adequate sensitivity and precision can be achieved.

[NOTE: If 1 μ L is used as injection volume, the injection volumes for all extracts, blanks, calibration solutions and the performance check samples must be 1 μ L.]

- 7.4.2 Gas Chromatograph-Mass Spectrometer Interface.
- The gas chromatograph is usually directly coupled to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless

steel. The interface components should be compatible with 300°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphic ferrules should be avoided in the GC injection area since they may adsorb TCDD. Vespel® or equivalent ferrules are recommended.

- 7.4.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with total cycle time (including voltage reset time) of one second or less (Section 12.3.4.1). At a minimum, the following ions which occur at these masses must be monitored:

<u>2,3,7,8-TCDD</u>	<u>1,2,3,4,7,8-H₇CDD</u>	<u>OCDD</u>
258.9300	326.8521	394.7742
319.8965	389.8156	457.7377
321.8936	391.8127	459.7347
331.9368		
333.93338		

- 7.4.4 Data System. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the base line.

- 7.4.5 GC Column. A fused silica column (60 M x 0.25 mm I.D.) coated with DB-5, 0.25 μ film thickness; (J & S Scientific, Inc., Crystal Lake, IL) is utilized to separate each of the several tetra-through octa PCDDs, as a group, from all of the other groups. This column also resolves 2,3,7,8-TCDD from all of the other 21 TCDD isomers and this isomer can therefore be determined quantitatively if proper calibration procedures are applied as described further in a later section. Other columns may be used for such analysis, but this separation must be demonstrated and documented. Minimum acceptance criteria must be determined per Section 12.1. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.
- 7.5 All required syringes, gases, and other pertinent supplies to operate the HRGC/HRMS system.
- 7.6 Airtight, screw-top containers to hold the sample cartridges (preferably glass with teflon seals or other non-contaminating seals) with labels for the sample number.
- 7.7 Data sheets for each sample for recording the location and sample time, duration of sample, the starting time, and the volume of air sampled.
- 7.8 Balance capable of weighing accurately to ± 0.001 g.
- 7.9 Pipettes, micropipets, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc. This includes syringes for accurately measuring volumes such as 25 μ L and 100 μ L of isotopically labeled dioxin solutions.
- 7.10 Soxhlet extractors capable of extracting GMW PS-1 PUF adsorbent cartridges (2.3" x 5" length), 500 mL flask and condenser.

- 7.11 Vacuum drying oven system capable of holding the PUF cartridges being evacuated to 240 torr, flushed with nitrogen, and held evacuated overnight.
- 7.12 Ice chest -- to store samples at 0°C after collection.
- 7.13 A glove box for working with extremely toxic standards and reagents with explosion proof hood for venting fumes from solvents reagents, etc.
- 7.14 Adsorbtion columns for column chromatography--1 cm x 10 cm and 1 cm x 30 cm--with stands.
- 7.15 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate.
- 7.16 A laboratory refrigerator with chambers operating at 0°C and 4°C.
- 7.17 Kuderna-Danish apparatus--500 mL evaporating flask, 10 mL graduated concentrator tubes with ground-glass stoppers, and 3 ball macro Snyder Column (Kontes K-570001-0500, K-50300-0121 and K-569001-219 or equivalent).
- 7.18 Two ball micro Snyder Column, Kuderna-Danish (Kontes 569001-0219 or equivalent).
- 7.19 Stainless steel spatulas and spoons.
- 7.20 Mini-vials-1 mL borosilicate glass with conical-shape reservoir and screw caps lined with teflon-faced silicone disks, and a vial holder.
- 7.21 Chromatographic columns for Carbopak cleanup--disposable 5-mL graduated glass pipets, 6 to 7 mm ID.
- 7.22 Desiccator.
- 7.23 Polyester gloves for handling PUF cartridges and filter.
- 7.24 Die - to cut PUF plugs.
- 7.25 Water bath equipped with concentric ring cover and capable of being temperature controlled within $\pm 2^\circ\text{C}$.
- 7.26 Erlenmeyer flask, 50 mL.
- 7.27 Glass vial, 40 mL.
- 7.28 Cover glass petri dishes for shipping filters.
- 7.29 Fritted glass extraction thimbles.
- 7.30 A Pyrex glass tube furnace system for activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually.

[NOTE: Reuse of glassware should be minimized to avoid the risk of cross contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry and heat in a muffle furnace at 400°C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace. In this case, rinsing with high-purity acetone and hexane may be substituted for muffle-furnace heating. After the glassware is dry and cool, rinse with hexane, and store inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8. Reagents and Materials

- 8.1 Ultra pure glass wool--silanized--extracted with methylene chloride and hexane and dried.
- 8.2 Ultra pure acid washed quartz fiber filters for PS-1 Sampler (Pallfex 2500 glass or equivalent).
- 8.3 Benzene (Burdick and Jackson, glass distilled, or equivalent).
- 8.4 Hexane (Burdick and Jackson, glass distilled, or equivalent).
- 8.5 Alumina, acidic--extract the alumina in a Soxhlet with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activate it by heating in a foil-covered glass container for 24 hours at 190°C.
- 8.6 Silica gel--high-purity grade, type 60, 70-230 mesh; extract the silica gel in a Soxhlet with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activate it by heating in a foil-covered glass container for 24 hours at 130°C.
- 8.7 Silica gel impregnated with 40 percent (by weight) sulfuric acid--add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw-capped glass bottle.

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- 8.8 Graphitized carbon black (Carbopak C or equivalent), surface of approximately 12 m²/g, 80/100 mesh--mix thoroughly 3.6 grams Carbopak C and 16.4 grams Celite 545® in a 40-mL vial. Activate at 130°C for six hours. Store in a desiccator.
- 8.9 Sulfuric Acid, ultra pure, ACS grade, specific gravity 1.84.
- 8.10 Sodium Hydroxide, ultra pure, ACS grade.
- 8.11 Native and isotopically labeled PCDD/PCDF isomers for calibration and spiking standards, from Cambridge Isotopes, Cambridge, MA.
- 8.12 n-decane (Aldrich Gold Label grade [D90-1] or equivalent).
- 8.13 Toluene (high purity, glass distilled).
- 8.14 Acetone (high purity, glass distilled).
- 8.15 Filters, quartz fiber - Pallflex 2500 QAST, or equivalent.
- 8.16 Ultra pure nitrogen gas (Scott chromatographic grade or equivalent).
- 8.17 Methanol (chromatographic grade).
- 8.18 Methylene chloride (chromatographic grade, glass distilled).
- 8.19 Dichloromethane/hexane (3:97, v/v) chromatographic grade.
- 8.20 Hexane/dichloromethane (1:1, v/v) chromatographic grade.
- 8.21 Perfluorokerosene (PFK), chromatographic grade.
- 8.22 Celite 545®, reagent grade, or equivalent.
- 8.23 Membrane filters or filter paper with pore sizes less than 25 um, hexane rinsed.
- 8.24 Granular anhydrous sodium sulfate, reagent grade.
- 8.25 Potassium carbonate-anhydrous, granular, reagent grade.
- 8.26 Cyclohexane, glass distilled.
- 8.27 Tridecane, glass distilled.
- 8.28 2,2,3-trimethylpentane, glass distilled.
- 8.29 isooctane, glass distilled.
- 8.30 sodium sulfate, ultra pure, ACS grade.
- 8.31 Polyurethane foam -- 3 inches thick sheet stock, polyether type used in furniture upholstery. Density 0.022 g/cm³.

8.32 Concentration calibration solutions (Table 1) --four tridecane solutions containing $^{13}\text{C}_{12}$ -1,2,3,4-TCDD (recovery standard) and unlabeled 2,3,7,8-TCDD at varying concentrations, and $^{13}\text{C}_{12}$ -2,3,7,8-TCDD (internal standard, CAS RN 80494-19-5). These must be obtained from the Quality Assurance Division, U.S. EPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. These must be used to calibrate the instrument. However, secondary standards may be obtained from commercial sources, and solutions may be prepared in the analytical laboratory. Traceability of standards must be verified against EPA supplied standards solutions. Such procedures must be documented by laboratory SOPs. Care must be taken to use the correct standard. Serious overloading of instruments may occur if concentration calibration solutions intended for low resolution MS are injected into the high resolution MS.

8.33 Column performance check mixture from Quality Assurance Division (EMSL/LV) dissolved in 1 mL tridecane. This solution will contain the following components(A) eluting closely to 2,3,7,8-TCDD, and the first (F) and last-eluting (L) TCDDs, when using the recommended columns at a concentration of 10 pg/uL of each of these isomers. Each ampule contains approximately 10 ng of:

- o unlabeled 2,3,7,8-TCDD;
- o $^{13}\text{C}_{12}$ -2,3,7,8-TCDD;
- o 1,2,3,4-TCDD (A);
- o 1,4,7,8-TCDD (A);
- o 1,2,3,7-TCDD (A);
- o 1,2,3,8-TCDD (A);
- o 1,3,6,8-TCDD (F); and
- o 1,2,8,9-TCDD (L).

If these solutions are unavailable from EPA, such solutions should be prepared by the analytical laboratory or a chemical supplier and analyzed in a manner traceable to the EPA performance check mixture. This mixture is designed for 2,3,7,8-TCDD monitoring. Similar mixtures of isotopically labeled compounds should be prepared to check performance for monitoring other specific forms of TCDD of interest.

