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SAC-ID-0008 (2,3,7,8-TCDD by 8280A)

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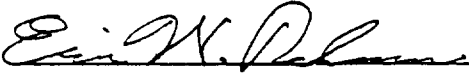
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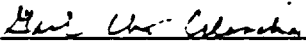
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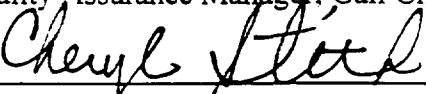
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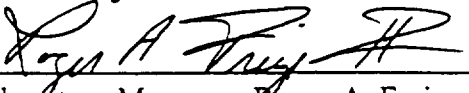
OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE
TITLE: ANALYSIS OF POLYCHLORINATED DIOXINS/FURANS BY LOW
RESOLUTION GC/MS
(SUPERSEDES: SEPTEMBER 20, 1993, REVISION 2.0)

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1. SCOPE AND APPLICATION

- 1.1. This SOP is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soil, oil, waste, plant and animal tissues, and air trains. The compounds and CAS numbers are listed in Appendix I, Table 7.
- 1.2. Detection limits: see Appendix I, Table 7.
- 1.3. Recommended range of concentration: 0.5-50 ppb in solids and 5-500 ppt in aqueous matrices.
- 1.4. Analysis time: approximately 30 minutes for a GC/MS run.

2. SUMMARY OF METHOD

- 2.1. The analysis is performed on a fused silica capillary column in a gas chromatograph (GC) interfaced to a mass spectrometer (MS). Identification of PCDDs/PCDFs is based on detection of the ions specified in Appendix I, Table 1 and measurement of the appropriate relative abundances (ratio) of two characteristic ions in the molecular ion cluster.
- 2.2. This method is a combination of isotope dilution and internal standard techniques. The PCDDs/PCDFs are quantitated by comparing the MS response of the detected analyte relative to the MS response of the appropriate internal standard. Labeled internal standards are added to the sample prior to extraction. The addition of the labeled internal standards prior to sample extraction causes the analytical results to be automatically recovery corrected. This procedure assumes that the internal standard losses are equal to the unlabeled PCDD/PCDF losses during sample preparation and analysis. The recovery standards are added to each sample extract and blank aliquot prior to injection. The recovery of the internal standards is related to the precision and quantitation limits of the analysis for the unlabeled PCDDs/PCDFs in the sample. (IS recovery should be >40%; if recovery is less than 40% then the chromatographic signal-to-noise ratio for the IS must be greater than 10-to-1.)

3. DEFINITIONS

- 3.1. Concentration Calibration Solution: A standard solution containing known amounts of the analytes (unlabeled 2,3,7,8-TCDD/TCDF; 1,2,3,7,8-PeCDD/PeCDF; 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD/HxCDF; 1,2,3,6,7,8-HxCDD/HxCDF; 1,2,3,7,8,9-HxCDD/HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDD/HpCDF; 1,2,3,4,7,8,9-

HpCDF; and OCDD/OCDF), the internal standards (^{13}C -2,3,7,8-TCDF; ^{13}C -2,3,7,8-TCDD; ^{13}C -1,2,3,6,7,8-HxCDD; ^{13}C -1,2,3,4,6,7,8-HpCDF; and ^{13}C -OCDD), the clean up recovery standard (^{37}Cl -2,3,7,8-TCDD), and the recovery standards (^{13}C -1,2,3,4-TCDD and ^{13}C -1,2,3,7,8,9-HxCDD) are analyzed prior to sample analysis. It is used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard, as well as the internal standards and clean-up recovery standard to that of the recovery standard (i.e., relative response factors or RRFs). See also Appendix I, Table 3.

- 3.2. Recovery Standards: ^{13}C -1,2,3,4-TCDD and ^{13}C -1,2,3,7,8,9-HxCDD are added to every blank, quality control sample, and sample extract aliquot prior to analysis. It is used to measure the recovery of the internal standards and the clean up recovery standard independent of the extraction process.
- 3.3. Internal Standards: ^{13}C -2,3,7,8-TCDF, ^{13}C -2,3,7,8-TCDD, ^{13}C -1,2,3,6,7,8-HxCDD, ^{13}C -1,2,3,4,6,7,8-HpCDF and ^{13}C -OCDD are added to every sample, blank, quality control sample, and concentration calibration solution. They are added to the sample before extraction and are used to measure the concentrations of the analytes or detection limits.
- 3.4. Clean Up Recovery Standard: ^{37}Cl -2,3,7,8-TCDD is added to every sample, blank, quality control sample, and concentration calibration solution. It is added to the samples after extraction but prior to extract clean up, and is used to judge the efficiency of the clean up procedures.
- 3.5. Response Factor: The ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of an internal standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used in the quantitation calculations.
- 3.6. Signal-to-noise: Defined as the ratio of analyte signal to random background signal.
- 3.7. Detection Limit (D.L.): When analytes are not detected in the sample, a calculation is performed to establish the maximum concentration of each analyte that could be present.
- 3.8. Window Defining Mix: This solution contains the first and last eluting isomer of each homologue and is used to verify that the switching times between the descriptors have been appropriately set.
- 3.9. Homologous Series: Defined as a series of organic compounds in which each successive member has one more chlorine atom than the preceding member.

- 3.10. Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.
- 3.11. Congener: Defined as any member of a particular homologous series, for example, pentachlorinated dibenzofurans.
- 3.12. Continuing Calibration Solution (Daily Standard): Analyzed every 12 hours to demonstrate continued acceptable GC/MS performance. The solution is the same as the CC3 medium standard in the initial calibration.
- 3.13. Column Performance Solution Mixture (CPSM): A mixture of TCDD isomers (including the 2,3,7,8-TCDD isomer) known to elute near each other on an SP-2331 column. Used to demonstrate acceptable resolution between the 2,3,7,8-TCDD isomer and all other TCDD isomers on the SP-2331 column (valley <25%).
- 3.14. Abbreviations

PCDD	-	Polychlorinated Dibenzo-p-dioxin
PCDF	-	Polychlorinated Dibenzofuran
TCDD	-	Tetrachlorinated Dibenzo-p-dioxin
TCDF	-	Tetrachlorinated Dibenzofuran
PeCDD	-	Pentachlorinated Dibenzo-p-dioxin
PeCDF	-	Pentachlorinated Dibenzofuran
HxCDD	-	Hexachlorinated Dibenzo-p-dioxin
HxCDF	-	Hexachlorinated Dibenzofuran
HpCDD	-	Heptachlorinated Dibenzo-p-dioxin
HPCDF	-	Heptachlorinated Dibenzofuran
OCDD	-	Octachlorinated Dibenzo-p-dioxin
OCDF	-	Octachlorinated Dibenzofuran
GC	-	Gas Chromatograph
MS	-	Mass Spectrometer (or Matrix Spike)
DS	-	Data System
SIM	-	Selected Ion Monitoring (or MID)
SICP	-	Selected Ion Current Profile (Chromatogram)
S/N	-	Signal-to-Noise
WDM	-	Window Defining Mix
CPSM	-	Column Performance Solution Mixture
CC	-	Calibration Check Standard
RRF	-	Relative Response Factor
IS	-	Internal Standard
RS	-	Recovery Standard

CRS	-	Clean Up Recovery Standard
OD	-	Outside Diameter
m/z	-	Mass-to-Charge Ratio
EMPC	-	Estimated Maximum Possible Concentration
DL	-	Detection Limit
DPE	-	Diphenyl Ether
PCB	-	Polychlorinated Biphenyls
NS	-	Native Spike (same as Matrix Spike)
NSD	-	Native Spike Duplicate (same as Matrix Spike Duplicate)

4. INTERFERENCES

- 4.1. Any compound that yields ions listed in Appendix I, Table 4 and also elutes within the retention time window of the corresponding congener is a potential interference. PCDDs/PCDFs are often associated with other interfering chlorinated compounds such as (PCBs) and polychlorinated biphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest.
- 4.2. 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 those materials must be demonstrated to be free from interferences under the conditions of analysis by running laboratory method blanks.
- 4.3. High-resolution capillary columns are used to resolve as many PCDD/PCDF isomers as possible; however, no single column is known to resolve all of the isomers.
- 4.4. GC syringes must be rinsed thoroughly before and after each injection of a standard, sample, or blank. Care must be taken to keep these syringes contaminant-free. If there is any doubt as to syringe integrity, clean the syringe and shoot a tetradecane blank or obtain a new syringe.
- 4.5. A 2 µL injection volume is used throughout this method.

NOTE: THE INJECTION VOLUME FOR ALL SAMPLE EXTRACTS, BLANKS, QUALITY CONTROL SAMPLES AND CALIBRATION SOLUTIONS MUST BE THE SAME.

5. SAFETY

- 5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

- 5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Neoprene, natural rubber and nitrile gloves provide varying degrees of protection against the solvents listed. Refer to permeation/degradation charts for the actual data.
- 5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.
- 5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: Dibenzo-p-dioxins and Dibenzofurans. 2,3,7,8-TCDD is a carcinogen, teratogen, and mutagen. Other PCDDs and PCDFs with chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. Exposure to these chemicals must be kept to a minimum by whatever means available.
- 5.3.2. Chemicals known to be **flammable** are: Methanol, Toluene, Hexane, and Acetone
- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.
- 5.7. Material Safety Data Sheets (MSDSs) are available to lab personnel, and must be read before samples or chemicals are handled.

6. EQUIPMENT AND SUPPLIES

- 6.1. Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

- 6.1.1. The GC is capable of temperature programming and equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port is designed for capillary columns; a splitless or an on-column injection technique is recommended.
- 6.2. Mass spectral data is obtained using a low resolution instrument, utilizing 70 volts (nominal) electron energy in the electron impact mode. The system is capable of selected ion monitoring (SIM) for at least 18 ions simultaneously, with a cycle time of 1 second or less. Minimum integration time for SIM is 25 millisecond per m/z. The integration time used to analyze samples is identical to the time used to analyze the calibration solutions and QC samples. Total data acquisition time per cycle (18 ions) must not exceed 1 second.
- 6.3. An interfaced data system (DS) is present to acquire, store, reduce, and output mass spectral data.
- 6.4. GC Columns: Fused silica capillary columns are used. Values for total concentrations of PCDDs and PCDFs are acquired using a 60m DB-5 column. In addition, a combination of the DB-5 column results, and the results of a separate analysis on an SP-2331 column can yield 2,3,7,8-substituted isomer results. If a client requests 2,3,7,8-TCDD and/or 2,3,7,8-TCDF values only, then the SP-2331 column analysis is sufficient.

7. REAGENTS AND STANDARDS

7.1. Calibration Gas

- 7.1.1. A solution of FC-43 is used to calibrate the GC/MS.

7.2. Standards and Quality Control Solutions

- 7.2.1. Solutions are purchased from outside sources.

- 7.2.2. See discussions under "Definitions" for the following:

7.2.2.1 Concentration calibration solutions.

- 7.2.2.1.1 See also Appendix I, Table 3 for complete lists of compounds and concentrations.

7.2.3. Recovery Standards

7.2.4. Internal Standards

7.2.5. Clean Up Recovery Standard

7.2.6. Window Defining Mix (Table 3A)

7.2.7. Continuing calibration solution (CC3)(Table 3)

7.2.8. Column performance solution mixture (Table 3B)

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples must be extracted within 30 days from collection and analyzed within 45 days of collection.
- 8.2. Samples must be stored at 4°C protected from light until the time of extraction.
- 8.3. Grab and composite samples must be collected in glass (preferably amber) containers.

9. QUALITY CONTROL

- 9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of laboratory reagent water or sodium sulfate processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance/Anomaly memo, then implemented when target analytes are detected in the method blank above the target detection limit or when internal standard recoveries are outside control limits. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable.
 - 9.1.1. Method blanks must have no target analytes detected greater than the required quantitation limit.
 - 9.1.2. If a target analyte is detected in the blank, but is not detected in the samples, the data may be reported, unless specified by the client. Note in the narrative. The analyst should review procedures to identify and eliminate any developing contamination trends.

- 9.1.3. If a target analyte is detected in the blank, and associated samples contain >20x the concentration of the contaminant in the blank, then the results may be reported unless specified by the client. Note in the narrative.
- 9.1.4. If the method blank contains any target analyte greater than the required quantitation limit, then an attempt to determine and eliminate the cause of contamination should be made. The associated QC and field samples affected by this contamination must then be reextracted.
- 9.2. Laboratory Control Sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner as the associated samples. Corrective actions must be documented on a Non-Conformance/Anomaly memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Reextraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable. See Quanterra Inc. QA Policy 003 for specific acceptance criteria. LCS components and spike concentrations are given in Appendix I, Table 6. The LCS controls the batch. LCS failure will trigger a batch reparation.
- 9.2.1. If the LCS is above control limits, and samples have no detected target analytes, then the data may be reported, unless specified by the client. Note in the narrative.
- 9.3. Matrix specific QC of a matrix spike (MS) and matrix spike duplicate (MSD) are performed at the request of the client or every 20 samples of a given matrix. Unless specified by the client, all QC and field samples are spiked and controlled by internal standards added at the time of extraction. The labeled internal standards may be used to assess matrix effects, and define corrective actions (see Section 9.4). When an MS/MSD are requested, matrix spike compounds and concentrations will be the same as those used for the LCS. See Appendix I, Table 6. These compounds will be spiked into aliquots of the sample specified by the client at the same concentration level as the LCS unless otherwise requested by the client.
- 9.4. Internal standard (IS) recovery should be greater than 40%. If recovery is less than 40%, then the signal-to-noise for the IS must be greater than 10-to-1. If these requirements are not met the sample may require reextraction using a smaller sample aliquot.
- 9.5. If the percent recovery of the clean-up recovery standard is less than 50%, then it is likely that the internal standard recoveries are also low. Evaluate sample and project history. If necessary, reextract and reanalyze the sample.

10. CALIBRATION

- 10.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo/Anomaly and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance/Anomaly Memo shall be filed in the project file.
- 10.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.
- 10.3. Calibration is comprised of instrument tuning (when needed), the setting/verification of switching times, the examination of chromatographic resolution on the SP-2331 column, and the analysis of a standard or standards.

10.3.1. Mass Calibration

Mass calibration (tuning) of the mass spectrometer is performed as needed based upon evaluation of the continuing calibration. It is desirable to tune the instrument to greater sensitivity in the high mass range to achieve better response to the later eluting compounds. Optimum results using FC-43 for mass calibration may be achieved by scanning from 50-550 amu every one second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode. Under these conditions, m/z 414 and m/z 502 should be greater than or equal to m/z 220. See Appendix II for instrument tuning instructions.

10.3.2. Window Defining Mix (WDM)

Prior to the calibration of the GCMS system, it is necessary to establish the appropriate switching times for the SIM descriptors. The switching times are determined by the analysis of the window defining mix containing the first and last eluting isomers in each homologue. The window defining mix must be analyzed at the frequency identified below:

- Before initial or continuing calibration on each instrument in which a DB-5 column is used for analysis.
- Each time a new initial calibration is performed, regardless of reason.
- Each time adjustments or instrument maintenance activities are performed that may affect retention times.

10.3.3. Column Performance Solution Mixture (CPSM)

The column performance solution mixture must be analyzed at the frequency listed below:

- At the beginning and end of every analytical sequence (not to exceed 12 hours) on a SP-2331 GC column for the determination of tetra-dioxins and -furans.
- On an SP-2331 GC column, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of a commercially available column performance mix that contains the TCDD isomers that elute most closely with the 2,3,7,8-TCDD isomer (1,4,7,8-TCDD, and 1,2,3,7/1,2,3,8-TCDD pair).
- The chromatographic peak separation between unlabeled 2,3,7,8-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of $\leq 25\%$ on the SP-2331 GC column.

10.3.4. Initial Calibration

The five calibration solutions outlined in Table 3 must be analyzed prior to sample analyses. The solutions must be analyzed in the order of CC3, CC1, CC2, CC4 and CC5 to avoid biasing the calibration.

10.3.4.1. Analyze a 2 μ L aliquot of each of the five concentration calibration solutions. The identical GC/MS/DS conditions used for the WDM (DB-5) or CPSM (SP-2331) solution must also be used for the concentration calibration solutions.

10.3.4.2. The laboratory must not proceed with the sample analyses until an acceptable initial calibration is determined and documented according to the following criteria.

- The relative ion abundance criteria listed for PCDDs/PCDFs in Appendix I, Table 4 must be met using areas to calculate the ratios.
- All analytes must fall within the appropriate retention time windows established by the Window Defining Mix (DB-5 column).

- MS Sensitivity. The signal-to-noise ratio (S/N) must be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10 for the internal standard and recovery standard ions (Table 4).
- The S/N must be ≥ 25 to 1 for the m/z 320 ion of the 2,3,7,8-TCDD obtained from the injection of the 100 ng/mL calibration standard.

10.3.4.3. Calculate the relative response factor for the native PCDDs/PCDFs relative to their appropriate internal standard. Calculate the relative response factor for the internal standards and the clean up recovery standard relative to the appropriate recovery standard.

NOTE: THE RELATIVE RESPONSE FACTORS OF GIVEN ISOMERS WITHIN ANY CONGENER ARE KNOWN TO BE DIFFERENT. HOWEVER, FOR THE PURPOSES OF THESE CALCULATIONS, IT WILL BE ASSUMED THAT EVERY ISOMER FOR A GIVEN CONGENER HAS THE SAME RELATIVE RESPONSE FACTOR. IN ORDER TO MINIMIZE THE EFFECT OF THIS ASSUMPTION ON RISK ASSESSMENT, 2,3,7,8- SUBSTITUTED ISOMERS WERE CHOSEN AS REPRESENTATIVE OF EACH CONGENER. THE RELATIVE RESPONSE FACTOR FOR A GIVEN CONGENER IS USED TO QUANTITATE THAT SPECIFIC 2,3,7,8-SUBSTITUTED ISOMER. THE TOTALS VALUE REPORTED FOR A GIVEN CONGENER CLASS WILL BE BASED AGAINST THE LOWEST RELATIVE RESPONSE FACTOR FOR THAT GIVEN CLASS. IF THE CONGENER CLASS IS NON-DETECT, THE HIGHEST RELATIVE RESPONSE FACTOR WILL BE USED TO CALCULATE THE CONGENER'S ESTIMATED DETECTION LIMIT.

10.3.5. Calculations are outlined below:

10.3.5.1. Response Factors

$$RRF_n = \frac{(An_1 + An_2) \times C_{is}}{(A_{is1} + A_{is2}) \times C_n}$$

$$RRF_{is} = \frac{(A_{is1} + A_{is2}) \times C_{rs}}{(A_{rs1} + A_{rs2}) \times C_{is}}$$

$$RRF_{crs} = \frac{A_{crs} \times C_{rs}}{(A_{rs_1} + A_{rs_2}) \times C_{crs}}$$

Where:

RRF_n = the response factor of the isomer of interest relative to that of the appropriate internal standard.

RRF_{crs} = the response factor of the clean up recovery standard relative to that of the recovery standard.

RRF_{is} = the response factor of the internal standard relative to that of the appropriate recovery standard.

C_n = concentration (ng/ μ L) of the native isomer present in the CC solution.

C_{is} = concentration (ng/ μ L) of the appropriate internal standard present in the CC solution.

C_{rs} = concentration (ng/ μ L) of the appropriate recovery standard present in the CC solution.

C_{crs} = concentration (ng/ μ L) of the clean up recovery standard present in the CC solution.

$A_{n_1} + A_{n_2}$ = integrated ion abundance area of the quantitation ions of the isomer of interest (Table 1).

$A_{is_1} + A_{is_2}$ = integrated ion abundance area of the quantitation ions of the appropriate internal standard (Table 1 and 2).

$A_{rs_1} + A_{rs_2}$ = integrated ion abundance of the quantitation ions of the appropriate recovery standard (Table 1).

A_{crs} = integrated ion abundance of the quantitation ion of the clean up recovery standard (Table 1).

