# THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

## 1.0 SCOPE AND APPLICATION

1.1 This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in Appendix B.

## 2.0 SUMMARY OF THE METHOD

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

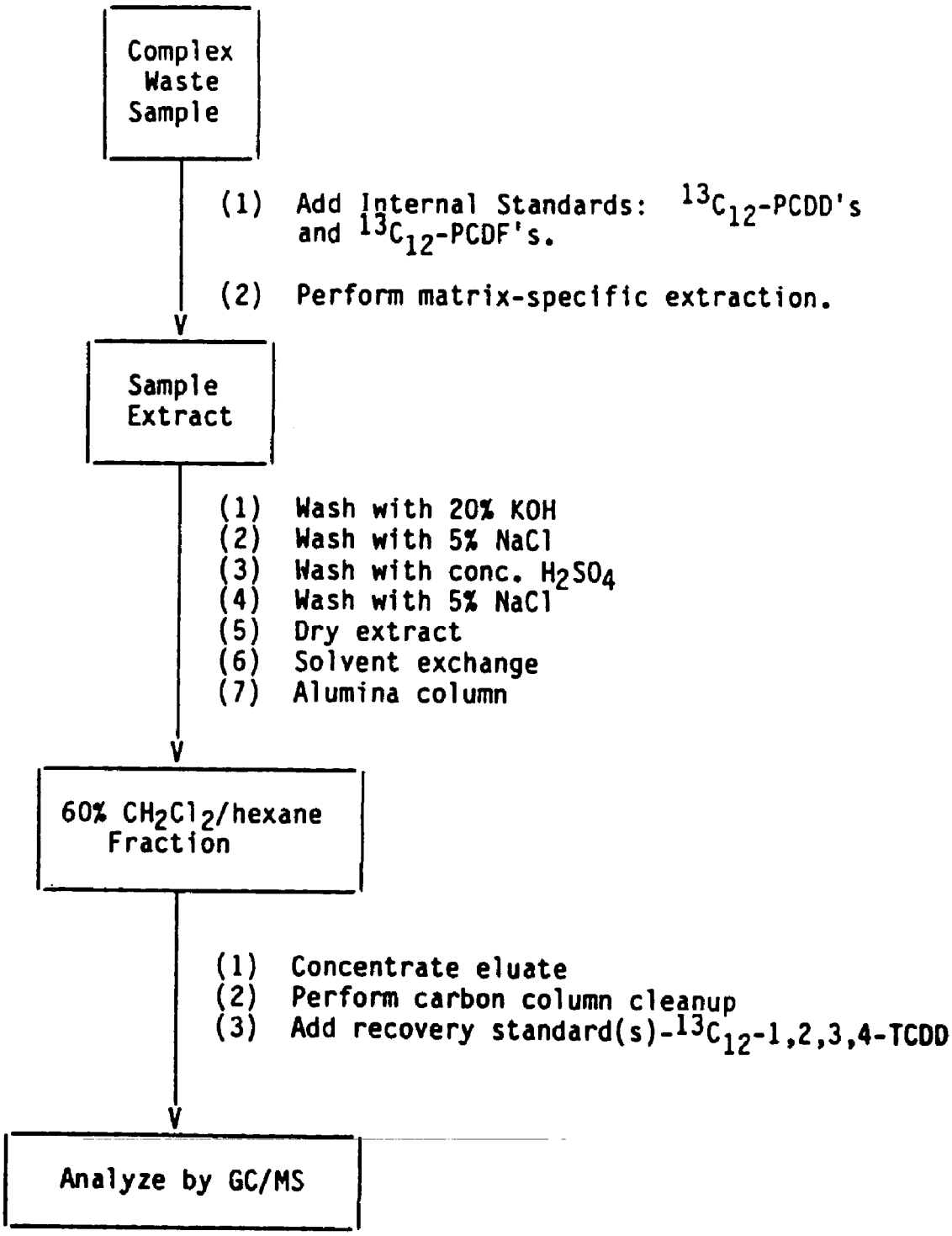


Figure 1. Method 8280 flow chart for sample extraction and cleanup as used for the analysis of PCDD's and PCDF's in complex waste samples.

## 3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 6-3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit (Section 11.6) stated in Table 8.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers.

3.5 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

## 4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling:

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottom.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control ($\pm$2°C). The bath should be used in a hood.

4.3 Gas chromatograph/mass spectrometer data system:

4.3.1 **Gas chromatograph:** An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, three columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 2,3,7,8-TCDD, 1,2,3,4,7 PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50-m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) DB-5 (30-m x 0.25-mm I.D.; 0.25-um film thickness) programmed 170° for 10 minutes, then 170°-320° at 8°/minute, hold at 320°C for 20 minutes; (c) 30-m SP-2250 programmed 70°-320° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) can also provide acceptable separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged, and may provide better separation from certain classes of interferents. Data presented in Figure 2 and Tables 1 to 8 of this Method were obtained using a DB-5 column with temperature programming described in (b) above. However, any capillary column which provides separation of 2,3,7,8-TCDD from all other TCDD isomers equivalent to that specified in Section 6.3 may be used; this separation must be demonstrated and documented using the performance test mixture described in Paragraph 6.3.

4.3.3 **Mass spectrometer:** A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms per m/z. The use of systems not capable of monitoring 11 ions simultaneously will require the analyst to make multiple injections.

4.3.4 **GC/MS interface:** Any GC-to-MS interface that gives an acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (see Paragraphs 6.1.-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.3.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot is

defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance, in any SICP, between specified time or scan number limits.

4.4 Pipets-Disposable, Pasteur, 150-mm long x 5-mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.4.1 Pipet, disposable, serological 10-mL (American Scientific Products No. P4644-10, or equivalent) for preparation of the carbon column specified in Paragraph 4.19.

4.5 Amber glass bottle (500-mL, Teflon-lined screw-cap).

4.6 Reacti-vial 2-mL, amber glass (Pierce Chemical Company). These should be silanized prior to use.

4.7 500-mL Erlenmeyer flask (American Scientific Products Cat. No. f4295 500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125-mL and 2-L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500-mL Kuderna-Danish fitted with a 10-mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300-mm x 10.5-mm glass chromatographic column fitted with Teflon stopcock.

4.13 15-mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen blowdown apparatus (N-Evap (reg. trademark) Analytical Evaporator Model 111, Organomation Associates Inc., Northborough, Massachusetts or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials 2.0-mL (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No. 54, or equivalent). Glass fiber filters or glass wool plugs are also recommended.

4.18 Solvent reservoir (125-mL) Kontes: (special order item) 12.5-cm diameter, compatible with gravity carbon column.

4.19 Carbon column (gravity flow): Prepare carbon/silica gel packing material by mixing 5 percent (by weight) active carbon AX-21 (Anderson Development Co., Adrain, Michigan), pre-washed with methanol and dried in vacuo at 110°C and 95 percent (by weight) Silica gel (Type 60, EM reagent 70 to 230 mesh, CMS No. 393-066) followed by activation of the mixture at 130° for 6 hr. Prepare a 10-mL disposable serological pipet by cutting off each end to achieve a 4-in. column. Fire polish both ends; flare if desired. Insert a glass-wool plug at one end and pack with 1 g of the carbon/silica gel mixture. Cap the packing with a glass-wool plug. (Attach reservoir to column for addition of solvents).

Option: Carbon column (HPLC): A silanized glass HPLC column (10 mm x 7 cm), or equivalent, which contains 1 g of a packing prepared by mixing 5 percent (by weight) active carbon AX-21, (Anderson Development Co., Adrian, Michigan), washed with methanol and dried in vacuo at 110°C, and 95 percent (by weight) 10 um silica (Spherisorb S10W from Phase Separations, Inc., Norwalk, Connecticut). The mixture must then be stirred and sieved through a 38-um screen (U.S. Sieve Designation 400-mesh, American Scientific Products, No. S1212-400, or equivalent) to remove any clumps.[1]

4.20 HPLC pump with loop valve (1.0 mL) injector to be used in the optional carbon column cleanup procedure.

4.21 Dean-Stark trap, 5- or 10-mL with T joints, (Fisher Scientific Company, No. 09-146-5, or equivalent) condenser and 125-mL flask.

4.22 Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915; or equivalent.).

4.23 Roto-evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10; or equivalent.

5.0 REAGENTS

5.1 Potassium hydroxide (ASC): 20 percent (w/v) in distilled water.

5.2 Sulfuric acid (ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tridecane, isooctane, toluene, cyclohexane. Distilled in glass or highest available purity.

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions (50 ppm) are stored in the dark at 4°C, and checked frequently for signs of degradation or evaporation, especially just prior to the preparation of working standards.

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1 The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade): Extracted by manual shaking with several portions of hexane and dried at 100°C.

5.8 Sodium chloride - (analytical reagent), 5 percent (w/v) in distilled water.

6.0 CALIBRATION

6.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, routine calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/mL (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraphs 6.3 and 6.6 is demonstrated and documented.

6.2 Initial calibration:

6.2.1 Prepare multi-level calibration standards[2] keeping one of the recovery standards and the internal standard at fixed concentrations (500 ng/mL). Additional internal standards ($^{13}C_{12}$-OCDD 1,000 ng/mL) are recommended when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Each calibration standard should contain the following compounds:

| | | |
|---|---|---|
| 2,3,7,8-TCDD, | | |
| 1,2,3,7,8-PeCDD | or any available | 2,3,7,8,X-PeCDD isomer, |
| 1,2,3,4,7,8-HxCDD | or any available | 2,3,7,8,X,Y-HxCDD isomer, |
| 1,2,3,4,6,7,8-HpCDD | or any available | 2,3,7,8,X,Y,Z-HpCDD isomer, |
| | | |
| 2,3,7,8-TCDF | | |
| 1,2,3,7,8,PeCDF | or any available | 2,3,7,8,X-PeCDF isomer, |
| 1,2,3,4,7,8-HxCDF | or any available | 2,3,7,8,X,Y,HxCDF isomer, |
| 1,2,3,4,6,7,8-HpCDF | or any available | 2,3,7,8,X,Y,Z-HpCDF isomer, |

OCDD, OCDF, $^{13}C_{12}$-2,3,7,8,-TCDD, $_{13}C_{12}$-1,2,3,4-TCDD and $_{13}C_{12}$-OCDD.