- 8.34 Sample fortification solution--an isooctane solution containing the internal standard at a nominal concentration of 10 pg/uL.
- 8.35 Recovery standard spiking solution--a tridecane solution containing the isotopically labeled standard ($^{13}\text{C}_{12}$ -2,3,7,8-TCDD and other PCDDs of interest) at a concentration of 10.0 pg/uL.
- 8.36 Field blank fortification solutions--isooctane solutions containing the following:
- Solution A: 10.0 pg/uL of unlabeled 2,3,7,8-TCDD
 - Solution B: 10.0 pg/uL of unlabeled 1,2,3,4-TCDD

[NOTE: These reagents and the detailed analytical procedures described herein are designed for monitoring TCDD concentrations of 6.0 pg/m³ to 37 pg/m³ of each isomer. If ambient concentrations should exceed these levels, concentrations of calibrations and spiking solutions will need to be modified, along with the detailed sample preparation procedures. The reagents and procedures described herein are based on Appendix B of the Protocol for the Analysis of 2,3,7,8-TCDD (Section 2.2.2) combined with the evaluation of the high volume air sampler for PCDD.

9. Preparation of PUF Sampling Cartridge

- 9.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm³). This type of foam is used for furniture upholstery.
- 9.2 The PUF inserts are 6.0 cm diameter cylindrical plugs cut from 3 inch sheet stock and should fit with slight compression in the glass cartridge, supported by the wire screen. See Figure 2. During cutting the die is rotated at high speed (e.g. in a drill press) and continuously lubricated with water.
- 9.3 For initial cleanup the PUF plug is placed in a Soxhlet extractor and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.
- 9.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

- 9.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane rinsed aluminum foil, placed in a labeled container and tightly sealed.
- 9.6 At least one assembled cartridge from each batch must be analysed, as a laboratory blank, using the procedures described in Section 11, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable.

10. Sample Collection

10.1 Description of Sampling Apparatus

- 10.1.1 The entire sampling system is diagrammed in Figure 1. A unit specifically designed for this method is commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio).
- 10.1.2 The sampling module (Figure 2) consists of a glass sampling cartridge and an air-tight metal cartridge holder. The PUF is retained in the glass sampling cartridge.

10.2 Calibration of Sampling System

- 10.2.1 The airflow through the sampling system is monitored by a venturi/Magnehelic assembly, as shown in Figure 1. Assembly must be audited every six months using an audit calibration orifice, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix B. A single point calibration must be performed before and after each sample collection, using the procedure described in Section 10.2.2.
- 10.2.2 Prior to calibration, a "dummy" PUF cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate is indicated on the magnehelic (based on the previously obtained multipoint calibration curve). The motor is allowed to warmup for 10 minutes and then the flow control

valve is adjusted to achieve the desired flow rate. The ambient temperature and barometric pressure should be recorded on an appropriate data sheet.

10.2.3 The calibration orifice is then placed on the sampling head and a manometer is attached to the tap on the calibration orifice. The sampler is momentarily turned off to set the zero level of the manometer. The sampler is then switched on and the manometer reading is recorded, once a stable reading is achieved. The sampler is then shut off.

10.2.4 The calibration curve for the orifice is used to calculate sample flow from the data obtained in Section 10.2.3, and the calibration curve for the venturi/magnehelic assembly is used to calculate sample flow from the data obtained in Section 10.2.2. The calibration data should be recorded on an appropriate data sheet. If the two values do not agree within 10%, the sampler should be inspected for damage, flow blockage, etc. If no obvious problems are found, the sampler should be recalibrated (multipoint) according to the U.S. EPA High Volume Sampling procedure (Section 10.2.1.)

10.2.5 A multipoint calibration of the calibration orifice, against a primary standard, should be obtained annually.

10.3 Sample Collection

10.3.1 After the sampling system has been assembled and calibrated as described in Sections 10.1 and 10.2, it can be used to collect air samples as described in Section 10.3.2

10.3.2. The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air.

- 10.3.3 A clean PUF sampling cartridge and quartz filter are removed from sealed transport containers and placed in the sampling head using forceps and gloved hands. The head is tightly sealed into sampling system. The aluminum foil wrapping is placed back in the sealed container for later use.
- 10.3.4 The zero reading of the Magnehelic is checked. Ambient temperature, barometric pressure, elapse time meter setting, sampler serial number, filter number and PUF cartridge number are recorded on a suitable data sheet, as illustrated in Figure 3.
- 10.3.5 The voltage variator and flow control valve are placed at the settings used in Section 10.2.3 and the power switch is turned on. The elapsed time meter is activated and the start time recorded. The flow (Magnehelic setting) is adjusted, if necessary using the flow control valve.
- 10.3.6 The Megnehelic reading is recorded ever six hours during the sampling period. The calibration curve (Section 10.2.4) is used to calculate the flow rate. Ambient temperature and barometric pressure are recorded at the beginning and end of the sampling period.
- 10.3.7 At the end of the desired sampling period the power is turned off and the filter and PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory.
- 10.3.8 The Magnehelic calibration is checked using the calibration orifice as described in Section 10.2.4. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

- 10.3.9 At least one field filter/PUF blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the filter/PUF cartridge assembly.
- 10.3.10 Samples are stored at 20°C in an ice chest until receipt at the analytical laboratory, at which time they are stored refrigerated at 4°C.

11. Sample Extraction

- 11.1 Immediately before use, charge the Soxhlet apparatus with 200 to 250 mL of benzene and reflux for 2 hours. Allow the apparatus to cool, disassemble and transfer the benzene to a clean glass container and retain as a blank for later analysis, if required. Following sampling, the cartridges and filters are spiked with an internal standard (Table 1). After spiking, place the PUF cartridge and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional). (The filter and PUF cartridge are analyzed together due to quantities needed to overcome detectable limits, questionable interpretation of the data and cost.) Add 200 to 250 mL of benzene to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.
- 11.2 Transfer the extract to a Kuderna-Danish (K-D) apparatus and concentrate to 2 to 3 mL and allow to cool. Rinse the column and flask with 5 mL of benzene, collecting the rinsate in the concentrator tube to 2 to 3 mL. Repeat the rinsing and concentration steps twice more. Remove the concentrator tube from the K-D apparatus and carefully reduce the extract volume to approximately 1 mL with a stream of nitrogen using a flow rate and distance above the solution such, that a gentle rippling of the solution surface is observed.

- 11.3 The column chromatographic procedures, for sample extraction cleanup, listed have been demonstrated to be effective for a mixture consisting of:
- 1,2,3,4-TCDD;
 - 1,2,3,4,7,8-H_xCDD;
 - OCDD; and
 - 2,3,7,8-TCDD
- 11.3.1 Prepare an acidic silica column as follows (Figure 4): Pack a 1 cm x 10 cm chromatographic column with a glass wool plug, a layer (1 cm) of Na₂SO₄/K₂CO₃(1:1), 1.0 g silica gel (Section 8.6) and 4.0 g of 40-percent (w/w) sulfuric acid-impregnated silica gel (Section 8.7). Pack a second chromatographic column (1 cm x 30 cm) with a glass wool plug, 6.0 g acidic alumina (Section 8.5) and top with a 1-cm layer of sodium sulfate (Section 8.30). Add hexane to the columns until they are free of channels and air bubbles.
- 11.3.2 Quantitatively transfer the benzene extract (1 mL) from the concentrator tub to the top of the silica gel column. Rinse the concentrator tube with 0.5-mL portions of hexane. Transfer the rinses to the top of the silica gel column.
- 11.3.3 Elute the extract from the silica gel column with 90 mL hexane directly into a Kudena-Danish concentrator tube. Concentrate the eluate to 0.5 mL, using nitrogen blow-down as necessary.
- 11.3.4 Transfer the concentrate (0.5 mL) to the top of the alumina column. Rinse the K-D assembly with two 0.5-mL portions of hexane and transfer the rinses to the top of the alumina columns. Elute the alumina column with 18 mL hexane until the hexane level is just below the top of the sodium sulfate. Discard the eluate. Columns must not be allowed to reach dryness (i.e., a solvent "head" must be maintained).

