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TMS

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TMS ANALYTICAL SERVICES, INC.

QUALITY ASSURANCE PLAN FOR DIOXINS

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GENERAL STATEMENT OF PURPOSE

TMS GENERAL STATEMENT OF PURPOSE

1.0 PURPOSE

Establishment of routine operating practices to ensure that all data generation in the laboratory conforms to specific requirements for accuracy, precision, and completeness. The purpose and goal of quality assurance/quality control (QA/QC) is to ensure that all data generated in the laboratory conforms to the specific requirements for accuracy, precision, and completeness as related to the appropriate type of analysis, analyte, and matrix. This quality assurance/quality control plan describes the organization and procedures routinely incorporated into all analyses performed by TMS ANALYTICAL SERVICES for the purpose of producing reliable data.

2.0 METHODS AND MODIFICATIONS

All methods of analyses will follow the specific EPA methodology for that specific type of analyses. This is to include all requirements for initial and daily calibration, method blanks, surrogates and internal standards, external standards, performance and/or matrix spike samples, and for all sample preparation procedures.

Customized, client-specific quality control measures can be added to these basic guidelines to satisfy the special needs of individual programs. Basic methods of analyses can also be modified to meet individual programs if no acceptable method of analysis is available. However, if such modification is necessary, the quality control/quality assurance criteria will be carried over in order to ensure accurate, precise, and complete data. Laboratory personnel are available to discuss the design, advantages, and disadvantages of any modifications to either the quality control measures or method of analysis.

3.0 ORGANIZATION

3.1 VICE PRESIDENT, OPERATIONS

The ultimate responsibility for the generation of reliable laboratory data rests with the Vice President of Operations. This person is vested with the authority to effect those policies and procedures which ensure that only data of the highest attainable caliber is produced.

3.2 ANALYTICAL SECTIONS

To assist the Vice President of Operations in achieving his/her goals, each Analytical Section as well as the Document Control Officer is responsible for the implementation of the established policies and procedures. Each section possess the authorities commensurate with its responsibilities for the day-to-day enforcement and monitoring of laboratory activities.

Unless otherwise specified, the Senior Analyst in each analytical section has the responsibility for ensuring that personnel within that section are adequately trained to perform analyses, that equipment and instrumentation are calibrated and functioning properly, and that system audits are performed on a periodic basis. These system audits will consist of analyses of external check samples to determine the analyst/instrument capability to identify and quantify routine analytes.

3.3 DOCUMENT CONTROL OFFICER

The Document Control Officer has the responsibility for the final review and evaluation of results from each analytical section. In addition, the preparation of quality assurance documentation for the laboratory is a function of the Document Control Officer. This officer will also review program plans for consistency with organizational and contractual requirements and will advise appropriate personnel of any changes or inconsistencies.

3.4 LABORATORY PERSONNEL

Any effective quality assurance and quality control program depends not only on organization and management but also on the efforts of each and every individual on the laboratory staff. The initial review for acceptability of analytical results rests with the analysts conducting the various tests. Observations made during the performance of an analytical method may indicate that the analytical system is not in control. Analysts must be constantly aware for indications of perturbations from the norm and be ready to verify that the system is in control before continuing analyses or reporting results or analyses.

In addition, laboratory personnel responsible for the receipt, breakdown, and preparation of samples should be aware of and note any observations which may affect the integrity of the final analytical data.

4.0 SAMPLE MANAGEMENT

An organized and efficient sample management system is a necessary and critical foundation on which actual analyses of samples are based. Sample management includes client file creation, sample preservation, sample receipt, sample storage, chain-of-custody documentation, reporting and invoicing, and sample retention and disposal.

4.1 CLIENT FILE

On notification of a sampling and analysis effort, the laboratory will create a client file to maintain records associated with the project. In addition to administrative information, the required analyses and any requested modifications will be included in the file. As the project progresses, chain-of-custody, tracking sheets, and analytical results as well as any other pertinent information will be added to the file.

4.2 BOTTLE PREPARATION/SAMPLE PRESERVATION

Sample bottles and sample preservation will be the responsibility of the client. In addition, sample homogenization will also be the responsibility of the client. In cases where counsel is sought regarding sampling, bottling, preservation, and/or shipping, TMS will advise according to the most recent recommendations from the U.S. Environmental Protection Agency as applicable.

4.3 CHAIN-OF-CUSTODY

Chain-of-custody procedures document the history of samples and constitute a crucial part of sampling and analysis programs. Chain-of-custody documentation assists and enables the identification and tracing of a sample from the time of collection through the time of analysis.

All samples which are received at the laboratory must be accompanies by a chain-of-custody. The chain-of-custody should include the following data:

* Date
* Sample Number
* Sample Description
* Client/Program
* Number of Containers
* Preservative (if present)
* Analyses Required

* Special Instructions/Notes
* Time/Date of Transfer
* Signature of Recipient

Sample containers should include the following data:

* Date
* Sample Description
* Analyses Required
* Client/Program

When samples are received at the laboratory, the sample custodian will verify each and every sample against the chain-of-custody forms, note any discrepancies or losses or samples, and then sign for receipt of the samples. Samples will remain under the control of the sample custodian until samples are transferred to the laboratory staff for processing. Following transfer to the laboratory staff, all samples must be in custody and such custody documented.

A sample is considered to be in custody if it:

* Is in the physical possession of the responsible party.
* Is in view of the responsible party
* Is secured by the responsible party to prevent tampering.
* Is secured by the responsible party in a restricted area.

4.4 SAMPLE RECEIPT

Samples received at the laboratory are inspected for integrity, and any field documentation is reviewed for accuracy and completeness. If chain-of-custody forms do not accompany the samples, the sample custodian will initiate these forms. When samples are received with missing or deficient chain-of-custody forms, the legal traceability of these samples cannot extend to the time of collection but must begin at the time of laboratory receipt.

Chain-of-custody and sample integrity problems are noted and recorded during sample log-in. Client Services is informed of the deficiencies and will advise the laboratory on the desired disposition of the samples after contacting the client.