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2 $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper quantification requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution.

Recommended concentration levels for standard analytes are 200, 500, 1,000, 2,000, and 5,000 ng/mL. These values may be adjusted in order to insure that the analyte concentration falls within the calibration range. Two uL injections of calibration standards should be made. However, some GC/MS instruments may require the use of a 1-uL injection volume; if this injection volume is used then all injections of standards, sample extracts and blank extracts must also be made at this injection volume. Calculation of relative response factors is described in Paragraph 11.1.2. Standards must be analyzed using the same solvent as used in the final sample extract. A wider calibration range is useful for higher level samples provided it can be described within the linear range of the method, and the identification criteria defined in Paragraph 10.4 are met. All standards must be stored in an isolated refrigerator at 4°C and protected from light. Calibration standard solutions must be replaced routinely after six months.

6.3 Establish operating parameters for the GC/MS system; the instrument should be tuned to meet the isotopic ratio criteria listed in Table 3 for PCDD's and PCDF's. Once tuning and mass calibration procedures have been completed, a column performance check mixture[3] containing the isomers listed below should be injected into the GC/MS system:

| | |
|---|---|
| TCDD | 1,3,6,8; 1,2,8,9; 2,3,7,8; 1,2,3,4; 1,2,3,7; 1,2,3,9 |
| PeCDD | 1,2,4,6,8; 1,2,3,8,9 |
| HxCDD | 1,2,3,4,6,9; 1,2,3,4,6,7 |
| HpCDD | 1,2,3,4,6,7,8; 1,2,3,4,6,7,9 |
| OCDD | 1,2,3,4,6,7,8,9 |
| | |
| TCDF | 1,3,6,8; 1,2,8,9 |
| PeCDF | 1,3,4,6,8; 1,2,3,8,9 |
| HxCDF | 1,2,3,4,6,8; 1,2,3,4,8,9 |
| HpCDF | 1,2,3,4,6,7,8; 1,2,3,4,7,8,9 |
| OCDF | 1,2,3,4,6,7,8,9 |

Because of the known overlap between the late-eluting tetra-isomers and the early-eluting penta-isomers under certain column conditions, it may be necessary to perform two injections to define the TCDD/TCDF and PeCDD/PeCDF elution windows, respectively. Use of this performance check mixture will enable the following parameters to be checked: (a) the retention windows for each of the homologues, (b) the GC resolution of 2,3,7,8-TCDD and 1,2,3,4-TCDD, and (c) the relative ion abundance criteria listed for PCDD's and PCDF's in Table 3. GC column performance should be checked daily for resolution and peak shape using this check mixture.

The chromatographic peak separation between 2,3,7,8-TCDD and 1,2,3,4-TCDD must be resolved with a valley of $\leq$25 percent, where

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

x = measured as in Figure 2
y = the peak height of 2,3,7,8-TCDD

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3 Performance check mixtures are available from Brehm Laboratory, Wright State University, Dayton, Ohio.

It is the responsibility of the laboratory to verify the conditions suitable for maximum resolution of 2,3,7,8-TCDD from all other TCDD isomers. The peak representing 2,3,7,8-TCDD should be labeled and identified as such on all chromatograms.

6.4 Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard.

6.5 From injections of the 5 calibration standards, calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described in Paragraph 11.1.2. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

6.6 For each analyte calculate the mean relative response factor (RRF), the standard deviation, and the percent relative standard deviation from triplicate determinations of relative response factors for each calibration standard solution.

6.7 The percent relative standard deviations (based on triplicate analysis) of the relative response factors for each calibration standard solution should not exceed 15 percent. If this condition is not satisfied, remedial action should be taken.

6.8 The Laboratory must not proceed with analysis of samples before determining and documenting acceptable calibration with the criteria specified in Paragraphs 6.3 and 6.7.

6.9 Routine calibration:

6.9.1 Inject a 2-uL aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of a 12 hr period. If the contractor laboratory operates during consecutive 12-hr periods (shifts), analysis of the performance check solution at the beginning of each 12-hr period and at the end of the final 12-hr period is sufficient.

Determine and document acceptable column performance as described in Paragraph 6.3.

6.9.2 Inject a 2-uL aliquot of the calibration standard solution at 500 ng/mL at the beginning of a 2-hr period. Determine and document acceptable calibration as specified in Paragraph 6.3, i.e., SIM sensitivity and relative ion abundance criteria. The measured RRF's of

all analytes must be within ±30 percent of the mean values established by initial analyses of the calibration standard solutions.

## 7.0 QUALITY CONTROL

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

7.2 A laboratory "method blank" must be run along with each analytical batch (20 or fewer samples). A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a sample. The method blank is also dosed with the internal standards. For water samples, one liter of deionized and/or distilled water should be used as the method blank. Mineral oil may be used as the method blank for other matrices.

7.3 The laboratory will be expected to analyze performance evaluation samples as provided by the EPA on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and acceptable performance must be demonstrated before sample analyses can resume.

7.4 Samples may be split with other participating labs on a periodic basis to ensure interlaboratory consistency. At least one sample per set of 24 must be run in duplicate to determine intralaboratory precision.

7.5 Field duplicates (individual samples taken from the same location at the same time) should be analyzed periodically to determine the total precision (field and lab).

7.6 Where appropriate, "field blanks" will be provided to monitor for possible cross-contamination of samples in the field. The typical "field blank" will consist of uncontaminated soil (background soil taken off-site).

7.7 GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hr period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

7.8 Before using any cleanup procedure, the analyst must process a series of calibration standards (Paragraph 6.2) through the procedure to validate elution patterns and the absence of interferents from reagents. Both alumina column and carbon column performance must be checked. Routinely check the 8 percent $CH_2C1_2$/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

NOTE: This fraction is intended to contain a high level of interferents and analysis near the method detection limit may not be possible.

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 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. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing, other potential sources of contamination which may absorb the target analytes.

8.2 All samples must be stored at 4°C, extracted within 30 days and completely analyzed within 45 days of collection.

## 9.0 EXTRACTION AND CLEANUP PROCEDURES

9.1 Internal standard addition. Use a sample aliquot of 1 g to 1,000 mL (typical sample size requirements for each type of matrix are provided in Paragraph 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and any other material which is to be used as an internal standard, (Paragraph 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give a concentration of 500 ng/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 uL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, assuming 100% recovery. Adoption of different calibration solution sets (as needed to achieve different quantification limits for different congeners) will require a change in the fortification level. Individual concentration levels for each homologous series must be specified.

9.2 Extraction

9.2.1 **Sludge/fuel oil.** Extract aqueous sludge samples by refluxing a sample (e.g. 2 g) with 50 mL of toluene (benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100-mL round bottom flask. Rinse the filter with 10 mL of toluene, combine the extract and rinsate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.4.

9.2.2 **Still bottom.** Extract still bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (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. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.2.4.

9.2.3 **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 (benzene) and extract for 16 hr using a three cycle/hour schedule. Cool and filter the toluene extract through a glass fiber filter paper into a 500-mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with Step 9.2.4.

9.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5-mL aliquots of hexane and add the rinses to the funnel. Shake 2 min with 50 mL of 5% NaCl solution, discard the aqueous layer and proceed with Step 9.3.

9.2.5 **Soil.** Extract soil samples by placing the sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether, in that order, to the flask. Shake on a wrist-action shaker for two hr. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Paragraph 9.2.5 through a glass funnel fitted with a glass fiber filter and filled with anhydrous sodium sulfate into a 500-mL Kuderna-Danish (KD) concentrator fitted with a 10-mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional 50-mL aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional 5-mL portions of petroleum ether.

9.2.5.2 Add a Teflon or PFTE 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 min.

9.2.5.3 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 min.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two 1-mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125-mL separatory funnel. Rinse the KD with two additional 5-mL portions of hexane, combine. Proceed with Step 9.3.

9.2.6 **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 Step 9.2.6.1.

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 using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 sec 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 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.2.6.1 and 9.2.6.2. Proceed with Paragraph 9.2.6.3.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. 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 (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (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.

9.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. 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 K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Paragraph 9.3.

9.3 In a 250-mL Separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 min.

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/PCDF's, contact time must be minimized.

9.4 Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard aqueous layer (bottom).
NOTE: Care should be taken due to the heat of neutralization and hydration.

9.5 Partition the solvent (15 mL hexane) against 40 mL of concentrated sulfuric acid. Shake for 2 min. Remove and discard 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.)

9.6 Partition the extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. 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 the separatory funnel with two 15-mL portions of hexane, pour through the funnel, and combine the hexane extracts. 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 blowdown with an inert gas to concentrate the extract is also permitted).

9.7 Pack a gravity column (glass 300-mm x 10.5-mm), fitted with a Teflon 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 super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but 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 prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present discard the column. Do not tap a wetted column.

9.8 Dissolve the residue from Step 9.6 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.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. Check by GC/MS analysis that no PCDD's or PCDF's are eluted in this fraction. See Paragraph 9.9.1.

9.8.2 Elute the PCDD's and PCDF's 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.

9.9 Carbon column cleanup:

Prepare a carbon column as described in Paragraph 4.18.

9.9.1 Using a carefully regulated stream of nitrogen (Paragraph 4.15), concentrate the 8 percent fraction from the alumina column (Paragraph 9.8.1) to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDD's and PCDF's. Concentrate the 60 percent fraction (Paragraph 9.8.2) to about 2 to 3 mL. Rinse the carbon 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, 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 (this 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.