- 11.3.5 Place 30 mL of 20-percent (v/v) methylene chloride in hexane on top of the alumina and elute the TCDDs from the column. Collect this fraction in a 50-mL Erlenmeyer flask.
- 11.3.6 Certain extracts, even after cleanup by column chromatography, contain interferences which preclude determination of TCDD at low parts-per-trillion levels. Therefore, a cleanup step is included using activated carbon which selectively retains planar molecules such as TCDDs. The TCDDs are then removed from the carbon by elution with toluene. Proceed as follows: Prepared a 18-percent Carbopak C/Celite 545® mixture by thoroughly mixing 3.6 grams Carbopak C (80/100 mesh) and 16.4 grams Celite 545® in a 40-mL vial. Activate at 130°C for 6 hours. Store in a desiccator. Cut off a clean 5-mL disposable glass pipet at the 4-mL mark. Insert a plug of glass wool (Section 8.1) and push to the 2-mL mark. Add 340 mg of the activated Carbopak/Celite mixture followed by another glass wool plug. Using two glass rods, push both glass wool plugs simultaneously towards the Carbopak/Celite plug to a length of 2.0 to 2.5 cm. Preelute the column with 2 mL toluene followed by 1 mL of 75:20:5 methylene chloride/methanol/benzene, 1 mL of 1:1 cyclohexane in methylene chloride, and 2 mL hexane. The flow rate should be less than 0.5 mL min.⁻¹. While the column is still wet with hexane, add the entire elute (30 mL) from the alumina column (Section 11.3.5) to the top of the column. Rinse the Erlenmeyer flask, which contained the extract, twice with 1 mL hexane and add the rinsates to the top of the column. Elute the column sequentially with two 1-mL aliquots hexane, 1 mL of 1:1 cyclohexane in methylene chloride, and 1 mL of 75:20:5 methylene

chloride/methanol/benzene. Turn the column upside down and elute the TCDD fraction with 6 mL toluene into a concentrator tube. Warm the tube to approximately 60°C and reduce the toluene volume to approximately 1 mL using a stream of nitrogen. Carefully transfer the residue into a 1-mL mini-vial and again at elevated temperature, reduce the volume to about 100 uL using a stream of nitrogen. Rinse the concentrator tube with 3 washings using 200 uL of 1% toluene in CH₂Cl₂. Add 50 uL tridecane and store the sample in a refrigerator until GC/MS analysis is performed.

12. HRGC/HRMS System Performance Criteria

The laboratory must document that the system performance criteria specified in Section 12.1, 12.2 and 12.3 have met prior to analysis of samples.

12.1 GC Column Performance

12.1.1 Inject 2 uL of the column performance check solution (Section 8.30) and acquire selected ion monitoring (SIM) data for m/z 258.930, 319.897, 321.894 and 333.934 within a total cycle time of <1 second.

12.1.2 The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of <25 percent, where

$$\text{Valley Percent} = (x/y)(100)$$

x = measured distance from extrapolated baseline to minimum of valley; and

y = the peak height of 2,3,7,8-TCDD.

[Note: It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The column performance check solution also contains the TCDD isomers eluting first and last under the analytical conditions specified in this protocol thus defining

the retention time window for total TCDD determination. The peaks representing 2,3,7,8-TCDD, the first and the last eluting TCDD isomers must be labeled and identified.]

12.2 Mass Spectrometer Performance

12.2.1 The mass spectrometer must be operated in the electron (impact) ionization mode. Static mass resolution of at least 10,000 (10 percent valley) must be demonstrated before any analysis of a set of samples is performed (Section 12.2.2). Static resolution checks must be performed at the beginning and at the end of each 12-hour period of operation. However, it is recommended that visual check (e.e., not documented) of the static resolution be made using the peak matching unit before and after each analysis.

12.2.2 Chromatography time for TCDD may exceed the long-term mass stability of the mass spectrometer and thus mass drift correction is mandatory. A reference compound (high boiling perflorokerosene (PFK) is recommended) is introduced into the mass spectrometer. An acceptable lock mass ion at any mass between m/z 250 and m/z 334 (m/z 318.979 from PFK is recommended) must be used to monitor and correct mass drifts.

[NOTE: Excessive PFK may cause background noise problems and contamination of the source resulting in an increase in "downtime" for source cleaning. Using a PFK molecular leak, tune the instrument to meet the minimum required mass resolution of 10,000 (10% valley) at m/z 254.986 (or any other mass reasonable close to m/z 259). Calibrate the voltage sweep at least across the mass range m/z 259 to m/z 344 and verify that m/z 330.979 from PFK (or any other mass close to m/z 334) is measured within ± 5 ppm (i.e., 1.7 mmu). Documentation of the mass resolution must then be accomplished by recording the peak profile of the PFK reference peak m/z 318.979 (or any other

reference peak at a mass close to m/z 320/322). The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (mmu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum) must appear on the hard copy and cannot exceed 31.9 mmu or 100 ppm.]

12.3 Initial Calibration

Initial calibration is required before any samples are analyzed for 2,3,7,8-TCDD. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 12.6.

- 12.3.1 All concentration calibration solutions listed in Table 1 must be utilized for the initial calibration.
- 12.3.2 Tune the instrument with PFK as described in Section 12.2.2.
- 12.3.3 Inject 2 μ L of the column performance check solution (Section 8.31) and acquired SIM mass spectral data for m/z 258.930, 319.897, 321.894, 331.937, and 333.934 using a total cycle time of ≤ 1 second. The laboratory must not perform any further analysis until it has been demonstrated and documented that the criterion listed in Section 12.1.2 has been met.
- 12.3.4 Using the same GC (Section 12.1) and MS (Section 12.2) conditions that produced acceptable results with the column performance check solution, analyze a 2- μ L aliquot of each of the 5 concentration calibration solutions in triplicate with the gas chromatographic/mass spectrometer operating parameters shown in Table 2.
 - 12.3.4.1 Total cycle time for data acquisition must be ≤ 1 second. Total cycle time includes the sum of all the dwell times and voltage reset times.

12.3.4.2 Acquire SIM data for the following selected characteristic ions:

<u>m/z</u>	<u>Compound</u>
258.930	TCDD - COCl
319.897	Unlabeled TCDD
321.894	Unlabeled TCDD
331.937	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD
333.934	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD

12.3.4.3 The ratio of integrated ion current for m/z 319.897 to m/z 321.894 for 2,3,7,8-TCDD must be between 0.67 and 0.87 ($\pm 13\%$).

12.3.4.4 The ratio of integrated ion current for m/z 331.937 to m/z 333.934 for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -1,2,3,4-TCDD must be between 0.67 and 0.87.

12.3.4.5 Calculate the relative response factor for unlabeled 2,3,7,8-TCDD [RRF(I)] relative to $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and for labeled $^{13}\text{C}_{12}$ -2,3,7,8-TCDD [RRF(II)] relative to $^{13}\text{C}_{12}$ -1,2,3,4-TCDD as follows:

$$\text{RRF(I)} = \frac{A_x \cdot Q_{IS}}{Q_x \cdot A_{IS}}$$

$$\text{RRF(II)} = \frac{A_{IS} \cdot Q_{RS}}{Q_{IS} \cdot A_{RS}}$$

where:

A_x = Sum of the integrated abundances of m/z 319.897 and m/z 321.894 for unlabeled 2,3,7,8-TCDD.

A_{IS} = Sum of the integrated abundances of m/z 331.937 and m/z 333.934 for $^{13}C_{12}$ -2,3,7,8-TCDD.

A_{RS} = Sum of the integrated abundances for m/z 331.937 and m/z 333.934 for $^{13}C_{12}$ -1,2,3,4-TCDD.

Q_{IS} = Quantity of $^{13}C_{12}$ -2,3,7,8-TCDD injected (pg).

Q_{RS} = Quantity of $^{13}C_{12}$ -3,4-TCDD injected (pg).

Q_x = Quantity of unlabeled 2,3,7,8-TCDD injected (pg).

12.4 Criteria for Acceptable Calibration

The criteria listed below for acceptable calibration must be met before analysis of any sample is performed.

12.4.1 The percent relative standard deviation (RSD) for the response factors from each of the triplicate analyses for both unlabeled and $^{13}C_{12}$ -2,3,7,8-TCDD must be less than ± 20 percent.

12.4.2 The variation of the 5 mean RRFs for unlabeled 2,3,7,8-TCDD obtained from the triplicate analyses must be less than ± 20 percent RSD.

12.4.4 SIM traces for $^{13}C_{12}$ -2,3,7,8-TCDD must present a signal-to-noise ratio ≥ 10 for 333.934.

12.4.5 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

NOTE: If the criteria for acceptable calibration listed in Sections 12.4.1 and 12.4.2 have been met, the RRF can be considered independent of the analyte quantity for the calibration concentration range. The mean RRF from 5 triplicate determinations for unlabeled 2,3,7,8-TCDD and for $^{13}C_{12}$ -2,3,7,8-TCDD will be used for all calculations until routine calibration criteria (Section 12.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of five triplicate determinations.

12.5 Routine Calibrations.

Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC column performance check runs.

12.5.1 Inject 2 μL of the concentration calibration solution which contains 5.0 pg/ μL of unlabeled 2,3,7,8-TCDD, 10.0 pg/ μL of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and 5.0 pg/ μL $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. Using the same GC/MS/DS conditions as used in Section 12.1, 12.2 and 12.3, determine and document acceptable calibration as provided in Section 12.6.

12.6 Criteria for Acceptable Routine Calibration.

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken and the instrument must be recalibrated.

12.6.1 The measured RRF for unlabeled 2,3,7,8-TCDD must be within ± 20 percent of the mean values established (Section 12.3.4.6) by triplicate analyses of concentration calibration solutions.

12.6.2 The measured RRF for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD must be within ± 20 percent of the mean value established by triplicate analyses of concentration calibration solutions (Section 12.3.4.6).

12.6.3 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

12.6.4 If one of the above criteria is not satisfied, a second attempt can be made before repeating the entire initialization process (Section 12.3).

[NOTE: An initial calibration must be carried out whenever any HRCC solution is replaced.]

13. Analytical Procedures

13.1 Remove the sample extract or blank from storage, allow it to warm to ambient laboratory temperature and add 5 μL recovery standard solution. With a stream of dry, purified nitrogen, reduce the extract/blank volume to 20 μL .

