

Standard Operating Procedure for Method 8280 Midland Area Soils (MAS)
Midland Area Soils Project – Site Specific Fast Analysis

1. SCOPE AND APPLICATION

1.1. This method is for the fast determination of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in soil by high resolution gas chromatography/high or low resolution mass spectrometry (HRGC/HRMS or HRGC/LRMS). It is specific for the Midland area soils (MAS).

1.2. The fast analysis is designed to dramatically speed up the analytical process and to reduce the costs of the analysis (1).

1.3. Selected 2,3,7,8-substituted PCDDs/PCDFs may be determined by this method. Due to the pattern distribution of the Midland area soil samples, an analysis of specific congeners allows a reliable estimation of the total TEQ concentrations present in the samples. In this sense, the Fast Analysis is used to calculate the total TEQ with a sufficient precision as described in the QAPP.

1.4. Due to the nature of this technique, the QA/QC of the methods 1613b, 8280 and 8290 will be adapted accordingly (2-5). Co-elutions and interferences in addition to those accepted by the methods 1613b, 8280 and 8290 may occur but will only bias the values high (6-10).

1.5. The method is for use only by analysts extensively experienced with the determination of PCDD and PCDF according to the methods 1613b, 8280 and 8290 or under the close supervision of such qualified persons.

1.6. This method is "performance-based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met.

2. SUMMARY OF THE METHOD

2.1. Extraction: At a minimum, a mixture of all 2,3,7,8-substituted ¹³C-labeled PCDD/PCDF standards is spiked into a sample containing up to 50g (dry weight) of sample (Table 1). The samples are homogenized prior to extraction. The samples are extracted with either a Soxhlet/Dean-Stark (SDS) extractor for a minimum of 16 hours (an application of shorter extraction time may be possible if the cycle rate is increased accordingly) or other extraction techniques proven to have a similar or better extraction efficiency and do not have measurable carry-over effects. The raw extract is split to create a retainer for potential re-analysis.

2.2. Cleanup: After extraction the sample extracts are concentrated and an aliquot is processed using simplified and especially adapted adsorption chromatographic cleanup method.

2.3. Concentration: After cleanup, the extract is concentrated to dryness, an internal standard is added to each extract, and the extract is injected into the gas chromatograph.

2.4. Determination: The target analytes are separated by the GC and detected by a mass spectrometer. Two exact m/z's are monitored for each analyte and standard.

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2.5. Identification: the target PCDD/PCDF are identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the retention time of the corresponding ¹³C labeled standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's.

2.6. Quantitation: Quantitative analysis is performed using selected ion current profile (SICP) areas: For the target PCDDs/PCDFs, the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.

2.7. The quality of the analysis is assured through an initial calibration and initial testing of the extraction and cleanup performance (IPR).

2.8. In addition to section 2.7, a daily calibration check (calibration verification), a detection verification standard (DVS), a method blank, and an OPR (on-going precision and recovery) will be performed and SQC-charts may be developed.

3. CONTAMINATION AND INTERFERENCES

3.1. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

3.2. Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

3.3. Glassware should be rinsed with solvent as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning.

3.4. If performing a detergent wash, glassware should be rinsed at a minimum with acetone.

3.5. Baking of the glassware can be used to effectively clean glassware and may be particularly warranted after dirty and/or highly contaminated samples are encountered to avoid carry-over.

3.6. All materials used in the analysis shall be free from interferences at significant levels. To monitor interferences, a method blank will be analyzed with each sample batch.

3.7. Interferences co-extracted from samples may be present at concentrations several orders of magnitude higher than the PCDDs/PCDFs. The cleanup step options given in Section 10 are used to reduce or eliminate these interferences for the target analytes and thereby permit reliable determination of the target PCDDs/PCDFs.

4. SAFETY

4.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should

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be available to all personnel involved in the chemical analysis of samples suspected to contain PCDDs/PCDFs.

4.2 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

4.3 The following safety practices are excerpts from EPA Method 1613, Sec. 5 (October 1994 version), amended as necessary for use in conjunction with this method. The 2,3,7,8-TCDD isomer has been found to be acrogenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should wear masks fitted with charcoal filters to prevent inhalation of dust.

4.4 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

4.5 Each laboratory must develop a strict safety program for the handling of PCDDs and PCDFs. The laboratory practices listed below are recommended.

4.5.1 Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood, or in a separate containment facility away from the main laboratory.

4.5.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols.

4.5.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps, or equivalent). Using this analytical method, analyze the irradiated liquid wastes and dispose of the solutions when 2,3,7,8-TCDD and 2,3,7,8-TCDF congeners can no longer be detected.

4.6 The following precautions for safe handling of 2,3,7,8-TCDD in the laboratory were issued by Dow Chemical U.S.A. (revised 11/78) and were amended for use in conjunction with this method. The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2,3,7,8-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Many techniques used in handling radioactive and infectious materials are applicable

4.6.1 Protective equipment -- Disposable plastic gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work. However, PVC gloves should not be used.

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4.6.2 Training -- Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

4.6.3 Personal hygiene -- Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

4.6.4 Confinement -- Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on bench tops.

4.6.5 Waste -- Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

4.6.6 Disposal of hazardous wastes -- Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin containing wastes.

4.6.7 Decontamination of personnel -- Apply a mild soap with plenty of scrubbing action.

4.6.8 Glassware, tools and surfaces -- Chlorothene NU Solvent™ (Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with chlorothene, then washing with a detergent and water. Dish water may be disposed to the sewer after percolation through a charcoal bed filter. It is prudent to minimize solvent wastes because they require special disposal through commercial services that are expensive.