10.3.6. Calibration Acceptance

10.3.6.1. Calculate the mean RRF (RRF_{AVE}) and percent relative standard deviation (%RSD) of the RRFs for the unlabeled PCDDs/PCDFs (CC1 through CC5).

$$RRF_{AVE} = \frac{\sum RRF_n}{n}$$

where n = number of calibration standards.

$$\text{Standard Deviation} = \sqrt{\sum_{i=1}^n [(RRF_{AVE} - RRF_i)^2 / (n-1)]}$$

$$\%RSD = \frac{\text{Standard Deviation} \times 100}{RRF_{AVE}}$$

10.3.6.2. The % RSD of the RRFs for the unlabeled PCDDs/PCDFs (CC1-CC5) must not exceed 15 percent.

10.3.6.3. If the initial calibration curve requirements are not met, the following suggestions may be useful:

- Reshoot the standard that is causing the problem.
- Check and adjust the GC and/or MS operating conditions.
- Adjust or replace the GC column.
- Adjust the MS for greater or lesser resolution using FC-43.
- Recalibrate.

10.3.6.4. The (RRF_{AVE}) is used for quantitation of target analytes detected in samples.

10.3.7. Continuing Calibration (i.e. Daily Standard)

10.3.7.1. Inject a 2 μ L aliquot of the continuing calibration solution (CC3, Mid-Point). The continuing calibration solution must be analyzed at the beginning of each 12-hour period.

10.3.7.2. The identical GC/MS/DS conditions used for the WDM or CPSM and the initial calibration solutions must also be used for the continuing calibration solution.

10.3.7.3. The measured RRFs of each analyte in the daily continuing calibration must be within $\pm 30\%$ of the RRF_{AVE} established by the analysis of the five-point (CC1-CC5) initial calibration.

10.3.7.4. The relative ion abundances listed in Table 4 must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.

10.3.7.5. The S/N ratio must be greater than 2.5 to 1 for the unlabeled PCDD/PCDF ions, and greater than 10.0 to 1 for the labeled internal and recovery standards.

10.3.7.6. If any of the criteria listed above are not met, the analyst must take corrective actions and reanalyze the continuing calibration standard. If the criteria are met after the corrective action, then sample analysis may begin.

10.3.7.7. If the criteria listed above are not met after the corrective action, then the analyst must perform a new initial calibration. This new initial calibration must meet all of the QC criteria in Section 10.

11. PROCEDURE

11.1. Sample Analysis

11.1.1. Prior to injection, 25 ng of ^{13}C -1,2,3,4-TCDD and ^{13}C -1,2,3,7,8,9-HxCDD (Recovery Standards) are added to each sample. These compounds are used to monitor the recovery of the internal standards that were added to each sample prior to the extraction method.

11.1.2. Inject a 2 μL aliquot of the sample into the GC/MS instrument. Analyze the sample by the identical GC/MS/DS conditions used for the continuing calibration.

11.2. Identification

11.2.1. Identification Criteria

11.2.1.1. All of the specified ions listed in Appendix I, Table 1, for each congener of PCDDs/PCDFs must be present in the reconstructed ion chromatogram and should maximize simultaneously.

11.2.1.2. The GC peaks assigned to a congener must have retention times within the windows established for that congener by the column window-defining mix.

11.2.1.3. The integrated ion current for each analyte ion listed in Table 1 must be at least 2.5 times background noise and must not have saturated the detector. However, if the $[M-COCl]^+$ ion does not meet the 2.5 times S/N requirement, but the target analyte meets all the other criteria listed and, in the judgment of the GC/MS operator, the peak is a PCDD/PCDF, the peak may be reported as positive, otherwise, use the peak area to report an "estimated maximum possible concentration" (EMPC).

11.2.1.4. The relative intensity (ratio) of the selected isotopic ions must lie within the range specified in Appendix I, Table 4. This applies to both the native analytes and the internal standards.

11.2.2. Confirmation/Quantitation of Qualitatively Identified 2,3,7,8-Substituted Isomers.

11.2.2.1. When 2,3,7,8-TCDD and/or 2,3,7,8-TCDF are qualitatively identified on the DB-5 column, then confirmation and quantitation by the SP-2331 column is required.

11.2.3. Identification Procedure

11.2.3.1. The identification of a GC peak as a PCDF cannot be made if a signal having S/N greater than 2.5 is detected at the same retention time (± 2 seconds) in the corresponding PCDPE channel (see Table 1). If a PCDPE is detected, an Estimated Maximum Possible Concentration (EMPC) shall be calculated for this GC peak, regardless of the ion abundance ratio.

11.2.3.2. If reintegration of any peak is necessary, how the reintegration was made must be indicated. All changes must be documented with an initial and date. An output of the original integration with the area counts must be included, or alternatively, the redrawn baselines and new area counts must be documented on the original output.

11.2.3.3. Analyze the continuing calibration every 12 hours. All criteria listed in Section 10.3.6 must be met.

11.3. Data Processing

11.3.1. Use the appropriate dump procedure to hardcopy specific MID runs. See project flowsheet for specific analysis.

TO60 - tetra-octa dioxins and furans

TD60 - tetra dioxin

TF60 - tetra dioxin and furan

TH60 - tetra-hexa dioxins and furans

11.3.2. Review data for acceptable internal standard recoveries and the need for TCDD/TCDF confirmation analysis.

11.3.2.1. If IS recovery is acceptable and the sample does not need second column analysis, proceed to Section 11.2.3.

11.3.2.2. If IS recovery is acceptable, but second column analysis is needed, transfer sample and associated paperwork to a GC/MS configured for TCDD/TCDF analysis.

11.3.2.3. If IS recovery is unacceptable, contact team leader or senior chemist for assistance. Reextraction of the sample may be necessary.

11.3.3. Package all associated paperwork for samples together prior to proceeding to data write-up.

11.3.3.1. Make certain that the following paperwork is included in every project.

11.3.3.2. Project flowsheet, including preparation/extraction log, benchsheet, and ticket report.

11.3.3.3. All samples in project, including method blank.

11.3.3.4. Copy of instrument log book page(s).

11.3.3.5. Copy of associated WDM.

11.3.3.6. Copy of all associated continuing calibrations.

11.4. Data Write-up

11.4.1. Use the Dioxin spreadsheet program on the VAX to write up dioxin data.

11.4.1.1. Enter data into dioxin program (appropriate scan numbers, heights, RRFs, areas, etc.).

11.4.1.2. Check ratios (see Table 5)

11.4.1.3. Check response factors on standards (must be +/- 30% of curve)

11.4.1.4. Calculate DL or concentration (if possible) for all samples.

11.4.1.5. DL for totals must take into consideration whole congener window.

11.4.1.6. Follow project specific criteria where noted.

11.5. Post Injection procedures

11.5.1. Have all data reviewed by another operator before giving data to team leader or senior chemist.

11.5.2. Include appropriate standards, logbook sheets, LCS forms, etc.

11.6. Trouble Shooting

11.6.1. The major problem is loss of sensitivity. If this occurs, the following is probably the cause.

11.6.1.1. Leaky septum

- Check head pressure, change septum.

11.6.1.2. Poor injection technique

- If septum is okay, check the needle and reinject.

11.6.1.3. Check voltages or filament. Replace filament if necessary.

11.6.1.4. Check System Status, type SS <cr>.

11.6.1.5. Check GC trace.

11.6.1.6.If the chromatography is poor, break off two feet from the back end of the column. If chromatography is still poor, break off six to twelve inches from the front portion of the column.

11.6.1.7.Ask team leader or senior chemist for assistance when trouble shooting, if necessary.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Definitions

C _n	=	concentration of native PCDD/PCDF found in the sample
W	=	weight (g) of sample extracted
V	=	volume (L) of sample extracted
Q _{is}	=	quantity (ng) of internal standard added to sample before extraction
Q _{rs}	=	quantity (ng) of recovery standard added to sample extract
Q _{crs}	=	quantity (ng) of cleanup recovery standard added to sample before cleanup.

NOTE: (A_{n1} + A_{n2}), (A_{is1} + A_{is2}), (A_{rs1} + A_{rs2}), RRF_n, RRF_{is}, and RRF_{crs} were defined in Section 10.3.5.1.

The concentrations of the various isomers of each congener shall be calculated using the RRF determined for that particular isomer from the continuing calibration.

12.2. Concentration

Determine the concentration of the total PCDDs/PCDFs (tetra-through octa-CDD, tetra- through octa- CDF) (C_n) according to the equations:

<u>SOIL</u>	<u>WATER</u>
$C_n \text{ (ng/g)} = \frac{Q_{is} \times (A_{n1} + A_{n2})}{W \times (A_{is1} + A_{is2}) \times RRF_n}$	$C_n \text{ (ng/L)} = \frac{Q_{is} \times (A_{n1} + A_{n2})}{V \times (A_{is1} + A_{is2}) \times RRF_n}$

12.3. Percent Recovery

12.3.1. Calculate the percent recovery of the internal standards (Ris) using the following equation:

$$R_{is} = \frac{(A_{is_1} + A_{is_2}) \times Q_{rs}}{(A_{rs_1} + A_{rs_2}) \times RRF_{is} \times Q_{is}} \times 100\%$$

12.3.2. Calculate the percent recovery of the cleanup recovery standard (³⁷Cl-2,3,7,8-TCDD, Rcrs) using the following equation:

$$R_{crs} = \frac{A_{crs} \times Q_{rs}}{(A_{rs_1} + A_{rs_2}) \times RRF_{crs} \times Q_{crs}} \times 100\%$$

12.3.3. For matrix spike samples, calculate the percent recovery of the isomer spiked using the following equations:

$$\text{Amt. (ng/L or ng/g) of Isomer Found in Spike} = \frac{(A_{n_1} + A_{n_2}) \times Q_{is}}{(A_{is_1} + A_{is_2}) \times RRF_n \times (W \text{ or } V)}$$

$$\% \text{Recovery} = \frac{\text{Amt of isomer in Spike} - \text{Amt of isomer in sample}}{\text{Amt of isomer added to the spiked sample}} \times 100\%$$

12.4. The Relative Percent Difference (RPD) between duplicate samples is calculated as follows:

$$RPD = \frac{[S1 - S2] \times 100}{\text{Mean Concentration}} = \frac{[S1 - S2] \times 100}{(S1 + S2) / 2}$$

S1 and S2 represent sample and duplicate sample results.

12.5. Detection Limits (See Table 7)

12.5.1. For samples in which no native PCDFs/PCDDs are detected, calculate the estimated detection limit (EDL) for each of the 10 congeners. The EDL is the concentration of a given PCDF/PCDD congener that would produce a signal

with peak height of 2.5 times the background signal level, or when no interference is present, if it were a PCDF/PCDD congener. The data must be carefully examined to determine which DL calculation will be used. Follow the rules below.

- 12.5.2. When only electronic noise is present, or if only one chemical peak is present at either the primary or secondary ion, use the following calculation:

$$\text{Estimated Detection Limit (EDL)} = \frac{2.5 \times (H_{n1} + H_{n2}) \times Q_{is}}{(His_1 + His_2) \times RRF_n \times (W \text{ or } V)}$$

where:

$(H_{n1} + H_{n2})$ = peak height of the quantitation ions of the compound of interest.

$(His_1 + His_2)$ = peak height of the quantitation ions of the appropriate internal standard.

- 12.5.3. When chemical peaks are present at both the primary and secondary ions that do not meet ratio criteria, but do meet the signal -to-noise criteria, use the formula below:

$$\text{EMPC} = \frac{(A_{n1} + A_{n2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times RRF_n \times (W \text{ or } V)}$$

EMPC = Estimated Maximum Possible Concentration

NOTE: Q_{is} , RRF_n , $(A_{n1} + A_{n2})$, $(A_{is1} + A_{is2})$, W and V were defined in Sections 10.3.5.1 and 12.1

12.6. Reporting Format

12.6.1. Reporting units

12.6.1.1.ng/L (ppt) for aqueous samples

12.6.1.2.ng/g (ppb) for solid samples

12.6.2. Detection Limits

12.6.2.1. All PCDD and PCDF analyses use a technique for calculating the estimated detection limit (EDL) for each of the chlorination levels and each congener by using the noise level present in the elution window and the heights of the chromatographic peak of the internal standard. Both signal to noise and peak heights are determined by the GC/MS data system and the result is a detection limit that is specific to the homologous series and sample. Since this method quantitates results using an isotope dilution technique, there is not a set reporting limit. Each sample will have its own sample specific estimated detection limit reported. (See Section 12.5 for calculations).

13. METHOD PERFORMANCE

- 13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

14. POLLUTION PREVENTION

- 14.1. No solvents of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

- 15.1. Waste management in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator or Hazardous Materials Technician should be contacted if additional information is required.
- 15.2. All waste must be disposed of according to the facility hazardous waste management procedures, Attachment C of the Chemical Hygiene Plan, Section WS002, Table 1.
- 15.3. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the facility hazardous waste management procedures, Attachment C of the Chemical Hygiene Plan, Section WS003, Disposal of Samples After Analysis.

16. REFERENCES

- 16.1. SW-846, 3rd Edition. Method 8280.

16.2. US EPA PCDD/PCDF Statement of Work, DFLM01.0, including Revision DFLM01.1, September 1991.

16.3. SW-846, Method 8280A. Update III Draft, January 1995.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Deviations from reference method (Method 8280)

- 17.1.1. Clean Up Recovery Standard: ^{37}Cl -2,3,7,8-TCDD is added to every sample, blank, quality control sample, and concentration calibration solution. It is added to the samples after extraction but prior to extract clean up, and is used to judge the efficiency of the clean up procedures. Addition and monitoring of this compound is not required by SW846 but is used as an additional diagnostic tool by the laboratory for isolating steps where analytes may be lost. No corrective action is required if recoveries are outside recommended control limits.
- 17.1.2. Column Performance Solution Mixture (CPSM): The CPSM is used to demonstrate acceptable resolution between the 2,3,7,8-TCDD isomer and all other TCDD isomers on the SP-2331 column. Quanterra Incorporated (West Sacramento) uses the SP-2331 column type as the primary column for the quantitation of 2,3,7,8-TCDD and 2,3,7,8-TCDF. Generally, the DB-5 column is used to determine presumptive results for the TCDD isomers and is not designated as the primary column for the quantitation of these analytes. Therefore, it is not necessary to evaluate the DB-5 column for resolution of these analytes.
- 17.1.3. A single injection of each multilevel standard (5 concentrations) instead of triplicate injections is used to construct the calibration curve as described in section 6.7 of Method 8280. For a calibration curve to be acceptable, the %RSD must be $\leq 15\%$. If this criteria is not met, then a new curve must be constructed. The triplicate analysis was required at the time of method development when HRGC/LRMS instruments were considerably less stable. The practice of using the average of triplicate injections would give the laboratory the best opportunity to meet the RSD criteria. Current instrumentation is more stable and the laboratory can meet the RSD criteria using single injections of each standard. If the %RSD criteria is not met, then the laboratory constructs a new calibration curve.
- 17.1.4. As recommended by the DFLM01.1 Statement of Work for Dioxins, five internal standards are used in the analysis.

17.1.5. Section 7.8 of Method 8280 indicates that the discarded fraction of the alumina column eluent is checked for target analytes. The laboratory assays the discarded fraction of the alumina column eluent for target analytes when out of control recoveries are observed in LCS or MS samples. Reagents will be checked and elution patterns will be reoptimized if target analytes are detected in the discarded fraction of the alumina column eluent.

17.1.6. The isotopic ratios listed in Table 4 for penta-, through octa-dioxins/furans as well as ratios for the hexa-,hepta-, and octa-dioxin or furan internal standards represent either the inverse of ratios specified in Method 8280 or a more accurate calculation of the theoretical relative intensity range. These ratios are provided in U.S. EPA Statement of Work DFLM01.0 including revision 1.1 (September 1991).

17.2. List of other SOPs cross-referenced in SOP.

17.2.1. SAC-QA-0041 Calibration and Calibration Check of Balances, Revision 1.1.

17.2.2. LP-CAL-0001 Laboratory Documentation Practices, Revision 3.0.

17.2.3. QA Policy 003 Quanterra Quality Control Program, Revision 0.

17.2.4. QA Policy 008 Data Recording Requirements, Rev. 0.

17.2.5. Chemical Hygiene Plan, Attachment C, Hazardous Waste Management Procedures, Current Edition.

17.3. Tables or figures referenced in body of SOP.

17.3.1. Table 1: Ions Specified for Selected Ion Monitoring for PCDDs and PCDFs

17.3.2. Table 2: Reference of Internal Standards and Corresponding Analytes

17.3.3. Table 3: Concentration Calibration Solutions

17.3.4. Table 3A: PCDD/PCDF Isomers in the Window Defining Mix for a 60m DB-5 Column

17.3.5. Table 3B: Column Performance Solution for a SP-2331 Column

17.3.6. Table 4: Criteria for Isotopic Ratio Measurements for PCDDs and PCDFs

17.3.7. Table 5: Operating Conditions Guidelines

17.3.8. Table 6: Laboratory Control Sample/Matrix Spike Solution

17.3.9. Table 7: Target Detection Limits

Appendix I

Table 1

**Ions Specified for Selected Ion
Monitoring for PCDDs and PCDFs**

<u>Analyte</u>	<u>Quantitation Ions</u>		<u>M-[COCl]⁺</u>
PCDFs			
Tetra	304	306	243
Penta	340	342	277
Hexa	374	376	311
Hepta	408	410	345
Octa	442	444	379
PCDDs			
Tetra	320	322	259
Penta	356	358	293
Hexa	390	392	327
Hepta	424	426	361
Octa	458	460	395
Internal Standards			
13C-2378-TCDF	316	318	
13C-2378-TCDD	332	334	
13C-123678-HxCDD	402	404	
13C-1234678-HpCDF	420	422	
13C-OCDD	470	472	
Recovery Standards			
13C-1234-TCDD	332	334	
13C-123789-HxCDD	402	404	
Clean Up Recovery Standard			
37Cl-2378-TCDD	328	---	

NOTE: Ions at m/z 376, 410, 446, 480 and 514 are also included to monitor for interferences from Diphenylethers.

Table 2

Reference of Internal Standards and Corresponding Analytes

<u>13C-TCDD</u>	<u>13C-TCDF</u>	<u>13C-HxCDD</u>	<u>13C-HpCDF</u>	<u>13C-OCDD</u>
TCDD	TCDF	HxCDD	HxCDF	OCDF
PeCDD	PeCDF	HpCDD	HpCDF	OCDD

Table 2A

**Reference of Recovery Standard to
Corresponding Internal Standards and Clean-up Recovery Standard**

<u>13C-1,2,3,4-TCDD</u>	<u>13C-1,2,3,7,8,9-HxCDD</u>
13C-2,3,7,8-TCDF	13C-1,2,3,6,7,8-HxCDD
13C-2,3,7,8-TCDD	13C-1,2,3,4,6,7,8-HpCDF
37Cl-2,3,7,8-TCDD	13C-OCDD

Table 3

Concentration Calibration Solutions²

<u>Native Compounds</u>	CC1	CC2	CC3	CC4	CC5
2,3,7,8-TCDD	0.1	0.25	0.5	1.0	2.0
2,3,7,8-TCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDD	0.1	0.25	0.5	1.0	2.0
2,3,4,7,8-PeCDF			0.5		
1,2,3,4,7,8-HxCDF			1.25		
1,2,3,6,7,8-HxCDF	0.25	0.625	1.25	2.5	5.0
2,3,4,6,7,8-HxCDF			1.25		
1,2,3,7,8,9-HxCDF			1.25		
1,2,3,4,7,8-HxCDD			1.25		
1,2,3,6,7,8-HxCDD	0.25	0.625	1.25	2.5	5.0
1,2,3,7,8,9-HxCDD			1.25		
1,2,3,4,6,7,8-HpCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,7,8,9-HpCDF			1.25		
1,2,3,4,6,7,8-HpCDD	0.25	0.625	1.25	2.5	5.0
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
<u>Internal Standards</u>					
13C-2378-TCDF	0.5	0.5	0.5	0.5	0.5
13C-2378-TCDD	0.5	0.5	0.5	0.5	0.5
13C-123678-HxCDD	0.5	0.5	0.5	0.5	0.5
13C-1234678-HpCDF	1.0	1.0	1.0	1.0	1.0
13C-OCDD	1.0	1.0	1.0	1.0	1.0
<u>Clean-up Recovery Standard</u>					
37Cl-2,3,7,8-TCDD			0.25		
<u>Recovery Standards</u>					
13C-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5

²: Concentrations are in ng/μL.