Each sample that is received by the laboratory is assigned a unique sequential sample number which will identify the

sample in the laboratory's internal tracking system. Reference to a sample in any communication will include the assigned sample number to specify which sample is of concern.

4.5 SAMPLE STORAGE

Samples will be stored in a secured area of the type dictated by the analytical methodology. If a refrigerated area, the Sample Custodian will monitor and record the temperature daily.

Sample fractions and extracts will also be stored under the conditions dictated by the analytical methodology.

4.6 SAMPLE RETENTION AND DISPOSAL

In the case of contracts entered into between TMS Analytical and the U.S. Environmental Protection Agency, samples and sample extracts will be retained for the specified time as outlined in the original contract. At the end of this time, samples and sample extracts will either be returned to the U.S. EPA or disposed of in an appropriate manner.

In the case of analyses conducted for private clients, the samples, sample extracts, packing materials, and shipping containers will be returned to the client upon verification of the data and transmission of the final data package.

5.0 ANALYTICAL METHODS

5.1 INSTRUMENT MAINTENANCE

Instruments will be maintained in accordance with manufacturers' specifications. More frequent maintenance may be dictated dependent on operational performance. Documentation pertaining to the date and type of maintenance performed will be kept by the Senior Analyst of each analytical section.

Service contracts via the manufacturer will be used on major instruments in order to provide routine preventative maintenance and to ensure rapid response for emergency repair service. Minimal instrument down time is experienced through the use of these contracts and is of major importance to TMS's goal of fast, accurate analysis.

5.2 INSTRUMENT CALIBRATION

Before any instrument can be used as a measurement device, the instrumental response to known reference materials must be determined. The manner in which the various instruments are calibrated will be dependent on the particular instrument and the intended use of the instrument. These calibrations will be based upon the strictest adherence to the guidelines published by the U.S. EPA for the intended analysis. All sample measurements will be made within the calibrated range of the instrument.

Laboratory balances will be calibrated annually and will be checked before use on a daily basis. A record of daily checks will be kept on the sample tracking record.

Temperature dependent devices will be checked daily. Thermometers used for such checks will be calibrated annually against a National Bureau of Standards certified thermometer in the range of interest.

5.3 PERSONNEL TRAINING

Prior to conducting analyses on an independent basis, analysts will be trained by experienced personnel in the complete performance of an analytical method. If instrumentation is particularly complicated, analysts may be trained at instrument manufacturers' training courses. The analyst is then required to independently generate data on several method and/or matrix spikes to demonstrate proficiency in that method analytical method. The type of data to be generated will be dependent on the analytical method to be performed. Results of this "certification" will be reviewed by the appropriate analyst for adequacy.

Since method blanks and matrix spikes are required routine samples in every lot, performance on a day-to-day basis can be monitored by comparison with the original and cumulative data on similar samples. Each analytical section and the document control officer are responsible for ensuring that samples are analyzed by competent analysts, and that the resultant data is of the highest level possible for precision and integrity.

5.4 STANDARD ANALYTICAL METHODS

Analytical methods are routinely conducted as outlined in published sources. These methods are included in the appended attachments. Modifications to these methods may be necessary in order to provide accurate analyses of

particularly complex matrices. When modifications to standard analytical methods are performed, the specific alterations as well as the reason for the change will be reported with the results of analyses. In all cases, the preferred method of analysis will be the most up to date method as published by the U.S. Environmental Protection Agency.

For a listing of currently used analytical methods, forward to the attachment directory.

5.5 METHODS DEVELOPMENT

When standard (published) methods of analyses are not applicable to analyses to be performed, methods can be developed to provide the desired information. However, the lack of a historical data base does not obviate the necessity for documented quality control data to demonstrate the validity of the generated results. Reference material sources must be identified, and proof of compound identity and purity must be available. Instrumental operating parameters as well as calibration data must be documented, and specific procedures must be noted. Quality control samples should be analyzed with greater frequency than with standard analytical methods to demonstrate the certainty and uncertainty of generated data. Exact requirements for demonstrating the reliability of developed methods are normally dictated by the specific program.

5.6 REFERENCE MATERIALS

Whenever possible, primary reference materials will be obtained from the National Bureau of Standards of the U.S. Environmental Protection Agency. In the absence of available reference materials from these organizations, other reliable sources will be sought. These reference materials will be used for instrument calibration, quality control spikes, internal standards, and/or performance evaluations. Secondary reference materials may be used for these functions provided that they are traceable to an NBS standard or have been compared to an NBS standard within the laboratory.

5.7 REAGENTS

Laboratory reagents will be of the highest quality obtainable to minimize or eliminate background concentrations of the analyte to be measured. Reagents must also not contain other contaminants that will interfere with the analyte of concern.

5.8 CORRECTIVE ACTIONS

When an analytical system or methodology is deemed to be questionable or out-of-control at any level of review, corrective action must be performed. If possible, the cause of the situation is determined, and efforts are made to bring the system back into control. Demonstration of the restoration to a reliable analytical system will normally be accomplished by generating satisfactory calibration and/or quality control sample data. The major consideration in performing corrective action is to ensure the production of reliable and precise data within the laboratory.

6.0 DATA MANAGEMENT

6.1 DATA COLLECTION

In addition to the data collected in the field and recorded on the chain-of-custody forms, data describing the processing of samples will be accumulated in the laboratory and recorded either on the sample tracking record or in laboratory notebooks. These records are pertinent to establishment of sample integrity and must be dated/initialized to ensure accuracy. All records are to be placed in the specific project file for project documentation.

6.2 DATA REDUCTION

Data reduction is performed by the individual analysts and consists of calculating concentrations in samples from the raw data obtained from the measuring instruments. The complexity of the data reduction will be dependent on the specific analytical method and the number of discrete operations involved in obtaining a sample that can be measured.