9.9.2 **Alternate carbon column cleanup.** Proceed as in Section 9.9.1 to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to an HPLC injector loop (1 mL). The injector loop is connected to the optional column described in Paragraph 4.18. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column. Elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/ methylene chloride 1:1 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is then discarded and 30 mL of cyclohexane/ methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0-mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of $N_2$. The final volume should be 100 uL for soil samples and 500 uL for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial (Paragraph 4.16). Add to this sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 uL aliquot of extract and 4 uL of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 uL) of the sample into the GC/MS instrument.

10.0 GC/MS ANALYSIS

10.1 When toluene is employed as the final solvent use of a bonded phase column from Paragraph 4.3.2 is recommended. Solvent exchange into tridecane is required for other liquid phases or nonbonded columns (CP-Sil-88).

NOTE: Chromatographic conditions must be adjusted to account for solvent boiling points.

10.2 Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8,-TCDD and $^{13}C_{12}$-OCDD (see Section 11). Add the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) to the samples prior to injection. The oncentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring, using all of the ions listed in Table 2. It is recommended that the GC/MS run be divided into five selected ion monitoring sections, namely: (1) 243, 257, 304, 306, 320, 322, 332, 334, 340, 356, 376 (TCDD's, TCDF's, $^{13}C_{12}$-labeled internal and recovery standards, PeCDD's, PeCDF's, HxCDE); (2) 277, 293, 306, 332, 338, 340, 342, 354, 356, 358, 410 (peCDD's, PeCDF's, HpCDE); (3) 311, 327, 340, 356, 372, 374, 376, 388, 390, 392, 446, (HxCDD's, HxCDF's, OCDE); (4) 345, 361, 374, 390, 406, 408, 410, 422, 424, 426, 480 (HpCDD's, HpCDF's, NCDE) and (5) 379, 395, 408, 424, 442, 444, 458, 460, 470, 472, 514 (OCDD, OCDF, $^{13}C_{12}$-OCDD, DCDE). Cycle time not to exceed 1 sec/descriptor. It is recommended that selected ion monitoring section 1 should be applied during the GC run to encompass the retention window (determined in Paragraph 6.3) of the first- and last-eluting tetra-chlorinated isomers. If a response is observed at m/z 340 or 356, then the GC/MS analysis must be repeated; selected ion monitoring section 2 should then be applied to encompass the retention window of the first- and last-eluting penta-chlorinated isomers. HxCDE, HpCDE, OCDE, NCDE, DCDE, are abbreviations for hexa-, hepta-, octa-, nona-, and decachlorinated diphenyl ether, respectively.

10.4 Identification criteria for PCDD's and PCDF's:

10.4.1 All of the characteristic ions, i.e. quantitation ion, confirmation ions, listed in Table 2 for each class of PCDD and PCDF, must be present in the reconstructed ion chromatogram. It is desirable that the M - COCl ion be monitored as an additional requirement. Detection limits will be based on quantitation ions within the molecules in cluster.

10.4.2 The maximum intensity of each of the specified characteristic ions must coincide within 2 scans or 2 sec.

10.4.3 The relative intensity of the selected, isotopic ions within the molecular ion cluster of a homologous series of PCDD's of PCDF's must lie within the range specified in Table 3.

10.4.4 The GC peaks assigned to a given homologous series must have retention times within the window established for that series by the column performance solution.

10.5 Quantitate the PCDD and PCDF peaks from the response relative to the appropriate internal standard. Recovery of each internal standard) vs. the recovery standard must be greater than 40 percent. It is recommended that samples with recoveries of less than 40 percent or greater than 120 percent be re-extracted and re-analyzed.

NOTE: These criteria are used to assess method performance; when properly applied, isotope dilution techniques are independent of internal standard recovery.

In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

## 11.0 CALCULATIONS

NOTE: The relative response factors of a given congener within any homologous series are known to be different. However, for purposes of these calculations, it will be assumed that every congener within a given series has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, a 2,3,7,8-substituted isomer that is commercially available was chosen as representative of each series. All relative response factor calculations for a given homologous series are based on that compound.

11.1 Determine the concentration of individual isomers of tetra-, penta, and hexa-CDD/CDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

$Q_{is}$ = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

$A_s$ = area of quantitation ion of the compound of interest.

$A_{is}$ = area of quantitation ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.1 Determine the concentration of individual isomers of hepta-CDD/CDF and the concentration of OCDD and OCDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

$Q_{is}$ = ng of internal standard $^{13}C_{12}$-OCDD, added to the sample before extraction.

G = g of sample extracted.

$A_S$ = area of quantitation ion of the compound of interest.

$A_{is}$ = area of quantitation ion (m/z 472) of the internal standard, $^{13}C_{12}$-OCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 472 of $^{13}C_{12}$-OCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.2 Relative response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

$A_S$ = area of quantitation ion of the compound of interest.

$A_{is}$ = area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

$C_{is}$ = concentration of the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD).

$C_S$ = concentration of the compound of interest.

11.1.3 The concentrations of unknown isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer.

The concentrations of unknown isomers of HxCDD shall be calculated using the mean RRF determined for 1,2,3,4,7,8-HxCDD or any available 2,3,7,8,-X,Y-HXCDD isomer.

The concentrations of unknown isomers of HpCDD shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer.

The concentrations of unknown isomers of TCDF shall be calculated using the mean RRF determined for 2,3,7,8-TCDF.

The concentrations of unknown isomers of PeCDF shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer.

The concentrations of unknown isomers of HxCDF shall be calculated using the mean RRF determined for 1,2,4,7,8-HxCDF or any available 2,3,7,8-X,Y-HxCDF isomer.

The concentrations of unknown isomers of HpCDF shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer.

The concentration of the octa-CDD and octa-CDF shall be calculated using the mean RRF determined for each.

Mean relative response factors for selected PCDD's and PCDF's are given in Table 4.

11.1.4 Calculate the percent recovery, $R_{is}$, for each internal standard in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_{r} \times Q_{is}} = 100\%$$

where:

$A_{rs}$ = Area of quantitation ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

$Q_{rs}$ = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_{r} = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

where:

$C_{rs}$ = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.1.5 Calculation of total concentration of all isomers within each homologous series of PCDD's and PCDF's.

Total concentration of PCDD's or PCDF's = Sum of the concentrations of the individual PCDD or PCDF isomers

11.4 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.5 Accuracy and Precision. Table 5 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 6 lists recovery data for the same analyses. Table 2 shows the linear range and variation of response factors for selected analyte standards. Table 8 provides the method detection limits as measured in specific sample matrices.

11.6 Method Detection Limit. The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The procedure used to determine the MDL values reported in Table 8 was obtained from Appendix A of EPA Test Methods manual, EPA-600/4-82-057 July 1982, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater."

11.7 Maximum Holding Time (MHT). Is that time at which a 10 percent change in the analyte concentration ($C_{t10}$) occurs and the precision of the method of measurement allows the 10 percent change to be statistically different from the 0 percent change ($C_{t0}$) at the 90 percent confidence level. When the precision of the method is not sufficient to statistically discriminate a 10 percent change in the concentration from 0 percent change, then the maximum holding time is that time where the percent change in the analyte concentration ($C_{tn}$) is statistically different than the concentration at 0 percent change ($C_{t0}$) and greater than 10 percent change at the 90 percent confidence level.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

| Analyte | 50-m CP-Sil-88 | 30-m DB-5 | 3--m SP-2250 |
|---|---|---|---|
| 2,3,7,8-TCDF | 25.2 | 17.8 | 26.7 |
| 2,3,7,8-TCDD | 23.6 | 17.4 | 26.7 |
| 1,2,3,4-TCDD | 24.1 | 17.3 | 26.5 |
| 1,2,3,4,7-PeCDD | 30.0 | 20.1 | 28.1 |
| 1,2,3,4,7,8-HxCDD | 39.5 | 22.1 | 30.6 |
| 1,2,3,4,6,7,8-HpCDD | 57.0 | 24.1 | 33.7 |
| OCDD | NM | 25.6 | NM |

*Retention time in min, using temperature programs shown below.

NM = not measured.

Temperature Programs:

| | |
|---|---|
| CP-Sil-88 | 60°C-190°C at 20°/min; 190°-240° at 5°/min. |
| DB-5<br>30 m x 0.25 mm<br>Thin film (0.25 um) | 170°, 10 min; then at 8°/min to 320°C, hold at 320°C 20 min (until OCDD elutes). |
| SP-2250 | 70°-320° at 10°/minute. |

Column Manufacturers

| | |
|---|---|
| CP-Sil-88 | Chrompack, Incorporated, Bridgewater, New Jersey |
| DB-5, | J and W Scientific, Incorporated, Rancho Cordova, California |
| SP-2250 | Supelco, Incorporated, Bellefonte, Pennsylvania |

TABLE 2. IONS SPECIFIED[a] FOR SELECTED ION MONITORING FOR PCDD'S AND PCDF'S

| | Quantitation ion | Confirmation ions | M-COC1 |
|---|---|---|---|
| PCDD's | | | |
| $^{13}C_{12}$-Tetra | 334 | 332 | --- |
| Tetra | 322 | 320 | 257 |
| Penta | 356 | 354;358 | 293 |
| Hexa | 390 | 388;392 | 327 |
| Hepta | 424 | 422;426 | 361 |
| Octa | 460 | 458 | 395 |
| $^{13}C_{12}$-Octa | 472 | 470 | |
| PCDF's | | | |
| Tetra | 306 | 304 | 243 |
| Penta | 340 | 338;342 | 277 |
| Hexa | 374 | 372;376 | 311 |
| Hepta | 408 | 406;410 | 345 |
| Octa | 444 | 442 | 379 |

[a]Ions at m/z 376 (HxCDE), 410 (HpCDE), 446 (OCDE), 480 (NCDE) and 514 (DCDE) are also included in the scan monitoring sections (1) to (5), respectively. See Paragraph 10.3.