- 13.2 Inject a 2-uL aliquot of the extract into the GC, operated under the conditions previously used (Section 12.1) to produce acceptable results with the performance check solution.
- 13.3 Acquire SIM data using the same acquisition time and MS operating conditions previously used (Section 12.3.4) to determine the relative response factors. Acquire SIM data for the following selected characteristic ions:

<u>m/z</u>	<u>Compound</u>
258.930	TCDD - COC1 (weak at detection limit level)
319.897	Unlabeled TCDD
321.894	Unlabeled TCDD
331.937	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD,
33.934	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD;

13.4 Identification Criteria

- 13.4.1 The retention time (RT) (at maximum peak height) of the sample component m/z 319.897 must be within -1 to +3 seconds of the retention time of the peak for the isotopically labeled internal standard at m/z 331.937 to attain a positive identification of 2,3,7,8-TCDD. Retention times of other tentatively identified TCDDs must fall within the RT window established by analyzing the column performance check solution (Section 12.1). Retention times are required for all chromatograms.
- 13.4.2 The ion current responses for m/z 258.930, 319.897 and 321.894 must reach maximum simultaneously (± 1 scan), and all ion current intensities must be ≥ 2.5 times noise level for positive identification of a TCDD.
- 13.4.3 The integrated ion current at m/z 319.897 must be between 67 and 87 percent of the ion current response at m/z 321.894.

- 13.4.4 The integrated ion current at m/z 331.937 must be between 67 and 87 percent of the ion current response at m/z 333.934.
- 13.4.5 The integrated ion currents for m/z 331.937 and 333.934 must reach their maxima within ± 1 scan.
- 13.4.6 The recovery of the internal standard $^{13}\text{C}_{12-2,3,7,8}$ -TCDD must be between 40 and 120 percent.

14. Calculations

- 14.1 Calculate the concentration of 2,3,7,8-TCDD (or any other TCDD isomer) using the formula:

$$C_x = \frac{A_x \cdot Q_{IS}}{A_{IS} \cdot V \cdot \text{RRF}(I)}$$

where:

C_x = Unlabeled 2,3,7,8-TCDD (or any other unlabeled TCDD isomer) concentration in pg.

A_x = Sum of the integrated ion abundances determined for m/z 319.897 and 321.894.

A_{IS} = Sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of $^{13}\text{C}_{12-2,3,7,8}$ -TCDD (IS = internal standard).

Q_{IS} = Quantity (in picograms) of $^{13}\text{C}_{12-2,3,7,8}$ -TCDD added to the sample before extraction ($Q_{IS} = 500$ pg).

V = Volume (in cubic meters) of air sampled.

 $\text{RRF}(I)$ = Calculated mean relative response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}\text{C}_{12-2,3,7,8}$ -TCDD. This represents the grand mean of the $\text{RRF}(I)$'s obtained in Section 12.3.4.5.

- 14.2 Calculate the recovery of the internal standard $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, measured in the sample extract, using the formula:

$$\text{Internal standard, percent recovery} = \frac{A_{\text{IS}} \cdot Q_{\text{RS}}}{A_{\text{RS}} \cdot \text{RRF(II)} \cdot Q_{\text{IS}}} \times 100$$

where:

A_{IS} and Q_{IS} = The same definitions as above (Section 14.1)

A_{RS} = Sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD (RS = recovery standard).

Q_{RS} = Quantity (in picograms) of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD added to the sample residue before HRGC-HRMS analysis. ($Q_{\text{RS}} = 500$ pg)

RRF(II) = Calculated mean relative response factor for labeled $^{13}\text{C}_{12}$ -2,3,7,8-TCDD. This represents the grand mean of the RRF(II)'s calculated in Section 12.3.4.5.

- 14.3 Total TCDD concentration. All positively identified isomers of TCDD must be within the RT window and meet all identification criteria listed in Sections 13.4.2, 13.4.3 and 13.4.4. Use the expression in Section 14.1 to calculate the concentrations of the other TCDD isomers, with C_x becoming the concentration of any unlabeled TCDD isomer.
- 14.4 Estimated Detection Limit. For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the estimated minimum detectable concentration. The background area is determined by integrating the ion abundances for m/z 319.897 and 321.894 in the appropriate region and relating that height area to an estimated concentration that would produce that product area. Use the formula:

$$\text{CE} = \frac{(2.5) \cdot (A_x) \cdot (Q_{\text{IS}})}{(A_{\text{IS}}) \cdot \text{RRF(I)} \cdot (W)}$$

where:

C_E = Estimated concentration of unlabeled 2,3,7,8-TCDD required to produce A_x .

A_x = Sum of integrated ion abundance for m/z 319.897 and 321.894 in the same group of ≥ 25 scans used to measure A_{IS} .

A_{IS} = Sum of integrated ion abundance for the appropriate ion characteristic of the internal standard, m/z 331.937 and m/z 333.934.

Q_{IS} , $RRF(I)$, and V retain the definitions previously stated in Section 14.1. Alternatively, if peak height measurements are used for quantification, measure the estimated detection limit by the peak height of the noise in the TCDD RT window.

14.5 The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|S_1 - S_2|}{(\text{Mean Concentration})} = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

14.6 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic) taken in Section 10.3.6 using the following equation:

$$V_m = \frac{Q_1 + Q_2 \cdots Q_N}{N} \times \frac{T}{1000}$$

where:

- V_m = Total sample volume (m^3).
- $Q_1 Q_2 \cdots Q_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling (L/minute).
- N = Number of data points averaged.
- T = Elapsed sampling time (minutes).

14.7 The concentration of compound in the sample is calculated using the following equation:

$$V_S = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where:

V_S = Total sample volume at 25°C and 760 mm Hg pressure (m^3)

V_m = Total sample flow under ambient conditions (m^3).

P_A = Ambient pressure (mm Hg).

t_A = Ambient temperature (°C).

14.8 The concentration of compound in the sample is calculated using the following equation:

$$C_A = \frac{A \times V_E}{V_i \times V_S}$$

where:

C_A = Concentration of analyte in the sample, ug/m^3 .

A = Calculated amount of material determined by HRGC/HRMS.

V_i = Volume of extract injected (μL).

V_E = Final volume of extract (mL).

V_S = Total volume of air samples corrected to standard conditions (m^3)

15. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory.

15.1 Standard Operating Procedures (SOPs)

15.1.1 Users should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system; 2) preparation, purification, storage and handling of sampling cartridges and filters; 3) assembly, calibration and operation of the HRGC/HRMS system; and 4) all aspects of data recording and processing.

- 15.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.
- 15.2 Process, Field, and Solvent Blanks
 - 15.2.1 One PUF cartridge and filter from each batch of approximately 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as process blank.
 - 15.2.2 During each sampling episode, at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.
 - 15.2.3 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.

TABLE 1
COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

<u>Recovery Standards</u>		<u>Analyte</u>	<u>Internal Standard</u>
$^{13}\text{C}_{12}$ -1,2,3,4-TCDD		2,3,7,8-TCDD	$^{13}\text{C}_{12}$ -1,2,3,7,8-TCDD
HRCC1	2.5 pg/uL	2.5 pg/uL	10.0 pg/uL
HRCC2	5.0 pg/uL	5.0 pg/uL	10.0 pg/uL
HRCC3	10.0 pg/uL	10.0 pg/uL	10.0 pg/uL
HRCC4	20.0 pg/uL	20.0 pg/uL	10.0 pg/uL
HRCC5	40.0 pg/uL	40.0 pg/uL	10.0 pg/uL

Sample Fortification Solution

5.0 pg/uL of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD

Recovery Standard Spiking Solution

100 pg/uL $^{13}\text{C}_{12}$ -1,2,3,4-TCDD

Field Blank Fortification Solutions

- A) 4.0 pg/uL of unlabeled 2,3,7,8-TCDD
- B) 5.0 pg/uL of unlabeled 1,2,3,4-TCDD

TABLE 2
RECOMMENDED HRGC/HRMS OPERATING PARAMETERS

Mass Resolution	10,000-12,000 (M/ M, 10% valley definition)
Electron Energy	70 eV
Accelerating Voltage	4,000 volts
Source Temperature	200°C
Preamplifier Gain	10 ⁷ volts/amp
Electron Multiplier Gain	10 ⁶
Transfer Line Temperature	280°C
Capillary Column	30 m DB-5 Fused Silica
Injector Temperature	300°C
Column Temp - Initial	160°C
Column Temp - Final	290°C
Carrier Gas	Helium
Flow Velocity	30 cm/sec
Injection Mode	Splitless
Injection Volume	2 μ L