For those methods utilizing a calibration curve, sample responses will be applied to the linear regression line to obtain an initial raw result which is then factored into equations to obtain the estimate of the concentration in the original sample. Rounding will not be performed until after the final result is obtained to minimize rounding errors, and results will not normally be expressed in more than two (2) significant figures.

Copies of all raw data and the spread sheets used to generate the final results will be retained in the project file to allow reconstruction of the data reduction process at a later date if necessary.

6.3 DATA REVIEW

System reviews are performed at all levels. The individual analyst constantly reviews the quality of data through calibration checks, quality control sample results, and performance evaluation samples. These reviews are performed prior to data reduction.

During data reduction, the individual analysts again review all data to ensure that all quality control/quality assurance criteria are met. Selected hard copy output of data will be reviewed by the Senior Analyst to ensure that results are interpreted correctly. Unusual or unexpected results will be reviewed by both the individual and Senior Analyst, and a resolution will be made as to whether the analysis should be repeated. In addition, the Senior Analyst will recalculate selected results to verify the calculation procedure.

The Document Control Officer independently conducts a complete review of projects to determine if laboratory and client quality assurance/quality control requirements have been satisfied. Discrepancies will be reported to the appropriate analytical section for resolution.

Final review is completed during the processing of the completed data package prior to transmission to the clients. In addition, non-routine audits are performed by regulatory agencies and client representatives. The level of detail and the areas of concern during these reviews are dependent on the specific program requirements.

6.4 DATA REPORTING

Reports will contain final results, methods of analysis, levels of detection, surrogate recovery data, and method blank data. In addition, special analytical problems and/or any modifications will be noted. The number of significant figures reported will be consistent with the limits of uncertainty inherent in the analytical method. Consequently, most analytical results will be reported to no more than two (2) significant figures. Final results will normally be reported in units commonly used for the analyses performed. Reported detection limits will be the concentration in the original matrix and will be calculated according to the specific methodology used for the analysis.

6.5 DATA ARCHIVING

The laboratory will maintain on file all data within the project file. This file will be maintained for three (3) years from the date of invoice unless a written request is received for an extended retention time.

All raw data files will be archived on a computer disc or magnetic tape for a period of one (1) year from date of invoice unless a written request is received for an extended retention time. For retrieval of data, a written work request to include a quotation must be submitted prior to data retrieval.

Client confidentiality will be maintained with retrieved data. Consequently, the laboratory can honor only those requests for data authorized by the original client.

7.0 SUBCONTRACTED ANALYSES

The subcontracting of analytical services does not relieve the laboratory of requirements set forth in this plan. Adherence to the provisions of this plan will be part of the subcontracting agreement, and data generated by the subcontractor laboratory will be reviewed with the same attitude as those analyses performed by the TMS laboratory.

KEY POSITION DESCRIPTIONS

LABORATORY MANAGER
DUTIES/RESPONSIBILITIES

1.0 PURPOSE

Establish minimum accountabilities for the Laboratory Manager to ensure that laboratory commitments are adequately met.

2.0 DUTIES AND RESPONSIBILITIES

2.1 Define project scope with analytical sections.

2.2 Review and approve analysis plans proposed by analytical sections.

2.3 Assign target completion date for analyses through client services and analytical sections.

2.4 Review client report completeness when last entry made on data report. Forward to Document Control.

2.5 Resolve technical problems with analytical sections.

2.6 Forward client file to document control for preparation of transmission and invoicing.

2.7 Review quality assurance/quality control data of client's file. Follow up with analytical sections if corrective action must be taken.

VICE PRESIDENT - OPERATIONS
DUTIES/RESPONSIBILITIES

1.0 PURPOSE

Establish overall goals and guidelines for growth of the laboratory. Ensure that data of the highest caliber is produced via the analytical sections.

2.0 DUTIES AND RESPONSIBILITIES

2.1 Define project with Laboratory Manager.

2.2 Approve proposal pricing.

2.3 Assign overall responsibilities in order to accomplish company's goals.

EPA CONTRACT LABORATORY PROGRAM

DUTIES AND RESPONSIBILITIES OF THE PROJECT MANAGER

1.0 **PURPOSE**

Establish minimum accountabilities for the Project Manager to ensure efficient operation, adequate technical guidance and adequate data review for the project.

2.0 **DUTIES AND RESPONSIBILITIES**

2.1 Direct the project to ensure that technical goals, project schedules and project costs are consistent with the contract.

2.2 Inform (by telephone and/or in writing) SMO and EPA Regional Technical Officer or client Project Officer of any discrepancies, technical difficulties or other items affecting smooth progress of sample preparation and analysis.

2.3 Review status, on regular basis with the Administrator Document Control, of all samples received for analyses.

2.4 Provide technical guidance, as required, to all project personnel.

2.5 Plan and direct work on a daily or weekly basis, as appropriate.

2.6 Handle client inquiries concerning status of samples.

2.7 Complete and submit to SMO a Weekly Progress Report for each case.

EPA CONTRACT LABORATORY PROGRAM

DUTIES AND RESPONSIBILITIES OF THE LABORATORY SUPPORT MANAGER

1.0 PURPOSE

Establish minimum accountabilities pertaining to the EPA-CLP for the Laboratory Support Manager to ensure proper coordination of support services such as bottle preparation, sample pick-up, sample log-in, and maintenance of client files.

2.0 DUTIES AND RESPONSIBILITIES

2.1 Coordinate scheduling of in-coming samples with the Section Managers and SMO.

2.2 Activate the client file by forwarding the file specifying case, number of samples expected, analytes required, and respective analyses requested to the Sample Custodian.

2.3 Supervise laboratory support personnel; (i.e., Sample Custodian, etc.) to ensure that laboratory operating practices pertaining to support services are adequately implemented.

2.4 Meet with Section Managers on a weekly basis to monitor in-house production needs so that in-coming work can be efficiently scheduled.

2.5 Initiate billing procedures on completion of a project.

2.6 Arrange for sample disposal after authorization has been received from the Project Officer, and ensure that proper documentation has been entered on the Chain-of-custody forms regarding final fate of the samples and extracts.