TABLE 3. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDD'S AND PCDF'S

| | Selected ions (m/z) | Relative intensity |
|---|---|---|
| PCDD's | | |
| Tetra | 320/322 | 0.65-0.89 |
| Penta | 358/356 | 0.55-0.75 |
| Hexa | 392/390 | 0.69-0.93 |
| Hepta | 426/424 | 0.83-1.12 |
| Octa | 458/460 | 0.75-1.01 |
| PCDF's | | |
| Tetra | 304/306 | 0.65-0.89 |
| Penta | 342/340 | 0.55-0.75 |
| Hexa | 376/374 | 0.69-0.93 |
| Hepta | 410/408 | 0.83-1.12 |
| Octa | 442/444 | 0.75-1.01 |

TABLE 4. MEAN RELATIVE RESPONSE FACTORS OF CALIBRATION STANDARDS

| Analyte | RRF[a] | RSD% (n = 5) | Quantitation ion (m/z) |
|---|---|---|---|
| 2,3,7,8-TCDD | 1.13 | 3.9 | 322 |
| 1,2,3,7,8-PeCDD | 0.70 | 10.1 | 356 |
| 1,2,3,4,7,8-HxCDD | 0.51 | 6.6 | 390 |
| 1,2,3,4,6,7,8-HpCDD[b] | 1.08 | 6.6 | 424 |
| OCDD[b] | 1.30 | 7.2 | 460 |
| 2,3,7,8-TCDF | 1.70 | 8.0 | 306 |
| 1,2,3,7,8-PeCDF | 1.25 | 8.7 | 340 |
| 1,2,3,4,7,8-HxCDF | 0.84 | 9.4 | 374 |
| 1,2,3,4,6,7,8-HpCDF[b] | 1.19 | 3.8 | 444 |
| OCDF[b] | 1.57 | 8.6 | 408 |
| $^{13}C_{12}$-2,3,7,8-TCDD | 1.00 | - | 334 |
| $^{13}C_{12}$-1,2,3,4-TCDD | 0.75 | 4.6 | 334 |
| $^{13}C_{12}$-OCDD | 1.00 | - | 472 |

[a]The RRF value is the mean of the five determinations made. Nominal weights injected were 0.2, 0.5, 1.0, 2.0 and 5.0 ng.

[b]RRF values for these analytes were determined relative to $^{13}C_{12}$-OCDD. All other RRF's were determined relative to $^{13}C_{12}$-2,3,7,8-TCDD.

Instrument Conditions/Tune - GC/MS system was tuned as specified in Paragraph 6.3. RRF data was acquired under SIM control, as specified in Paragraph 10.3.

GC Program - The GC column temperature was programmed as specified in Paragraph 4.3.2(b).

TABLE 5. PRECISION DATA FOR REVISED METHOD 8280

| Compound | Matrix[a] | Analyte level (ng/g) Native | Native + spike | N | Percent RSD |
|---|---|---|---|---|---|
| 2,3,7,8-TCDD | clay | ND[b] | 5.0 | 4 | 4.4 |
| | soil | 378 | 378 | 4 | 2.8 |
| | sludge | ND | 125 | 4 | 4.8 |
| | fly ash | ND | 46 | 2 | - |
| | still bottom | 487 | 487 | 4 | 24 |
| 1,2,3,4-TCDD | clay | ND | 5.0 | 3 | 1.7 |
| | soil | ND | 25.0 | 4 | 1.1 |
| | sludge | ND | 125 | 4 | 9.0 |
| | fly ash | 38.5 | 38.5 | 4 | 7.9 |
| | still bottom | ND | 2500 | 4 | - |
| 1,3,6,8-TCDD | clay | ND | 2.5 | 4 | 7.0 |
| | soil | ND | 25.0 | 4 | 5.1 |
| | sludge | ND | 125 | 4 | 3.1 |
| | fly ash | 19.1 | 19.1 | 2 | - |
| | still bottom | 227 | 2727 | 2 | - |
| 1,3,7,9-TCDD | clay | ND | 2.5 | 4 | 19 |
| | soil | ND | 25.0 | 4 | 2.3 |
| | sludge | ND | 125.0 | 4 | 6.5 |
| | fly ash | 58.4 | 58.4 | 2 | - |
| | still bottom | ND | 2500 | 2 | - |
| 1,3,7,8-TCDD | clay | ND | 5.0 | 4 | 7.3 |
| | soil | ND | 25.0 | 4 | 1.3 |
| | sludge | ND | 125 | 4 | 5.8 |
| | fly ash | 16.0 | 16.0 | 4 | 3.5 |
| | still bottom | 422 | 2920 | 2 | - |
| 1,2,7,8-TCDD | clay | ND | 5.0 | 4 | 7.7 |
| | soil | ND | 25.0 | 4 | 9.0 |
| | sludge | ND | 125 | 4 | 7.7 |
| | fly ash | 2.6 | 2.6 | 3 | 23 |
| | still bottom | ND | 2500 | 2 | - |
| 1,2,8,9-TCDD | clay | ND | 5.0 | 4 | 10 |
| | soil | ND | 25.0 | 4 | 0.6 |
| | sludge | ND | 125 | 4 | 1.9 |
| | fly ash | ND | 46 | 2 | - |
| | still bottom | ND | 2500 | 2 | - |

TABLE 5 (Continued)

| Compound | Matrix[a] | Analyte level (ng/g) Native | Native + spike | N | Percent RSD |
|---|---|---|---|---|---|
| 1,2,3,4,7-PeCDD | clay | ND | 5.0 | 4 | 10 |
| | soil | ND | 25.0 | 4 | 2.8 |
| | sludge | ND | 125 | 4 | 4.6 |
| | fly ash | 25.8 | 25.8 | 2 | 6.9 |
| | still bottom | ND | 2500 | 2 | - |
| 1,2,3,7,8-PeCDD | clay | ND | 5.0 | 4 | 25 |
| | soil | ND | 25.0 | 4 | 20 |
| | sludge | ND | 125 | 4 | 4.7 |
| | fly ash | ND | 46 | 2 | - |
| | still bottom | ND | 2500 | 2 | - |
| 1,2,3,4,7,8-HxCDD | clay | ND | 5.0 | 4 | 38 |
| | soil | ND | 25.0 | 4 | 8.8 |
| | sludge | ND | 125 | 4 | 3.4 |
| | fly ash | ND | 46 | 2 | - |
| | still bottom | ND | 2500 | 2 | - |
| 1,2,3,4,6,7,8-HpCDD | clay | ND | 5.0 | 4 | - |
| | soil | ND | 25.0 | 4 | - |
| | sludge[c] | 8760 | 8780 | 4 | - |
| | fly ash | ND | - | - | - |
| | still bottom | ND | - | - | - |
| 1,2,7,8-TCDF | clay | ND | 5.0 | 4 | 3.9 |
| | soil | ND | 25.0 | 4 | 1.0 |
| | sludge | ND | 125 | 4 | 7.2 |
| | fly ash | 7.4 | 7.4 | 3 | 7.6 |
| | still bottom | ND | 2500 | 2 | - |
| 1,2,3,7,8-PeCDF | clay | ND | 5.0 | 4 | 6.1 |
| | soil | ND | 25.0 | 4 | 5.0 |
| | sludge | ND | 125 | 4 | 4.8 |
| | fly ash | ND | 46 | 2 | - |
| | still bottom[3] | 25600 | 28100 | 2 | - |
| 1,2,3,4,7,8-HxCDF | clay | ND | 5.0 | 4 | 26 |
| | soil | ND | 25.0 | 4 | 6.8 |
| | sludge | 13.6 | 139 | 4 | 5.6 |
| | fly ash | 24.2 | 24.2 | 4 | 13.5 |
| | still bottom | ND | 2500 | 2 | - |

TABLE 5. (Continued)

| Compound | Matrix[a] | Analyte level (ng/g) Native | Native + spike | N | Percent RSD |
|---|---|---|---|---|---|
| OCDF | clay | ND | - | - | - |
| | soil | ND | - | - | - |
| | sludge | 192 | 317 | 4 | 3.3 |
| | fly ash | ND | - | - | - |
| | still bottom | ND | - | - | - |

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only. (Carbon column not used.)

[b]ND - not detected at concentration injected (final volume 0.1 mL or greater).

[c]Estimated concentration out of calibration range of standards.