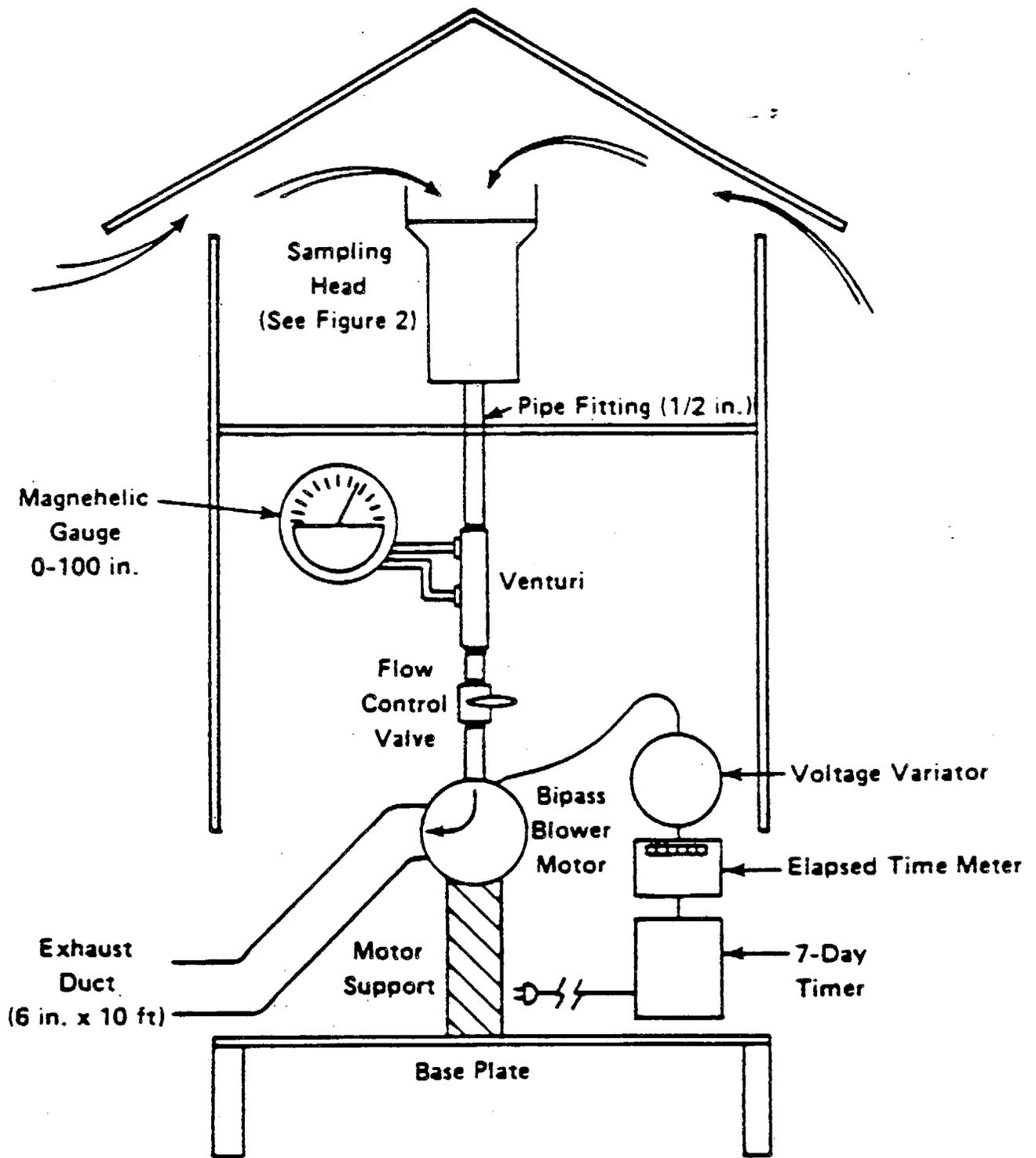


FIGURE 1. HIGH VOLUME AIR SAMPLER
GENERAL METAL WORKS (MODEL PS-1)

T09-35

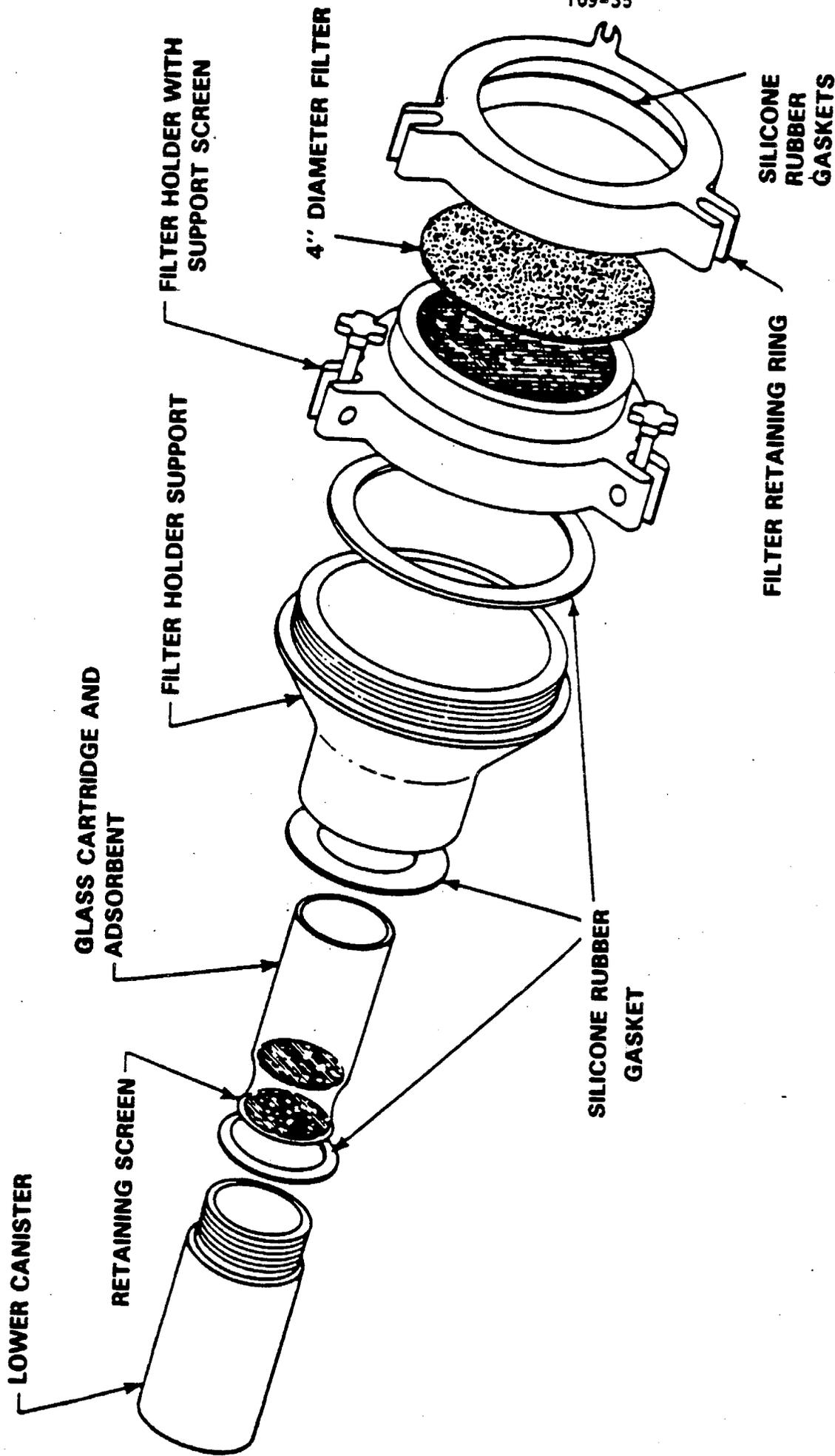
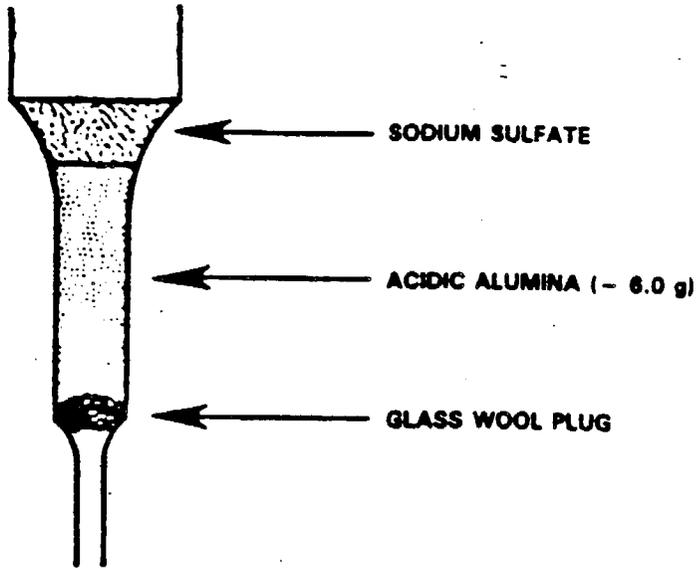
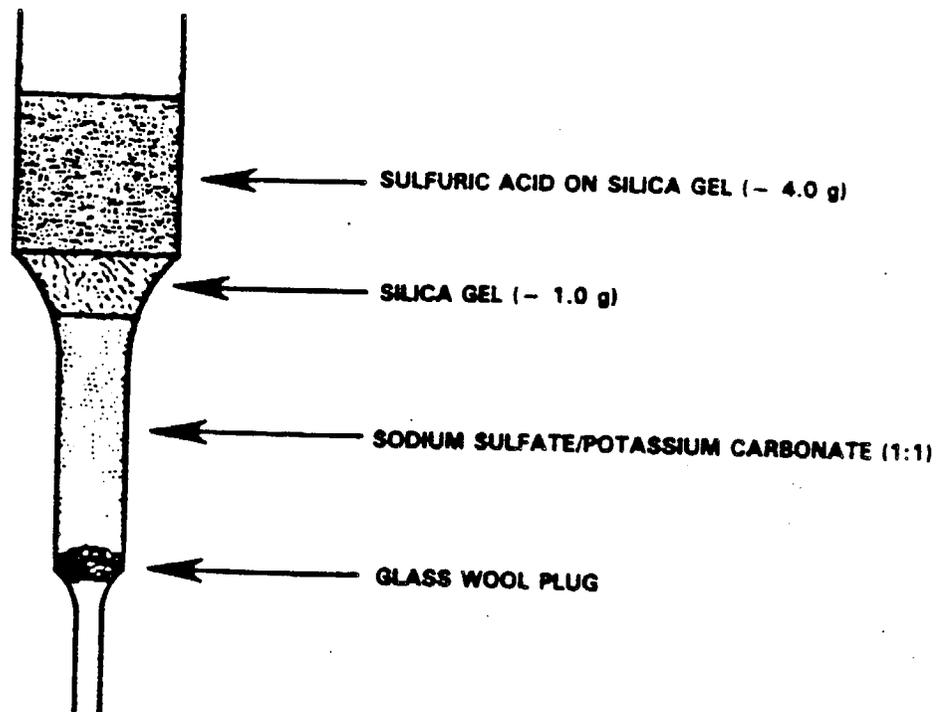