4.6.9 Laundry -- Clothing known to be contaminated should be disposed according to the precautions of the source described under Sec. 5.6.6. Laboratory coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through one full cycle before being used again for other clothing.

4.6.10 Wipe tests -- A useful method for determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, extract the filter paper and analyze the extract. NOTE: A procedure for the collection, handling, analysis, and reporting requirements of wipe tests performed within the laboratory is described in Appendix A of Method 8290. The results and decision-making processes are based on the presence of 2,3,7,8-substituted PCDDs/PCDFs.

4.6.11 Inhalation -- Any procedure that may generate airborne contamination must be carried out with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no significant inhalation hazards except in case of an accident.

4.6.12 Accidents -- Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

4.7 It is recommended that personnel working in laboratories where PCDDs/PCDFs are handled be given periodic physical examinations (at least annually). 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 PCDDs/PCDFs. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

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5. APPARATUS AND MATERIALS

Note: Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the laboratory.

5.1. Equipment for Glassware Cleaning

5.1.1. Laboratory sink with overhead fume hood.

5.1.2. Kiln (optional)

5.2. Equipment for Sample Preparation

5.2.1. Laboratory fume hood of sufficient size to contain the sample preparation equipment.

5.2.2. Glove box (optional).

5.2.3. Top loading balance for samples: Capable of weighing to 0.01 g. Analytical balance capable of weighing 0.001 g (optional)

5.2.4. Aluminum weighing boats.

5.2.5. Spatulas: Stainless steel.

5.3. Extraction Apparatus

5.3.1. Soxhlet/Dean-Stark (SDS) extractor

5.3.1.1. Soxhlet: 50mm ID, 200mL capacity with 500mL flask (Cal-Glass LG-6900, or equivalent, except substitute 300mL round-bottom flask 500mL flat-bottom flask).

5.3.1.2. Thimble: 30 × 100 to fit Soxhlet (Whatman Glass Microfibre thimbles, or Cal-Glass LG-6901-122, or equivalent).

5.3.1.3. Moisture trap: Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet.

5.3.1.4. Heating mantle: Hemispherical, to fit 300mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent).

5.3.1.5. Variable transformer: Powerstat (or equivalent), 110 volt, 10 amp.

5.3.2. Beakers: Assorted volumes.

5.3.3. Spatulas: Stainless steel

5.3.4. Extract storage: assorted sample vials

5.4. Cleanup Apparatus.

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5.4.1. Laboratory Oven: For baking and storage of adsorbents, capable of maintaining a constant temperature ($\pm 5^{\circ}\text{C}$) in the range of 100–250°C.

5.4.2. Tube furnace with heating range from 100 - 250°C

5.4.3. Disposable glass tubes: approximately 25 cm in length and 1 mm in diameter

5.5. Concentration Apparatus.

5.5.1. Nitrogen blowdown apparatus: Equipped with water bath controlled in the range of 30–60°C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood.

5.5.2. Sample Vials.

5.5.2.1. Glass: 2–5mL with fluoropolymer-lined screw-cap.

5.5.2.2. Glass: 0.3mL, conical, with fluoropolymer-lined screw or crimp cap.

5.6. Gas Chromatograph: Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

5.6.1. GC column for PCDDs/PCDFs: for instance 30 \pm 5m long \times 0.32 \pm 0.02mm ID; 0.25 μm silicone bonded-phase fused-silica capillary column (e.g. DB-5MS, or equivalent). An attached guard column is recommended.

5.7. Mass Spectrometer: low or high resolution mass spectrometry capable of analyzing the target PCDD/PCDF

5.7.1. Data System: Capable of collecting, recording, and storing MS data.

6. REAGENTS AND STANDARDS

6.1. Extraction.

6.1.1. Solvent: Acetone, toluene, benzene, hexane, methanol, ethyl acetate, methylene chloride, and nonane; distilled in glass, HPLC grade or better recommended

6.1.2. White quartz sand, 60/70 mesh: For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450°C for four hours minimum or extract for 16 hours with benzene or toluene.

6.2. Adsorbents for Sample Cleanup.

6.2.1 Silica gel

6.2.1.1 Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methanol and methylene chloride (optional), baked at approximately 180°C for a minimum of

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one hour, cooled in a dessicator, and stored in a precleaned glass bottle with screwcap that prevents moisture from entering.

6.2.1.2 Acid silica gel (44% w/w)—Thoroughly mix 44.0 g of concentrated sulfuric acid with 56g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

6.2.1.3 Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

6.2.2. Carbon.

6.2.2.1. Carbpak B: (Supelco 20274, or equivalent).

6.2.2.2. Celite 545: (Supelco 2-0199, or equivalent).

6.2.2.3. Thoroughly mix Carbpak B and Celite 545 to produce an 18% w/w mixture (Carbpak B/Celite 545). Extract the mixture in toluene for at least 16 hours. Dry the mixture above 130°C for a minimum of six hours. Store in a dessicator.

6.3. Reference Matrices: Playground sand or similar material. Prepared by extraction with benzene or toluene and/or baking at 450°C for a minimum of four hours and spiked with the PAR solution (see section 6.7.)

6.4. Standard Solutions: Purchased as solutions or mixtures with certification of their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards should be stored in the dark at room temperature in screw-capped vials with fluoropolymerlined caps. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.

6.5. Selected isomer standard solutions: The 13 target congeners for the fast analysis of the MAS samples are 2,3,7,8-TCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PeCDD; 2,3,4,7,8-PeCDF; 1,2,3,4,7,8 + 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,7,8 + 1,2,3,6,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; OCDD; OCDF. These are referred to as "target PCDDs/PCDFs" in this method.