TABLE 6. RECOVERY DATA FOR REVISED METHOD 8280

| Compound | Matrix[a] | Native[b] (ng/g) | Spiked[c] level (ng/g) | Mean percent recovery |
|---|---|---|---|---|
| 2,3,7,8-TCDD | clay | ND | 5.0 | 61.7 |
| | soil | 378 | - | - |
| | sludge | ND | 125 | 90.0 |
| | fly ash | ND | 46 | 90.0 |
| | still bottom | 487 | - | - |
| 1,2,3,4-TCDD | clay | ND | 5.0 | 67.0 |
| | soil | ND | 25.0 | 60.3 |
| | sludge | ND | 125 | 73.1 |
| | fly ash | 38.5 | 46 | 105.6 |
| | still bottom | ND | 2500 | 93.8 |
| 1,3,6,8-TCDD | clay | ND | 2.5 | 39.4 |
| | soil | ND | 25.0 | 64.0 |
| | sludge | ND | 125 | 64.5 |
| | fly ash | 19.1 | 46 | 127.5 |
| | still bottom | 227 | 2500 | 80.2 |
| 1,3,7,9-TCDD | clay | ND | 2.5 | 68.5 |
| | soil | ND | 25.0 | 61.3 |
| | sludge | ND | 125 | 78.4 |
| | fly ash | 58.4 | 46 | 85.0 |
| | still bottom | ND | 2500 | 91.7 |
| 1,3,7,8-TCDD | clay | ND | 5.0 | 68.0 |
| | soil | ND | 25.0 | 79.3 |
| | sludge | ND | 125 | 78.9 |
| | fly ash | 16.0 | 46 | 80.2 |
| | still bottom | 615 | 2500 | 90.5 |
| 1,2,7,8-TCDD | clay | ND | 5.0 | 68.0 |
| | soil | ND | 25.0 | 75.3 |
| | sludge | ND | 125 | 80.4 |
| | fly ash | 2.6 | 46 | 90.4 |
| | still bottom | ND | 2500 | 88.4 |
| 1,2,8,9-TCDD | clay | ND | 5.0 | 59.7 |
| | soil | ND | 25.0 | 60.3 |
| | sludge | ND | 125 | 72.8 |
| | fly ash | ND | 46 | 114.3 |
| | still bottom | ND | 2500 | 81.2 |

TABLE 6. (Continued)

| Compound | Matrix[a] | Native[b] (ng/g) | Spiked[c] level (ng/g) | Mean percent recovery |
|---|---|---|---|---|
| 1,2,3,4,7-PeCDD | clay | ND | 5.0 | 58.4 |
| | soil | ND | 25.0 | 62.2 |
| | sludge | ND | 125 | 79.2 |
| | fly ash | 25.8 | 46 | 102.4 |
| | still bottom | ND | 2500 | 81.8 |
| 1,2,3,7,8-PeCDD | clay | ND | 5.0 | 61.7 |
| | soil | ND | 25.0 | 68.4 |
| | sludge | ND | 125 | 81.5 |
| | fly ash | ND | 46 | 104.9 |
| | still bottom | ND | 2500 | 84.0 |
| 1,2,3,4,7,8-HxCDD | clay | ND | 5.0 | 46.8 |
| | soil | ND | 25.0 | 65.0 |
| | sludge | ND | 125 | 81.9 |
| | fly ash | ND | 46 | 125.4 |
| | still bottom | ND | 2500 | 89.1 |
| 1,2,3,4,6,7,8-HpCDD | clay | ND | 5.0 | ND |
| | soil | ND | 25.0 | ND |
| | sludge[d] | 8780 | 125 | - |
| | fly ash | ND | - | - |
| | still bottom | ND | - | - |
| 2,3,7,8-TCDD (C-13) | clay | ND | 5.0 | 64.9 |
| | soil | ND | 25.0 | 78.8 |
| | sludge | ND | 125 | 78.6 |
| | fly ash | ND | 46 | 88.6 |
| | still bottom | ND | 2500 | 69.7 |
| 1,2,7,8-TCDF | clay | ND | 5.0 | 65.4 |
| | soil | ND | 25.0 | 71.1 |
| | sludge | ND | 125 | 80.4 |
| | fly ash | 7.4 | 46 | 90.4 |
| | still bottom | ND | 2500 | 104.5 |
| 1,2,3,7,8-PeCDF | clay | ND | 5.0 | 57.4 |
| | soil | ND | 25.0 | 64.4 |
| | sludge | ND | 125 | 84.8 |
| | fly ash | ND | 46 | 105.8 |
| | still bottom | 25600 | 2500 | - |

TABLE 6. (Continued)

| Compound | Matrix[a] | Native[b] (ng/g) | Spiked[c] level (ng/g) | Mean percent recovery |
|---|---|---|---|---|
| 1,2,3,4,7,8-HxCDF | clay | ND | 5.0 | 54.2 |
| | soil | ND | 25.0 | 68.5 |
| | sludge | 13.6 | 125 | 82.2 |
| | fly ash | 24.2 | 46 | 91.0 |
| | still bottom | ND | 2500 | 92.9 |
| OCDF | clay | ND | - | - |
| | soil | ND | - | - |
| | sludge | 192 | 125 | 86.8 |
| | fly ash | ND | - | - |
| | still bottom | ND | - | - |

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator: resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[b]Final volume of concentrate 0.1 mL or greater, ND means below quantification limit, 2 or more samples analyzed.

[c]Amount of analyte added to sample, 2 or more samples analyzed.

[d]Estimated concentration out of calibration range of standards.

TABLE 7. LINEAR RANGE AND VARIATIOIN OF RESPONSE FACTORS

| Analyte | Linear range tested (pg) | n[b] | Mean RF | %RSD |
|---|---|---|---|---|
| 1,2,7,8-TCDF[a] | 50-6000 | 8 | 1.634 | 12.0 |
| 2,3,7,8-TCDD[a] | 50-7000 | 7 | 0.721 | 11.9 |
| 2,3,7,8-TCDF | 300-4000 | 5 | 2.208 | 7.9 |

[a]Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

[b]Each value of n represents a different concentration level.

TABLE 8. METHOD DETECTION LIMITS OF $^{13}C_{12}$ - LABELED PCDD'S and PCDF'S

IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

| $^{13}C_{12}$-Labeled Analyte | Reagent Water[a] | Missouri Soil[b] | Fly-Ash[b] | Industrial Sludge[c] | Still-Bottom[d] | Fuel Oil[d] | Fuel Oil/ Sawdust[b] |
|---|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 0.44 | 0.17 | 0.07 | 0.82 | 1.81 | 0.75 | 0.13 |
| 1,2,3,7,8-PeCDD | 1.27 | 0.70 | 0.25 | 1.34 | 2.46 | 2.09 | 0.18 |
| 1,2,3,6,7,8-HxCDD | 2.21 | 1.25 | 0.55 | 2.30 | 6.21 | 5.02 | 0.36 |
| 1,2,3,4,6,7,8-HpCDD | 2.77 | 1.87 | 1.41 | 4.65 | 4.59 | 8.14 | 0.51 |
| OCDD | 3.93 | 2.35 | 2.27 | 6.44 | 10.1 | 23.2 | 1.48 |
| 2,3,7,8-TCDF | 0.63 | 0.11 | 0.06 | 0.46 | 0.26 | 0.48 | 0.40 |
| 1,2,3,7,8-PeCDF | 1.64 | 0.33 | 0.16 | 0.92 | 1.61 | 0.80 | 0.43 |
| 1,2,3,4,7,8-HxCDF | 2.53 | 0.83 | 0.30 | 2.17 | 2.27 | 2.09 | 2.22 |

[a]Sample size 1,000 mL.
[b]Sample size 10 g.
[c]Sample size 2 g.
[d]Sample size 1 g.
Note: The final sample-extract volume was 100 uL for all samples.

Matrix types used in MDL Study:

- Reagent water: distilled, deionized laboratory water.
- Missouri soil: soil blended to form a homogeneous sample.
- Fly-ash: alkaline ash recovered from the electrostatic precipitator of a coal-burning power plant.
- Industrial sludge: sludge from cooling tower which received creosotic and pentachlorophenolic wastewaters. Sample was ca. 70 percent water, mixed with oil and sludge.
- Still-bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.
- Fuel oil: wood-preservative solution from the modified Thermal Process tanks. Sample was an oily liquid (>90 percent oil) containing no water.
- Fuel oil/Sawdust: sawdust was obtained as a very fine powder from the local lumber yard. Fuel oil (described above) was mixed at the 4 percent (w/w) level.

Procedure used for the Determination of Method Detection Limits was obtained from "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" Appendix A, EPA-600/4-82-057, July 1982. Using this procedure, the method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero.