EPA CONTRACT LABORATORY PROGRAM

DUTIES AND RESPONSIBILITIES OF THE ADMINISTRATOR DOCUMENT CONTROL

1.0 **PURPOSE**

Establish minimum accountabilities for the Document Control Operation to ensure that sample data and related documentation for a specified case (group or samples) will be accounted for when the project is completed.

2.0 **DUTIES AND RESPONSIBILITIES**

2.1 Review quality control data for conformance to laboratory control limits and contract required acceptance criteria.

2.2 Perform quality assurance/quality control (QA/QC) review/audit of all analytical case files according to QA/QC check point procedures.

2.3 Waste stream inventory control management and disposition.

2.4 Maintain and facilitate EPA case file purges as defined by procedure/Statement of Work.

2.5 Maintain and facilitate archive storage of Private Client case files as defined by procedure.

2.6 Research all Sample Management Office (SMO) disallowed payments and prepare documentation for disputes.

2.7 Maintain laboratory signature list to current status.

2.8 Update and maintain laboratory standard operating procedures.

2.9 Maintain library of analytical procedures.

2.10 Function as contact for Contract Evidence Audit Team (CEAT-TechLaw) on all EPA related audits.

2.11 Provide support to Client Services as needed for case file research.

2.12 Provide back up to other administration staff as required.

EPA CONTRACT LABORATORY PROGRAM

DUTIES AND RESPONSIBILITIES OF THE ANALYSTS

1.0 **PURPOSE**

Establish minimum accountabilities for analytical laboratory personnel to ensure adequate bench level data evaluation and documentation in a timely, efficient manner.

2.0 **DUTIES AND RESPONSIBILITIES**

2.1 Meet with the Project Manager on a daily basis to discuss priorities and assignments.

2.2 Perform analyses according to the work schedule assigned and analytical SOP's required.

2.3 Check samples as appropriate for proper preservations/ preparation before beginning analyses.

2.4 Bring instrument problems, analytical problems, any abnormal occurrences, etc. to the attention of the Section Manager and/or Supervisor for resolution. Document the problem and the respective resolution in the appropriate instrument/laboratory notebook.

2.5 Record all observations and results which cannot be recorded on preprinted data sheets into a bound laboratory notebook. At the top of each page, record:

- Title: EPA-CLP SMO Case #/TMS #
- Notebook Number
- Date/analyst's signature

Data from only one case is recorded per page. If the entire page is not used, a line is drawn diagonally through the unused portion. The appropriate block at the bottom of the page is dated and initialed by the analyst.

When all of the data from a case are compiled, copies of all applicable notebook entries must be forwarded to the Document Control Administrator, who will inventory and file these copies in the appropriate case file.

2.6 Record all documents made in logbooks, and other documents, in ink. If an error is made, corrections are made by crossing a single line through the error, entering the correct information, and initialing and dating the correction.

2.7 Complete calculations at the end of each run or batch of similar runs and enter data into the appropriate laboratory notebook.

2.8 Review quality control data for conformance to laboratory control limits and contract required acceptance criteria.

2.9 Submit results into the laboratory data management system at the end of each work shift.

CLIENT SERVICES
DUTIES/RESPONSIBILITIES

1.0 PURPOSE

Establish minimum accountabilities for Client Services to ensure that client's needs are accomplished.

2.0 DUTIES AND RESPONSIBILITIES

2.1 Develop and maintain geographical profile of client base.

2.2 Develop and maintain categorical profile of client base.

2.3 Develop, co-ordinate, and maintain interface between client base and analytical sections.

2.4 Co-ordinate sample prioritization within analytical sections and laboratory operations.

2.5 Monitor and provide sample status reports to the operations management.

2.6 Provide technical support to the design, implementation, and operation of the marketing program.

2.7 Provide technical support to the client base in order to meet their needs for data and reporting.

FACILITIES DESCRIPTION

FACILITY DESCRIPTION

TMS Analytical Services, Inc. occupies a 17000 square foot facility located in Indianapolis, Indiana, approximately 15 minutes from the airport. The facility contains separate/ dedicated laboratory preparation rooms with state of the art air handling and exhaust systems, three dedicated mass spectrometry laboratories, an inorganic laboratory, dedicated glassware cleaning area, and document control areas.

TMS has the capability to perform standard GC/MS and GC/HRMS methods as well as a variety of specialized MS/MS methods. The laboratory staff includes low resolution, high resolution, and tandem mass spectrometer operators, along with staff who are experienced in sample preparation. The laboratory holds national EPA contracts for the analysis of samples for dioxin, and is one of the few laboratories in the CLP program for that analysis.

Laboratory equipment available includes gas chromatographs, liquid chromatographs, assorted spectrophotometers, and support equipment. The principle laboratory instrumentation includes a sophisticated tandem quadrapole mass spectrometer, an EBE geometry computer controlled double focusing mass spectrometer, and several conventional Hewlett-Packard GC/MS systems.

The tandem quadrapole mass spectrometer is a top-of-the-line SCIEX TAGA 6000E. The instrument is equipped with extended mass range to 1500 amu, and all available interfaces including GC, APCI, LPCI, LC, probes, and gas sampling. The instrument is computer controlled and is capable of all forms of MS/MS operation, including SIM, parent/daughter SIM, parent scans, daughter scans, and neutral loss scans. The instrument is cryopumped and capable of handling continuous gas loads directly into the source as high as 40 ml/min. The low pressure CI source is a bright Townsend discharge that generates an extremely high ion density.

The high resolution mass spectrometer is a VG AutoSpec hybridized magnetic sector with OPUS data analysis and chemical information system. The present configuration includes EI, CI, and probe sources. Due to the great sensitivity of this instrument, an injection of 1 picogram of 2,3,7,8-TCDD shows a signal-to-noise ratio greater than 500:1.