6.6. Stock Solutions.

6.6.1. Preparation: Prepare in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories (CIL), Woburn, MA, or equivalent). Observe the safety precautions in Section 4, and the recommendation in Section 4.2. Alternatively purchased certified reference standards may be used.

6.6.2. Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1–2mg of 2,3,7,8-TCDF to three significant figures in a 10mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the TCDF is completely dissolved, transfer the solution to a clean 15mL vial with fluoropolymerlined cap.

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6.6.3. Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from CIL and may be available from other vendors.

6.7. Precision and Recovery (PAR) Stock Solution

6.7.1. Used for determination of initial and ongoing precision and recovery

6.7.2. PCDDs/PCDFs: Using the solutions in Section 6.6 or purchased solutions, prepare the PAR stock solution to contain the PCDDs/PCDFs at the concentrations shown in Table 2.

6.8. Labeled Compound Spiking Solution.

6.8.1. PCDDs/PCDFs: From stock solutions, or from purchased mixtures, prepare this solution to contain the labeled compounds in nonane at the concentrations shown in Table 2.

6.9. Internal (injection) Standard

6.9.1. Prepare the internal standard solution to contain any $^{13}\text{C}_{12}$ -labeled PCDD/PCDF-standard other than the PCDD/PCDF standards in nonane at the concentration shown in Table 2.

6.10. Calibration Standards (CS1 through CS5): Combine the solutions in Sections 6.6 through 6.9 to produce a minimum of five calibration solutions in nonane (Table 3). These solutions permit the relative responses (labeled to native) and response factors to be measured as a function of concentration. A standard close to the middle of the calibration range should be used for calibration verification (VER).

6.11. Detection Verification Standard (DVS): A standard at the low end of the calibration curve that will be run daily (24-hour) to determine the daily quantification level. Sample concentrations determined from peak areas below the DVS peak areas will be flagged.

6.12. Stability of Solutions: Standard solutions used for quantitative purposes should be analyzed periodically, and should be assayed against reference standards.

6.13. Quality Check standard (QC): a standard, containing at a minimum, the analytes of interest obtained from a source independent of solution used for the calibration curve.

7. SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

7.1. Collect samples in amber glass containers following guidelines put forth in the project QAPP.

7.2. Maintain solid samples in the dark at $<-10\text{ }^{\circ}\text{C}$.

7.3. Sample extracts, will be kept long term, at room temperature in the dark with the volume marked.

8. QUALITY ASSURANCE/QUALITY CONTROL

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- 8.1. The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method.
- 8.2. Analyses of method blanks are required to indicate freedom from significant contamination.
- 8.3. The laboratory shall spike all samples with labeled compounds to monitor method performance.
- 8.4. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery aliquot that the analytical system is in control.
- 8.5. The laboratory shall maintain records to define the quality of data that is generated.
- 8.6. Initial Precision and Recovery (IPR): To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations. Alternatively, an analyst can perform sections of the procedure and therefore be qualified to run those steps of this procedure.
- 8.6.1. Analyze four aliquots of reagent sand spiked with the diluted labeled compound spiking solution and the PAR standard (10 μ L for both solutions based on Table 2 concentrations). All sample processing steps that are to be used for processing samples, including preparation, extraction, and cleanup, shall be included in this test.
- 8.6.2. Using results of the set of four analyses, compute the average concentration (X) of the extracts and the standard deviation of the concentration (s) for each target compound, by isotope dilution for the PCDDs/PCDFs with a labeled analog.
- 8.6.3. For each target PCDD/PCDF compound, compare s and X with the corresponding limits for initial precision and recovery in Table 4. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.
- 8.7. The laboratory shall spike all samples with labeled compound spiking solution to assess method performance on the sample matrix for the target compounds.
- 8.7.1. Analyze each sample according to the procedures outlined below.
- 8.7.2. Compute the percent recovery of the labeled target compounds using the internal standard method.
- 8.7.3. The recovery of each labeled target compound should be within the limits in Table 5. If the recovery of any compound falls outside of these limits, an assessment of the acceptability will be done. The assessment of acceptability will involve determining the peak height of the labeled compound. If the peak height is greater than 10:1 signal:noise (meaning quantifiable) the recovery will be deemed acceptable and reported with a flag. If the peak height is below 10:1, the value will not be reported and action to correct the problem will need to be taken.

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8.8. Recovery of labeled target compounds from samples should be assessed and records should be maintained.

8.9. Method Blanks: Reference matrix method blanks are analyzed to indicate freedom from significant contamination.

8.9.1. Prepare, extract, clean up, and concentrate a method blank with each sample batch (samples started through the extraction process on the same 12-hour shift). The matrix for the method blank shall be sand. Analyze the blank immediately after analysis of the OPR to indicate freedom from significant contamination.

8.9.2. If any of the target PCDD/PCDFs is found in the blank at a significant level, the result will be flagged and an assessment of the acceptability will be done.

8.10. The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration, calibration verification, and for initial and ongoing precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of PCDDs/PCDFs by this method.

8.11. A QC standard will be analyzed after the initial calibration curve has been built.

9. CALIBRATION

9.1. Suggested GC operating conditions for a 30m DB-5MS column:

9.1.1. Injector: temperature 250°C, constant pressure 12 psi

9.1.2. Interface temperature: 280°C

9.1.3. Initial temperature: 120°C

9.1.4. Initial time: One minute

9.1.5. Temperature program:

9.1.5.1. 120 to 240°C, at 40°C/minute

9.1.5.2. 240 to 295°C, at 5°C/minute

9.1.5.3 295 to 325°C, at 30°C/minute

9.1.5.4. 325°C for 6.5 minutes

9.1.6. Optimize GC and MS conditions for compound sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.

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As long as all method QC and project requirements are met the GC conditions should be optimized for short analysis times.