FIGURE 2. SAMPLING HEAD



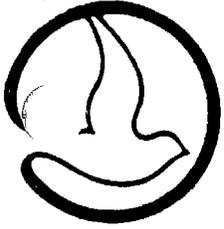
(a) ALUMINA COLUMN



(b) SILICA GEL COLUMN

FIGURE 4. MULTILAYERED EXTRACT CLEANUP COLUMNS

APPENDIX I
HOSPITAL AND WIRE RECLAMATION INCINERATORS
SCAQMD SOURCE INVENTORY



South Coast
AIR QUALITY MANAGEMENT DISTRICT

9150 FLAIR DRIVE, EL MONTE, CA 91731 (818) 572-6200

April 28, 1987

ERT
975 Business Center Circle
Newberry Park, CA 91320

Attn: Alan C. Lloyd

Subject: Incinerator Locations in the South Coast Air Basin

Ref: ERT letter, "same subject", dated April 22, 1987

Enclosed are the names and locations of hospital and wire reclamation incinerators in the South Coast Air Basin. The computer print-out category codes are identified as follows:

Category Code

Description

000182	Multi-chamber, with pathological retort
← 000190	Wire-insulation burner
00013X	Multi-chamber, retort
00014X	Multi-chamber, in line
00015X	Pathological
X	Incinerator Ratings
0.	0- 50 lbs/hr
1.	51- 100 lbs/hr
2.	101- 249 lbs/hr
3.	250- 349 lbs/hr
4.	350- 499 lbs/hr
5.	500- 749 lbs/hr
6.	750- 999 lbs/hr
7.	1,000-1,999 lbs/hr
8.	2,000-3,999 lbs/hr
9.	4,000+ lbs/hr

ERT

-2-

April 28, 1987

An invoice of \$363.99 for services will be mailed to you under separate cover. If you have any questions, please contact Mr. Louis D. Yuhas at (818) 572-6132.

Very truly yours,

William J. Dennison
Acting Director of Engineering

Louis D. Yuhas
Louis D. Yuhas
Acting Supervising A.Q. Engineer

LDY:et

Enclosure

cc: W. Dennison
W. Zwiacher

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
EQUIPMENT 00013XX,00014X,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
010905	AEROJET ORG & MFG CO	END OF PIPE LINE AVE	CHINO	91710	000140 000140
024905	ALTA VISTA CONVALESCENT HOSP	9020 GARFIELD	RIVERSIDE	92503	000151
045864	ANGELS REST PET CEMETERY & CREMATORY, OBA	18247 COLLIER AVE	LAKE ELSINORE	92330	000150
006472	ANTELOPE VALLEY UNION HI SCH DIST	44900 ND. DIVISION STREET	LANCASTER	93534	000134
007528	ARMEC DEFENSE PRUD. INC, DIV CRITTON	85-901 AV 53	COACHELLA	92236	000141
021372	ARTESIA HI SCH	1210R DEL AMU BLVD.	LAKEMOOD	90701	000132
025273	BARLOW HOSP	2000 STADIUM WAY	LUS ANGELES	90026	000134
024505	BEAR VALLEY COMM HOSP DIST	41870 GARSTIN DRIVE	BIG BEAR LAKE	92315	000152
012129	BEVERLY HOSP	309 W. BEVERLY BLVD.	MUNTEBELLO	90641	000133
009063	BEVERLY MANOR CONVALESCENT HOSPITAL	4768 PALM AVE.	RIVERSIDE	92501	000151
010833	BURNS INC	PLANT ENG DEPT	RIVERSIDE	92507	000145
020364	BOY SCOUTS OF AMERICA-CAMP TAHQUITZ	STAR RT. BOX 1	ANGELUS OAKS	90807	000134
011437	BROADVIEW SANITARIUM	4570 GRIFFIN AVE.	LOS ANGELES	90031	000130
009672	BURBANK COMM HOSP	466 EAST OLIVE AVE	BURBANK	91501	000130
011772	CARRILLO LAINE SCH	20122 CARRILLO LANE	CERRITOS	90701	000133
003823	CAL MEDICAL CTR - LOS ANGELES	1414 S. HOPE ST.	LOS ANGELES	90015	000182
008522	CAL NURSING & REHAB CTR OF PALM SPRINGS	2299 W INDIAN AV	PALM SPRINGS	92262	000150

04/25/87

PAGE 2

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
024620	CAL PEY CREMATORY	9595 GLENDAKS BLVD	SUN VALLEY	91352	000131
002961	CAL ST COL, DOMINGUEZ HILLS	1000 EAST VICTORIA ST.	DOMINGUEZ HILLS	90247	000150
015507	CAL ST UNIV FULLERTON	800 N STATE COLLEGE BL	FULLERTON	92631	000151
024006	CAL ST UNIV LA	5151 STATE UNIVERSITY DR.	LOS ANGELES	90032	000151
004565	CAL ST UNIV NORTHRIDGE	18111 NORDHUFF STREET	NORTHRIDGE	91324	000151
023043	CAL ST UNIV, SAN BERN	5500 STATE UNIVERSITY PKWY	SAN BERNARDINO	92407	000150
015840	CAL ST, FRANK D. LANTERMAN ST HOSP	3530 W. POMONA BLVD.	POMONA	91766	000150
004351	CAL ST, POLYTECHNIC UNIV	3801 W. TEMPLE AVE.	POMONA	91766	000150
020170	CAL-MODE FURNITURE MFG CO	9909 JEFFERSON BLVD.	CULVER CITY	90230	000133
002154	CAREHOUSE CONVALESCENT HOME	1800 N. OLD TUSTIN AVE.	SANTA ANA	92701	000130
020156	CARMELA SCH	13300 LAKELAND RD.	WHITTIER	90605	000133
011464	CASA COLINA HOSP FOR REHABILITATIVE MED	255 E. BONITA AVE.	POMONA	91767	000132
016389	CEDARS-SINAI MEDICAL CTR	6700 ALDEN DRIVE	LOS ANGELES	90039	000182
036792	CENTRALAB INC	4561 COLORADO BLVD	LOS ANGELES	90039	000132
000104	CERES AV SCH	10621 S. CERES AVE.	WHITTIER	90604	000133
010685	CHILDREN'S HOSP OF LA	4614 SUNSET HLVD.	LOS ANGELES	90027	52
044460	CHP AN HOSP MEDICAL CTR	2224 RUBY DR	PERRIS	92370	000150

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,000162,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
018001	CHURCH OF JESUS CHRIST LATTER DAY SAINTS	10777 SANTA MONICA BLVD.	LOS ANGELES	90025	000133
017914	CIGNA	1711 TEMPLE ST	LOS ANGELES	90026	000150
000662	CITY OF HOPE MED CTR	2104 HUENA VISTA ST.	DUARTE	91010	000152
023194	CITY OF HOPE MED CTR	1500 DUARTE ROAD	DUARTE	91010	000135
001132	CITY VIEW HOSP	3711 BALDWIN ST.	LOS ANGELES	90031	000131
014156	CLOVERLEAF HEALTH CARE	275 NORTH SAN JACINTO STREET	HEMET	92343	000150
018930	COACHELLA VALLEY UNI SCH DIST WESTSIDE	82-225 AIRPORT BL.	THERMAL	92274	000132
021736	COACHELLA VALLEY UNI SCH DIST, JOHN KELL	87-163 CENTER ST.	THERMAL	92274	000132
023764	COMM CONVALESCENT HOSP	4070 JUNUPA AVE.	RIVERSIDE	92506	000140
002732	COMMERCIAL ELECTRIC MOTORS INC	1101 MERIDIAN AV	ALHAMBRA	91803	000190
019970	COMPRESSOR PARTS & REPAIR INC	1501 NO. PECK RD.	SOUTH EL MONTE	91733	000190
009001	CONRAC CORP, SYS WEST DIV	1700 SO. MOUNTAIN AV.	DUARTE	91010	000131
009561	CORDONA ELECTRIC MOTORS,BILL MARKET D&A	1781 CAPITAL ST. UNIT 1	CORDONA	91720	000190
017133	CRESTVIEW CONVALESCENT HOSP	1471 RIVERSIDE	RIALTO	92376	000130
013961	DAPPLE GRAY SCH	3011 N. PALOS VERDES DR.	ROLLING HILLS	90274	000133
055548	DESERT MOTOR REPAIR, JOSE G RUIZ	84191 INDIO BLVD	INDIO	92201	000190
023091	DOCTORS HOSP OF LAKEWOOD	3700 EAST SOUTH ST.	LAKEWOOD	90712	000151
009353	DON PERITO SCH	3700 DEJAIR ST.	PASADENA	91109	