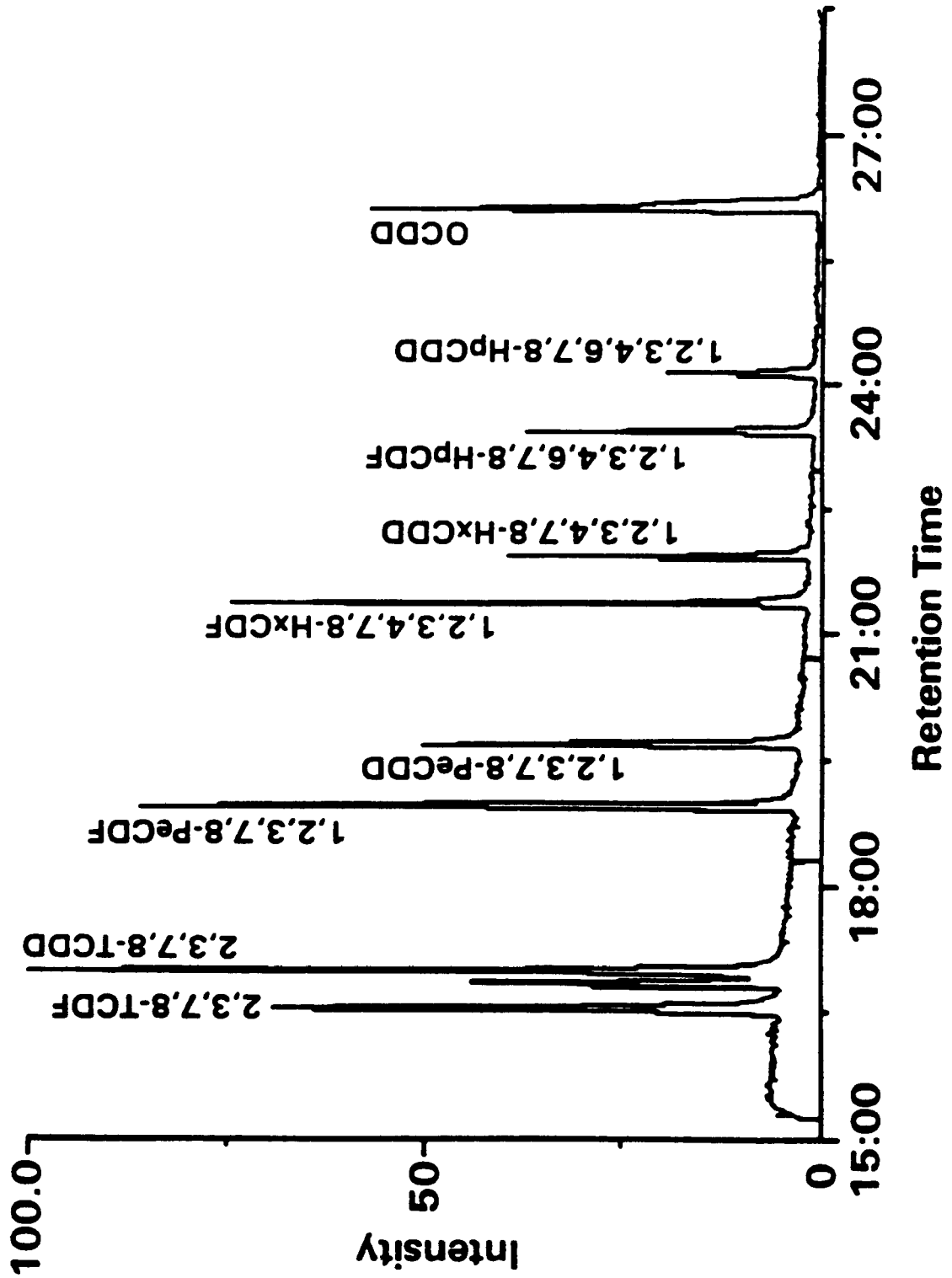
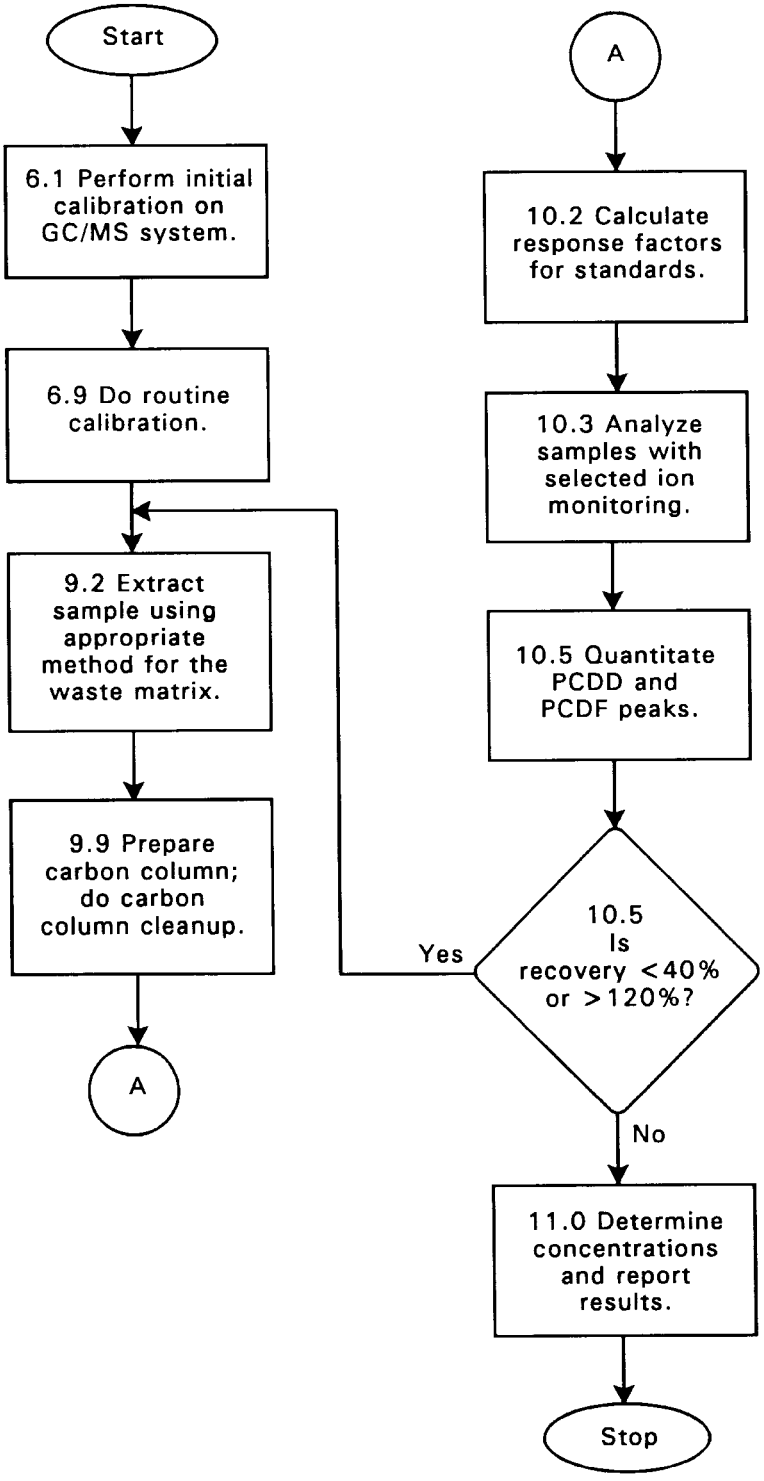



Figure 2. Mass Chromatogram of Selected PCDD and PCDF Congeners.


Start
6.1 Perform initial calibration on GC/MS system.
6.9 Do routine calibration.
9.2 Extract sample using appropriate method for the waste matrix.
9.9 Prepare carbon column; do carbon column cleanup.
A
A
10.2 Calculate response factors for standards.
10.3 Analyze samples with selected ion monitoring.
10.5 Quantitate PCDD and PCDF peaks.
10.5 Is recovery <40% or >120%?
Yes
No
11.0 Determine concentrations and report results.
Stop

APPENDIX A

SIGNAL-TO-NOISE DETERMINATION METHODS

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 1 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 in Figure 1. 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.

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.

INTERACTIVE COMPUTER GRAPHICAL METHOD

This method calls for the measurement of the GC/MS peak area using the computer data system and Eq. 1:

$$S/N = \frac{A/t}{\frac{A_1/2t + A_r/2t}{2}}$$

where t is the elution time window (time interval, $t_2$-$t_2$, at the base of the peak used to measure the peak area A). (Refer to Figure 2, for the following discussion).

$A_1$ and $A_r$ correspond to the areas of the noise level in a region to the left ($A_1$) and to the right ($A_r$) of the GC peak of interest.

The procedure to determine the S/N is as follows:

1. Estimate the average negative peak excursions of the noise (i.e., the low segment-$E_2$-of the noise envelope). Line $E_2$ should pass through the estimated statistical mean of the negative-going noise excursions. As stated earlier, it is important to have the signal offset (O) set high enough such that negative-going noise is recorded.

2. Using the cross-hairs of the video display terminal, measure the peak area (A) above a baseline corresponding to the mean negative noise value ($E_2$) and between the time $t_1$ and $t_2$ where the GC/MS peak intersects the baseline, $E_2$. Make note of the time width $t=t_2-t_1$.

3. Following a similar procedure as described above, measure the area of the noise in a region to the left ($A_1$) and to the right ($A_r$) of the GC/MS signal using a time window twice the size of t, that is, 2 x t.

The analyst must sound judgement in regard to the proper selection of interference-free regions in the measurement of $A_1$ and $A_r$. It is not recommended to perform these noise measurements ($A_1$ and $A_r$) in remote regions exceeding ten time widths (10t).

4. Compute the S/N using Eq. 1.

NOTE: If the noise does not occupy at least 10 percent of the vertical axis (i.e., the noise envelope cannot be defined accurately), then it is necessary to amplify the vertical axis so that the noise occupies 20 percent of the terminal display (see Figure 3).

## FIGURE CAPTIONS

Figure 1. 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.

Figure 2. Interactive determination of S/N.
The peak area (A) is measured above the baseline average negative noise $E_2$ and between times $t_1$ and $t_2$. The noise is obtained from the areas $A_1$ and $A_r$ measured to the left and to the right of the peak of interest using time windows $T_1$ and $T_r$ ($T_1$=$T_r$=2t).

Figure 3. Interactive determination of S/N.
A) Area measurements without amplification of the vertical axis. Note that the noise cannot be determined accurately by visual means. B) Area measurements after amplification (10X) of the vertical axis so that the noise level occupies approximately 20 percent of the display, thus enabling a better visual estimation of the baseline noise, $E_1$, $E_2$, and C.