9.2. Ion Abundance Ratios, Minimum Levels: Choose an injection volume of either 1 μ L or 2 μ L, consistent with the capability of the HRGC/MS instrument. Inject a 1 μ L or 2 μ L aliquot of the Detection Verification Standard (DVS) solution using the GC/MS conditions listed above.

9.2.1. Measure the SICP areas for each target analyte, and compute the ion abundance ratios at the m/z's specified in Table 6. Compare the computed ratio to the theoretical ratio given in Table 6.

9.2.2. All target PCDDs/PCDFs and labeled target compounds in the DVS standard shall be within the QC limits in Table 6 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified .

9.3. Isomer Specificity. Target analyte co-elutions can be accepted as long as the TEQ values are biased high and the interferences are known and limited.

9.3.1. Check system performance ensuring adequate separation between the ¹³C 2378-TCDF and the native 2378-TCDD.

9.3.2. Ensure that all target analytes are detected in VER standard in the proper windows.

9.4. Calibration by Isotope Dilution: Isotope dilution calibration is used for the target PCDDs/PCDFs for which the labeled compounds are added to samples prior to extraction.

9.4.1. A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (RR) (labeled to native) vs. concentration in standard solutions is plotted or computed using a linear regression. Relative response is determined according to the procedures described below. At a minimum a five point calibration is employed.

9.4.2. The response of each target PCDD/PCDF relative to a labeled analog is determined using the area responses of either the primary or secondary exact m/z's specified in Table 6, for each calibration standard, as follows:

$$RR1 = (A1n/A21)(Cl/Cn)$$

$$RR2 = (A2n/A21)(Cl/Cn)$$

where:

A1n and A2n = The areas of the primary and secondary m/z's for the PCDD/PCDF.

A21 = The area of the primary or secondary m/z's for the labeled compound.

Cl = The concentration of the labeled compound in the calibration standard (Table 4).

Cn = The concentration of the native compound in the calibration standard (Table 4).

9.4.3. To calibrate the analytical system by isotope dilution, inject a volume of calibration standards CS1 through CS5. Compute the relative responses (RR1 and RR2) at each concentration.

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9.4.4. Linearity: If the relative response for any compound is constant (less than 20% coefficient of variation) over the five-point calibration range, an averaged relative response may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point calibration range.

9.5. Data Storage: MS data shall be collected, recorded, and stored.

9.5.1. Data acquisition: The signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

9.5.2. Response factors and multipoint calibrations: The data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity. Statistics on initial performance and ongoing performance should be computed and maintained, either on the instrument data system, or on a separate computer system.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Sample preparation involves modifying the physical form of the sample so that the PCDDs/PCDFs can be extracted efficiently.

10.1.2. For samples known or expected to contain high levels of the PCDDs/PCDFs, the smallest sample size representative of the entire sample should be used.

10.1.3. For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes. If the set contains a field duplicate, it must also be processed through the same steps as the other samples in the batch.

10.1.4. Sample Sub-Dividing

10.1.4.1. The homogenization, or blending procedures may be carried out in fume hood to prevent particles from contaminating the work environment.

10.1.4.2. Mixing: Place sample in a zip-lock plastic bag. Thoroughly homogenize the sample for several minutes until completely mixed. Take care to exclude plant material and obvious rocks or other non-representative components before mixing. Treat the blank and reference matrix aliquots using a clean spatula.

10.1.4.3. Homogenization or blending: Particles that are not ground effectively, or particles greater than 1mm in size after grinding, may often be reduced in size by high speed homogenization or blending.

10.1.4.4. Each size-reducing preparation procedure shall be verified before the procedure is employed routinely.

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10.2. Sample spiking

10.2.1. Weigh 10-50g of the homogenized or blended sample into a soxhlet thimble.

10.2.2. Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

10.2.3. Spike an appropriate amount of the diluted labeled compound spiking solution into the sample (See Table 2).

10.2.4. For each sample or sample batch to be extracted during the same 12 hour shift weigh out two 10-50g aliquots of the sand reference matrix in clean soxhlet thimbles.

10.2.5. Spike an appropriate amount of the diluted labeled compound spiking solution into each reference matrix aliquot (See Table 2). One aliquot will serve as the method blank. Spike an appropriate amount of the PAR solution into the other reference matrix aliquot (See Table 2). This will serve as the OPR.

10.3. Extraction

10.3.1. SDS Extraction

10.3.1.1. Charge a clean extraction thimble with the sample and spike according to section 10.2.

10.3.1.2. Place the thimble in a clean extractor. Place 30-40mL of toluene or benzene in the receiver and 200-300mL of toluene or benzene in the flask with boiling stones added.

10.3.1.3. Assemble the SDS apparatus, and apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sample until water removal lessens the restriction to toluene or benzene flow. Frequently check the apparatus for foaming during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

10.3.1.4. Drain the water from the receiver at one to two hours and/or eight to nine hours, or sooner if the receiver fills with water. Reflux the sample for a minimum of 16 hours.

10.3.1.5. Drain the water from the Dean-Stark receiver

10.3.1.6. Concentrate the extract using one of the macro-concentration procedures.

10.4. Macro-Concentration

10.4.1. Extracts in benzene or toluene are concentrated using a heating mantle

10.4.2. Turn heating mantle off. Disassemble SDS apparatus once it has cooled for approx. 10 minutes. Leave round flat bottom flasks in heating mantle with sample and prepare them for boil

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down. Place a vigreux in each flask and set mantle to desired temp. Boil sample to 20ml or under. Pour sample into pre-marked 40 ml vial and bring final volume to 40ml using hexane.