Table 3A

PCDD/PCDF Isomers In The Window Defining Mix For A 60m DB-5 Column

<u>Homologue</u>	<u>First Eluted</u>	<u>Last Eluted</u>
TCDD	1,3,6,8-	1,2,8,9-
TCDF	1,3,6,8-	1,2,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-

Additional Isomers

13C-1,2,3,4-TCDD
13C-2,3,7,8-TCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
OCDD
OCDF

Table 3B

Column Performance Solution For A SP-2331 Column

Isomers

1,4,7,8-TCDD
2,3,7,8-TCDD
1,2,3,7/1,2,3,8-TCDD
1,2,3,4-TCDD
13C-2,3,7,8-TCDD
13C-1,2,3,4-TCDD

Table 4

Criteria for Isotopic Ratio Measurements for PCDDs and PCDFs

<u>Analyte</u>	<u>Selected Ions</u>	<u>Relative Intensity</u>
PCDFs		
Tetra	304/306	0.65-0.89
Penta	340/342	1.24-1.86 ³
Hexa	374/376	1.05-1.43 ³
Hepta	408/410	0.88-1.20 ³
Octa	442/444	0.76-1.02 ³
PCDDs		
Tetra	320/322	0.65-0.89
Penta	356/358	1.24-1.86 ³
Hexa	390/392	1.05-1.43 ³
Hepta	424/426	0.88-1.20 ³
Octa	458/460	0.76-1.02 ³
Internal Standards		
13C-2,3,7,8-TCDF	316/318	0.65-0.89
13C-2,3,7,8-TCDD	332/334	0.65-0.89
13C-1,2,3,6,7,8-HxCDD	402/404	1.05-1.43 ³
13C-1,2,3,4,6,7,8-HpCDF	420/422	0.88-1.20 ³
13C-OCDD	470/472	0.76-1.02 ³
Recovery Standards		
13C-1,2,3,4-TCDD	332/334	0.65-0.89
13C-1,2,3,7,8,9-HxCDD	402/404	1.05-1.43 ³

³: Relative intensity ratios are from SOW DFLM01.0 including Revision DFLM01.1 (September 1991).

Table 5

Operating Conditions Guidelines

Column Coating	DB-5 (or SP-2331 for isomer specific analyses)
Film Thickness	0.25 μ m
Column Dimensions	60m x 0.32mm
Helium Linear Velocity	35-40 cm/sec at 240°C
Initial Temperature	170°
Initial Time	1 minute
Temperature Program	increase to 310° at 8°/min
Hold Time	until OCDF elutes

Table 6

Laboratory Control Sample/Matrix Spike Solution

<u>Compounds</u>	<u>Concentration</u>	<u>Compounds</u>	<u>Concentration</u>
2,3,7,8-TCDF	25	2,3,7,8-TCDD	25
1,2,3,7,8-PeCDF	62.5	1,2,3,7,8-PeCDD	62.5
1,2,3,6,7,8-HxCDF	62.5	1,2,3,6,7,8-HxCDD	62.5
1,2,3,4,6,7,8-HpCDF	62.5	1,2,3,4,6,7,8-HpCDD	62.5
OCDF	125	OCDD	125

units = ng/sample

Table 7

**Target Detection Limits
Soil/Solid/Aqueous**

<u>PCDD/PCDF</u>	<u>CAS Number</u>	<u>Water (ng/L)</u>	<u>Quantitation Limits¹</u>		
			<u>Soil (ug/Kg)</u>	<u>Fly Ash (ug/Kg)</u>	<u>Chemical Waste² (ug/Kg)</u>
2378-TCDD	1746-01-6	5.0	0.5	0.5	5.0
2378-TCDF	51207-31-9	5.0	0.5	0.5	5.0
12378-PeCDF	57117-41-6	12.5	1.25	1.25	12.5
12378-PeCDD	40321-76-4	12.5	1.25	1.25	12.5
23478-PeCDF	57117-31-4	12.5	1.25	1.25	12.5
123478-HxCDF	70648-26-9	12.5	1.25	1.25	12.5
123678-HxCDF	57117-44-9	12.5	1.25	1.25	12.5
123478-HxCDD	39227-28-6	12.5	1.25	1.25	12.5
123678-HxCDD	57653-85-7	12.5	1.25	1.25	12.5
123789-HxCDD	19408-74-3	12.5	1.25	1.25	12.5
234678-HxCDF	60851-34-5	12.5	1.25	1.25	12.5
123789-HxCDF	72918-21-9	12.5	1.25	1.25	12.5
1234678-HpCDF	67562-39-4	12.5	1.25	1.25	12.5
1234678-HpCDD	35822-46-9	12.5	1.25	1.25	12.5
1234789-HpCDF	55673-89-7	12.5	1.25	1.25	12.5
OCDD	3268-87-9	25	2.5	2.5	25
OCDF	69001-02-0	25	2.5	2.5	25

¹ All CRQL Values listed here are based on the wet weight of the sample.

² Chemical waste includes the matrices of oils, stillbottoms, oily sludge, wet fuel oil, oil-laced soil, and surface water heavily contaminated with these matrices.

Appendix II:
Operating instructions for the
Finnigan -Mat. 4500

I. System Check-out and Start-up

A. Vacuum

1. High vacuum should be in the 10^{-6} to 10^{-8} range with a capillary column installed and all other gases shut off. Normal column head pressure should be: 08-12 psi for 30m narrow bore columns and 18-20 psi for 60m wide bore.

B. Temperatures

1. Transfer line temperature should be set high enough to allow the last eluting compound to have good peak shape. Approximate temperatures are 10° C above the final column temperature.
2. Manifold temperature: Approximately 100° C.
3. Ion source temperature: 150° C, (LED blinking).

C. Rf Generator for 4500 Model

1. Depress multiple mass marker button on scope module. Check that these mass markers extend to the full range on both.

D. Tuning

1. Place the GC/MS in the manual mode by entering SS, type: EM1, FI1 and CA1 to turn on multiplier, filament and cal gas.
2. Check to see that the following conditions are met:
 - a. Filament: ON
 - b. EM voltage/DS: ON
 - c. Dynode: ON
 - d. Helium GC Carrier: ON
 - e. Cal Gas: ON
 - f. Vacuum Protect: ON
 - g. 2010 Interface power: ON
3. Set up Q3 with m/z 219 and m/z 502 on the split screen.
4. Tune for:

- a. Peak Shape
- b. Resolution
- c. Peak Intensities

Use the front panel adjustments as well as the source magnet.

II. System Shut-down

1. Check to see that the following conditions are met:

- a. Filament: OFF
- b. EM voltage/DS: STBY
- c. Dynode: STBY
- d. Helium GC Carrier: ON
- e. Cal Gas: OFF
- f. Vacuum Protect: ON
- g. 2010 Interface power: ON

III. Basic Maintenance

A. Removal of the Ion Source

1. Venting the Manifold.
 - a. Turn the filament OFF; the dynode and multiplier to STBY.
 - b. Turn the ionizer heater OFF by dialing in 00 on the thumbwheel switches.
Allow the ionizer to cool about 0.5 hr.
 - c. Turn the Vacuum Protect and Ion Gauge OFF.
 - d. Turn OFF the turbos; then the mechanical pumps or close baffle valve on the diffusion pump.
 - e. Insert the back fill plug assembly into the solid inlet port.
 - f. Open the solids inlet valve and wait for the pressure to equalize.
2. Loosen the O-ring fitting on the inlet evacuation solenoid and disconnect the ionizer cable and cal gas cables from the front flange assembly.
3. Slide back the transfer line by loosening the nut on the left side of the manifold.
4. Loosen and remove all but the top one of the flange bolts.
5. Holding the front flange firmly, remove the last flange bolt.

6. Looking through the viewing port, remove the source, being careful not to scrape it against the transfer line.
7. Place the ion source on the stand provided.

B. Steps to cleaning the source

1. Refer to pages 6-3 through 6-9 in the 4500 series GC/MS operators manual.

C. Installation of the ion source

1. Check to see that the copper gasket is in good condition. If not, replace it.
2. Check with an ohmmeter that the lens leads are not touching each other.
3. Slip the O-ring nut and O-ring over the inlet evacuation line.
4. Carefully take the ionizer flange assembly in two hands and insert the ionizer into the vacuum manifold. Looking through the viewing port, guide the flange into place.
5. Put in the bolts and hand-tighten.
6. Wrench-tighten the bolts using the opposite bolt technique.
7. Fasten the inlet evacuation line to the solenoid.
8. Reposition the transfer line into the ion source.
9. Re-evacuating the manifold.
 - a. Turn on mechanical pumps and turbomolecular pumps by pressing MECH Pumps and TURBO Pumps or turn on the diffusion pump by toggling the diffusion pump switch.
 - b. When the manifold forepressure is reduced to at least 0.04 torr and/or the turbopump is at least 80%, start the ion gauge.
 - c. With the ion gauge operating, place the system in the protect mode by pressing the VACUUM PROTECT button.

D. Removing the ion volume

1. Make sure that the filament and electron multiplier are OFF.

2. Make sure that the release knob in the handle of the insertions/removal (I/R) tool is retracted and locked.
3. Insert the tip of the tool into the vacuum seal at the entrance of the solids inlet valve, with the guide pin in the groove of the guide bar.
4. Slide the tool until the guide pin reaches the first step in the guide bar.
5. Tighten the seal by rotating the black vacuum seal nut clockwise until finger tight.
6. Evacuate the solids inlet valve by depressing the INLET EVAC push button on the vacuum controller.
7. Set the FOREPRESSURE switch to INLET.
8. Monitor the inlet pressure, and when it is reduced to 0.05 torr (after 5 or 10 seconds) disengage the INLET EVAC push button.
9. Open the solids inlet valve by rotating the handle fully counterclockwise.
10. Slowly slide the I/R tool collet all the way into the ion volume adapter.
11. Pull the release knob away from the handle and let it slide forward to expand the collet inside the adapter.
12. Slowly and carefully withdraw the I/R tool, with ion volume assembly attached, until the guide pin reached the offset stop.
13. Close the solids inlet valve by turning the handle fully clockwise.
14. Loosen the vacuum seal nut, rotate the pin past the offset stop, and withdraw the tool.
15. Release the ion volume by pulling back the release knob until it locks in the handle of the tool. Using clean gloves (or tweezers if it is hot), place the ion volume in the storage box provided. Close lid to keep out dust.

E. Installing the ion volume

1. Ensure that the release knob is retracted and insert the collet end of the I/R tool into the adapter of the selected ion volume assembly.

2. Pull the release knob out and let it go forward so as to expand the collet. Be sure that the adapter is fully seated on the collet and that the alignment bracket orientation is correct. The forks on the alignment bracket should be on the spring near the collar of the adapter.
3. Insert the I/R tool with the ion volume assembly through the solids inlet valve as described in steps 3 through 9 under Volume Removal, above.
4. Carefully slide the tool through the solids inlet valve, stopping about 20 mm short of complete insertion.
5. Look through the window on the top of the manifold and make sure the collector hole is pointing straight up.
6. Slowly slide the I/R tool the rest of the way in and check the proper seating of the ion volume assembly. If it is not properly seated, slide the I/R tool back about 20 mm and make sure that the collector hole is up and the detent flats down. If the collector hole is up and the detent flats, down, and the ion volume does not seat properly, it usually means there is an alignment problem.
7. Retract and lock the release knob (close and collet) and remove the tool as directed in steps 12 through 14 of the removal procedure.
8. Store the I/R tool in the accessory rack on the side of the instrument.

F. Column Installation

1. Bring the manifold to atmospheric pressure in A-1 and cool the injector and transfer line.
2. Uncoil a few turns of both ends of the column from its cage.
3. Using a diamond pencil, score and break about 6 inches from each of the sealed ends of the column.
4. Mount the column on its cage inside the GC oven, and slide a 1/16 inch Swagelok nut and graphite vespel ferrule onto the front end of the column.
5. Again, using a diamond cell pencil, score and break about 1 inch from the front end to ensure that no pieces of the ferrule are inside the column.
6. Insert the fused-silica capillary column into the bottom of the injector 57 mm.

7. Attach the 1/16 inch Swagelok nut and tighten finger-tight first, then tighten with a 5/16 inch wrench.
8. For a 30m x 0.25 mm ID fused-silica capillary column, set the column head pressure, using the pressure regulator on the front panel, to 8-12 psi. For a 60m x 0.32 ID, set the head pressure to 8-15 psi.
9. Using a bubble flow meter, adjust the SPLIT ADJUST valve to approximately 75 cc/min.
10. Slide a 1/16 inch Swagelok nut and a graphite vespel onto the detector end of the column.
11. Using a diamond pencil, score and break about 1 inch off the end of the column to ensure that no pieces of the ferrule get into the column.
12. Attach the 1/16 inch Swagelok, tighten with at 5/16 inch wrench, and bring the system back to high vacuum as in Section C-8 of Appendix III.
13. Using a flashlight, look through the vacuum view port and thread the column through the transfer-line to the point where it appears out the end of the transfer-line nozzle.
14. Now, thread the column to the entrance of the source block.

Caution: If the column is inserted too far into the source block, it will be shaved off by insertion or removal of the ion volume. This piece of column could end up in the instrument's vacuum system.

QUANTERRA INC. (West Sacramento)

STANDARD OPERATING PROCEDURE CHANGE FORM

SOP Number:	SAC-ID-0008, version 3.0
SOP Title:	ANALYSIS OF POLYCHLORINATED DIOXINS/FURANS BY LOW RESOLUTION GC/MS
SOP Sections Affected by Change:	Section 7.2 Section 3.12
Reason for Addition or Change:	Standards made in tetradecane have a viability of one year. Working calibration standards may be stored at room temperature.
Change Effective From [Date]:	10/8/98
Change or Addition (Specific Section; use additional sheets if necessary.):	<i>Section 7.2 All PCDD/PCDF calibration, internal standard, clean-up recovery standards, and spiking solutions are stable for one year from preparation. After one year, solutions may be revalidated. The revalidated solution may be used for an additional year or until there is evidence of compound degradation or concentration. The revalidation must be performed using an unexpired, not previously validated solution from a second lot or second vendor.</i> <i>Section 3.12 Working calibration standards may be stored at room temperature.</i>

Submitted by/Date:

Approved by:*

Technical Reviewer:



Date:

10/8/98

EH&S Signature:

Date:

QA Signature: 

Date: 10/7/98

Management Signature:



Date 10/8/98

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QUANT
DIOXIN/FURAN REVIEW SHEET

(Higher Molecular Wt. Ion used in Calculations)

Analysis: SAS: C14 - C18 - subst.

LR/HR: LR

Client Name: City of San Diego

CAL Project No.: CALLAB-089101

Client Sample ID: Method Blank

Quanterra Sample ID: 429275

Date Sampled:

Date Authorized:

Date Analyzed: 27 AUG 96

Sample Wt./Vol.: 1.0 L

RRF's from: ST27960827C

Units: NG/L

A = Amount added to the sample

CAL Sample Number.: 0002-MB

Matrix: AQUEOUS

Date Received: 17 AUG 96

Date Extracted: 22 AUG 96

GC Column: DB-5

Percent Moisture: NA

Data Prepared by: MBAQUERFO

	SCANS	TOTAL AREA	TOTAL AREA	DL HEIGHT	AREA RATIO	RRF	AMOUNT FOUND	DETECTION LIMIT	PERCENT RECOVERY
FURANS									
13C-2378-TCDF	2021	263162	336772	122339	0.78	1.85	25	(A)	51.53
Tetra (total)				1544		0.88	ND	0.8963543	
(2378)				1544		0.88	ND	0.8963543	
Penta (total)				540		0.70	ND	0.3941039	
(12378)				540		0.70	ND	0.3941039	
(23478)				540		0.64	ND	0.4310512	
Hexa (total)				520		1.10	ND	0.4031032	
(123478)				520		0.99	ND	0.4478925	
(123678)				520		1.10	ND	0.4031032	
(123789)				520		0.81	ND	0.5474242	
(234678)				520		0.95	ND	0.4667511	
13C-HpCDF	2838	410531	407687	146590	1.01	1.42	50	(A)	61.42
Hepta (total)				380		0.85	ND	0.3812153	
(1234678)				380		0.85	ND	0.3812153	
(1234789)				380		0.72	ND	0.4500458	
Octa (total)				332		1.70	ND	0.3834589	

QUANTERRA

Review, pg 2

Sample ID: CALLAB-089101 0002-MB

	SCANS	TOTAL AREA	TOTAL AREA	DL HEIGHT	AREA RATIO	RRF	AMOUNT FOUND	DETECTION LIMIT	PERCENT RECOVERY
DIOXINS									
13C-1234-TCDD	2055	282871	346472		0.82		25	(A)	
13C-123789-HxCDD	2678	254863	214225		1.19		25	(A)	
13C-2378-TCDD	2066	158601	200041	71262	0.79	1.17	25	(A)	48.71
37Cl-2378-TCDD	2068		142681	29249	0.00	1.14	10	(A)	49.72
Tetra (total)				424		0.85	ND	0.4374908	
(2378)				424		0.85	ND	0.4374908	
Penta (total)				676		0.85	ND	0.6975089	
(12378)				676		0.85	ND	0.6975089	
13C-123678	2678	145731	121087	52281	1.20	0.98	25	(A)	58.04
Hexa (total)				460		0.80	ND	0.6873912	
(123478)				460		0.76	ND	0.7235696	
(123678)				460		0.80	ND	0.6873912	
(123789)				460		0.78	ND	0.7050166	
Hepta (total)				664		0.91	ND	0.8722938	
(1234678)				664		0.91	ND	0.8722938	
13C-OCDD	3188	197796	224436	63662	0.88	0.72	50	(A)	62.51
OCDD (total)				292		1.01	ND	0.5676638	

ENSECO - California Analytical Laboratory
EPA SAS
Dioxin/Furan Standard - CC3

STD ID : ST27960827C
Column : DB-5
Date : 8-27-96 TIME : 22:00
Chemist : MCB
Std Mix : LR-III-55C

FURANS	IONS	SCANS	AREA	AREA	AMOUNT	RATIO	RRF
-----	----	-----	----	----	-----	-----	---
13C-2378-TCDF	316/318	2020	388246	492031	0.50	0.79	1.85
2378-TCDF	304/306	2021	342658	435496	0.50	0.79	0.88
12378-PnCdf	340/342	2293	371891	244727	0.50	1.52	0.70
23478-PnCdf	340/342	2348	336562	224736	0.50	1.50	0.64
123478-HxCDF	374/376	2582	873504	694435	1.25	1.26	0.99
123678-HxCDF	374/376	2591	966488	762246	1.25	1.27	1.10
234678-HxCDF	374/376	2635	837266	663435	1.25	1.26	0.95
123789-HxCDF	374/376	2700	712375	566016	1.25	1.26	0.81
13C-1234678-HpCDF	420/422	2840	641088	621347	1.00	1.03	1.42
1234678-HpCDF	408/410	2841	566880	669158	1.25	1.00	0.85
1234789-HpCDF	408/410	2960	572023	563459	1.25	1.02	0.72
OCDF	442/444	3203	1266100	1451100	2.50	0.87	1.70
DIOXINS							

13C-1234-TCDD	332/334	2054	211868	263405	0.50	0.80	
13C-2378-TCDD	332/334	2066	246021	310026	0.50	0.79	1.17
CL37-2378-TCDD	328	2067		272766	0.25		1.14
2378-TCDD	320/322	2067	208236	266011	0.50	0.78	0.85
12378-PnCDD	356/358	2376	290681	182595	0.50	1.59	0.85
13C-123789-HxCDD	402/404	2680	242212	202687	0.50	1.20	
123478-HxCDD	390/392	2647	463218	363235	1.25	1.28	0.76
123678-HxCDD	390/392	2654	487411	380716	1.25	1.28	0.80
13C-123678-HxCDD	402/404	2653	238240	197027	0.50	1.21	0.98
123789-HxCDD	390/392	2680	480378	368754	1.25	1.30	0.78
1234678-HpCDD	424/426	2925	495647	493841	1.25	1.00	0.91
13C-OCDD	470/472	3191	300309	338154	1.00	0.89	0.72
OCDD	458/460	3192	773156	842596	2.50	0.92	1.01

ENSECO - California Analytical Laboratory
EPA SAS
CONTINUING STANDARD COMPARISON SHEET

CONGENER -----	DAILY RRF -----	CURVE RRF -----	% D ---
FURANS			
13C-2378-TCDF	1.85	1.80	-2.8
2378-TCDF	0.88	0.96	8.3
12378-PnCdf	0.70	0.73	4.1
23478-PnCdf	0.64	0.67	4.5
123478-HxCdf	0.99	0.97	-2.1
123678-HxCdf	1.10	1.17	6.0
234678-HxCdf	0.95	1.01	5.9
123789-HxCdf	0.81	0.87	6.9
13C-1234678-HpCdf	1.42	1.45	2.1
1234678-HpCdf	0.85	0.94	9.6
1234789-HpCdf	0.72	0.78	7.7
OCDF	1.70	1.62	-4.9