The conventional Hewlett-Packard GC/MS systems are capillary gas chromatographs coupled with mass selective detectors. The data system supporting the three GC/MSD units is an HP 1000 A-Series computer, Real-Time Executive (RTE-A) operating system, HP mass spectrometer applications/ data reduction software and HP peripheral hardware (scanning interface, disc drives, terminals, printers, etc.) It controls or assists in instrument tuning; data aquistion, data reduction, report production and automation.

LABORATORY SECURITY

LABORATORY SECURITY

The entire laboratory space of TMS is considered to be a limited access and secure facility. No persons who are not employees of the company are allowed on the premises unescorted at any time. Handling of visitors will be in accordance with regulations governing the laboratories controlled drug permits.

All visitors must sign in the visitors log-book upon arrival at either TMS facilities. Delivery personnel (such as Federal Express people need not sign in to conduct routine business, but must be escorted at all times.

Refer to section on Sample Security for measures that are taken to secure samples.

The facility is protected by an automatic alarm system.

All employees shall be issued one key to the system. Lost or stolen keys shall be reported to the office manager who shall determine the need for a new key system and issue appropriate new or replacement keys as necessary.

The first person into the laboratory in the morning shall disarm the alarm system, leaving the system in the "announcement of intrusion" mode. The last person to leave shall arm the system into the "away" position. All employees shall be instructed in the security codes to respond to the automatic call of police or fire units in the event of an alarm violation occuring.

WASTE DISPOSAL

TMS ANALYTICAL SERVICES STANDARD OPERATING PROCEDURE

EPA CONTRACT LABORATORY PROGRAM
HAZARDOUS WASTE DISPOSAL

Metal containers, lined with plastic bags shall be available in the laboratory areas so that any contaminated glassware can be immediately placed in the container. When the container is full, the lid will be crimped shut and then labeled as contaminated glassware.

Also available and handled in the same way will be metal containers for possible contaminated conbustables such as paper, gloves, plastic bench cover, etc. These containers will be handled in a similar manner and labeled accordingly.

Liquid wastes will be concentrated, evaporated to dryness, and the residue handled as solid waste.

The Laboratory Support Manger will dispose of accumulated solid waste by use of approved EPA or commercial disposal facilities.

Any remaining unused samples will be disposed of according to the requirements of the IFB contract.

VIAR AND COMPANY

SPECIAL ANALYTICAL SERVICES

STATEMENT OF WORK

FOR ANALYSIS OF

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD)

AND POLYCHLORINATED DIBENZOFURANS (PCDF)

IN WATERS, SOILS, SEDIMENTS, FLY ASH

AND CHEMICAL WASTES

INTRODUCTION

This document comprises part of the Statement of Work (SOW) to be used for analysis of environmental samples for PCDDs and PCDFs under Viar and Company's Special Analytical Services (SAS) program. The document includes the target compound list (see Exhibit C), the extraction procedures and analytical procedures to be employed (see Exhibit D), the reporting and deliverable requirements, including the data reporting forms (see Exhibit B), and a glossary of terms used in the SOW (see Exhibit G).

Certain terms used in this document are designed for use in EPA's Routine Analytical Services (RAS) programs, and may not be directly applicable to analyses performed under SAS, for instance, Case, SDG, and Traffic Report. It must be understood by the users of this document that such terms may be replaced by SAS-specific terms.

The requirements described in this document are supplemented by other specific requirements contained in the SAS Scope of Work, Contract Letter, and Regional Client Request Form. Any questions regarding the requirements in the SOW or any of these other documents should be directed to Viar and Company.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

C. Sample Data Summary Package

One Sample Data Summary Package shall be delivered to SMO concurrently with delivery of other required sample data. The Sample Data Summary Package consists of copies of specified items from the Sample Data Package. These items are listed below and are described under Part D, Sample Data Package.

The Sample Data Summary Package shall be ordered as follows and shall be submitted separately (i.e., separated by rubber bands, clips or other means) directly preceding the Sample Data Package. Sample data forms shall be arranged in increasing EPA sample number order, considering both letters and numbers. For example, DBE400 is a lower sample number than DBF100, as E precedes F in the alphabet.

The Sample Data Summary Package shall contain data for samples in one SDG of the Case as follows:

1. SDG Narrative.

2. Completed Forms I (PCDD-1, PCDD-2 and PCDD-3) for all samples. Original and rerun sample data shall be provided on separate forms.

D. Sample Data Package

The Sample Data Package shall include data for analyses of all samples in one SDG, including field samples, reanalyses, blanks, matrix spikes, and duplicate analyses. The Sample Data Package is divided into the three major units described below.

The Contractor shall retain a copy of the Sample Data Package for 365 days after final acceptance of data. After this time, the Contractor may dispose of the package.

1. SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name; Case number; sample numbers in the SDG, differentiating between initial analyses and reanalyses; SDG number; Contract number; and detailed documentation of any quality control, sample, shipment and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample reanalyses are submitted, the Contractor shall state in the SDG Narrative for each reanalysis, whether it considers the reanalysis to be billable, and if so, why.

The Contractor must also include any problems encountered, both technical and administrative, the corrective actions taken and the resolutions, and an explanation for all flagged edits (i.e., manual edits) on quantitation lists.

NOTE: If a column is used that has different first and last eluting isomers than the DB-5 column, the Contractor shall

fully document, in the SDG Narrative, the order of elution of the isomers and identify the first and last eluting isomers for that particular column for the window defining mix and CC3 solution.

The SDG Narrative shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by the signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature. Additionally, the SDG Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated. All copies of the SDG Narrative shall be signed in original signature.

2. Traffic Reports

A copy of the TRs submitted in Part A for all of the samples in the SDG shall be delivered. The TRs shall be arranged in increasing EPA sample numbering order, considering both letters and numbers in ordering samples. Copies of the SDG Cover Sheet shall be included with the copies of the TRs.

If samples are received at the laboratory with multi-sample TRs, all the samples on one multi-sample TR may not necessarily be in the same SDG. In this instance, the Contractor must make the appropriate number of photocopies of the TR so that a copy is submitted with each data package to which the TR applies.