10.5. Extract Cleanup

10.5.1 Acid Silica column

10.5.1.1. Insert glass wool plug into a disposable pipette. In the following manner, add approximately 0.5 g of dried silica, 0.5 g of acid silica, and 0.2 g of dried silica into the pipette.

10.5.2. Carbon Column.

10.5.2.1. Insert a glass-wool plug at one end of the disposable glass tube, and pack the column with 0.55g +/- 0.05 grams of Carbopak/Celite to form an adsorbent bed approximately 2cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place. With a marker, mark one end of the tube.

10.5.3. Two column clean-up using Acid Silica and Carbon Columns

10.5.3.1. Set up column system that the acid silica column drains into the carbon column (make sure mark on carbon column is on top). Pre-elute the columns by adding approximately 10mL of benzene or toluene to the acid column which drains into the carbon column. Add additional 10mL of 50/50 hexane/methylene chloride to the carbon column.

10.5.3.2. Apply not more than 20mL of the sample extract to the column (if less than 20mL of the sample extract is added to the column, after the column drains, apply additional hexane so that the sample extract and hexane amount totals 20mL). Apply 5 mL of hexane to complete the elution. Discard acid column

10.5.3.3. Invert the carbon column (mark on carbon column on bottom), and wash the column with 10mL of 50/50 hexane/methylene chloride. Discard the eluate. Elute the PCDDs/PCDFs with 10mL of toluene. If carbon particles are present in the eluate, filter through glass-fiber filter paper or glass wool.

10.5.3.4. Concentrate the eluate for further cleanup or injection into the GC/MS.

10.6. Micro-Concentration and Solvent Exchange.

10.6.1. Transfer the vial containing the sample extract to a nitrogen blowdown device. Adjust the flow of nitrogen so that the surface of the solvent is visibly disturbed.

10.6.2. Lower the vial into a 40-60°C water bath and continue concentrating to dryness.

10.6.3. Transfer sample by adding hexane into a 0.3mL conical vial for final concentration

10.6.4. Evaporate to dryness in the conical vial

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10.6.5. Add a known amount (e.g. 20 μ L) of the appropriate injection standard to the vial. Seal the vial and label with the sample number. If an extract is to be reanalyzed and evaporation has occurred, do not add more instrument internal standard solution. Rather, bring the extract back to its previous volume with nonane.

10.7. HRGC/LRMS Analysis

10.7.1. Establish the operating conditions.

10.7.2. Inject 1.0 μ L or 2.0 μ L of the concentrated extract containing the internal standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration. Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the last peaks of interest have eluted. Return the column to the initial temperature for analysis of the next extract or standard.

10.8. System and Laboratory Performance

10.8.1. For each 12-hour shift where analyses are performed, GC/MS system performance and calibration are verified for all target PCDDs/PCDFs and labeled target compounds. Adjustment and/or recalibration shall be performed until all performance criteria are met. Only after all performance criteria are met samples, blank, and OPR may be analyzed.

10.8.2. Calibration Verification.

10.8.2.1. Inject the DVS and VER standard.

10.8.2.2. The m/z abundance ratios for all target PCDDs/PCDFs shall be within the limits in Table 6; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated.

10.8.2.3. For VER, compute the concentration of each target PCDD/PCDF compound by isotope dilution.

10.8.2.4. For each target compound, compare the concentration with the calibration verification limit in Table 4. If all target compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any target compound fails its respective limit, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the verification test, or recalibrate.

10.8.3. Ongoing Precision and Recovery.

10.8.3.1. Analyze the extract of the ongoing precision and recovery (OPR) aliquot prior to analysis of samples from the same batch.

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10.8.3.2. Compute the concentration of each target PCDD/PCDF by isotope dilution. Compute the concentration of each labeled target compound by the internal standard method.

10.8.3.3. For each target PCDD/PCDF, compare the concentration with the OPR limits given in Table 4. If all target compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual target compound concentration falls outside of the range given, the extraction/concentration process may have been performed improperly for that compound. In this event, the result will be flagged and an assessment of the acceptability will be done.

10.8.3.4. Blank: Analyze the method blank extracted with each sample batch immediately following analysis of the OPR aliquot to indicate freedom from significant contamination and freedom from significant carryover from the OPR analysis.

10.9. Qualitative Determination

10.9.1. A PCDD, PCDF, or labeled compound is identified in a standard, blank, or sample when all of the criteria below are met.

10.9.2. The signals for the two m/z's in Table 6 must be present and must maximize within the same two seconds.

10.9.3. The signals for the native m/z's must maximize within the two seconds of the corresponding ¹³C-standard.

10.9.4. The ratio of the integrated areas of the two m/z's specified in Table 6 must be within the limit in Table 6, or within ±15% of the ratio in the midpoint calibration.

10.10. Quantitative Determination.

10.10.1. Isotope Dilution Quantitation: By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the PCDD/PCDF can be made because the PCDD/PCDF and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative response (RR) values are used in conjunction with the initial calibration data to determine concentrations directly, as long as labeled compound spiking levels are constant, using the following equation:

$$C1_{ex} \text{ (pg/g)} = [(A1_n/A2_1) \cdot CI] / RR1 / \text{sample weight dry (g)}$$

$$C2_{ex} \text{ (pg/g)} = [(A2_n/A2_1) \cdot CI] / RR2 / \text{sample weight dry (g)}$$

where:

A1_n and A2_n = The areas of the primary and secondary m/z's for the PCDD/PCDF.

A2_l = The area of the primary or secondary m/z's for the labeled compound.