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EQUIPMENT 00013XX,00014X,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
009792	EAST WHITTIER INTERMEDIATE SCH	14421 E WHITTIER BL	WHITTIER	90605	000132
917288	EL CAMINO COL	16007 S CRENSHAW BL	TORRANCE	90506	000134
025227	EL MONTE HI SCH	3048 TYLER AVE.	EL MONTE	91731	000150
012249	EL MONTE UNION HI SCH DIST	3537 N JOHNSON AV	EL MONTE	90731	000132
020697	ELLA P. MELBOURN ELEM SCH	21314 CLAREITA AV	LAKEMOOD	90715	000131
016675	EMERSON ELECTRIC CO, INDUSTRIAL SERV DIV	1988A QUIROZ CT	WALNUT	91789	000133
014365	ESTHER WALTER SCH	10802 RUSTIC LN	ANAHEIM	92804	000190
021852	EXTENDED CARE HOSP OF RIVERSIDE INC	8171 MAGNOLIA AV	RIVERSIDE	92504	000143
004867	FAYE ROSS SCH	17707 S ELAINE AV	ARTESIA	90701	000150
017323	FOREST LAWN CO, SUNNYSIDE MORTUARY O&A	4725 CHERRY AV	LUNG BEACH	91205	000133
022165	FOREST LAWN MEM PARK ASSOC	21300 VIA VERDE RD	COVINA	91723	000141 000141 000141 000141
122465	FOREST LAWN MEM PARK ASSOC	1712 S GLENDALE AV	GLENDALE	91209	000130 000151
014449	FRANKEL IRON & METAL CU	15615 AMRON HWY	FONTANA	92335	000152 000152
024007	FUKUJ MORTUARY INC	707 E. TEMPLE	LOS ANGELES	90012	000190 000190
017627	GARF 'S' MEDICAL CTR	525 N GARFIELD AV	MONTEREY PARK	91754	000130

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SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,000162,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
005002	GATEWAYS HOSP	1891 EFFIE ST.	LOS ANGELES	90026	000133
012528	GEN VENEER MFG CO	8652 OTIS ST.	SOUTH GATE	90280	000147 000147
002124	GLENDALE ADVENTIST MEDICAL CTR	1509 WILSON TERRACE	GLENDALE	91206	000150
009682	GLENDALE MEMORIAL HOSPITAL & HEALTH CTR	1420 S. CENTRAL AVE.	GLENDALE	91204	000151
019353	GOLDEN WEST COL. COAST COMM COL DIST	15749 GOLDEN WEST ST.	HUNTINGTON BEACH	92621	000150
003523	GRANADA SCH	15337 E. LEMON DR.	WHITTIER	90605	000135
002155	GRAND VIEW MEM PARK	1341 GLENWOOD RD.	GLENDALE	91201	000152 000151 000152
022138	H. G. TULLY VETERINARY HOSP	11966 VENTURA BLVD.	STUDIO CITY	91604	000130
014882	HANDY & HARMAN	4140 GIBSON RD.	EL MONTE	91734	000141 000153
017329	HARBOR FURNITURE MFG CO INC	12508 CENTER ST	SOUTH GATE	90282	000153
013557	HARBOR LANN MEM PARK	1625 GISLER AVE.	COSTA MESA	92626	000182 000182 000182 000182
010441	HEMET CONVALESCENT HOSP	40300 DEVONSHIRE AV	HEMET	92343	000150
007714	HEMET ELECTRIC MOTOR SERV	141 SOUTH INEZ ST.	HEMET	92343	000190
011559	HILLHAVEN HIGHLAND HOUSE, HILLHAVEN INC	7534 PALM AVE.	HIGHLAND	92346	000141
019839	HOLLYWOOD PRESBYTERIAN MEDICAL CTR	1300 NORTH VERMONT AVE.	LOS ANGELES	90027	000151

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
EQUIPMENT 000154X,00014K,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
021001	HOME FURNITURE MFG CO	2330 SANTA ANA BLVD.	LOS ANGELES	90059	000134
016071	HUNTINGTON MEM HOSP	100 N. CONGRESS ST.	PASADENA	91105	000150
016448	INGLEWOOD ANIMAL HOSP INC	817 N. MANCHESTER BLVD.	INGLEWOOD	90301	000130
005156	INGLEWOOD PARK CEMETERY	720 E. FLORENCE AVE.	INGLEWOOD	90307	000154 000150
038264	INIL IMMUNOLOGY CORP	22549 ADAMS AV	MURRIETA	92362	000131
014361	JAMES L. RALPHS INC	49744 GURMAN POST RD.	GORMAN	93534	000135
004456	JEFFERSON ELEM SCH	4285 JEFFERSON STREET	RIVERSIDE	92501	000131
012156	JERSEY AV SCH	9400 S. JERSEY AVE.	SANTA FE SPRINGS	90670	000133
012732	JOHN F. KENNEDY MEM HOSP	47-111 MONROE ST	INDIO		000151
010218	JOHN F. KENNEDY SCH, ABC SCH DIST	17500 BELSHIRE AV	ARTESIA	90701	000133
012557	JOHN H. NIEMES SCH	16715 S. JERSEY AVE.	ARTESIA	90701	000133
011732	KAISER FONTANA HOSP	9961 SIERRA AV	FONTANA	92335	000150
022593	KATHERINE EDWARDS SCH	6012 S WOHWALK BL	WHITTIER	90606	000133
012648	KEIRO NURSING HOME INC	2221 LINCOLN PARK AV	LOS ANGELES	90031	000131
020910	LA CITY, CENTRAL MEDICAL CTR	1401 W SIXTH ST	LOS ANGELES	90017	000182
002984	LA CITY, GREATER LA ZOO	5333 ZOO DR	LOS ANGELES	90027	000182
008537	LA C. PUB WKS DEPT, BUREAU PUB BLDG	27234 BOUQUET CYN	SANJUAN	91405	000150

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SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
022390	LA CO., ADM. HEADQUARTERS, HEALTH DEPT	313 N FIGUEROA ST	LOS ANGELES	90012	000152
006556	LA CO., ANIMAL CONTROL DEPT	5210 W AV I	LANCASTER	93534	000150
014335	LA CO., BELLFLOWER HEALTH CTR	10005 E FLOWEN ST	BELLFLOWER	90706	000130
014317	LA CO., EL MONTE HEALTH CTR	3550 EASTMONT	EL MONTE	91731	000130
017326	LA CO., GLENDALE HEALTH CTR	501 N GLENDALE AV	GLENDALE	91206	000130
000457	LA CO., HARBOR GEN HOSP	1000 W CARSON ST	TORRANCE	90509	000150 000145
014026	LA CO., LA PUENTE HEALTH CTR	15930 CENTRAL AV	LA PUENTE	91746	000130
003093	LA CO., OLIVE VIEW MEDICAL CTR	14445 OLIVE VIEW DRIVE	SYLMAR		000151
067723	LA CO., POMONA HEALTH CTR	750 SOUTH PARK	POMONA	91766	000131
018753	LA CO., SHERIFF'S DEPT, CENTRAL JAIL	401 BAUCHET ST.	LOS ANGELES	90012	000130 000131
010686	LA CO., SOUTH DIST HEALTH CTR	1522 E 102 ST	LOS ANGELES	90002	000130
010134	LA CO., SYBIL BRAND INST FOR WOMEN	4500 E. CITY TERRACE DR	LOS ANGELES	90063	000150
020041	LA CO., TORRANCE HEALTH CTR	2300 WEST CARSON STREET	TORRANCE	90501	000130
020197	LA CO., UNIV SO CAL MEDICAL CTR	1200 N. STATE ST.	LOS ANGELES	90033	000150 000130
017904	LA COLIMA SCH	11225 SOUTH MILLER RD.	WHITTIER	90605	000133
010677	LA FEIRA SCH	547 W. BENNETT AVE.	GLENDALE	91740	000133
011445	LA MIRADA HI SCH, MAINT & OPER	13520 ADELFA UP.	LA MIRADA	90650	000133