DIOXINS

13C-1234-TCDD			
13C-2378-TCDD	1.17	1.16	-0.9
CL37-2378-TCDD	1.14	1.35	15.6
2378-TCDD	0.85	0.99	14.1
12378-PnCDD	0.85	0.79	-7.6
13C-123789-HxCDD			
123478-HxCDD	0.76	0.79	3.8
123678-HxCDD	0.80	0.94	14.9
13C-123678-HxCDD	0.98	1.02	3.9
123789-HxCDD	0.78	0.84	7.1
1234678-HpCDD	0.91	0.87	-4.6
13C-OCDD	0.72	0.64	-12.5
OCDD	1.01	1.20	15.8

DAILY :ST27960827C

CURVE :8-26-96

DATE :8-27-96

OPERATOR :MCB

ADVANCED TECHNOLOGY LOW RESOLUTION DIOXIN/FURAN ANALYSIS

PROJECT: _____
RECEIPT DATE: _____
IN PREP DATE: _____
TO GCMS DATE: _____
HTV DATE: _____

ANALYSIS: _____
DCS REF: _____
MB REF: _____
SAMPLE STORAGE LOCATION: _____
% MOISTURE REQUIRED YES NO

SAMPLE NUMBER	EXTRACTION/VOLUME		QC			13C INTERNAL STDS	
			MB			25 ng	13C-2378 TCDD
			DU	MS	SD	25 ng	13C-2378 TCDF
						25 ng	13C-123678 HxCDD
						50 ng	13C-1234678 HpCDF
			DCS		LCS	50 ng	13C-OCDD

CRS: 12.5 ng 37Cl-2378 TCDD

optional
OPTION "C"

IFB COLUMN

OPTION D2

RS:

25 ng 13C-1234 TCDD
25 ng 13C-123789 HxCDD

50 ul

DB-5

SP-2331

COMMENTS:

% SOLID	
/	/
/	/
/	/
/	/
/	/
/	/
/	/
/	/
/	/
/	/

Sample(s): _____
submitted for re-extraction on: _____
due to: _____

RELINQUISHED BY: _____

DUE DATE: _____

ACCEPTED BY: _____

GCMS LOCATION: _____

QUANTERRA INCORPORATED
West Sacramento

LOW RESOLUTION DIOXIN PROJECT CHECKLIST

PREP	REVIEW 1	REVIEW 2
Percent moisture results present		
LIMS entry completed with the correct dates		
ANALYSIS	REVIEW 1	REVIEW 2
Standards		
CPSM/WDM criteria met		
Standard criteria met		
Blank/Samples		
Blank criteria met		
IS recovery met		
S/N ratio checked		
Chromatography checked		
All samples run within 12 hours of standard		
Logbook pages included		
DATA WRITE-UP	REVIEW 1	REVIEW 2
DCS included		
CPSM/WDM correctly labeled and included		
All associated standards included		
All samples and associated blanks reported		
Correct RRF's used in calculations		
IS recoveries met		
All ratios met		
Correct sample volume used in calculations		
IS raw data included		
Manual integrations documented and verified		
LIMS ENTRY	REVIEWED	RELEASED

Anomaly: _____

Name List: LR
File Name: ST27970217

Entry # 1 of 6

2/17/97 11:51

(1)Format: FIN
(2)Sample: LR-IV-66A WDM
(3)Conditions: 60M X 0.32MM DB-5 F-27
(4)Formula: QUANTERRA (5)Submitted: SAC
(6)Analyst: RBH

Name List: LR
File Name: ST27970217A

Entry # 2 of 6

2/17/97 12:25

(1)Format: FIN
(2)Sample: LR-IV-72C CC3
(3)Conditions: 60M X 0.32MM DB-5 F-27
(4)Formula: QUANTERRA (5)Submitted: SAC
(6)Analyst: RBH

Name List: LR
File Name: ST27970217B

Entry # 3 of 6

2/17/97 12:59

(1)Format: FIN
(2)Sample: LR-IV-72A CC1
(3)Conditions: 60M X 0.32MM DB-5 F-27
(4)Formula: QUANTERRA (5)Submitted: SAC
(6)Analyst: RBH

Name List: LR
File Name: ST27970217C

Entry # 4 of 6

2/17/97 13:33

(1)Format: FIN
(2)Sample: LR-IV-72B CC2
(3)Conditions: 60M X 0.32MM DB-5 F-27
(4)Formula: QUANTERRA (5)Submitted: SAC
(6)Analyst: RBH

Name List: LR
File Name: ST27970217D

Entry # 5 of 6

2/17/97 14:07

(1)Format: FIN
(2)Sample: LR-IV-72D CC4
(3)Conditions: 60M X 0.32MM DB-5 F-27
(4)Formula: QUANTERRA (5)Submitted: SAC
(6)Analyst: RBH

Name List: LR
File Name: ST27970217E

Entry # 6 of 6

2/17/97 14:41

(1)Format: FIN
(2)Sample: LR-IV-72E CC5
(3)Conditions: 60M X 0.32MM DB-5 F-27
(4)Formula: QUANTERRA (5)Submitted: SAC
(6)Analyst: RBH

148 PM

APPENDIX B9

SAC-ID-0005 (Dioxins by 8290)

Controlled Copy

Copy No. _____



Environmental
Services

SOP No.: SAC-ID-0005

Revision No. 4.0

Revision Date: 9/11/98

Implementation Date:

Page: 1 of 76

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE
TITLE: METHOD 8290 - POLYCHLORINATED DIOXINS & FURANS
BY HRGC/HRMS

(SUPERSEDES: SAC-ID-0005, REVISION 3.0 OF 4/97)

Prepared by: Eric Redman

Reviewed by:

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Approved by:

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Environmental Health and Safety Coordinator, Cheryl Ann Stith

Approved by:

Robert Dovi
Laboratory Manager, Robert Dovi

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1. SCOPE AND APPLICATION

- 1.1. This method provides procedures for the detection and quantitative measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologs; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologs; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) concentrations by SW 846 Method 8290. The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits and other pertinent information. Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper calibration limit (Table 1). Samples containing concentrations of specific congeners (PCDDs and PCDFs) considered within the scope of this method that are greater than the calibration limit should be analyzed by a protocol designed for such concentrations of specific congeners such as 8280. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is described.
- 1.2. The sensitivity of this method is dependent upon the level of interferences within a given matrix.
- 1.3. This method is designed for use by analysts who are experienced with residue analysis and skilled in high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

2. SUMMARY OF METHOD

- 2.1. This procedure uses matrix-specific extraction, analyte-specific cleanup, and high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.
- 2.2. If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is show in Figure 1.
- 2.3. A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still-bottom, fuel oil, chemical reactor residue, or fish tissue, is spiked with a solution containing specified amounts of each of nine isotopically (^{13}C) labeled PCDDs/PCDFs listed in Table 2. The sample is then extracted according to a

matrix-specified extraction procedure. The extraction procedures are: a) toluene Soxhlet extraction for soil, sediment, fly ash samples and aqueous sludges; b) methylene chloride liquid-liquid extraction for water samples; c) dilution of a small sample aliquot in solvent for wastes/chemical products; and d) toluene (or hexane/methylene chloride) extraction for fish tissue.

- 2.4. If interferences are present, the extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the residue is cleaned up by column chromatography on acid base silica, acid alumina and carbon on silica. The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 10 μ L (depending on the matrix type) of a tetradecane solution containing 100 pg/ μ L of each of the two recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD (Table 2) to the concentrated carbon column eluate. The former is used to determine the percent recoveries of tetra- and penta-chlorinated PCDD/PCDF congeners while the latter is used for the determination of hexa-, hepta- and octa-chlorinated PCDD/PCDF congeners percent recoveries.
- 2.5. One to two μ L of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).
- 2.6. The identification of OCDD and fourteen of the fifteen 2,3,7,8-substituted congeners (Table 3), for which a 13C-labeled standard is included as a spiked compound, is based on their elution at their exact retention time (-1 to +3 seconds from the respective internal or recovery standard signal) and simultaneous detection of the two most abundant ions in the molecular ion region. All other identified PCDD/PCDF congeners are identified by their relative retention times falling within their respective PCDD/PCDF retention time windows, as established by using a GC column performance evaluation solution, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to 13C-OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation is based on a comparison of the ratio of the integrated ion abundance of the molecular ion species to their theoretical abundance ratio.
- 2.7. Quantification of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homolog, during which each calibration solution is analyzed once.

3. DEFINITIONS

- 3.1. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs): compounds (Figure 2) that contain from one to eight chlorine atoms. The fifteen 2,3,7,8-substituted PCDDs (totaling 75) and PCDFs (totaling 135) are shown in Table 3. The number of isomers at different chlorination levels is shown in Table 4.
- 3.2. Homologous series: Defined as a group of chlorinated dibenzodioxins or dibenzofurans having a specific number of chlorine atoms.
- 3.3. Isomer: Defined by the arrangement of chlorine atoms within an homologous series. For example, 2,3,7,8-TCDD is a TCDD isomer.
- 3.4. Congener: Any isomer of any homologous series.
- 3.5. Internal Standard: An internal standard is a ¹³C-labeled analog of a congener chosen from the compounds listed in Table 3 and of OCDD. Internal standards are added to all samples including method blanks and quality control samples before extraction, and they are used to quantitate the concentration of the analytes. Nine internal standards are used in this method. There is one for each of the dioxin and furan homologs (except for OCDF) with the degree of chlorination ranging from four to eight. Additional internal standards may be added to act as retention time references.
- 3.6. Recovery Standard: Recovery standards (two) are used to determine the percent recoveries for the internal standards. The ¹³C-1,2,3,4-TCDD is used to measure the percent recoveries of the tetra- and pentachlorinated dioxins and furans while ¹³C-1,2,3,7,8,9-HxCDD is used to determine the recovery of the hexa-hepta- and octachlorinated homologs and acts as a retention time reference for the unlabeled analog present in sample extracts. They are added to the final sample extract before HRGC/HRMS instrument analysis.
- 3.7. High-Resolution Concentration Calibration Solutions (Table 5): Solutions (tetradecane) containing known amounts of 17 selected PCDDs and PCDFs, a minimum of nine internal standards (¹³C-labeled PCDDs/PCDFs), and two carbon-labeled recovery standards; the set of five solutions is used to determine the instrument response of the unlabeled analytes relative to the internal standards and of the internal standards relative to the recovery standards.
- 3.8. Sample Fortification Solution (Table 2): A solution (isooctane or toluene) containing the nine internal standards, which is used to spike all samples before extraction and cleanup.

- 3.9. Recovery Standard Solution (Table 2): A tetradecane solution containing the two recovery standards, which is added to the final sample extract before HRGC/HRMS analysis.
- 3.10. Field Blank: A portion of a sample representative of the matrix under consideration, which is free of any PCDDs/PCDFs.
- 3.11. Rinsate: A portion of solvent used to rinse sampling equipment. The rinsate is analyzed to demonstrate that samples were not contaminated during sampling.
- 3.12. GC Column Performance Check Mixture: A tetradecane solution containing a mixture of selected PCDD/PCDF standards including the first and last eluters for each homologous series, which is used to demonstrate continued acceptable performance of the capillary column (i.e., ≤ 25 percent valley separation of 2,3,7,8-TCDD from all the other 21 TCDD isomers) and to define the homologous PCDD/PCDF retention time windows.
- 3.13. Performance Evaluation Materials: Representative sample portions containing known amounts of certain unlabeled PCDD/PCDF congeners (in particular the ones having a 2,3,7,8-substitution pattern). Representative interferences may be present. PEMs are obtained from the EPA EMSL-LV and submitted to potential contract laboratories, which must analyze these and obtain acceptable results before being awarded a contract for sample analyses (see IFB Pre-Award Bid Confirmations). PEMs may also be included as unspecified ("blind") quality control (QC) samples in any sample batch submitted to a laboratory for analysis.
- 3.14. Relative Response Factor: Response of the mass spectrometer to a known amount of a native analyte relative to a known amount of an internal standard, or a known amount of internal standard to a known amount of a recovery standard.
- 3.15. Batch: A group of samples processed at the same time.
- 3.16. Sample Rerun: Extraction of another portion of the sample followed by extract cleanup and extract analysis.
- 3.17. Extract Reanalysis: Instrument analysis by HRGC/HRMS of another aliquot of the final extract.
- 3.18. Tuning (Mass Resolution Check): Standard method used to demonstrate a static resolving power of 10,000 minimum (10 percent valley definition).

- 3.19. **Method Calibration Limits:** For a given sample size, a final extract volume, and the lowest and highest concentration calibration solutions, the lower and upper calibration limits delineate the region of quantification for which the HRGC/HRMS system was calibrated with standard.
- 3.20. **Matrix Spike Fortification Solution:** Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes listed in Table 5. The solution also contains all internal standards used in the sample fortification solution per the method

4. **INTERFERENCES**

- 4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks. Analysts should avoid using PVC gloves.
- 4.2. The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.
- 4.3. Re-use of glassware is to be minimized to avoid the risk of contamination.
- 4.4. Interferents co-extracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated xanthenes that may be found at concentrations several orders of magnitude higher than 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. While certain clean-up techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.
- 4.5. A high-resolution capillary column (60m DB-5) is used to resolve as many PCDD and PCDF isomers as possible. However, no single column is known to resolve all isomers. The DB-225 column is used for the quantitation of 2,3,7,8-TCDF.

5. **SAFETY**

- 5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

- 5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.2.1. N-Dex nitrile gloves provide varying degrees of intermittent splash protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.
- 5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.
- 5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: methylene chloride.
- 5.3.2. Chemicals known to be **flammable** are: toluene, hexane, acetone. Hexane is also a neurotoxic agent.
- 5.3.3. The following materials are known to be **corrosive**: H_2SO_4 , NaOH, KOH.
- 5.3.4. 2,3,7,8-TCDD is identified as a carcinogen, teratogen, and mutagen. 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.
- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.
- 5.7. 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. Such samples are to be processed in a confined environment, such as a hood or a glove box. If additional protection (i.e. respirators) are required, associates must notify the Environmental Health and Safety (EH&S) Manager. A hazard assessment must be conducted. Only the EH&S Manager is able to select and issue respiratory protection.

- 5.8. Safety practices described in Section 5.10 are adapted from EPA Method 613, Section 4 (July 1982 version).
- 5.9. Each laboratory must develop a strict safety program for the handling of 2,3,7,8-TCDD. The laboratory practices listed below are recommended.
 - 5.9.1. Contamination of the laboratory will be minimized by conducting the manipulations in a fume hood.
 - 5.9.2. 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.

6. EQUIPMENT AND SUPPLIES

- 6.1. High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS).
 - 6.1.1. The GC must be equipped for temperature programming. All required accessories must be available, such as syringes, gases, and capillary columns. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2- μ L injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2 μ L). 1 μ L injections are allowed; however, laboratories are encouraged to remain consistent throughout the analyses by using the same injection volume at all times on a given HRGC/HRMS/DS.
 - 6.1.2. Gas Chromatograph/Mass Spectrometer (GC/MS) Interface--The GC/MS interface components should withstand 350° C. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that

the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel® or equivalent ferrules are recommended.

- 6.1.3. Mass Spectrometer-The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less
- 6.1.4. Data System - A dedicated data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass-spectral peak profiles and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should also permit the measurement of noise on the base line.

6.2. GC Column

- 6.2.1 In order to have an isomer-specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, the 60-m DB-5 fused-silica capillary column is recommended. At the beginning of each 12-hour period during which samples are analyzed and after tuning, acceptable compound separation on the GC column must be demonstrated through the analysis of a column performance check solution. Operating conditions known to produce acceptable results with the recommended column are shown in Table 7.

6.3. Miscellaneous Equipment and Materials

The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

- 6.3.1. Nitrogen evaporation apparatus with variable flow rate.
- 6.3.2. Balances capable of accurately weighing to 0.01 g and 0.0001 g.
- 6.3.3. Centrifuge.
- 6.3.4. Water bath, equipped with concentric ring covers and capable of maintaining temperature control within $\pm 2^{\circ}\text{C}$.
- 6.3.5. Stainless steel or glass containers large enough to hold contents of one-pint sample containers.
- 6.3.6. Glove box.
- 6.3.7. Drying oven.
- 6.3.8. Stainless steel spoons and spatulas.
- 6.3.9. Laboratory hoods.
- 6.3.10. Pipettes, disposable, Pasteur, 150 mm long x 5 mm ID.
- 6.3.11. Pipettes, disposable, serological, 10 mL, for the preparation of the carbon column specified in Section 7.1.
- 6.3.12. Reacti-vial, 2 mL, silanized amber glass.
- 6.3.13. Stainless steel meat grinder with a 3- to 5-mm hole size inner plate.
- 6.3.14. Separatory funnels, 125 mL.
- 6.3.15. Kuderna-Danish concentrator, 500 mL, fitted with 10-mL concentrator tube and three-ball Snyder column.
- 6.3.16. Teflon® boiling chips (or equivalent), washed with DCM before use.
- 6.3.17. Chromatographic column, glass, 300 mm x 10.5 mm, fitted with Teflon® stopcock.
- 6.3.18. Adapters for concentrator tubes.

6.3.19. Glass fiber filters.

6.3.20. Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125 mL flask.

6.3.21. Continuous liquid-liquid extractor.

6.3.22. All-glass Soxhlet apparatus, 500 mL flask.

6.3.23. Glass funnels, sized to hold 170 mL of liquid.

6.3.24. Desiccator.

6.3.25. Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

6.3.26. Rotary evaporator with a temperature controlled water bath.

6.3.27. High speed tissue homogenizer, equipped with an EN-8 probe or equivalent.

6.3.28. Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.

Note: Re-use of glassware should be minimized to avoid the risk of contamination. All glassware that is re-used must be scrupulously cleaned as soon as possible after use, applying the following procedure:

6.4. 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 glassware surface.

6.4.1. Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with Teflon stopcocks, must be disassembled prior to detergent washing.

6.4.2. After detergent washing, glassware should be immediately rinsed with acetone, toluene, hexane, and then methylene chloride.

6.4.3. Do not kiln reusable glassware in an oven as a routine part of cleaning. Kilning may be warranted after particularly dirty samples are encountered, but

should be minimized, as repeated kilning of glassware may cause the formation of active sites on the glass surface that will irreversibly adsorb PCDDs/ PCDFs.

- 6.4.4. Immediately prior to use, Soxhlet extraction glassware should be pre-extracted with toluene for approximately 3 hours.

7. REAGENTS AND STANDARDS

7.1. Column Chromatography Reagents

- 7.1.1. Silica Gel - Kieselgel 60 or equivalent, activate for 1 hour at 184°C before use. Store at 130°C in covered flask.
- 7.1.2. Acid Alumina - ICN or equivalent, activated as necessary.
- 7.1.3. Basic Alumina - ICN or equivalent. No activation required.
- 7.1.4. Granular carbon/silica gel - Mix 3.6 g granular carbon and 16.4 g activated silica gel; (alternatively, prepare AX-21/silica gel (5%/95%); i.e., combine 5 g precleaned AX-21 with 95 g silica gel). Activate mix for >12 hours at 130°C before use. Store at 130°C in covered flask. The first LCS prepared with a new batch of column packing material is the quality control check of the packing materials. Please refer to historical control limits before accepting the new batch of material.
- 7.1.5. 44% H₂SO₄ /silica gel - Mix 24 mL conc. H₂SO₄ and 56 g activated silica gel. Stir and shake until free flowing. Store at room temperature.
- 7.1.6. 33% NaOH/silica gel - Mix 34 mL 1N NaOH and 67 g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.2. Reagents

- 7.2.1. Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.
- 7.2.2. Potassium hydroxide, ACS grade, 20 percent (w/v) in distilled water.
- 7.2.3. Distilled water demonstrated to be free of interferents
- 7.2.4. Potassium carbonate, anhydrous, analytical reagent.

7.2.5. Silica gel.

7.3. Desiccating Agent

7.3.1. Sodium sulfate, granular, anhydrous.

7.4. Solvents

7.4.1. High-purity, distilled-in-glass or highest available purity: Methylene chloride, hexane, benzene, methanol, tetradecane, isooctane, toluene, cyclohexane, and acetone.