CI = The amount in pg of the labeled compound in the calibration standard (Table 4).

C_{nex} = The concentration (pg/g) of the PCDD/PCDF in the sample.

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10.10.2 Reporting Concentrations:

10.10.2.1 If C1ex and C2ex are within 15% RPD (relative percent difference), average the two values for reporting final concentration. If the values do not agree within 15% then report the lower value and the value will be flagged.

10.11. Internal Standard Quantitation and Labeled Compound Recovery.

10.11.1. Compute the concentrations of ¹³C-labeled analogs in the extract using the response factors determined from the initial calibration data and the following equation:

$$\text{RRF} = (A1is/A2ij) * (Aij/Ais)$$

$$\% \text{ recovery} = (A1iss/A2ijs) * (Aij/Amis) / \text{RRF} * Af$$

A1is - area of internal standard in calibration standard

A1iss - area of internal standard in sample

A2ij – area of injection standard in calibration standard

A2ijs – area of injection standard in sample

Aij – amount of injection standard in pg

Ais – amount of internal standard in pg

Amis – amount of internal standard in pg in the sample

Af – aliquot factor (taking into account the aliquot taken in step 10.5.3.2.). Value will always be 1 or greater

10.11.2. If the SICP area at either quantitation m/z for any compound exceeds the calibration range, determine if the value is within the linear range of the instrument. If the SICP area is within the linear range of the instrument, no further dilution is necessary and the value will be flagged as outside the calibration range but within the linear range of the instrument. If the SICP area is not within the linear range of the instrument, dilute the extract until the SICP area is within the linear range of the instrument.

10.11.3. Results are reported to three significant figures for the PCDDs/PCDFs and two significant figures for recovery rate found in the OPR, blank, and samples.

10.12. Reporting units

10.12.1. Report results in ng/kg based on the dry weight of the sample. Also calculate and report TEQ for the target analytes and an estimated total TEQ (E_{TEQ}).

10.13. Reporting level

10.13.1. Data will be reported down to the sample specific estimated detection level. In general, the method should be able to achieve the estimated detection limits listed in Table 8.

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10.14. Polychlorinated Diphenyl Ethers: For the purposes of this method polychlorinated diphenyl ethers will be quantified as polychlorinated dibenzofurans resulting in a high ETEQ bias.

11. POLLUTION PREVENTION

11.1. The solvents used in this method pose little threat to the environment when managed properly. The solvent evaporation techniques used in this method are amenable to solvent recovery, and it is recommended that the laboratory recover solvents wherever feasible.

11.2. Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standards.

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12. WASTE MANAGEMENT

12.1. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

12.2. The PCDDs/PCDFs decompose above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

12.3. Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the PCDDs/PCDFs can no longer be detected.

12.4. Further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better—Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

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14. TABLES AND FIGURES

Table 1

Chlorinated Dibenzo-p-Dioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/Low Resolution Mass Spectrometry (LRMS)

PCDD/PCDF	CAS Registry
2,3,7,8-TCDD	1746-01-6
2,3,7,8-TCDF	51207-31-9
1,2,3,7,8-PeCDD	40321-76-4
1,2,3,7,8-PeCDF	57117-41-6
2,3,4,7,8-PeCDF	57117-31-4
1,2,3,4,7,8-HxCDD	39227-28-6
1,2,3,6,7,8-HxCDD	57653-85-7
1,2,3,7,8,9-HxCDD	19408-74-3
1,2,3,4,7,8-HxCDF	70648-26-9
1,2,3,6,7,8-HxCDF	57117-44-9
2,3,4,6,7,8-HxCDF	60851-34-5
1,2,3,7,8,9-HxCDF	72918-21-9
1,2,3,4,6,7,8-HpCDD	35822-46-9
1,2,3,4,6,7,8-HpCDF	67562-39-4
1,2,3,4,7,8,9-HpCDF	55673-89-7
OCDD	3268-87-9
OCDF	39001-02-0
13C-2,3,7,8-TCDD	76523-40-5
13C-2,3,7,8-TCDF	89059-46-1
13C-1,2,3,7,8-PeCDD	109719-79-1
13C-1,2,3,7,8-PeCDF	109719-77-9
13C-2,3,4,7,8-PeCDF	116843-02-8
13C-1,2,3,4,7,8-HxCDD	109719-80-4
13C-1,2,3,6,7,8-HxCDD	109719-81-5
13C-1,2,3,7,8,9-HxCDD	109719-82-6
13C-1,2,3,4,7,8-HxCDF	114423-98-2
13C-1,2,3,6,7,8-HxCDF	116843-03-9
13C-2,3,4,6,7,8-HxCDF	116843-05-1
13C-1,2,3,7,8,9-HxCDF	116843-04-0
13C-1,2,3,4,6,7,8-HpCDD	109719-83-7
13C-1,2,3,4,6,7,8-HpCDF	109719-84-8
13C-1,2,3,4,7,8,9-HpCDF	109719-94-0
13C-OCDD	114423-97-1
13C-OCDF	109719-78-0

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Table 2

Concentration of Stock and Spiking Solutions Containing PCDDs/PCDFs and Labeled Compounds