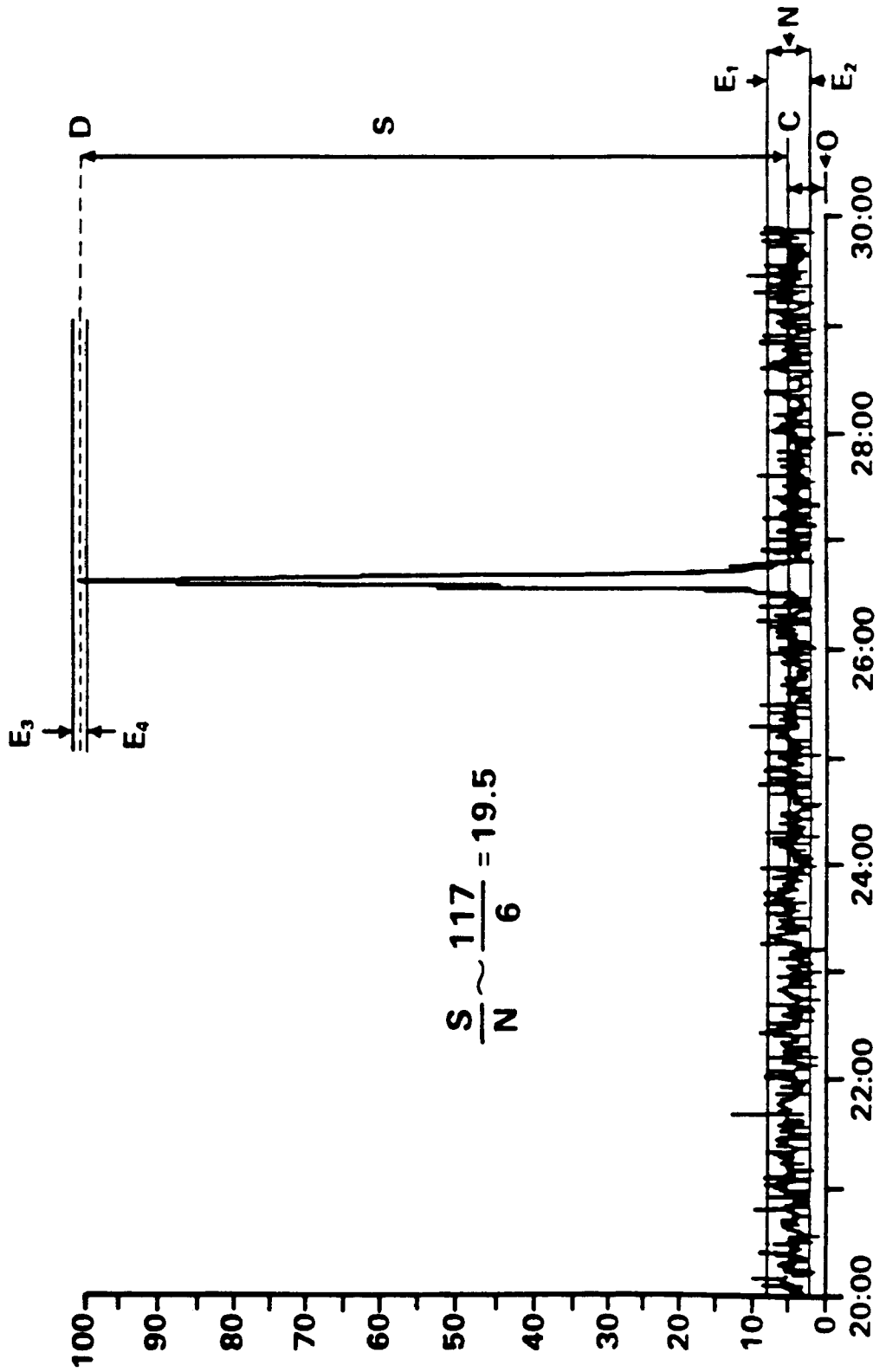



Figure 1. Manual Determination of S/N.

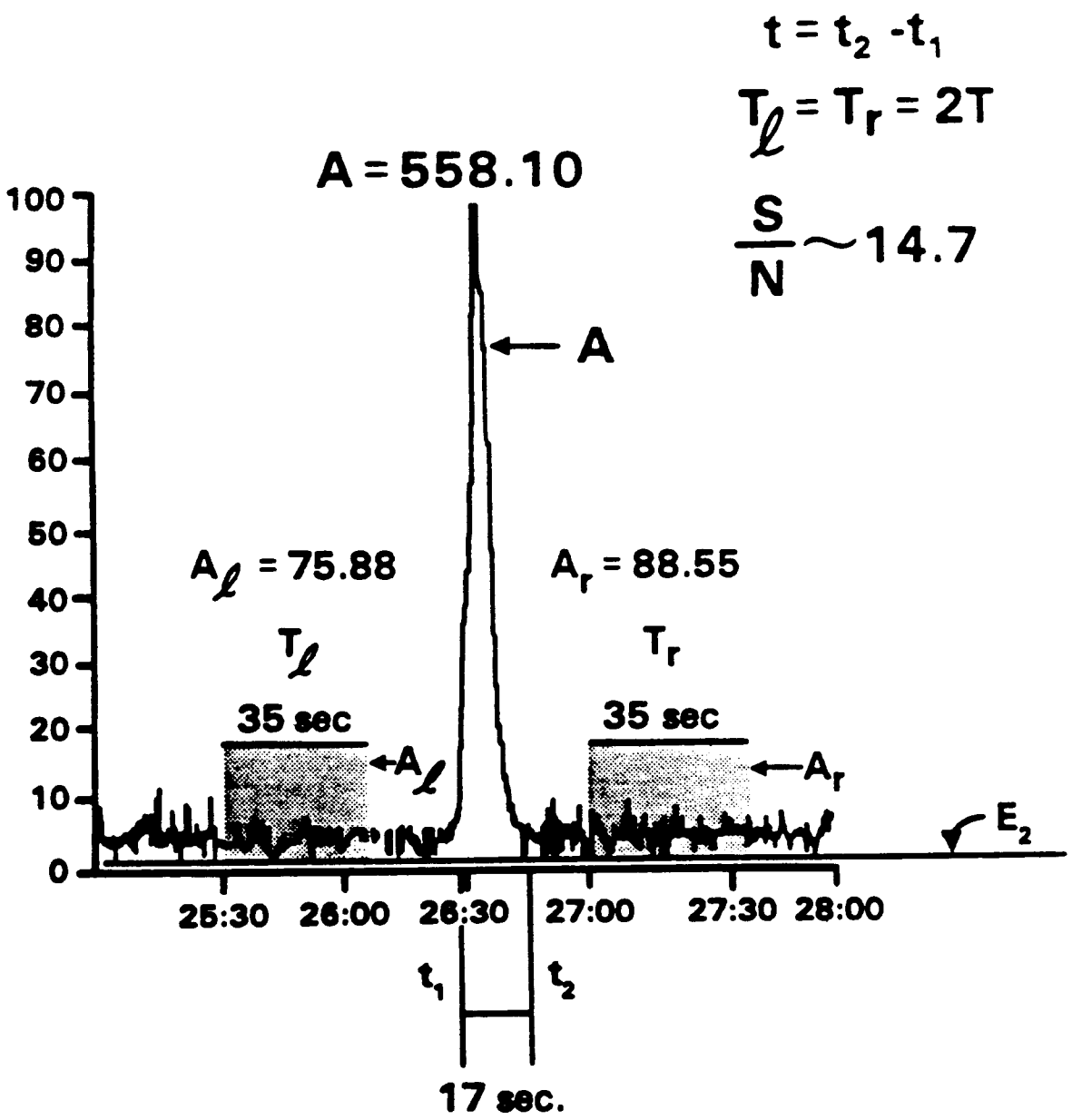



Figure 2. Interactive Determination of S/N.

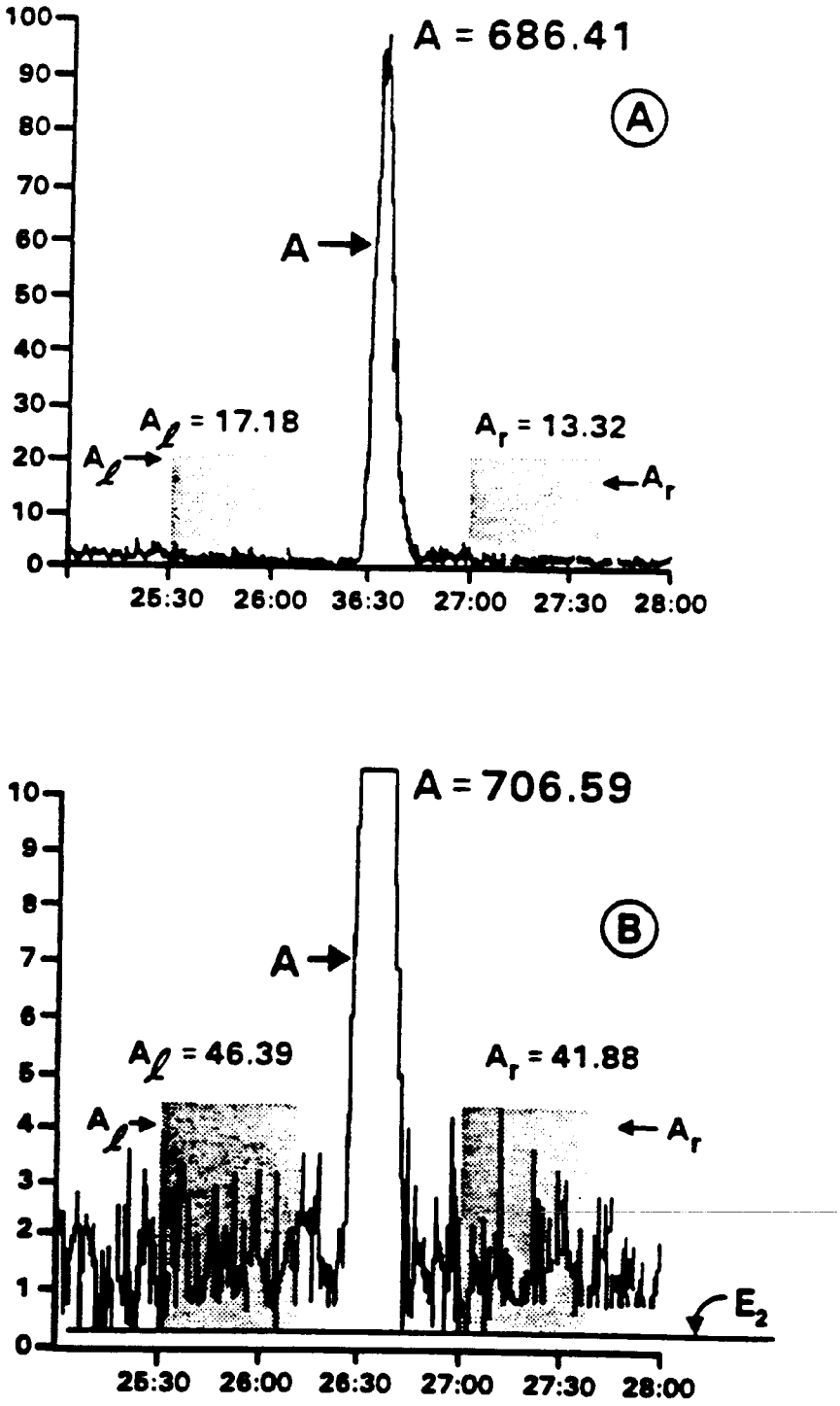



Figure 3. Interactive Determination of S/N.