7.5. All calibration, internal standard, clean up recovery standards, and spiking solutions are stable for one year from preparation. After 1 year, solutions may be revalidated. The revalidated solution may be used for an additional year, or until there is evidence of compound degradation or concentration. The revalidation must be performed using an unexpired, not previously validated solution from a second lot or second vendor.

7.5.1. Sealed ampules may be used until the manufacturer's expiration date is exceeded. If no expiration date is provided, then the expiration date will be 1 year from the date the ampule is opened.

7.6. Calibration Solutions

7.6.1. High-Resolution Concentration Calibration Solutions (Table 5) - Five tetradecane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations used to calibrate the instrument. The concentration ranges are homolog dependent, with the lowest values associated with the tetra chlorinated dioxins and furans (0.5 pg/μL) and the highest for the octachlorinated congeners (2000 pg/μL).

7.6.2. Individual isomers that make up the high-resolution concentration calibration solutions are obtained from commercial sources and prepared in the laboratory. These standards are traceable back to EPA-supplied standard solutions.

7.6.3. Store the calibration solutions in appropriate containers and at room temperature in the dark.

7.7. GC Column Performance Check Solution

- 7.7.1. This solution contains the first and last eluting isomers for each homologous series from tetra- through hepta-chlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The 13C-2,3,7,8-TCDD is also present. The laboratory is required to use tetradecane as the solvent and adjust the volume so that the final concentration does not exceed 100 pg/ μ L per congener. Table 8 summarizes the qualitative composition (minimum requirement) of this performance evaluation solution for the DB-5 column
- 7.7.2. For the DB-225 column, the column performance check solution contains a series of TCDF isomers in addition to the 2,3,7,8-TCDF. The solution is injected and evaluated at the start of each analytical sequence on the DB-225 column to ensure that 2,3,7,8-TCDF is resolved from its closest eluting isomers with a baseline-to-valley ratio of $\leq 25\%$.

7.8. Sample Fortification Solution (Matrix Spike Mix)

- 7.8.1. This isooctane (or toluene) solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note that 13C-OCDF is not present in the solution.)

7.9. Recovery Standard Solution

- 7.9.1. This tetradecane solution contains two recovery standards (13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,HxCDD). An appropriate volume of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

- 8.2. Grab and composite samples must be collected in glass containers.
- 8.3. Conventional sampling practices must be followed. Do not rinse the bottle with sample before collection. Sampling equipment must be free of potential sources of contamination.
- 8.4. Grinding or Blending of Fish Samples.
 - 8.4.1. If not otherwise specified by the client, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3- to 5-mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the client. If so requested by the client, the above whole fish requirement is superseded.
 - 8.4.2. Hearing protection **must** be worn when grinding samples.
- 8.5. With the exception of the fish tissues, which must be stored at - 20°C, all samples must be stored at 4°C $\pm$ 2, extracted within 30 days and completely analyzed within 45 days of collection.
- 8.6. All extracts must be stored capped, in the dark, at room temperature (approximately 21°C to 28°C).
- 8.7. Phase Separation
 - 8.7.1. To ensure that a suitable aliquot is extracted, the analyst may air dry a very wet soil/sediment. The analyst will determine the residual percent moisture on the air dried aliquot, then extract the air dried aliquot. The specific sample results will be reported with the residual moisture value.
 - 8.7.1.1. Subsample the wet soil/sediment.
 - 8.7.1.2. Dry the subsample in the drying cabinet at room temperature for 1-3 days.
 - 8.7.1.3. Weigh two aliquots of the air dried subsample. Perform a percent solids determination on one aliquot as described in Section 8.7, and extract the second aliquot in accordance with this SOP.

8.7.2. Phase separation on very wet (>25 percent water) soil and sediment samples may be accomplished as follows. Place a 50-g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipette, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent moisture determination, extraction). Return the remaining solid portion to the original sample bottle (empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil and sediment method. Take note of the estimated volume of liquid before disposing of the liquid as a liquid waste.

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

8.8. Soil, Sediment or Paper Sludge (Pulp) Percent Moisture Determination.

The percent moisture of soil or sediment samples showing detectable levels (see note below) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined according to the following recommended procedure.

Generally, depending on sample availability, a 5-10 g sample, weighed to three significant figures, is used for % solids determination. The sample is then dried to constant weight at $110^{\circ}\text{C} \pm 10$ in an adequately ventilated oven. Weigh the dried solid to three significant figures. Calculate and report the percent moisture on the appropriate form. Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste.

NOTE: The lower calibration limit (Table 1) may be used to estimate the minimum detectable levels.

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

8.9. Fish Tissue Lipid Content Determination

The percent lipid of fish samples showing detectable levels of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined as follows:

Concentrate the extract from Section 11.3.5 on a rotary evaporator until constant weight is attained. The percent lipid is calculated using the following expression:

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

9. QUALITY CONTROL

9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of laboratory reagent water processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when target analytes are detected in the method blank above the reporting limit or when surrogate recoveries are outside control limits. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable.

9.1.1. If the accompanying samples are aqueous, use distilled water as a matrix. Take the method blank through all steps detailed in the analytical procedure.

9.1.2. Use sodium sulfate as the method blank laboratory matrix when solids are extracted. Take the MB through all steps detailed in the analytical procedure.

9.1.3. The method blank must be spiked prior to extraction with the same amount of ¹³C-labeled internal standards as added to samples.

9.1.4. If method blank contamination is present, check solvents, reagents, fortification solutions, apparatus and glassware to locate and eliminate the source of contamination before any further samples are extracted and analyzed.

9.1.4.1. OCDD is a ubiquitous laboratory contaminant. A method blank and the associated samples are deemed acceptable if the OCDD concentration is <5x the specified reporting limit. Flag data appropriately. The analyst is expected to investigate and eliminate potential sources of systematic contamination.

9.1.4.2. If a target analyte is detected in the blank but the associated samples are ND (not detected), then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

9.1.4.3. If a target analyte is detected in the blank, but the concentration of the contaminant in the samples $>20\times$ the blank concentration, then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

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

9.2. A Laboratory Control Sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Reextraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable. See Quanterra Inc. QA Policy 003 for specific acceptance criteria.

9.2.1. A LCS is deemed acceptable if control analytes are above control limits and the associated samples are ND, unless otherwise specified by the client. Note any actions in the narrative.

9.3. A Matrix Spike/Matrix Spike Duplicate (MS/MSD or MS/SD) pair are extracted at the client's request only. An MS/MSD pair are aliquots of a selected field sample spiked with analytes of known identity and concentration. When requested by the client, the MS/MSD pair shall be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spike analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, an LCS, the selected field sample, the MS/MSD may be required after evaluation and review.

9.3.1. Matrix Spike (MS): A sample which is spiked with a known amount of the matrix spike fortification solution prior to the extraction step. The recoveries of the matrix spike compounds are determined; they are used to estimate the effect of the sample matrix upon the analytical methodology.

9.3.2. Matrix Spike Duplicate (MSD): A second portion of the same sample as used in the matrix spike analysis and which is treated like the matrix spike sample.

- 9.3.3. Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").
 - 9.3.4. Add an appropriate volume of the matrix spike fortification solution, adjusting the fortification level as specified in Table 1, under IS Spiking Levels.
 - 9.3.5. Analyze the MS and MSD samples as described in Section 11.
 - 9.3.6. The results obtained from the MS and MSD samples (percent recovery and concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference. Report all results and flag outliers.
 - 9.3.7. Internal standard recoveries are flagged if they are outside the recovery goals. Re-extraction of affected samples should be performed if signal-to-noise for any internal standard is less than 10:1.
- 9.4. Duplicates
- 9.4.1. Upon client request, duplicates may be processed. Locate the sample specified for duplicate analysis, and prepare and analyze a second 10-g soil or sediment sample portion or 1-L water sample, or an appropriate amount of the type of matrix under consideration.
 - 9.4.1.1. The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference. Report all results and flag outliers.
 - 9.4.2. Internal standard recoveries are flagged if they are outside the recovery goals. Re-extraction of affected samples should be performed if signal-to-noise for any internal standard is less than 10:1.
- 9.5. Field Blanks
- 9.5.1. Each batch of samples may contain a field blank sample of uncontaminated soil, sediment or water that is to be fortified before analysis. Fortified Field Blank
 - 9.5.1.1. Weigh a 10-g portion or use 1 L (for aqueous samples) of the specified field blank sample and add 100 μ L of the solution containing the nine internal standards (Table 2) diluted with 1.5 mL acetone.

9.5.1.2. Extract by using the procedures described in Section 11.3. As applicable, add 10 μ L of the recovery standard solution and analyze a 1-2 μ L aliquot of the concentrated extract.

9.5.1.3. Calculate the concentration of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards.

9.6. Rinsate Samples

9.6.1. In addition to the field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment.

9.6.2. The rinsate sample must be fortified like a regular sample.

9.6.3. Take a 100-mL (+ 0.5 mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100 μ L of the solution containing the nine internal standards (Table 2).

9.6.4. Using appropriate methods, concentrate to approximately 10 mL.

9.6.5. Just before analysis, add 10 μ L tetradecane recovery standard solution (Table 2), and reduce the volume to a final volume of 20 μ L, as necessary. No column chromatography is required.

9.6.6. Analyze an aliquot following the same procedures used to analyze samples.

9.6.7. Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds in pg/mL of rinsate solvent.

9.7. Surrogate/Clean Up Recovery Standard

9.7.1. A surrogate compound ^{37}Cl -2,3,7,8-TCDD may be spiked into all samples and QC samples for this method. The spike concentration is 0.8 ng per sample extract. This surrogate is spiked following extraction and just prior to cleanup as a "cleanup recovery standard", in order to monitor relative loss of internal standard during both extraction and cleanup.

9.8. Internal Standards

- 9.8.1. Internal standards must be spiked into all samples, QC samples, and included in all calibrations.
- 9.8.2. For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.
- 9.8.3. A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data. Internal standard recoveries are flagged if they are outside the recovery goals. Re-extraction of affected samples should be performed if signal-to-noise for any internal standard is less than 10:1.

9.9. Recommended Corrective Actions and Troubleshooting Steps

- Verify satisfactory instrument performance.
- If possible, verify that no error was made while weighing the sample portions.
- Review the analytical procedures with the performing laboratory personnel.

9.10. Identification Criteria

- 9.10.1. If either one of the identification criteria appearing in Sections 11.5.4.1 is not met for an homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit.
- 9.10.2. If the criteria specified in sections 11.5.4.1 and 11.5.4.2 are not met (i.e. retention time and ion abundance ratios), that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form. The sample may be rerun or the extract reanalyzed as directed by the client.

10. CALIBRATION AND STANDARDIZATION

Calibration and Standardization requires a check of mass resolution (tuning), a check of compound resolution, a verification of switching times (i.e. descriptors), and a verification of calibration curve validity.

10.1. Tuning (Mass Resolution Check)

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

Corrective actions must be implemented whenever the resolving power does not meet the requirement.

- 10.1.2. Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in downtime for source cleaning.

- 10.1.3. By using a PFK molecular leak, tune the instrument to meet minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). Verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).
- 10.1.4. Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760). The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 6) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to

the 10-percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

10.2. Performance Checks

10.2.1. At the beginning of each 12-hour period during which sample are to be analyzed, aliquots of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3) shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended). If the required criteria are not met, remedial action must be taken before any samples are analyzed.

10.2.1.1. Method blanks or solvent blanks are used to demonstrate that the analytical system is free of contamination after the analysis of calibration standards or high level samples. The blank must demonstrate that the system has returned to appropriate background levels prior to continued analysis.

10.2.2. At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that the PeCDF masses ($M+2$ & $M+4$) are also monitored in the first descriptor. This is because the first PeCDF isomer elutes prior to elution of the final tetra isomer. The selection (Table 6) of the molecular ions M and $M+2$ for ^{13}C -HxCDF and ^{13}C -HpCDF rather than $M+2$ and $M+4$ (for consistency) is to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory. The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 6.

10.2.2.1. The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-CIN. However, if not available from the EMSL-CIN, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDDs/PCDFs, which are not obtained from the EMSL-CIN, must be verified by comparison with second-source standard solutions.

10.3. Initial Calibration

Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (Section 10.5) does not meet the required criteria listed in Section 10.6.

10.3.1. Five high-resolution concentration calibration solutions, listed in Table 5, must be used for the initial calibration.

10.3.2. Tune the instrument with PFK.

10.3.3. Inject 1 or 2 μL of the GC column performance check solution and acquire SIM mass spectral data as described earlier in Section 6.1.3. The total cycle time must be ≤ 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criterion listed in Section 13.1 is met.

10.3.3.1. Select the injection volume based upon the expected target analyte concentration, or expected matrix interferences.

10.3.3.2. The same injection volume must be used for all samples, QC, and standards.

10.3.4. By using the same GC and mass spectrometer conditions that produced acceptable results with the column performance check solution, analyze a 1 or 2- μL portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameter.

10.3.4.1. The total cycle time for data acquisition must be ≤ 1 second. The total cycle time includes the sum of all dwell times and voltage reset times.

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

10.3.4.3. The ratio of integrated ion current for the ions appearing in Table 9 (homologous series quantification ions) must be within the indicated control limits (set for each homologous series).

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

NOTE: Section 10.4.3 requires that ion ratios be within the specified control limits simultaneously in one run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

10.3.5. For each SICP and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 10. This measurement is suggested for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question.

10.3.5.1. Referring to Table 10, calculate the 17 relative response factors (RRF) for unlabeled target analytes [RRF(n); n=1 to 17] relative to their appropriate internal standards (Table 5) and the nine RRFs for the labeled ¹³C internal standards [RRF(m); m=18 to 26] relative to the two recovery standards according to the following formulae:

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

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

Where:

A_x = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for the labeled recovery standards,

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

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

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

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

10.3.5.2. Calculate the RRF(n)s and their respective percent relative standard deviations (%RSD) for the five calibration solutions:

$$\overline{\text{RRF}(n)} = (1/5) \sum_{j=1}^5 \text{RRF}_j(n)$$

where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17; Table 10), and j is the injection number (or calibration solution number; j = 1 to 5).

10.3.5.3. The relative response factors to be used for the determination of the concentration of total isomers in a homologous series (Table 10) are calculated as follows:

10.3.5.3.1. For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF determined in Section 10.3.5.2.

NOTE: The calibration solutions do not contain ^{13}C -OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[\text{M}+6]^+$ ion of ^{13}C -OCDF from the $[\text{M}+2]^+$ ion of OCDD (and $[\text{M}+4]^+$ from ^{13}C -OCDF with $[\text{M}]^+$ of OCDD). Therefore, the RRF for OCDF is calculated relative to ^{13}C -OCDD.

10.3.5.3.2. For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the mean RRF used for those homologous series will be the mean of the RRFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

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

Where:

k = 27 to 30 (Table 10), with 27 = PeCDF; 28 = HxCDF; 29 = HxCDD; and 30 = HpCDF, t = total number of 2,3,7,8-substituted isomers present in the calibration solutions (Table 5) for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

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

10.3.5.4. Relative response factors [RRF(m)] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

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

$$\text{RRF}(m) = (1/5) \sum_{j=1}^5 \text{RRF}_j(m)$$

Where:

m = 18 to 26 (congener type) and j = 1 to 5 (injection number),

- A_{is}^m = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for a given internal standard ($m = 18$ to 26),
- A_{rs} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for a given internal standard ($m = 18$ to 26),
- Q_{rs} & Q_{is}^m = quantities of, respectively, the recovery standard (rs) and a particular internal standard (m) injected (pg),
- $RRF(m)$ = relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from one injection, and
- $\overline{RRF}(m)$ = calculated mean relative response factor of a particular internal standard, as determined from the five initial calibration injections (j).

10.4. Criteria for acceptable calibration

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

10.4.1. The percent relative standard deviations for the mean response factors [$RRF(n)$ and $RRF(m)$] from the 17 unlabeled standards must be ≤ 20 percent, and those for the nine labeled reference compounds must be ≤ 30 percent.

10.4.2. The signal/noise ratio (S/N) for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10 .

10.4.3. The isotopic ratios (Table 9) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section 10.4.1 is met, the analyte-specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the routine calibration criteria (Section 10.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

10.5. Routine Calibration (continuing calibration check)

Routine calibrations must be performed at the beginning of, following a successful tune and GC column performance check, and after a 12 hour period. The routine calibration initiates the 12 hour clock during which samples may be subsequently analyzed. The last sample in the sequence must be injected within 12 hours of the

routine calibration, followed by the analysis of a closing calibration check. An acceptable closing calibration check standard may be used to initiate the next 12 hour analysis sequence when consecutive acquisition sequences occur. The ending mass resolution check shall be performed after the closing calibration check of an analysis acquisition sequence or after the final bracketing standard when consecutive 12 hour acquisition sequences are run.

10.5.1. Inject 1 or 2 μL of the concentration calibration solution HRCC-3 containing 10 $\text{pg}/\mu\text{L}$ of tetrachlorinated congeners, 50 $\text{pg}/\mu\text{L}$ of penta-, hexa-, and heptachlorinated congeners, 100 $\text{pg}/\mu\text{L}$ of octachlorinated congeners, and the respective internal and recovery standards (Table 5). By using the same HRGC/HRMS conditions as used in Sections 6.1.3 through 6.2, determine and document an acceptable calibration as provided in Section 10.6.

10.6. Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken, including recalibration if needed.

10.6.1. The measured RRFs [RRF(n) for the unlabeled standards] obtained during the opening continuing calibration must be ± 20 percent of the mean values established during the initial calibration (Section 10.3.5.).

10.6.1.1. The bracketing continuing calibration must be $\pm 25\%$ of the average RRF calculated from the initial calibration.

10.6.2. The measured RRFs [RRF(m) for the labeled standards] obtained during the opening continuing calibration must be ± 30 percent of the mean values established during the initial calibration (Section 10.1.5).

10.6.2.1. The bracketing continuing calibration must be $\pm 35\%$ of the average RRF calculated from the initial calibration.

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

10.6.4. If either one of the above criteria (Sections 10.6.1 and 10.6.2) is not satisfied, the entire initial calibration process (Section 10.3) must be repeated. If either criteria in Sections 10.6.1.1 or 10.6.2.1 are not met, additional samples may not be analyzed. Sample data collected must be evaluated for usability. Narrate any reported data from the analytical sequence. If the ion-abundance ratio criterion is not satisfied, refer to the note in Section 10.3.4.4 for resolution.

Note: An initial calibration must be carried out whenever the HRCC-3, the sample fortification or the recovery standard solution is replaced by a new solution from a different lot.

11. PROCEDURE

- 11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.
- 11.2. Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.
- 11.3. Extraction
 - 11.3.1. Internal Standard Addition. A 1.0 mL aliquot of the internal standard mixture is added to all samples, regardless of sample size. As an example, for 13C-2,3,7,8-TCDD, a 10-g soil sample requires the addition of 1000 pg of 13C-2,3,7,8-TCDD to give the requisite 100 ppt fortification level.
 - 11.3.2. Sludges. Paper Pulp Sludges are generally air-dried and ground. Because of the drying procedure, a Dean-Stark water separator may, or may not, be used for extraction. Extraction is generally done by Soxhlet with 200-300 mL of toluene.
 - 11.3.2.1. Non-Paper Pulp Sludges are extracted with 200-300 mL of toluene.
 - 11.3.2.2. Soxhlet sample for a minimum of 16 hours. Cool the sample, filter the toluene extract, if needed, through a glass-fiber filter, or equivalent, into a round-bottom flask. Rinse the filter with 10 mL toluene, and combine the extract and rinsate. Concentrate the combined solutions to near dryness on a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 11.4 as necessary.
 - 11.3.3. Still-Bottom/Fuel Oil. All organic liquids, fuel oils, and solids that will dissolve in a solvent and are treated as a solvent dilution will be dissolved in 1-2 mL of an appropriate solvent; then diluted with 5-10 mL of Hexane if no

option C is required. Spike with appropriate Internal Standards and proceed with Section 11.4 as necessary.

- 11.3.4. Fly Ash. Extract fly ash samples by jar shake with hydrochloric acid before soxhlet extraction. Weigh 2-10g of sample aliquot into a clean glass jar. Add 1.0mL of the internal standard mixture with 2 mL of acetone. Add 150mL of 1N hydrochloric acid and shake for 4 hours. If the sample reacts violently with acid, then allow the sample to equilibrate for 4 hours with no shaking. The contents of the jar are then filtered. The solids are soxhlet extracted for 16 hours. The aqueous filtrate is extracted with 100 mL of toluene and twice with 100 mL of hexane. Concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Section 11.4 as necessary.