In addition, in any instance where samples from more than one multi-sample TR are in the same data package, the Contractor must submit a copy of the SDG Cover Sheet with copies of the TRs.

3. PCDD/PCDF Data

a. Sample Data - in order by EPA sample number

(1) Target Compound List Results (Form I PCDD-1).

(2) Calculation of the Toxicity Equivalence (Form I PCDD-2).

(3) Second Column Confirmation Summary (Form I PCDD-3).

If the TEF is greater than the limits specified in Exhibit D, analysis on a column capable of resolving all 2378-substituted PCDDs/PCDFs is required.

(4) Selected Ion Current Profile (SICP) for each sample and each analysis of each sample. SICPs must contain the following header information:

- o EPA sample number.
- o Date and time of analysis.
- o GC/MS instrument ID.
- o Lab file ID.

(5) Total Congener Concentration Results (Form II PCDD).

b. Quality Control Data

(1) Spiked Sample Results (Form III PCDD-1) - in order by EPA sample number.

(2) Duplicate Sample Results (Form III PCDD-2) - in order by EPA sample number.

(3) Method Blank Summary (Form IV PCDD) - in order by EPA sample number assigned to the blanks.

(4) Window Defining Mix Summary (Form V PCDD-1) - in order by EPA sample number assigned to the window defining mix.

(5) Chromatographic Resolution Summary (Form V PCDD-2) - in order by EPA sample number assigned to the standard used to evaluate the column resolution.

(6) SICP for each analysis above [b.(1) - (5)]. SICPs must contain the header information described in a. (4) above.

c. Calibration Data

(1) Initial Calibration Data (Form VI PCDD-1 and Form VI PCDD-2) - in order by instrument, if more than one instrument used.

(a) PCDD/PCDF standard(s) SICPs for the initial (five-point) calibration shall be labeled as stated above.

(b) When more than one initial calibration is performed, the data must be arranged in chronological order by instrument.

(2) Continuing Calibration Data (Form VII PCDD-1 and Form VII PCDD-2) - in order by instrument, if more than one instrument is used.

(a) PCDD/PCDF standard(s) SICPs for all continuing calibrations shall be labeled as stated above.

(b) When more than one continuing calibration is performed, the data must be arranged in chronological order, by instrument.

d. Raw Quality Control Data

(1) Blank Data - in order by EPA sample number assigned to the blank. SICPs shall be submitted for each blank analyzed and labeled as above.

(2) Spiked Sample Data - in order by EPA sample number. SICPs shall be submitted for each spiked sample analyzed and labeled as above.

G. Extracts

The Contractor shall preserve sample extracts in the dark at room temperature in bottles/vials with Teflon-lined septa. Extract bottles/vials shall be labeled with EPA sample number, Case number and SDG number. A logbook of stored extracts, listing EPA sample numbers and associated Case and SDG numbers, shall be maintained.

The Contractor is required to retain extracts for 365 days following data submission. During that time, the Contractor shall submit extracts and associated logbook pages within seven days following receipt of a written request from the APO or SMO.

SECTION III

FORM INSTRUCTION GUIDE

This section includes specific instructions for the completion of all required forms. These instructions are arranged in the following order:

A. General Information and Header Information

B. PCDD/PCDF Sample Data (Form I PCDD-1, PCDD-2 and PCDD-3)

C. PCDD/PCDF Total Congener Concentration Summary (Form II)

D. PCDD/PCDF Spiked Sample and Duplicate Sample Results (Form III PCDD-1 and PCDD-2)

E. PCDD/PCDF Method Blank Summary (Form IV)

F. PCDD/PCDF Window Defining Mix Summary, Chromatographic Resolution Summary, and Analytical Sequence (Form V PCDD-1, PCDD-2 and PCDD-3)

G. PCDD/PCDF Initial Calibration Data Summary (Form VI PCDD-1 and PCDD-2)

H. PCDD/PCDF Continuing Calibration Data Summary (Form VII PCDD-1 and PCDD-2)

I. Sample Log-In Sheet (Form DC-1)

J. Document Inventory Sheet (Form DC-2)

A. General Information and Header Information

The data reporting forms presented in Section IV have been designed in anticipation of the development of a computer-readable data format. Although a "diskette deliverable" is not a requirement at this time, the design of the data reporting forms have taken such a future requirement into consideration. Therefore, the specific length of each field on the forms is the approximate length that would be included in a data element dictionary, with exceptions made in some instances for additional space on the hardcopy forms for visual clarity.

All characters which appear on the data reporting forms presented in Section IV must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the APO. The names of the various fields and compounds (e.g., "Lab Code," "2378-TCDD") must appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix: (Soil/Water/Waste/Ash)" must appear, not just "Matrix"). For items appearing on the uncompleted forms (Section IV), the use of uppercase and lowercase letters is optional.

Alphabetic entries made onto the forms by the Contractor shall be in ALL UPPERCASE letters (e.g., "SOIL," not "Soil" or "soil"). If an entry does not fill the entire blank space provided on the form, null characters shall be used to remove the remaining underscores that comprise the blank line. However, do not remove the underscores or vertical bar characters that delineate "boxes" on the forms. The only exception would be those underscores at the bottom of a "box" that are intended as a data entry line. (For instance, on Form II, if data must be entered on the last line of the box, it will replace the underscores).

Six pieces of information are common to the header section of each data reporting form. They are Lab Name, Contract, Lab Code, Case No., SAS No., and SDG No. Except as noted below for SAS No., this information must be entered on every form and must match on every form.

The "Lab Name" shall be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.

The "Lab Code" is an alpha-numeric abbreviation of up to six letters and numbers assigned by EPA to identify the laboratory and aid in data processing. This lab code shall be assigned by EPA at the time a contract is awarded and shall not be modified by the Contractor, except at the direction of EPA. If a change of name or ownership occurs at the laboratory, the lab code will remain the same unless and until the Contractor is directed by EPA to use another lab code assigned by EPA.