APPENDIX B

RECOMMENDED SAFETY AND HANDLING PROCEDURES FOR PCDD'S/PCDF'S

1. The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001 perent to 0.14 percent. The physical properties of the 135 other tetra- through octachlorinated PCDD/PCDF have not been well established, although it is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer. On the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personel entering these laboratories should wear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves are also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are processed, removal of these from sample contaners, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing, and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-aproved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than 50 ng/$m^2$, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500 ng/$m^2$. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scurbbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgeable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

# DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No._____

CASE No. _____

QUANTITY FOUND (ng/g)

| SAMPLE NO. | FILE NAME | TCDD | PeCDD | HxCDD | HpCDD | OCDD |
|---|---|---|---|---|---|---|
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DATA RELEASE AUTHORIZED BY _____

# DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No._____

CASE No. _____

QUANTITY FOUND (ng/gL)

| SAMPLE NO. | FILE NAME | TCDF | PeCDF | HxCDF | HpCDF | OCDF |
|---|---|---|---|---|---|---|
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# DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No._____

CASE No. _____

QUANTITY FOUND (ug/L)

| SAMPLE NO. | FILE NAME | TCDD | PeCDD | HxCDD | HpCDD | OCDD |
|---|---|---|---|---|---|---|
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DATA RELEASE AUTHORIZED BY _____

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No._____

CASE No. _____

QUANTITY FOUND (ug/L)

| SAMPLE NO. | FILE NAME | TCDF | PeCDF | HxCDF | HpCDF | OCDF |
|---|---|---|---|---|---|---|
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DIOXIN RAW SAMPLE DATA FORM 8280-2

LAB NAME _____ ANALYST(s) _____ CASE No. _____

SAMPLE No. _____ TYPE OF SAMPLE _____CONTRACT No. _____

SAMPLE SIZE _____ % MOISTURE _____ FINAL EXTRACT VOLUME _____

EXTRACTION METHOD _____ ALIQUOT USED FOR ANALYSIS _____

CLEAN UP OPTION _____

CONCENTRATION FACTOR _____ DILUTION FACTOR _____

DATE EXTRACTED _____ DATA ANALYZED _____

VOLUME $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____ TO SAMPLE VOLUME _____

VOLUME INJECTED _____ Wt $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____

Wt $^{13}C_{12}$-2,3,7,8-TCDD ADDED _____ $^{13}C_{12}$-2,3,7,8-TCDD % RECOVERY _____

Wt $^{13}C_{12}$-2,3,7,8-OCDD ADDED _____ $^{13}C^{12}$-OCDD % RECOVERY _____

$^{13}C_{12}$-2,3,7,8-TCDD RRF _____ $^{13}C_{12}$-2,3,7,8-OCDD RRF _____

$^{13}C_{12}$-2,3,7,8-TCDD

AREA 332 _____ AREA 334 _____ RATIO 332/334 _____

$^{13}C_{12}$-OCDD AREA 470 _____ AREA 472 _____ RATIO 470/472 _____

RT 2,3,7,8-TCDD (Standard) _____ RT 2,3,7,8-TCDD (Sample) _____

$^{13}C_{12}$-2,3,7,8-TCDD -$^{13}C_{12}$-1,2,3,4-TCDD Percent Valley _____

DIOXIN INITIAL CALIBRATION STANDARD DATA SUMMARY

FORM 8280-3

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s)_____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD_____or $^{13}C_{12}$-1,2,3,$^{4-}$TCDD_____

| CALIBRATION STANDARD | RRF 1 | RRF 2 | RRF 3 | RRF 4 | RRF 5 | MEAN | %RSD |
|---|---|---|---|---|---|---|---|
| TCDD | | | | | | | |
| PeCDD | | | | | | | |
| HxCDD | | | | | | | |
| HpCDD | | | | | | | |
| OCDD | | | | | | | |
| TCDF | | | | | | | |
| PeCDF | | | | | | | |
| HxCDF | | | | | | | |
| HpCDF | | | | | | | |
| OCDF | | | | | | | |

CONCENTRATIONS IN PG/UL

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| TCDD | | | | | |
| PeCDD | | | | | |
| HxCDD | | | | | |
| HpCDD | | | | | |
| OCDD | | | | | |
| TCDF | | | | | |
| PeCDF | | | | | |
| HxCDF | | | | | |
| HpCDF | | | | | |
| OCDF | | | | | |

DIOXIN CONTINUING CALIBRATION SUMMARY

FORM 8280-4

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s) _____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD_____ or $^{13}C_{12}$-1,2,3,4-TCDD_____

| COMPOUND | $\overline{RRF}$ | RRF | %D |
|---|---|---|---|
| TCDD | | | |
| PeCDD | | | |
| HxCDD | | | |
| HpCDD | | | |
| OCDD | | | |
| TCDF | | | |
| PeCDF | | | |
| HxCDF | | | |
| HpCDF | | | |
| OCDF | | | |

DIOXIN RAW SAMPLE DATA FORM 8280-5-A

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

TCDD REQUIRED 320/322 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 322 | AREA 320 | AREA 257 | 320/ 322 | CONFIRM AS TCDD Y/N | CONC. |
|---|---|---|---|---|---|---|---|

TOTAL TCDD _____

TCDF REQUIRED 304/306 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 322 | AREA 320 | AREA 257 | 320/ 322 | CONFIRM AS TCDF Y/N | CONC. |
|---|---|---|---|---|---|---|---|

TOTAL TCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-B

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

PeCDD REQUIRED 320/322 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 356 | AREA 358 | AREA 354 | AREA 293 | 358/ 356 | CONFIRM AS PeCDD Y/N | CONC. |
|---|---|---|---|---|---|---|---|---|

TOTAL PeCDD _____

PeCDF REQUIRED 342/340 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 340 | AREA 342 | AREA 338 | AREA 227 | 342/ 340 | CONFIRM AS PeCDF Y/N | CONC. |
|---|---|---|---|---|---|---|---|---|

TOTAL PeCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-C

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

HxCDD REQUIRED 392/390 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 390 | AREA 392 | AREA 388 | AREA 327 | 392/ 390 | CONFIRM AS HxCDD Y/N | CONC. |
|---|---|---|---|---|---|---|---|---|

TOTAL HxCDD _____

HxCDF REQUIRED 376/374 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 376 | AREA 374 | AREA 372 | AREA 311 | 376/ 374 | CONFIRM AS HxCDF Y/N | CONC. |
|---|---|---|---|---|---|---|---|---|

TOTAL HxCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-D

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

HpCDD REQUIRED 426/444 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 424 | AREA 426 | AREA 422 | AREA 361 | 426/ 424 | CONFIRM AS HpCDD Y/N | CONC. |
|---|---|---|---|---|---|---|---|---|

TOTAL HpCDD _____

HpCDF REQUIRED 410/408 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 408 | AREA 410 | AREA 406 | AREA 345 | 410/ 408 | CONFIRM AS HpCDF Y/N | CONC. |
|---|---|---|---|---|---|---|---|---|

TOTAL HpCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-E

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

OCDD REQUIRED 458/460 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 460 | AREA 458 | AREA 395 | 458/ 460 | CONFIRM AS OCDD Y/N | CONC. |
|---|---|---|---|---|---|---|---|

TOTAL OCDD _____

OCDF REQUIRED 442/444 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

| SCAN # | RRT | AREA 444 | AREA 442 | AREA 379 | 442/ 444 | CONFIRM AS OCDF Y/N | CONC. |
|---|---|---|---|---|---|---|---|

TOTAL OCDF _____

DIOXIN SYSTEM PERFORMANCE CHECK ANALYSIS FORM 8280-6

LAB NAME _____ CASE No. _____

BEGINNING DATE _____ TIME _____ CONTRACT No._____

ENDING DATE _____ TIME _____ ANALYST(s) _____

PC SOLUTION IDENTIFIER _____

ISOTOPIC RATIO CRITERIA MEASUREMENT

| PCDD's | IONS RATIOED | RATIO AT BEGINNING OF 12 HOUR PERIOD | RATIO AT END OF 12 HOUR PERIOD | ACCEPTABLE WINDOW |
|---|---|---|---|---|
| Tetra | 320/322 | | | 0.65-0.89 |
| Penta | 358/356 | | | 0.55-0.75 |
| Hexa | 392/390 | | | 0.69-0.93 |
| Hepta | 426/424 | | | 0.83-1.12 |
| Octa | 458/460 | | | 0.75-1.01 |
| PCDF's | | | | |
| Tetra | 304/306 | | | 0.65-0.89 |
| Penta | 342-340 | | | 0.55-0.75 |
| Hexa | 376-374 | | | 0.69-0.93 |
| Hepta | 410/408 | | | 0.83-1.12 |
| Octa | 442/444 | | | 0.75-1.01 |

Ratios out of criteria

| | Beginning | End |
|---|---|---|
| PCDD | _____ out of _____ | _____ out of _____ |
| PCDF | _____ out of _____ | _____ out of _____ |

NOTE: One form is required for each 12 hour period samples are analyzed.

# ERRATA FOR METHOD 8280

In Section **1.1**, **delete** the following text:

"reactor residues" with no replacement.

In Section **1.5**, **replace** the following text:

"the analyst must take necessary precautions to prevent exposure to himself, or to others, of"

with:

"the analyst must take necessary precautions to prevent human exposure from" and

**delete** the following text:

"to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH 548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450)."

In Section **6.3**, **replace** the following text:

"x = measured as in Figure 2"

with:

"x = height of the valley between 2,3,7,8-TCDD and 1,2,3,4-TCDD, using the column performance check mixture."

In Section **6.9.2**, **replace** "a 2-hr period" with "a 12 hr period".

In Section **7.4**, **replace** "24" with "20".