	Labeled Spiking solution (ng/mL)	PAR Stock Solution (ng/mL)	Injection Standard (ng/mL)	Labeled Spiked Amount (ng)	PAR Spiked Amount (ng)
PCDD/PCDF					
2,3,7,8-TCDD		1000			10
2,3,7,8-TCDF		1000			10
1,2,3,7,8-PeCDD		2500			25
1,2,3,7,8-PeCDF		2500			25
2,3,4,7,8-PeCDF		2500			25
1,2,3,4,7,8-HxCDD		2500			25
1,2,3,6,7,8-HxCDD		2500			25
1,2,3,7,8,9-HxCDD		2500			25
1,2,3,4,7,8-HxCDF		2500			25
1,2,3,6,7,8-HxCDF		2500			25
2,3,4,6,7,8-HxCDF		2500			25
1,2,3,7,8,9-HxCDF		2500			25
1,2,3,4,6,7,8-HpCDD		2500			25
1,2,3,4,6,7,8-HpCDF		2500			25
1,2,3,4,7,8,9-HpCDF		2500			25
OCDD		5000			50
OCDF		5000			50
13C-2,3,7,8-TCDD	1000, 10000			110	
13C-2,3,7,8-TCDF	1000			10	
13C-1,2,3,7,8-PeCDD	1000			10	
13C-1,2,3,7,8-PeCDF	1000			10	
13C-2,3,4,7,8-PeCDF	1000			10	
13C-1,2,3,4,7,8-HxCDD	1000			10	
13C-1,2,3,6,7,8-HxCDD	1000			10	
13C-1,2,3,7,9-HxCDD	1000			10	
13C-1,2,3,4,7,8-HxCDF	1000			10	
13C-1,2,3,6,7,8-HxCDF	1000			10	
13C-2,3,4,6,7,8-HxCDF	1000			10	
13C-1,2,3,7,8,9-HxCDF	1000			10	
13C-1,2,3,4,6,7,8-HpCDD	1000			10	
13C-1,2,3,4,6,7,8-HpCDF	1000			10	
13C-1,2,3,4,7,8,9-HpCDF	1000			10	
13C-OCDD	2000			20	
13C-OCDF	2000			20	
<i>Injection Standard</i>					
13C-1,2,7,8-TCDF			50		

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Table 3

An Example Set of PCDDs/PCDFs in Calibration and Calibration Verification Solutions

PCDD/PCDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	4	50	250	1000	5000
2,3,7,8-TCDF	4	50	250	1000	5000
1,2,3,7,8-PeCDD	10	125	625	2500	12500
1,2,3,7,8-PeCDF	10	125	625	2500	12500
2,3,4,7,8-PeCDF	10	125	625	2500	12500
1,2,3,4,7,8-HxCDD	10	125	625	2500	12500
1,2,3,6,7,8-HxCDD	10	125	625	2500	12500
1,2,3,7,8,9-HxCDD	10	125	625	2500	12500
1,2,3,4,7,8-HxCDF	10	125	625	2500	12500
1,2,3,6,7,8-HxCDF	10	125	625	2500	12500
2,3,4,6,7,8-HxCDF	10	125	625	2500	12500
1,2,3,7,8,9-HxCDF	10	125	625	2500	12500
1,2,3,4,6,7,8-HpCDD	10	125	625	2500	12500
1,2,3,4,6,7,8-HpCDF	10	125	625	2500	12500
1,2,3,4,7,8,9-HpCDF	10	125	625	2500	12500
OCDD	20	250	1250	5000	25000
OCDF	20	250	1250	5000	25000
13C-2,3,7,8-TCDD	10	10	10	10	10
13C-2,3,7,8-TCDF	10	10	10	10	10
13C-1,2,3,7,8-PeCDD	10	10	10	10	10
13C-1,2,3,7,8-PeCDF	10	10	10	10	10
13C-2,3,4,7,8-PeCDF	10	10	10	10	10
13C-1,2,3,4,7,8-HxCDD	10	10	10	10	10
13C-1,2,3,6,7,8-HxCDD	10	10	10	10	10
13C-1,2,3,7,8,9-HxCDD	10	10	10	10	10
13C-1,2,3,4,7,8-HxCDF	10	10	10	10	10
13C-1,2,3,6,7,8-HxCDF	10	10	10	10	10
13C-2,3,4,6,7,8-HxCDF	10	10	10	10	10
13C-1,2,3,7,8,9-HxCDF	10	10	10	10	10
13C-1,2,3,4,6,7,8-HpCDD	10	10	10	10	10
13C-1,2,3,4,6,7,8-HpCDF	10	10	10	10	10
13C-1,2,3,4,7,8,9-HpCDF	10	10	10	10	10
13C-OCDD	20	20	20	20	20
13C-OCDF	20	20	20	20	20

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Table 4

Acceptance Criteria for Performance Tests

PCDD/PCDF	amount [ng]	S [ng]	x [ng]	OPR [ng]	OPR [%]	VER [ng/mL]	VER [%]
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	67-158	80-120	80-120
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8	75-158	80-120	80-120
1,2,3,7,8-PeCDD	25	3.8	19-33	17-36	68-144	200-300	80-120
1,2,3,7,8-PeCDF	25	3.8	21-31	20-34	80-136	200-300	80-120
2,3,4,7,8-PeCDF	25	4.3	18-38	17-40	68-160	200-300	80-120
1,2,3,4(6),7,8-HxCDD	50	4.7	39-76	35-82	70-164	400-600	80-120
1,2,3,7,8,9-HxCDD	25	5.6	18-36	16-42	64-168	200-300	80-120
1,2,3,4(6),7,8-HxCDF	50	4.4	42-61	36-67	76-134	400-600	80-120
2,3,4,6,7,8-HxCDF	25	3.7	18-37	17-39	68-156	200-300	80-120
1,2,3,7,8,9-HxCDF	25	3.2	21-31	19-33	76-132	200-300	80-120
1,2,3,4,6,7,8-HpCDD	25	3.9	19-33	17-35	68-140	200-300	80-120
1,2,3,4,6,7,8-HpCDF	25	3.2	22-28	20-32	80-128	200-300	80-120
1,2,3,4,7,8,9-HpCDF	25	4.1	21-32	18-35	76-140	200-300	80-120
OCDD	50	10	44-64	39-72	78-144	400-600	80-120
OCDF	50	14	37-73	31-85	62-170	400-600	80-120