The "Case No." is the EPA-assigned Case number associated with the sample and reported on the Traffic Report or sample shipping paperwork.

The "Contract" is the number of the EPA contract under which the analyses were performed. In the case of multiple laboratories operating under a corporate-wide contract, the contract number entered shall be that of the corporate contract, regardless of the facility performing the analyses.

The "SDG No." is the EPA sample number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services (SAS). If samples are to be analyzed under SAS only and reported on these forms, then enter "SAS No.," and leave "Case No." blank. If samples are analyzed according to the Routine Analytical Services (IFB) protocols <u>and</u> have additional SAS requirements, enter <u>both</u> "Case No." and "SAS No." on all forms. If the analyses have no SAS requirements, leave "SAS No." blank. NOTE: Some samples in a SDG may have a SAS No., while others do not.

The other information common to most of the forms is the "EPA Sample No." This number appears either in the upper right-hand corner of the form, or as the left column of a table summarizing data from a number of samples. When the "EPA Sample No." is entered into the triple-spaced box in the upper right-hand corner of Form I, III or IV, it should be entered on the middle line of the three lines that comprise the box.

All samples, spiked samples, duplicate samples, blanks and standards shall be identified with an EPA sample number. For field samples, spiked samples, and duplicates samples, the EPA sample number is based on the unique identifying number given in the Traffic Report or sample shipping records for that sample.

In order to facilitate data assessment, the following sample suffixes <u>must</u> be used:

XXXXX	-	EPA sample number
XXXXXS	-	Spiked aliquot of sample "XXXXX"
XXXXXD	-	Duplicate aliquot of sample "XXXXX"
XXXXXRE	-	Reextracted and reanalyzed aliquot of sample "XXXXX"
XXXXXDL	-	Diluted analysis of sample "XXXXX"

Form V PCDD-3 requires that <u>all</u> samples analyzed in a given 12-hour analytical sequence be listed, regardless of whether or not they are part of the SDG being reported, and regardless of whether or not they are EPA samples. Therefore, use "ZZZZZ" as the EPA sample number for any sample analysis <u>not</u> associated with the SDG being reported.

For blanks and standards, the following identification scheme <u>must</u> be used as the "EPA Sample No."

1. Method blanks shall be identified as DFBLK==.

2. Calibration standards shall be identified as CC1==, CC2==, CC3==, CC4== and CC5==, corresponding to the calibration solutions identified in Exhibit D.

3. The window defining mixture shall be identified as WDM==.

4. The column performance solution shall be identified as CPS==.

The "EPA Sample No." <u>must be unique</u> within a SDG. Therefore, the Contractor must replace the two-character "==" terminator of the identifier with one or two characters or numbers, or a combination of both, to create a unique EPA sample number for each blank and standard within the SDG. For example, possible identifiers for method blanks would be DFBLK1, DFBLK2, DFBLKA1, DFBLKB2, DFBLKAB, etc.

Several other pieces of information are common to many of the data reporting forms. These include "Matrix," "Lab Sample ID," "Lab File ID," "Instrument," and "GC Column."

For "Matrix," enter "SOIL" for a soil/sediment sample, "WATER" for an aqueous sample, and "WASTE" for a chemical waste sample, including the matrices of oily sludge, wet fuel oil, stillbottoms, oils, or other materials significantly contaminated with these matrices. Enter "ASH" for fly ash samples.

"Lab Sample ID" is an optional laboratory-generated internal identifier. Up to 12 alpha-numeric characters may be reported here. If the Contractor does not have a lab sample ID, this field may be left blank. However, if this identifier is used on <u>any</u> of the forms, <u>or</u> accompanying hardcopy data deliverables, it must be reported on <u>all</u> the appropriate forms.

"Lab File ID" is the laboratory-generated name of the GC/MS data system file containing information pertaining to a particular analysis. Up to 14 alpha-numeric characters may be used here.

"Instrument" is common to many of the forms, particularly those containing calibration data. The identifier used by the laboratory must include some indication of the manufacturer and/or model of the instrument, and contain additional characters or numbers that differentiate between all instruments of the same type in the laboratory. The instrument identifier must be consistent on all forms within the SDG.

"GC Column" and "ID (mm)" are common to various other forms. These two fields are to be used to identify the stationary phase of the GC column (previously called GC Column ID), and the internal diameter of the GC column in millimeters (mm). For packed columns, convert the ID from inches to millimeters as necessary, and enter in the "ID" field.

For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round

up). If the figure following the last digit to be retained equals 5, round up if the digit to be retained is odd, and round down if that digit is even.

B. PCDD/PCDF Sample Data

1. Form I PCDD-1

This form is used for tabulating and reporting the sample analysis results for target analytes. It is related to Form I PCDD-2, and for each sample for which there is a Form I PCDD-1, there must be a corresponding Form I PCDD-2.

Complete all header information according to the instructions in Part A and as follows:

Enter the "Matrix" of the sample being analyzed. The designation of matrix must reflect which one of the matrix-specific extraction procedures in Exhibit D was used for extraction of the sample.

For "Sample wt/vol," enter the number of grams (for soil) or milliliters (for water) of sample used in the first blank line, and the units, either "G" or "ML," in the second blank.

For water samples, indicate the extraction procedure used by entering "SEPF" for separatory funnel extraction or "CONT" for continuous liquid-liquid extraction in the field labeled "Water Sample Prep."

Enter the actual volume of the most concentrated sample extract, in microliters, under "Conc. Extract Volume:" This volume will typically be 100 microliters, although this volume is split into two aliquots before analysis.

Enter "GC Column," "Instrument," "Lab Sample ID," and "Lab File ID" as described in Part A.

"Date Received" is the date of sample receipt at the laboratory, as noted on the Traffic Report (i.e., the validated time of sample receipt, VTSR) for that sample. It must be entered as MM/DD/YY.