Note: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

- 11.3.5. Solids. Add anhydrous sodium sulfate to the soil sample portion in a ratio of 2 to 1 (e.g. 20 g sodium sulfate to 10 g of sample) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass-wool plug (the use of an extraction thimble is optional). Add 200 to 250 mL toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system at least five times per hour. Proceed with Section 11.3.3.

- 11.3.6. 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.

- 11.3.6.1. Add 100 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel. The internal standard mixture is added to samples by first mixing well in 2 mL of acetone then it is added to the separatory funnel. Each aliquot of spike mixture is added similarly. Extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Extraction is repeated two additional times with methylene chloride.

- 11.3.6.2. Determine the original sample volume by filling the sample bottle to the mark with water and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.
- 11.3.6.3. Dry extract with sodium sulfate: Place glass wool in a precleaned filter funnel. Rinse glass wool with DCM and load funnel with DCM-rinsed Na_2SO_4 . Pour extract through Na_2SO_4 to remove water. Rinse Na_2SO_4 with fresh DCM and collect in round bottom flask.
- 11.3.6.4. Transfer the extract to a 500-mL round-bottom, add 100 μL of tetradecane and concentrate on a rotary evaporator or TurboVap.
- 11.3.7. 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 when using a separatory funnel.
- 11.3.7.1. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface.
- 11.3.7.2. Transfer the solvent to the extractor.
- 11.3.7.3. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinsate to the extractor.
- 11.3.7.4. Add 200 to 500 mL methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 hours.
- 11.3.7.5. Allow to cool, then detach the distilling flask. Proceed with Section 11.4 as necessary.
- 11.4. Optional Extract Clean-Ups
- 11.4.1. Acid/Base Partitioning
- 11.4.1.1. Partition the extract in 50-125 mL of hexane against 40 mL concentrated H_2SO_4 in a separatory funnel. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.4.1.2. Partition the extract against 50 mL distilled H_2O (w/v). Shake for two minutes. Remove and discard the aqueous layer (bottom).

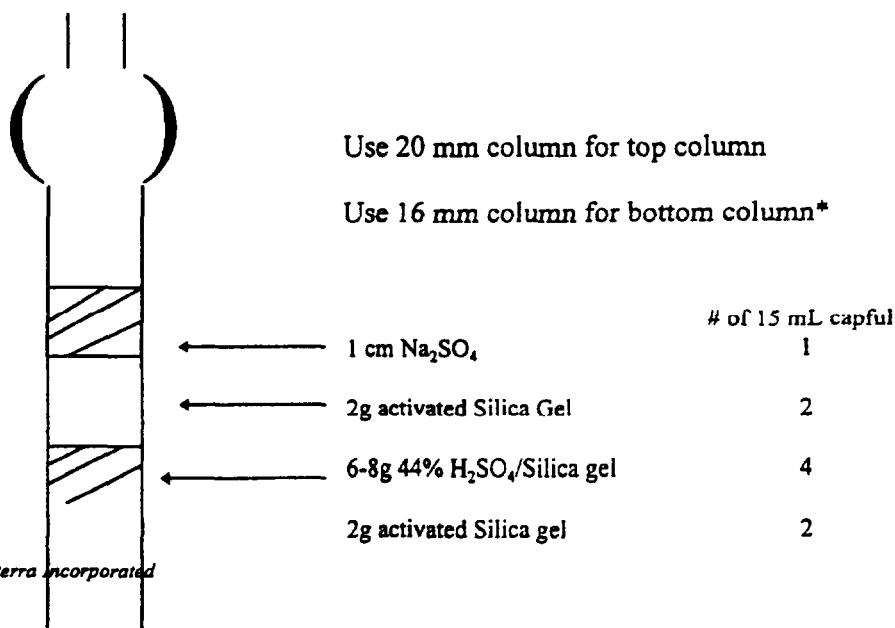
11.4.1.3. Partition the extract using 50 mL of 10 N NaOH. Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform a maximum of four base washings). Strong base is known to degrade certain PCDDs/PCDFs, so contact time must be minimized. The NaOH partition is applied only as samples warrant it at the discretion of the analyst.

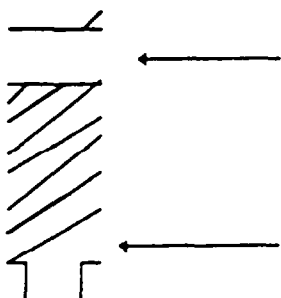
11.4.1.4. Partition the extract against 50 mL of distilled H_2O . Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the extract by pouring it through a funnel containing anhydrous sodium sulfate and collect it in a round-bottom flask. Rinse the sodium sulfate with two 15-mL portions of hexane, add the rinsates to the flask, and concentrate the hexane solution to near dryness on a rotary evaporator (35°C water bath), making sure all traces of toluene (when applicable) are removed. (Use of blow-down with an inert gas to concentrate the extract is also permitted.) The DI H_2O partition is applied only as samples warrant it at the discretion of the analyst.

11.4.2. IFB Column Clean-Up "Exhibit A"

11.4.3. For NON paper pulp mill solids & effluents proceed with clean-up step exhibit "A".

EXHIBIT A IFB Column Clean-up





*Upper and lower columns are piggy backed

11.4.3.1. Pre-rinse both columns with hexane - 20 mL Top and 20 mL Bottom.

11.4.3.2. Put one column above the other.

11.4.3.3. Add extract to the top column. Rinse extract vessel 2 times with 1 mL each of hexane and add to column.

11.4.3.4. Elute 60 mL hexane directly onto acid silica column (upper piggy backed columns).

11.4.3.5. Discard upper column.

11.4.3.6. Elute with 10 mL of 10% methylene chloride/hexane. Discard in proper waste stream.

11.4.3.7. Elute with 30 mL of 65% methylene chloride/hexane. Save and collect in culture tube.

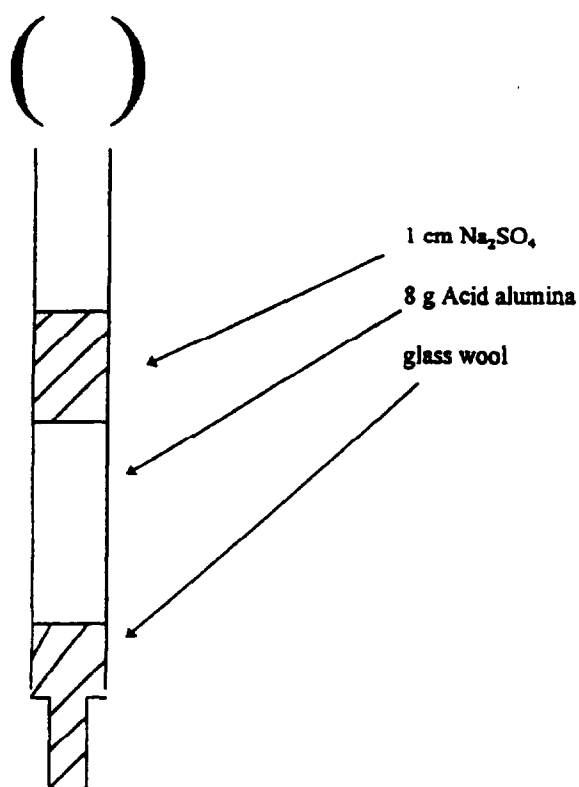
11.4.3.8. Proceed with additional cleanups as necessary.

11.4.4. Acid Alumina Column Clean-Up "Exhibit B"

11.4.4.1. Use for paper pulp mill solids and effluents.

Exhibit B Acid Alumina Column Clean-up





11.4.4.2. Add extract in 2 mL hexane with 2 x 2 mL hexane rinse of container.

11.4.4.3. Elute with "pre-analyte" solvent system. Collect, label and store this fraction.

11.4.4.4. Elute with "analyte" solvent system. Collect, label, and proceed to additional cleanups or final volume with this fraction.

11.4.4.5. Alumina activity may vary with the matrix or environmental conditions. Monitor internal standard and cleanup recovery standard recoveries in extract analysis. Low recoveries of cleanup recovery standard may indicate loss of alumina activity. If loss of internal standard can be attributed to alumina activity variation, recombine the stored "pre-analyte" fraction with the extract, reduce to final volume and reanalyze. Additionally, reassess stability of alumina activity and apply corrective action as appropriate (reactivate and reprofile).

11.4.4.6. Profile each vendor lot of activated alumina as corrective actions to low internal standard and C.R.S. recoveries dictate. If necessary, proceed as follows:

11.4.4.6.1. Set up and label 3 acid alumina columns.

11.4.4.6.2. Pre-rinse with 20 mL hexane.

11.4.4.6.3. Add 2 mL hexane spiked with internal standards and natives (spike amounts equivalent to those for LCS) with 2X2 mL hexane rinse of fractions.

11.4.4.6.4. Elute each column with 20 mL hexane. Collect and label these fractions.

11.4.4.6.5. Elute each column with 5 x 10 mL methylene chloride/hexane at the appropriate v/v percent. Collect and label these fractions separately.

11.4.4.6.6. Elute each column with 10 mL of 100% methylene chloride. Collect and label these fractions. Reduce all fractions to final volume and add recovery standard.

11.4.4.7. Review data and select an elution scheme. Group the fraction from each solvent system as follows:

- Pre-analyte fraction - consists of all eluent prior to elution of first target analytes..
- Analyte fraction - consists of all which contain detectable levels of target analytes.
- Post-analyte fraction - consists of all eluents after elution of the last target analyte.

11.4.4.8. Select the solvent system which best meets the following two conditions:

- Pre-analyte fraction consists of 20 mL hexane and no more than 20 mL mixed solvent.

- Analyte fraction consists of no more than 20 mL of mixed solvent and contains greater than 90% of all target analytes and greater than 80% of all internal standards.

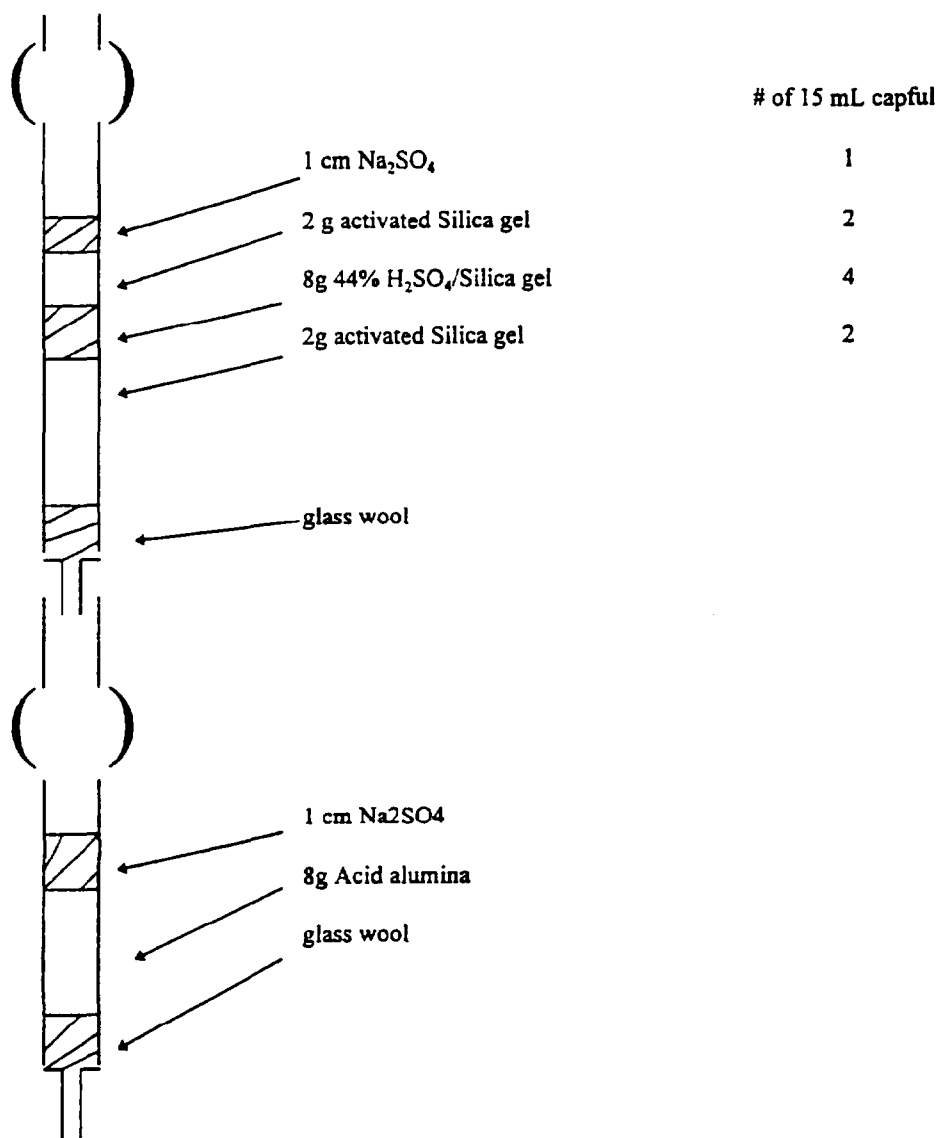
11.4.4.9. After selection of the appropriate solvent system and fractionation pattern, perform triplicate acid alumina cleanups on spiked hexane to ensure reproducibility of the fractionation pattern. Document each elution scheme and append to this SOP.

11.4.4.10. Each subsequent batch of acid alumina used in the lab (from the same vendor lot) must be checked for stable activity.

11.4.5. Combined Exhibit A and Exhibit B Clean-Up

Combined Exhibit A and Exhibit B NCASI Paper Pulp IFB Column Clean-up

Use 20 mm column for top column
 Use 16 mm column for bottom column



- 11.4.5.1.Pre-rinse both columns with hexane - 40 mL Top and 20 mL Bottom.
- 11.4.5.2.Put one column above the other.
- 11.4.5.3.Add extract to the top column with hexane. Rinse.
- 11.4.5.4.Extract Vessel 2 times with 1 mL each of hexane and add to column.
- 11.4.5.5.Concentrate 120 mL of hexane to tetradecane, add to bottom column.
- 11.4.5.6.Elute the bottom column with 20 mL of hexane. Discard in proper waste stream.
- 11.4.5.7.Elute with 23 mL of 20% methylene chloride/hexane.
- 11.4.5.8.Collect eluate in TurboVap tube.
- 11.4.5.9.Use tetradecane and N₂ as appropriate per flow chart.

11.4.6. Carbon Column Clean-up "Exhibit D"

11.4.6.1. Prepare an AX-21 Carbon & Silica Gel column as described in EXHIBIT D, below.

Exhibit D

Carbon Column Clean-up Special D2

"A"	
	- Cut off both ends of a 10 mL pipette.
	- Push a glasswool plug down to the 6 mL mark.
	- Add 1g of 5% AX-21/silica and top with another glasswool plug.
0 mL	
1 mL	- Pre-elute with 5 mL 1:1 MeCl ₂ :cyclohexane. Direction "A"
2 mL	- Turn over and pre-elute with 5 mL 1:1 MeCl ₂ :cyclohexane in direction "B".
3 mL	
4 mL	- Discard pre-eluates.
5 mL	
6 mL	- Dilute extract to 1 mL with hexane and transfer to the column.
7 mL	
8 mL	- Rinse sample vial onto the column with 2 X 2 mL 1:1 MeCl ₂ :cyclohexane.
9 mL	
10 mL	- Elute with 6mL 1:1 MeCl ₂ :cyclohexane 5mL 75:20:5 MeCl ₂ :MeOH:Benzene
"B"	
	- Discard Evaluates
	-After flipping column back to the "A" direction, the column is eluted with 30 mL of toluene and collected
	- N ₂ or roto-vap to NEAR dryness and proceed to next step.

11.5. Analytical Procedures

11.5.1. With a stream of dry, purified nitrogen, reduce the extract volume to 10 μL . Add 20 μL of the recovery standard solution (Table 2). With a stream of dry, purified nitrogen, reduce the extract to volume to 20 μL .

11.5.1.1. Transfer the extract to an autoinjection vial and store in the dark at room temperature.

11.5.2. Inject a 1 or 2 μL aliquot of the extract into the GC, operated under the conditions previously used (Section 6.2) to produce acceptable results with the performance check solution.

11.5.3. Acquire SIM data according to Section 6.1.3. Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (Section 10). Ions characteristic for polychlorinated diphenyl ethers are included in the descriptors listed in Table 6. Their presence is to monitor their interference during the characterization of PCDFs.

11.5.4. Identification Criteria

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

11.5.4.1. Retention Times

11.5.4.1.1. For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract, the retention time (at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 6) must be within -1 and +3 seconds of the retention time of the peak for the isotopically labeled internal or recovery standard at m/z corresponding to the first characteristic ion (of the set of two; Table 6) to obtain a positive identification of these nine 2,3,7,8-substituted PCDDs/PCDFs and OCDD.

11.5.4.1.2. For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract, the relative retention time (relative to the appropriate internal standard) must fall within 0.005 relative retention time units of the relative retention times measured in the daily routine calibration. Identification of OCDF is based on its

retention time relative to ^{13}C -OCDD as determined from the daily routine calibration results.

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

11.5.4.1.4. The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach a maximum simultaneously (+ 2 seconds).

11.5.4.1.5. The ion current responses for both ions used for the labeled standards (e.g., for ^{13}C -TCDD: m/z 331.9368 and m/z 333.9339) must reach a maximum simultaneously (+ 2 seconds).

11.5.4.2. Ion Abundance Ratios

11.5.4.2.1. The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned. See Table 9.

11.5.4.3. Signal-To-Noise Ratio

11.5.4.3.1. All ion current intensities must be >2.5 times noise level for positive identification of the PCDD/PCDF compound or a group of coeluting isomers. Figure 7 describes the procedure to be followed for the determination of the S/N.

11.5.4.4. Polychlorinated Diphenyl Ether Interferences

11.5.4.4.1. In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N >2.5 is detected, at the same retention time (+2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 6) channel.

12. DATA ANALYSIS AND CALCULATIONS

- 12.1. For gas chromatographic peaks that have met the criteria outlined in Section 11.5.4 calculate the concentration of the PCDD or PCDF compounds using the formula:

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

Where:

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

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

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

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

W = Sample size in g (if solid) or L (if liquid).

$RRF(n)$ = Calculated mean relative response factor for the analyte

[$RRF(n)$ with $n = 1$ to 17; Section 10.3.5].

If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs, $RRF(n)$ is the value calculated using the equation in Section 10.3.5.1. However, if it is a non-2,3,7,8-substituted congener, the $RRF(k)$ value is the one calculated using the equation in Section 10.3.5.3.2 [$RRF(k)$ with $k = 27$ to 30.].

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

$$\text{Internal Standard Percent Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times RRF(m)} \times 100$$

Where:

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

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

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

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

$RRF(m)$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5, footnotes) recovery standard. This represents the mean obtained in Section 10.3.5.4 [$RRF(m)$ with $m = 18$ to 26].

12.3. If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limit(MCL) for that compound listed in Table 1, the linear range of response versus concentration may have been exceeded. In such cases, the following corrective actions will be undertaken:

- If the signal for the analyte has saturated the detector, a single dilution and re-analysis of the extract will be made in an attempt to bring the signal within the range of the detector. If the measured concentration of the analyte is still above the MCL, the reported concentration for the analyte will be qualified appropriately.
- If the signal for the analyte is above the MCL but does not saturate the detector, the concentration will be reported and qualified appropriately.

In either case, **with the approval of the client**, the sample may be re-extracted and/or re-analyzed with one or more of the following adjustments made to the analytical procedure in order to provide a concentration which meets client-specific data quality objectives.

- Extraction and analysis of a one tenth aliquot. This is appropriate if it will provide analyte concentration within the MCL and will also provide a representative sample aliquot.
- Extraction of an aliquot large enough to be representative with an increased concentration of internal standard and surrogate spike components added prior to

the extraction. The extract is then diluted either prior to or after the cleanup procedures.

- Dilution of the original extract. Internal standard components are re-spiked at an appropriate level prior to analysis. In this case, the internal standard recoveries are taken from the original analysis.

For the other congeners (including OCDD and OCDF), however, report the measured concentration and indicate that the value exceeds the upper calibration standard.