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Table 5

Labeled Compound Recovery in Samples

PCDD/PCDF	lower limit [%]	upper limit [%]
13C-2,3,7,8-TCDD	5	100
13C-2,3,7,8-TCDF	5	100
13C-1,2,3,7,8-PeCDD	5	100
13C-1,2,3,7,8-PeCDF	5	100
13C-2,3,4,7,8-PeCDF	5	100
13C-1,2,3,4,7,8-HxCDD	5	100
13C-1,2,3,6,7,8-HxCDD	5	100
13C-1,2,3,7,8,9-HxCDD	5	100
13C-1,2,3,4,7,8-HxCDF	5	100
13C-1,2,3,6,7,8-HxCDF	5	100
13C-2,3,4,6,7,8-HxCDF	5	100
13C-1,2,3,7,8,9-HxCDF	5	100
13C-1,2,3,4,6,7,8-HpCDD	5	100
13C-1,2,3,4,6,7,8-HpCDF	5	100
13C-1,2,3,4,7,8,9-HpCDF	5	100
13C-OCDD	5	100
13C-OCDF	5	100

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Table 6

Descriptors, M/Z's, M/Z Types, and Elemental Compositions, Theoretical Ion Abundance Ratios and QC Limits of the PCDDs and PCDFs

	selected ions	Theoretical Abundance	Control Limits
PCDD/PCDF			
2,3,7,8-TCDD	320/322	0.77	0.65 - 0.89
2,3,7,8-TCDF	304/306	0.77	0.65 - 0.89
1,2,3,7,8-PeCDD	356/358	1.53	1.30 - 1.76
1,2,3,7,8-PeCDF	340/342	1.53	1.30 - 1.76
2,3,4,7,8-PeCDF	340/342	1.53	1.30 - 1.76
1,2,3,4,7,8-HxCDD	390/392	1.22	1.04 - 1.40
1,2,3,6,7,8-HxCDD	390/392	1.22	1.04 - 1.40
1,2,3,7,8,9-HxCDD	390/392	1.22	1.04 - 1.40
1,2,3,4,7,8-HxCDF	374/376	1.23	1.05 - 1.42
1,2,3,6,7,8-HxCDF	374/376	1.23	1.05 - 1.42
2,3,4,6,7,8-HxCDF	374/376	1.23	1.05 - 1.42
1,2,3,7,8,9-HxCDF	374/376	1.23	1.05 - 1.42
1,2,3,4,6,7,8-HpCDD	424/426	1.02	0.87 - 1.17
1,2,3,4,6,7,8-HpCDF	408/410	1.02	0.87 - 1.17
1,2,3,4,7,8,9-HpCDF	408/410	1.02	0.87 - 1.17
OCDD	462/464	2.45	2.08 - 2.82
OCDF	442/444	0.88	0.75 - 1.01
13C-2,3,7,8-TCDD	332/334	0.77	0.65 - 0.89
13C-2,3,7,8-TCDF	316/318	0.77	0.65 - 0.89
13C-1,2,3,7,8-PeCDD	366/368	0.62	0.53 - 0.71
13C-1,2,3,7,8-PeCDF	350/352	0.62	0.53 - 0.71
13C-2,3,4,7,8-PeCDF	350/352	0.62	0.53 - 0.71
13C-1,2,3,4,7,8-HxCDD	400/402	0.51	0.43 - 0.59
13C-1,2,3,6,7,8-HxCDD	400/402	0.51	0.43 - 0.59
13C-1,2,3,7,8,9-HxCDD	400/402	0.51	0.43 - 0.59
13C-1,2,3,4,7,8-HxCDF	384/386	0.51	0.43 - 0.59
13C-1,2,3,6,7,8-HxCDF	384/386	0.51	0.43 - 0.59
13C-2,3,4,6,7,8-HxCDF	384/386	0.51	0.43 - 0.59
13C-1,2,3,7,8,9-HxCDF	384/386	0.51	0.43 - 0.59
13C-1,2,3,4,6,7,8-HpCDD	438/436	0.97	0.82 - 1.12
13C-1,2,3,4,6,7,8-HpCDF	422/420	0.97	0.82 - 1.12
13C-1,2,3,4,7,8,9-HpCDF	422/420	0.97	0.82 - 1.12
13C-OCDD	474/472	0.65	0.55 - 0.75
13C-OCDF	456/454	1.14	0.97 - 1.31

Document Date: 6/29/2011
Revision Date: 10/5/2011

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Table 7

Example for elution order on a DB-5MS column

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

Note: elution orders may change on other column types

Table 8

Target Estimated Detection Levels (TEDL)

PCDD/PCDF	TEDL (ng/kg dry weight)
2,3,7,8-TCDD	10
2,3,7,8-TCDF	10
1,2,3,7,8-PeCDD	10
1,2,3,7,8-PeCDF	10
2,3,4,7,8-PeCDF	10
1,2,3,4 (6),7,8-HxCDD	20
1,2,3,7,8,9-HxCDD	10
1,2,3,4 (6),7,8-HxCDF	20
2,3,4,6,7,8-HxCDF	10
1,2,3,7,8,9-HxCDF	10
1,2,3,4,6,7,8-HpCDD	25
1,2,3,4,6,7,8-HpCDF	25
1,2,3,4,7,8,9-HpCDF	25
OCDD	50
OCDF	50

Document Date: 6/29/2011
 Revision Date: 10/5/2011