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
000059	LA ODD FELLOWS CEMETERY ASSOC	3640 WHITTIER BLVD.	LOS ANGELES	90023	000133
011350	LA SIERRA CONVALESCENT HOSP	11162 PALM TERRACE LN.	RIVERSIDE	92505	000183 000152
023038	LINDA VALLEY CONVALESCENT HOSP	25383 COLE ST	LOMA LINDA	92354	000130
011433	LITTLEJOHN-REULAND CORP	4575 PACIFIC BLVD.	VERNON	90058	000130
001846	LOMA LINDA COMM HOSP	25333 BARTON RD	LOMA LINDA	92354	000190
001203	LOMA LINDA UNIV	POWER PLANT	LOMA LINDA	92350	000131
022770	LONG BEACH CITY, UNI SCH DIST,MAINT DEPT	151 E. 27TH ST.	LONG BEACH	90806	000135 000135
011427	LONG BEACH POLYTECHNIC HI SCH	16TH ST. & ATLANTIC AVE.	LONG BEACH	90813	000136
009118	LORO BADEN-POWELL SCH	2911 STONYBROOK DR	ANAHEIM	92804	000134
016057	LOS NIETOS SCH	11425 E. RIVERA RD.	LOS NIETOS	90606	000143
002020	LDYOLA MARYMOUNT UNIV	7101 W. 80TH STREET	LOS ANGELES	90045	000133
014626	MANUEL DOMINGUEZ HI SCH	15301 SAN JUSE AVE.	COMPTON	90221	000150
024277	MARSHALL SCHOOL	2627 CRESCENT AV	ANAHEIM	92804	000133
005648	MAXWELL SCH	2613 W ORANGE AV	ANAHEIM	92804	000143
000081	MEADONKOOK CONVALESCENT HOSP INC	401 E. JOHNSTON ST.	HEMET	92343	000144
018281	MONTE VISTA SCH	1615 ELJURED AVE.	WEST COVINA	91723	000150
022585	MOYER S	6313 MAYWOOD AVE	HUNTINGTON PARK	90256	001

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SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,00016Z,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
000189	MOUNTAIN VIEW CEMETERY	2400 N FAIR OAKS AV	ALTADENA	91001	000143
015952	MT. RUBIDOUX REHABILITATION HOSP	6401 33RD ST.	RIVERSIDE	92509	000151
005192	NORTH PARK JR HI SCH	4450 S. OURFEE AVE.	PICO RIVERA	90661	000151
014481	NORTHRIDGE JR HI SCH	17960 CHASE ST.	NORTHRIDGE	91324	000145
000561	NORWALK-LA MIRADA SCHOOL DIST	12820 PIONEER BLVD.	NORWALK	90650	000150
023790	PALMDALE MEM PARK	1401 S GRAND AV	GLENDORA	91740	000133
016812	OAKWOOD MEM PARK	22601 LASSEN ST.	CHATSWORTH	91311	000141
005930	OCEAN VIEW SCH	14359 E. 2ND ST.	WHITTIER	90605	000151
022678	PACUJIMA JR HI SCH	9919 LAUREL CANYON BL	PACUJIMA	91331	000133
024491	PALMDALE HI SCH	2137 E AV R	PALMDALE	93534	000133
052400	PAN METAL CORP	720 E 59TH ST	LOS ANGELES	19135	000134
705218	PARKVIEW COMM HOSP	3865 JACKSON ST	RIVERSIDE	92503	000190
024921	PARKVIEW HOSP	1514 E LINCOLN AV	ANANEIM	92805	000190
019430	PET HAVEN CEMETERY & CREMATORY	18300 S FIGUEROA ST	CARSON	90905	000152
009808	PILGRIM PINES	39570 OAK GLEN RD	YUCAIPA	92399	000182
002487	PIONEER HI SCH	10800 E BENAVIDA ST	WHITTIER	90606	000151
					000131
					000135

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
EQUIPMENT 00013XX,00014X,00015X,000182,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
042074	PRECIOUS METALS IND INC	120 S LINDEW AV	RIALTO	92376	000130
011508	PRESBYTERIAN INTER COMM HOSP INC	12401 E WASHINGTON HL	WHITTIER	90602	000134
023736	PYLES SCH	10411 S DALE	STANTON	92804	000143
017738	RAINBOW CANYON GOLF RESORT CORP	44-501 RAINBOW CANYON RD	TEMECULA	92590	000143
017045	RANCHO SANTA GERTRUDES SCH	11233 CHARLESWORTH RD	SANTA FE SPRINGS	90670	000133
023857	RESEDA HI SCH	18230 KITTRIDGE ST	RESEDA	91335	000135
003159	RIVERSIDE COMM HOSP	4445 MAGNOLIA AV	RIVERSIDE	92501	000145
013332	RIVERSIDE SCH DIST	8362 COLORADO AV	RIVERSIDE	92501	000131
017298	RIVERSIDE UNI SCH DIST, MT VIEW ELEM SCH	6180 STREETER AV	RIVERSIDE	92501	000133
014656	RIVERSIDE UNI SCH DIST, RAMONA HI SCH	7675 MAGNOLIA AV	RIVERSIDE	92501	000133
005008	ROSEN'S ELECTRICAL EQUIP CO INC	8226 E WHITTIER BL	PICO RIVERA	90661	000190 000190
015182	ROYAL OAKS SCH	2499 ROYAL OAKS DR	BRADBURY	91010	000132
013752	SALK SCH	1411 S GILBERT	ANAHEIM	92804	000144
014437	SAN ANTONIO COMMUNITY HOSP	999 SAN BERNARDINO	UPLAND	91786	000150
017724	SAN BEKY. CO., MEDICAL CTR	780 E GILBERT	SAN BERNARDINO	92404	000182
018451	SAN GORGONIO PASS MEM HOSP	600 N HIGHLAND SPRINGS AV	BANING	92220	000152 000152
022854	SAN ANICA HOSP MEDICAL CTR	1225 15TH ST	SANTA MONICA	90404	000150

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SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

EQUIPMENT 00013XX,00014X,00015X,00016Z,000190

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
005157	SAVANNAH SCH	3720 N MID HOUND AV	ROSEMEAD	91770	000133
009132	SCHWEITZER SCH	229 S DALE ST	ADAMS	92804	000143
009243	SIDNEY JAMES TERRANCE MEM HOSP	3330 LONITA BL	TERRANCE	90505	000151
009786	SIERRA EDUCATION CTR	9001 S FAIRIER AV	WHITTIER	90605	000135
012940	SIX-PAC RECYCLING CTR	14292 E 6TH ST	CORONA	91720	000190 000190
017181	SULHEIM LUTHERAN HOME	2236 MERTON AVE.	LUS ANGELES	90041	000133
001751	SOUTH COAST MEDICAL CTR	31872 COAST HIGHWAY	SOUTH LAGUNA	92677	000150
007939	SOUTH WHITTIER INTERMEDIATE SCH	13243 E. LOS NIETOS RD.	WHITTIER	90605	000133
012659	ST SALVAGE CO INC	22500 SO. ALAMEDA ST	CARSON	90810	000190
006324	ST. BERNARDINE HOSP	2101 N. WATERMAN AVE	SAN BERNARDINE	92404	000141
009220	ST. JOSEPHS HOSP & MEDICAL CTR	501 S. BUENA VISTA AVE.	BURBANK	91503	000151
024546	ST. JUDE HOSP AND REHAB. CTR	101 E VALENCIA MESA DR	FULLERTON	92631	000151
024964	ST. JUDES HOSP, YORBA LINDA	16650 GASTACHURRY RD.	YORBA LINDA	92635	000150
012646	STAUFFER CHEM CO UNIT LG. 2	20720 S WILMINGTON AV	CAPSON	90810	000150
024797	STUMP ELECTRIC CO INC	3414 E. 14TH ST.	LUS ANGELES	90023	000190
021096	SUN CITY REHABILITATION CTR	27600 ESCOBADO DRIVE	SUN CITY	92361	000150
025457	TEMPLE HOSP	255 N HOOVER ST	LUS ANGELES	90004	000182

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
EQUIPMENT 00013XX,00014X,00015X,000182,00019G

ID	COMPANY NAME	ADDRESS	CITY	ZIP	CATEGORY
003973	TYLER TROUPE	VARIOUS LOCATIONS IN SCAGMO		92692	000131
003103	UNIV CAL IRVINE MEDICAL CTR	101 CITY DR S	ORANGE	92668	000150
018452	UNIV CAL LA	405 HILGARD AV	LUS ANGELES	90024	000155
009670	UNIV CAL RIVERSIDE	STEAM PLANT-UCR	RIVERSIDE	92502	000153
000056	UNIV SO CAL, PHYSICAL PLANT DEPT	2011 ZONAL AV	LUS ANGELES	90007	000152 000153
005791	UNIV SO CAL, PHYSICAL PLANT DEPT	UNIVERSITY PARK	LOS ANGELES	90007	000152
005351	US GOVT, AF DEPT, MARCH AFB UNIT NU. 1	EAST OF HWY 395	MARCH AFB	92518	000162
018815	US GOVT, AF DEPT, HORTON AFB UNIT 1	63RD MILITARY AIRLIFT WING	HORTON AFB		000133 000133
003885	US GOVT, VETERANS ADM HOSP	11201 BENJUM ST	LOMA LINDA	92354	000152
005679	US GOVT, VETERANS ADM HOSP	16111 PLUMMER ST	SEPULVEDA	91383	000151
014956	US GOVT, VETERANS ADM HOSP, WADSWORTH	WILSHIRE & SANTELE	LOS ANGELES		000151 000151 000151
018800	VALLEY HOSP MEDICAL CTR, DIV HEALTH WEST	14500 SHERMAN CIR	VAN NUYS	91318	000162
006768	VERNON CITY, PUB WKS FAC	4305 S SANTA FE AV	VERNON	90058	000132
050098	WEST COAST FERTILIZER AND RENDERING CO	4105 BANDINGI BL	VERNON		000151
017046	WILLIAM W. URR SCH	12130 S JERSEY AV	NORWALK	90651	000132
007819	WRIGHT INTERMEDIATE SCH	12250 CIVIC CTR	NORWALK	90650	00