- 12.4. The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value may be specified in the report.

12.5. Sample-Specific Estimated Detection Limit

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

- 12.5.1. Samples giving a response for both quantitation ions (Tables 6 and 9) that is less than 2.5 times the background level.

12.5.1.1. Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e., $S/N < 2.5$). The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions (Table 6) of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C -labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that product height.

NOTE: The quantitation ions for both the unlabeled PCDDs/PCDFs and their internal standard must be consistently paired (using either both lighter mass ions or both heavier mass ions).

Use the formula:

$$\text{EDL}(\text{specific 2,3,7,8-subst.PCDD/PCDF}) = \frac{2.5 \times H_s \times Q_{is}}{H_{is} \times W \times \text{RRF}(n)}$$

Where:

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

H_s = height of the average noise for one of the quantitation ions (Table 6) for the unlabeled PCDDs/PCDFs.

H_{is} = height of one of the quantitation ions (Table 6) for the labeled internal standards.

W, RRF (n), and Q_{is} retain the same meanings as defined in Section 12.1

12.5.2. Samples characterized by a response above the background level with a S/N of at least 2.5 for at least one of the quantitation ions (Tables 6 and 9).

12.5.2.1. When the response of a signal having the same retention times as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in Section 11.5.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section 12.1, except that Ax in Section 12.1 should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio. Alternatively, an EDL can be calculated using the above formula and the height of one of the ions as appropriate.

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

$$\text{RPD} = \frac{|S1 - S2|}{(S1 + S2) / 2} \times 100$$

S1 and S2 represent sample and duplicate sample results.

- 12.7. The 2,3,7,8-TCDD toxic equivalents (TE) of PCDDs and PCDFs present in the sample are calculated, only at the data user's request. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs (Table 3 and the non-2,3,7,8-substituted compounds as shown in Table 11). The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 11. The exclusion of other homologous series such as mono-, di-, and tri- and chlorinated dibenzodioxins and dibenzofurans does not mean that they are non-toxic.

12.7.1. Two-GC Column TEF Determination

12.7.1.1. The concentration of 2,3,7,8-TCDD (see note below), is calculated from the analysis of the sample extract on the 60m DB-5 fused silica capillary column. The chromatographic separation of this isomer must be $\leq 25\%$ valley.

12.7.1.2. For samples that have a presumptive positive result for 2,3,7,8-TCDF or the DB-5 column, the extract is reanalyzed on a 30m DB-225 fused silica column. The GC/MS conditions are altered so that only the first descriptor (Table 6) is used. The reported concentration for 2,3,7,8-TCDF is then the result calculated from the DB-225 analysis. The chromatographic separation between 2,3,7,8-TCDF and any other unlabeled TCDF isomers must be $\leq 25\%$ valley using the column performance check solution for the DB-225 column. Concentration calculations are performed as in Section 12.1 through 12.6.

12.7.1.3. A DB-225 column can be used in the quantitative analysis of 2,3,7,8-TCDF and 2,3,7,8-TCDD analytes. Since the DB-225 cannot resolve 2,3,7,8-TCDD, any positively identified 2,3,7,8-TCDD analytes which exceed the reporting limit shall be confirmed on a DB-5 column.

12.7.1.4. For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance (Section 11.5.4) and signal-to-noise ratio criteria. In addition, the retention time identification criterion described in Section 11.5.4 applies here for congeners for which a carbon-labeled analog is available in the sample extract. However, the relative retention time

(RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogs are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described in Table 12 and the results from the routine calibration run on the DB-5 column.

13. METHOD PERFORMANCE

The laboratory may use the recommended GC column. It must be documented that all applicable system performance criteria specified were met before analysis of any sample is performed. Table 7 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 4 provides a typical 12-hour analysis sequence. A GC column performance check is only required at the beginning of each 12-hour period during which samples are analyzed.

13.1. GC Column Performance

13.1.1. Inject 1 or 2 μL of the column performance check solution and acquire selected ion monitoring (SIM) data as described in Section 6.1.3 within a total cycle time of < 1 second.

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

Where:

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

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

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

13.1.3. It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used for qualitative and quantitative purposes. The peak for 2,3,7,8-TCDD must be labeled on the chromatograms. The chromatograms showing the first and last eluters of a homologous series must be included.

13.1.4. The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds.

14. POLLUTION PREVENTION

14.1. No solvents/wastes of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

15.1. Waste management in the procedure must be segregated and disposed according to the waste streams identified in the facility hazardous waste procedures, Attachment B of the Chemical Hygiene Plan, Section WS002, Table 1.

15.2. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the facility hazardous waste management procedures, Attachment B of the Chemical Hygiene Plan, Section WS003, Disposal of Samples After Analysis.

16. REFERENCES

16.1. SW846, Third Edition, Method 8290, USEPA, November, 1992.

16.2. Protocol for the Analysis of 2,3,7,8-TCDD by HRGC/HRMS". J. S. Stanley and T. M. Sack, EPA 600/4-86-004.

16.3. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety (3rd Edition, 1979.)

16.4. "Carcinogens - Working with Carcinogens". Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.

16.5. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910) Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Deviations from reference method.

- 17.1.1. The method specifies that 2 μ L injections are used throughout the analysis. If an instrument demonstrates adequate sensitivity and chromatographic resolution, then the analyst may use 1 μ L injections for all performance checks, standards, QC samples, and samples.
- 17.1.2. In Section 2.7 of Method 8290, a retention time window of 0.005 RT units is used to tentatively identify unlabeled PCDD/PCDFs for which there are no corresponding labeled internal standards. All available labeled internal standards are used; therefore, a retention time window of -1 to +3 seconds is used to identify all compounds. See Section 7.8.4.1 of Method 8290.
- 17.1.3. Tetradecane instead of nonane is used as the final solvent to increase the stability of extracts and standards. Tetradecane is less volatile than nonane. Loss of analyte as a result of solvent incompatibility is monitored through recovery checks and calibration acceptance criteria.
- 17.1.4. Extract clean-ups are performed at the discretion of the analyst when interferences are observed. Then, the analyst should select the clean-up procedure appropriate to the interferent.
- 17.1.5. Section 7.4.6.4 of Method 8290 indicates that extracts should be transferred with hexane, then toluene. Toluene is used to transfer extracts to maintain compound solubility and minimize analyte loss.
- 17.1.6. Section 7.5.1.2 of Method 8290 specifies that a NaCl solution should be used for partitioning. Instead the laboratory uses laboratory water only. NaCl is used to break up emulsions that may form. An analyst may use NaCl or any other mechanical means to break up an emulsion.
- 17.1.7. Section 7.5.3 of Method 8290 specifies that hexane is used as a column elution solvent. The laboratory uses cyclohexane to achieve better and more reproducible separation of the target analyte from the interferent.
- 17.1.8. Carbon columns are packed with silica gel in place of celite. Elution solvents are changed accordingly. (SOP Section 11.4; Method 8290 Section 7.5.3.2).
- 17.2. Summary of modifications to SOP from previous revisions
 - 17.2.1. The SOP format was updated.
 - 17.2.2. Extraction cycle time was changed from three to five.

- 17.2.3. Percent solids oven temperature was changed from 100 to $110^{\circ}\text{C} \pm 10$.
- 17.2.4. An bracketing continuing calibration standard is required to be analyzed and evaluated.
- 17.2.5. A bracketing resolution check is required to be analyzed and evaluated.
- 17.3. Tables or figures referenced in body of SOP.
 - 17.3.1. Table 1 - Types of Matrices
 - 17.3.2. Table 2 - Composition of The Sample Fortification and Recovery Standard Solutions.
 - 17.3.3. Table 3 - The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners
 - 17.3.4. Table 4 - Isomers of Chlorinated Dioxins and Furans
 - 17.3.5. Table 5 - Concentrations of Calibration Solutions
 - 17.3.6. Table 6 - Ions Monitored for PCDDs/PCDFs
 - 17.3.7. Table 7 - Recommended GC Operating Conditions
 - 17.3.8. Table 8 - Congeners in the GC Performance Evaluation Solution (DB-5)
 - 17.3.9. Table 9 - Theoretical Ion Abundance Ratios and Control Limits
 - 17.3.10. Table 10 - Relative Response Factor Attributes
 - 17.3.11. Table 11 - 2,3,7,8-TCDD Equivalent Factors
 - 17.3.12. Table 12 - TEF: Analyte Relative Retention Time Reference Attributes
 - 17.3.13. Figure 1 - Analysis Flowchart
 - 17.3.14. Figure 2 - Compound Structure
 - 17.3.15. Figure 3 - PFK Resolution Example
 - 17.3.16. Figure 4 - Analysis Scheme

17.3.17. Figure 5 - GC Performance Check Chromatogram on the DB-5 Column

17.3.18. Figure 6 - PFK Peak Profile

17.3.19. Figure 7 - Manual Determination of Signal-to-Noise

17.3.20. Appendix A - Periodic Wipe Test Performance

TABLE 1

**Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based
Method Calibration Limits (Parts per Trillion)**

	Water	Soil Sediment Paper Pulp	Fly Ash	Human/ Fish Tissue	Adipose Tissue	Sludges, Fuel Oil	Still- Bottom
Lower MCL(a)	0.02	2.0	2.0	2.0	2.0	10	20
Upper MCL(a)	4.0	400	400	400	400	2000	4000
Weight (g)	1000	10	10	10	10	2.0	1.0
IS Spiking Levels (ng)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Final Extract Volume (μ L)	20	20	20	20	20	20	20

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

TABLE 2
Composition of the Sample Fortification
and Recovery Standard Solutions

Analyte	Sample Fortification Solution Concentration pg/ μ L; Solvent: Isooctane	Sample Fortification Solution Concentration pg/ μ L; Solvent: Tetradecane
13C-2,3,7,8-TCDD	10	--
13C-2,3,7,8-TCDF	10	--
13C-1,2,3,4-TCDD	--	100
13C-1,2,3,7,8-PeCDD	10	--
13C-1,2,3,7,8-PeCDF	10	--
13C-1,2,3,6,7,8-HxCDD	25	--
13C-1,2,3,4,7,8-HxCDF	25	--
13C-1,2,3,7,8,9-HxCDD	--	100
13C-1,2,3,4,6,7,8-HpCDD	25	--
13C-1,2,3,4,6,7,8-HpCDF	25	--
13C-OCDD	50	--

(*) The 13C-labeled analog is used as an internal standard.

(+) The 13C-labeled analog is used as a recovery standard.

TABLE 3

The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

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

(*)The ¹³C-labeled analog is used as an internal standard.

(+)The ¹³C-labeled analog is used as a recovery standard.

TABLE 4

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

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

TABLE 5

High Resolution Concentration Calibration Solutions

Compound	Concentration (ng/mL)				
	CS1	CS2	CS3 (VER(6))	CS4	CS5
Native CDDs and CDFs					
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
Labeled CDDs and CDFs					
¹³ C ₁₂ -2,3,7,8-TCDD	100	100	100	100	100
¹³ C ₁₂ -2,3,7,8-TCDF	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	100	100	100	100
¹³ C ₁₂ -2,3,4,7,8-PeCDF	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	100	100	100	100	100
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	100	100	100	100	100
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	100	100	100	100
¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
¹³ C ₁₂ -OCDD	200	200	200	200	200
Cleanup Standard					
³⁷ Cl ₄ -2,3,7,8-TCDD	0.5	2	10	40	200
Recovery Standards					
¹³ C ₁₂ -1,2,3,4-TCDD	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 6*
Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate ^(a) Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	C ₁₂ H ₄ ³⁵ Cl ₄ O	TCDF
	305.8987	M+2	C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO	TCDF
	315.9419	M	¹³ C ₁₂ H ₄ ³⁵ Cl ₄ O	TCDF (S)
	317.9389	M+2	¹³ C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO	TCDF (S)
	319.8965	M	C ₁₂ H ₄ ³⁵ Cl ₄ O ₂	TCDD
	321.8936	M+2	C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO ₂	TCDD
	331.9368	M	¹³ C ₁₂ H ₄ ³⁵ Cl ₄ O ₂	TCDD (S)
	333.9338	M+2	¹³ C ₁₂ H ₄ ³⁵ Cl ₃ ³⁷ ClO ₂	TCDD (S)
	375.8364	M+2	C ₁₂ H ₄ ³⁵ Cl ₅ ³⁷ ClO	HxCDFE
2	[354.9792]	LOCK	C ₉ F ₁₃	PFK
	339.8597	M+2	C ₁₂ H ₃ ³⁵ Cl ₄ ³⁷ ClO	PeCDF
	341.8567	M+4	C ₁₂ H ₃ ³⁵ Cl ₃ ³⁷ Cl ₂ O	PeCDF
	351.9000	M+2	¹³ C ₁₂ H ₃ ³⁵ Cl ₄ ³⁷ ClO	PeCDF (S)
	353.8970	M+4	¹³ C ₁₂ H ₃ ³⁵ Cl ₃ ³⁷ Cl ₂ O	PeCDF (S)
	355.8546	M+2	C ₁₂ H ₃ ³⁵ Cl ₄ ³⁷ ClO ₂	PeCDD
	357.8516	M+4	C ₁₂ H ₃ ³⁵ Cl ₃ ³⁷ Cl ₂ O ₂	PeCDD
	367.8949	M+2	¹³ C ₁₂ H ₃ ³⁵ Cl ₄ ³⁷ ClO ₂	PeCDD (S)
	369.8919	M+4	¹³ C ₁₂ H ₃ ³⁵ Cl ₃ ³⁷ Cl ₂ O ₂	PeCDD (S)
	409.7974	M+2	C ₁₂ H ₃ ³⁵ Cl ₆ ³⁷ ClO	HpCDFE
	[354.9792]	LOCK	C ₉ F ₁₃	PFK
3	373.8208	M+2	C ₁₂ H ₂ ³⁵ Cl ₅ ³⁷ ClO	HxCDF
	375.8178	M+4	C ₁₂ H ₂ ³⁵ Cl ₄ ³⁷ Cl ₂ O	HxCDF
	383.8639	M	¹³ C ₁₂ H ₂ ³⁵ Cl ₆ O	HxCDF (S)
	385.8610	M+2	¹³ C ₁₂ H ₂ ³⁵ Cl ₅ ³⁷ ClO	HxCDF (S)
	389.8156	M+2	C ₁₂ H ₂ ³⁵ Cl ₅ ³⁷ ClO ₂	HxCDD
	391.8127	M+4	C ₁₂ H ₂ ³⁵ Cl ₄ ³⁷ Cl ₂ O ₂	HxCDD
	401.8559	M+2	¹³ C ₁₂ H ₂ ³⁵ Cl ₅ ³⁷ ClO ₂	HxCDD (S)
	403.8529	M+4	¹³ C ₁₂ H ₂ ³⁵ Cl ₄ ³⁷ Cl ₂ O ₂	HxCDD (S)

TABLE 6 (cont.)*
Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate ^(a) Mass	Ion ID	Elemental Composition	Analyte
4	407.7818	M+2	C ₁₂ H ³⁵ Cl ₆ ³⁷ ClO	HpCDF
	409.7788	M+4	C ₁₂ H ³⁵ Cl ₅ ³⁷ Cl ₂ O	HpCDF
	417.8250	M	¹³ C ₁₂ H ³⁵ Cl ₇ O	HpCDF (S)
	419.8220	M+2	¹³ C ₁₂ H ³⁵ Cl ₆ ³⁷ ClO	HpCDF
	423.7767	M+2	C ₁₂ H ³⁵ Cl ₆ ³⁷ ClO ₂	HpCDD
	425.7737	M+4	C ₁₂ H ³⁵ Cl ₅ ³⁷ Cl ₂ O ₂	HpCDD
	435.8169	M+2	¹³ C ₁₂ H ³⁵ Cl ₆ ³⁷ ClO ₂	HpCDD (S)
	437.8140	M+4	¹³ C ₁₂ H ³⁵ Cl ₅ ³⁷ Cl ₂ O ₂	HpCDD (S)
	479.7165	M+4	C ₁₂ H ³⁵ Cl ₇ ³⁷ Cl ₂ O	NCDPE
	[430.9728]	LOCK	C ₉ F ₁₇	PFK
5	441.7428	M+2	C ₁₂ ³⁵ Cl ₇ ³⁷ ClO	OCDF
	443.7399	M+4	C ₁₂ ³⁵ Cl ₆ ³⁷ Cl ₂ O	OCDF
	457.7377	M+2	C ₁₂ ³⁵ Cl ₇ ³⁷ ClO ₂	OCDD
	459.7348	M+4	C ₁₂ ³⁵ Cl ₆ ³⁷ Cl ₂ O ₂	OCDD
	469.7780	M+2	¹³ C ₁₂ ³⁵ Cl ₇ ³⁷ ClO ₂	OCDD (S)
	471.7750	M+4	¹³ C ₁₂ ³⁵ Cl ₆ ³⁷ Cl ₂ O ₂	OCDD (S)
	513.6775	M+4	¹³ C ₁₂ ³⁵ Cl ₈ ³⁷ Cl ₂ O	DCDPE
	[442.9728]	LOCK	C ₁₀ F ₁₇	PFK

^(a) The following nuclidic masses were used:

H = 1.007825	O = 15.994915
C = 12.000000	³⁵ Cl = 34.968853
¹³ C = 13.003355	³⁷ Cl = 36.965903
F = 18.9984	

S = Internal/recovery standard

*The homologous groups for functions 1-3 do not use the same lockmass as described in Table 6. They use masses 316.9824, 366.9792, and 380.9760, respectively.

TABLE 7

Recommended GC Operating Conditions

The GC Operating Conditions (Temperatures (°C), and Times (minutes))
Are as Follows:

Injector Temperature: 280°C

Interface Temperature: 280°C

Initial Temperature and Time: 190°C / 1 Minute

Temperature Program: 190°C, increasing at a rate of 4°C per minute up to 240°C, and maintaining at this temperature until the last of the tetra- group has eluted from the column. (The total time required for this is approximately 25 minutes, depending on the length of the column). The maintained temperature of 240°C is then increased to 320°C at the rate of 20°C per minute and held at this level until the last compound (octa-group) has eluted from the column.

TABLE 8

PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and Used for Defining the Homologous GC Retention Time Windows on a 60-M DB-5 Column^(b)

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

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

- (b) The PCDF Congeners present in GC the Performance Evaluation Solution for the 30 m DB-225 column include:

- 1,2,3,9-TCDF
- 2,3,7,8-TCDF
- 2,3,4,7-TCDF
- ¹³C₁₂-2,3,7,8-TCDF

Column performance criteria is met when the percent valleys between the 2,3,7,8-TCDF analyte and the closest eluting isomers are ≤ 25%.

TABLE 9

Theoretical Ion Abundance Ratios and Their
Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	$\frac{M}{M+2}$	0.77	0.65	0.89
5	$\frac{M+2}{M+4}$	1.55	1.32	1.78
6	$\frac{M+2}{M+4}$	1.26	1.05	1.43
6 ^m	$\frac{M}{M+2}$	0.51	0.43	0.59
7 ^m	$\frac{M}{M+2}$	0.44	0.37	0.51
7	$\frac{M+2}{M+4}$	1.04	0.88	1.20
8	$\frac{M+2}{M+4}$	0.89	0.76	1.02

^m Used only for ¹³C-HxCDF (IS).

^m Used only for ¹³C-HpCDF (IS).

TABLE 10

Relative Response Factor [RRF (number)] Attributes

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

TABLE 11

2,3,7,8-TCDD Equivalent Factors (TEFs) for the Polychlorinated
Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

TABLE 12

Toxicity Equivalency Factor:
Analyte Relative Retention Time Reference Attributes

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

(a) The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to $^{13}\text{C}_{12}$ -1,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF.

FIGURE 1

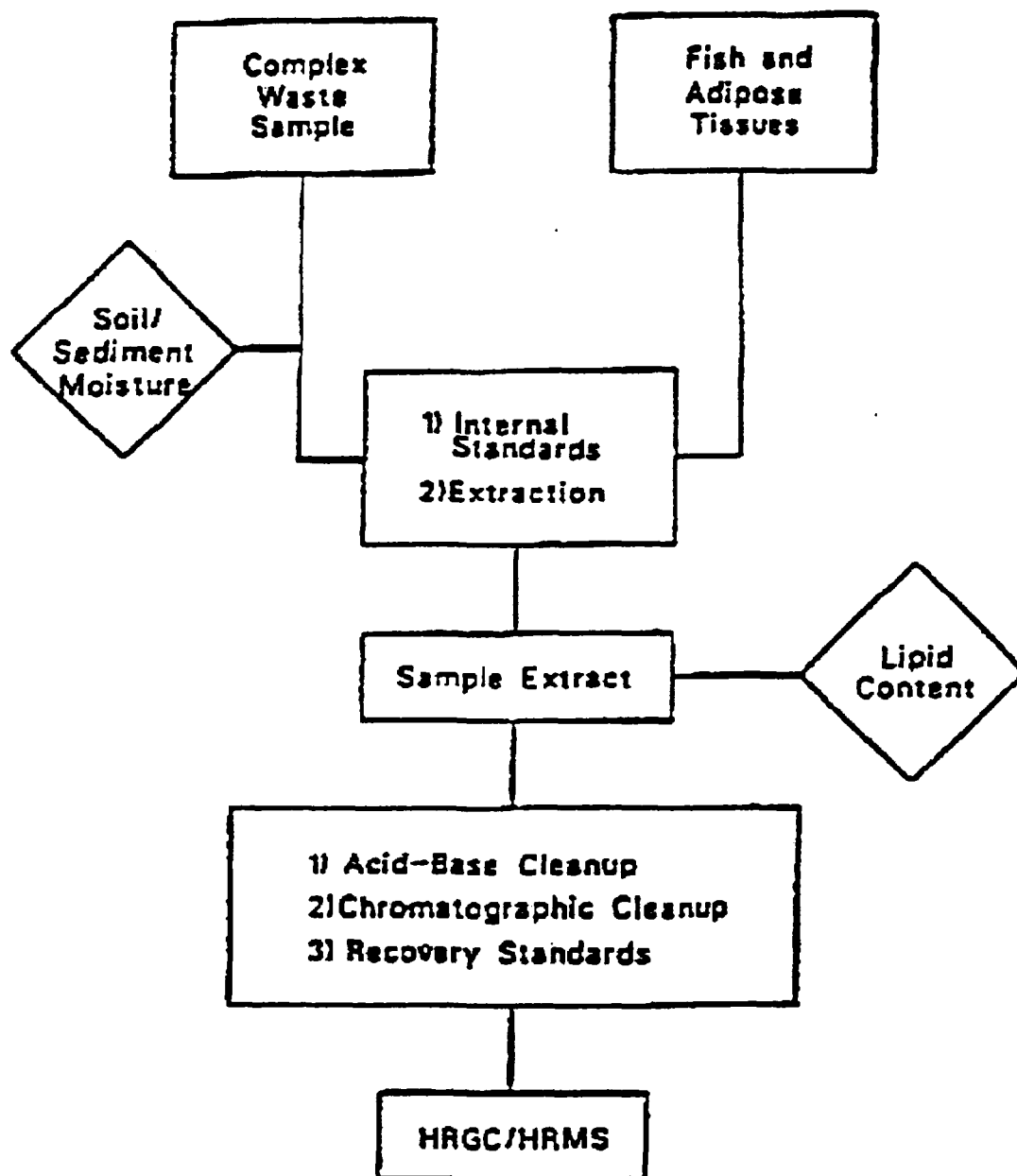
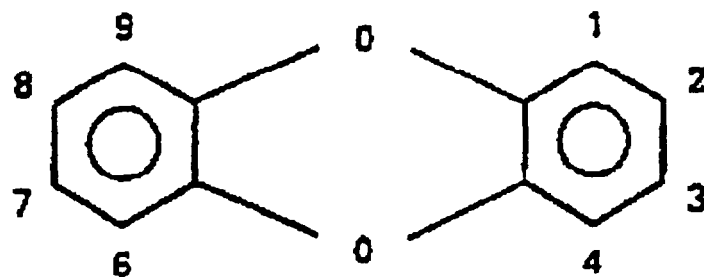
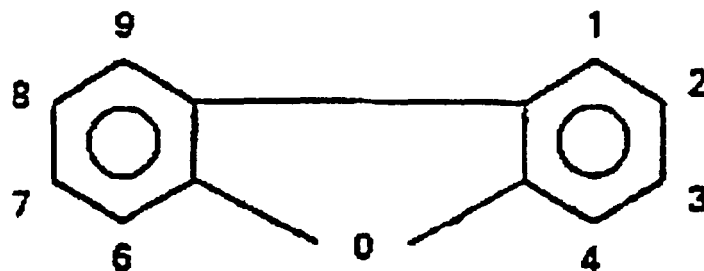


FIGURE 2

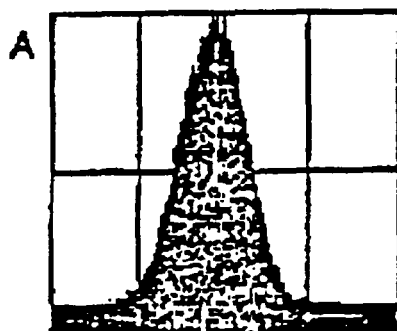


Dibenzodioxin

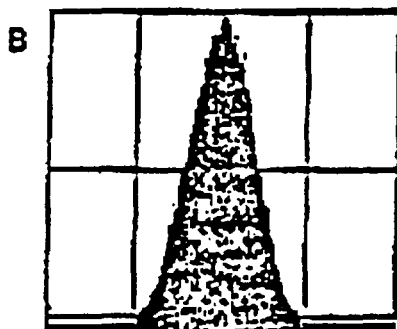


Dibenzofuran

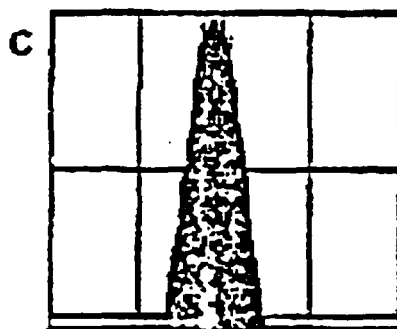
FIGURE 3



5,600



5,600



8,550

← 400 ppm →

FIGURE 4

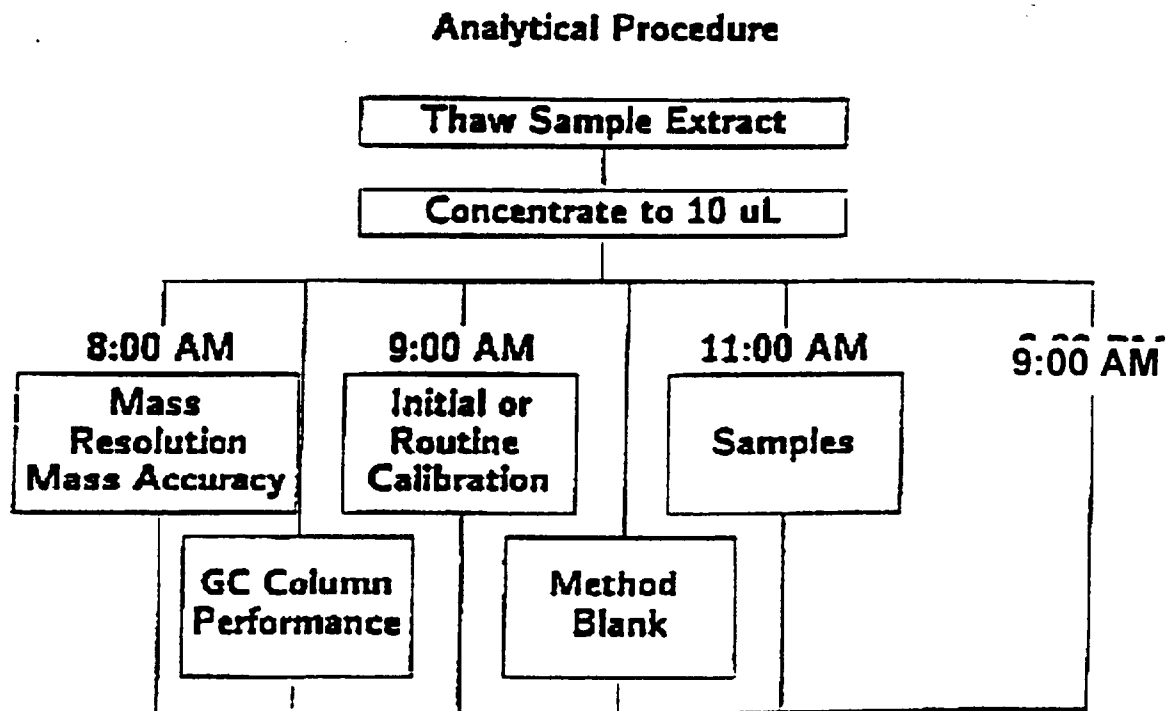
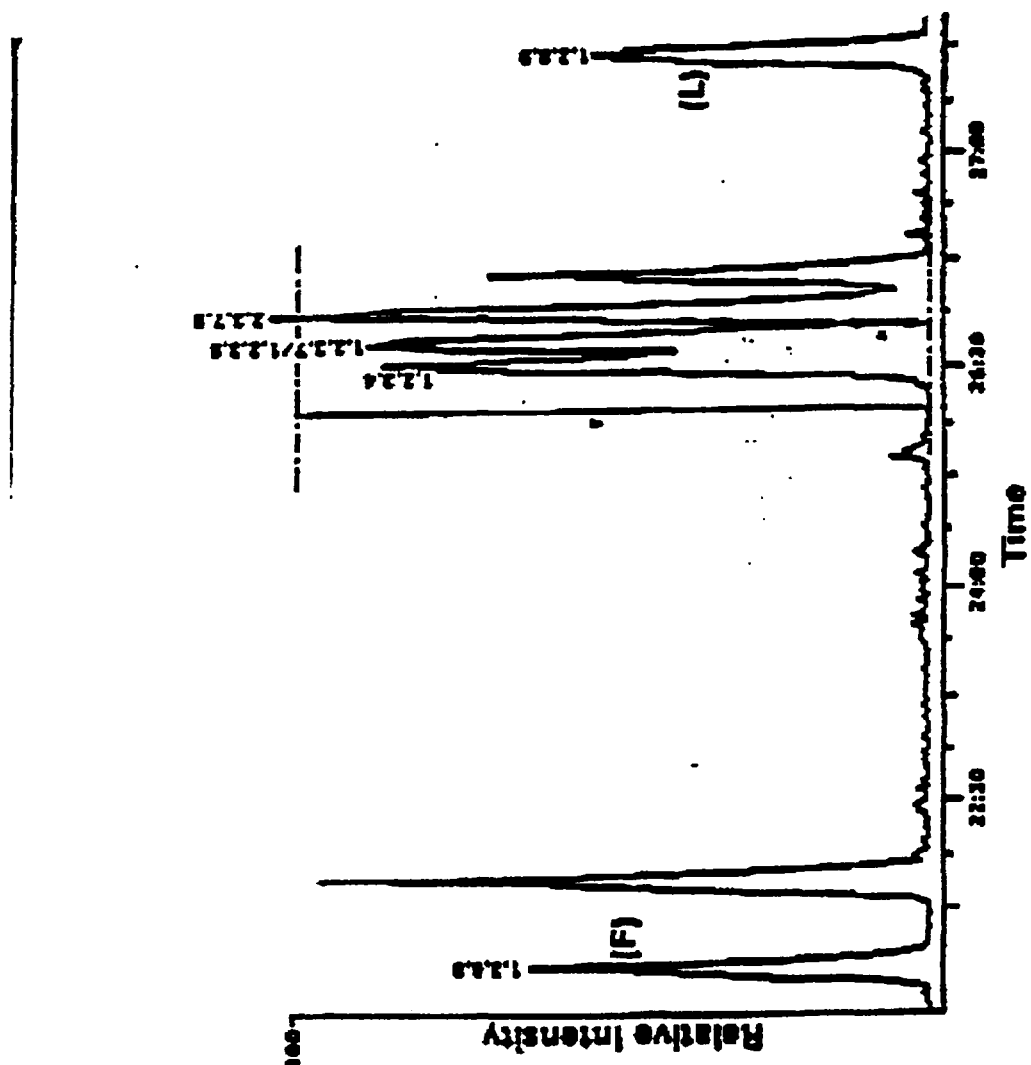


FIGURE 5

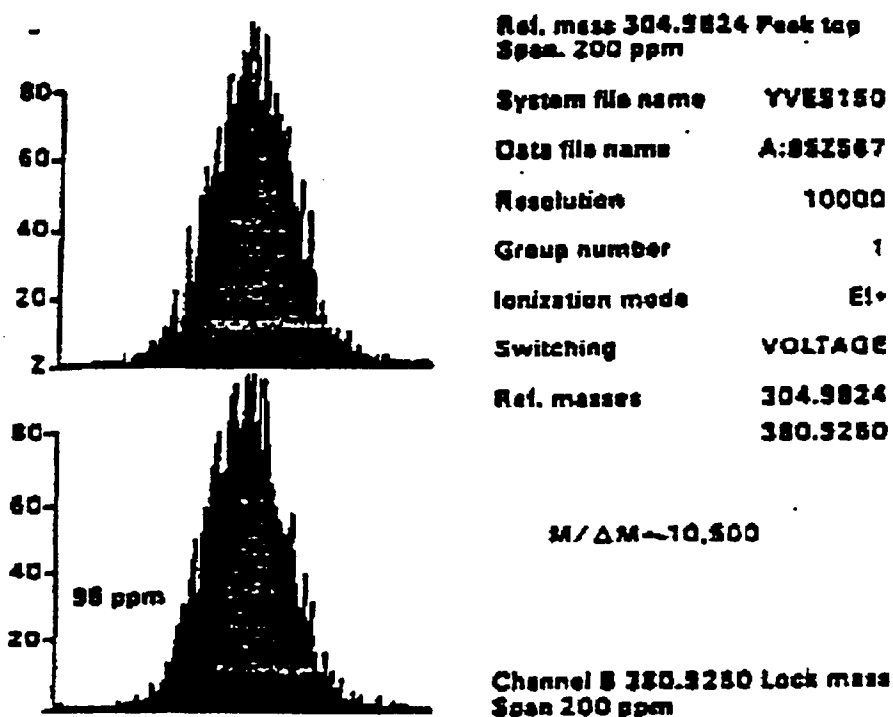


Selected ion current profile for m/z 322 (TCDOs) produced by MS analysis of the GC performance check solution on a 60 m DB-3 fused silica capillary column under the conditions listed in Section 7.6.

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FIGURE 6

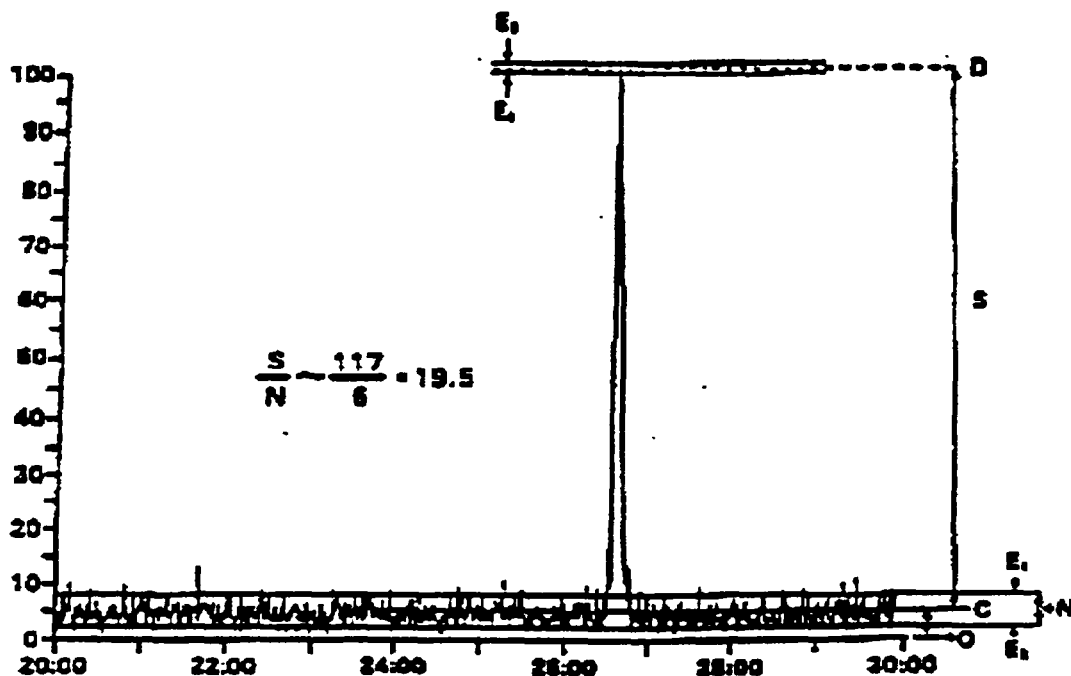


Peak profiles representing two PFK reference ions at m/z 305 and 381. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power $M/\Delta M$ of 10,500 (10 percent valley definition).

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FIGURE 7



Manual determination of S/N.

The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE:

It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

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- 17.6 Record Management and Documentation. (Sample benchsheets, logbook pages, data review checklists, etc.).
- 17.7 Method appendices.



QUANTERRA INCORPORATED

West Sacramento

Initial Calibration Checklist

High Resolution

ICAL ID _____ Method ID _____

Column ID _____ Instrument ID _____

STD ID's _____ Multiplier Setting _____

Analyzed By _____ Date Analyzed _____

Prepared By _____ Date Prepared _____

Reviewed By _____ Date Reviewed _____

ANALYSIS OFICAL	INITIATED	REVIEWED
Curve summary present?		
CS1-CS5, CPSM, solvent blank present?		
Copy of logfile present?		
CPSM blowup/static resolution check present?		
Target file RT's correct?		
RRFs within method-specified limits?		
Signal-to-noise criteria met?		
Isotopic ratios within limits?		
Chromatographic windows correct?		
CPSM valley < 25%?		
Manual reintegrations checked and hardcopies included?		

COMMENTS: _____

Method 8290: %RSD $\leq$ 20% for natives, $\leq$ 30% for labelled analytes; S/N $\geq$ 10Method 1613A: %CV $\leq$ 35% (See Table 7, Method 1613A); S/N $\geq$ 10Method 23: %RSD $\leq$ values specified in Table 5, Method 23; S/N $>$ 2.5PAH: %RSD $\leq$ 30% for natives and labelled compounds; S/N $\geq$ 10PCB: %RSD $\leq$ 25% for natives, $\leq$ 30% for labelled compounds; S/N $\geq$ 2.5NCASI 551: %RSD $\leq$ 20% for natives and labelled compounds; $\geq$ 5

APPENDIX A

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

PERFORMING WIPE TEST

Perform the wipe tests on surface areas of two inches by one foot with laboratory wipers saturated with distilled-in-glass acetone using a pair of clean stainless steel forceps. Use one wiper for each of the designated areas. Combine the wipers to one composite sample in an extraction jar containing 200 mL distilled-in-glass hexane. Place an equal number of unused wipers in 200 mL hexane and use this as a control.

SAMPLE PREPARATION

Close the jar containing the wipers and 200 mL hexane and extract for 20 minutes using a wrist-action shaker. Use an appropriate means to reduce the volume to approximately 1.0 mL. Put through an alumina column to clean up potential interfering compounds. Add appropriate amount of recovery standard.

EXTRACT ANALYSIS

Concentrate the contents of the vial to a final volume of 20 μ L (either in a minivial or in a capillary tube). Inject 2 μ L of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDDs/PCDFs as specified in the analytical method Section 11 (this exhibit). Perform calculations according to Section 12 (this exhibit).

REPORTING FORMAT

Report the presence of 2,3,7,8-substituted PCDDs and PCDFs as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 25 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 8 pg of 2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is $25 \times 5 = 125$ pg/WTE and the positive response for the blank would be $8 \times 5 = 40$ pg). Also, report the recoveries of the internal standards during the simplified cleanup procedure.

FREQUENCY OF WIPE TESTS

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

CORRECTIVE ACTION

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

The test results and the decontamination procedure must be reviewed with EH&S.

QUANTERRA INC. (West Sacramento)
STANDARD OPERATING PROCEDURE CHANGE FORM

SOP Number:	
SOP Title:	
SOP Sections Affected by Change:	
Reason for Addition or Change:	
Change Effective From [Date]:	
Change or Addition (Specific Section; use additional sheets if necessary.):	

Submitted by/Date:

Approved by:*

Technical Reviewer:

Date:

EH&S Signature:

Date:

QA Signature:

Date:

Management Signature:

Date

*Must be same signature authorities of SOP being revised.

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