"Date Extracted" and "Date Analyzed" must also be entered as MM/DD/YY. If continuous liquid-liquid extraction procedures are used for water samples, enter the date on which the procedure was started as the "Date Extracted." If separatory funnel procedures are used for water samples, enter the date on which the procedure was completed. The "Date Analyzed" must be the date of the analysis for which the results are reported on Form I. (If the sample requires a second column confirmation and is reported on Form I PCDD-3, the "Date Analyzed" on Form I PCDD-3 must be the date of the second analysis, while the date on Form I PCDD-1 and PCDD-2 will be the date of the first analysis.)

If the sample has been diluted for analysis, enter the "Dilution Factor" as a single number, not a fraction. For example, enter "100.0" for a 1 to 100 dilution of the extract. Enter "0.1" for a concentration of 10 to 1. If the sample was not diluted, enter "1.0."

NOTE: "Dilution" refers to sample handling steps other than those outlined in Exhibit D. If the weight or volume of the sample taken for extraction is not the weight or volume specified in the protocol, this is not a dilution but is accounted for in the weight/volume term. A dilution refers specifically to the addition of clean solvent to a measured volume of the most concentrated sample extract.

The appropriate concentration units, "NG/L" for water samples or "UG/KG" for all other matrices, must be entered in the field for "CONCENTRATION UNITS:"

For each analyte detected in a sample, enter the absolute retention time of the detected peak under "PEAK RT." Enter the retention time in minutes and decimal minutes, not seconds or minutes and seconds. The retention time must be entered even if the peak did not meet all of the identification criteria in Exhibit D.

Enter the ion abundance ratio for the two m/z's (listed under "Selected Ions") in the column labeled "ION RATIO." If the ion abundance ratio falls outside the acceptance limits listed in Exhibit D, place an asterisk (*) in the column under the number (#) symbol.

For target analytes that meet all the identification criteria in Exhibit D, the Contractor shall report the concentrations detected as uncorrected for blank contaminants in the column in the lower portion of the form labeled "CONCENTRATION." Report all results to two significant figures.

Under the column labeled "Q" for qualifier, flag each result with the specific data reporting qualifiers listed below. The Contractor is encouraged to use additional flags as needed, but the definition of such flags must be explicit, must not contradict the qualifiers listed below, and must be included in the accompanying Narrative.

For reporting results to EPA, the following contract-specific qualifiers are to be used. The seven qualifiers listed below are not subject to modification by the laboratory. Up to five qualifiers may be reported on Form I for each analyte.

The seven EPA-defined qualifiers to be used are as follows:

U - Indicates compound was analyzed for but not detected. The CONCENTRATION column is left blank in this instance, and an estimated detection limit (EDL) must be calculated based on the signal-to-noise ratio, as described in Exhibit D. This

calculation takes into account the sample weight/volume extracted, the volume of the most concentrated extract, the injection volume, and dilution of the most concentrated extract prior to analysis. The calculation does not consider the percent solids content of the sample, as all results are reported on a wet weight basis.

J - Indicates an estimated value. This flag is used when the mass spectral data indicate presence of an analyte meeting all the identification criteria in Exhibit D, but the result is less than the sample quantitation limit, but greater than zero.

B - This flag is used when the analyte is found in the associated blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action.

E - This flag identifies analytes whose concentrations exceed the calibration range of the GC/MS instrument for that specific analysis. If one or more compounds have a response greater than full scale, except as noted in Exhibit D, the sample extract must be diluted and reanalyzed according to the specifications in Exhibit D. All such compounds with a response greater than full scale should have the concentration flagged "E" on the Form I for the original analysis. If the dilution of the extract causes any compounds identified in the first analysis to be below the calibration range in the second analysis, the results of both analyses shall be reported on separate copies of Form I. The Form I for the diluted sample shall have the "DL" suffix appended to the EPA sample number.

D - This flag indicates all compounds identified in an analysis at a secondary dilution factor. If a sample extract is reanalyzed at a higher dilution factor, as in the "E" flag above, the "DL" suffix is appended to the EPA sample number on the Form I for the diluted sample, and all concentration values reported on that Form I are flagged with the "D" flag. This flag alerts data users that any discrepancies between the concentrations reported may be due to dilution of the sample extract.

S - This flag indicates that the analyte in question is, in the opinion of the GC/MS Interpretation Specialist, a PCDD/PCDF, even though the M-[COCl]+ ion did not meet the requirement of 2.5 times signal-to-noise (see Exhibit D, Section 11.3).

H - This flag indicates that the analyte in question was quantitated using peak heights rather than peak areas for both the analyte and its internal standard (see Exhibit D, Section 11.4).

X - Other specific flags may be required to properly define the results. If used, they must be fully described, and such description must be attached to the Sample Data Summary

Package and the SDG Narrative. Begin using "X." If more than one flag is needed, use "Y" and "Z" as needed. The laboratory-defined flags are limited to the letters "X," "Y," and "Z."

The combination of flags "BU" or "UB" is expressly prohibited. Blank contaminants are flagged "B" only when they are detected in the sample associated with the blank.

If a peak detected in the sample meets all of the identification criteria except the ion abundance ratio, flag the ion ratio as indicated above, and report the "Estimated Maximum Possible Concentration" as calculated in Exhibit D under the "EMPC/EDL" column. Do not report the value of the EMPC under the column labeled "CONCENTRATION," as that column is only for analytes meeting all the identification criteria.

If an analyte was not detected in the sample, enter "U" in the qualifier column, as described above, and report the Estimated Detection Limit" as calculated in Exhibit D under the "EMPC/EDL" column. Do not report the value of the EDL if there is an entry under "CONCENTRATION." The presence of the "U" alerts the data user that the reported value is an EDL, otherwise it is assumed to be an EMPC.

The bottom portion of Form I PCDD-1 contains the fields for reporting the recoveries of the internal standard and the cleanup standard. The recoveries of these standards are crucial in evaluating the effectiveness of this isotope dilution method. For each internal standard and the cleanup standard, enter the absolute retention time of the standard in the sample in minutes and decimal minutes, as above. Report the ion abundance ratio of each of the five internal standards under the "ION RATIO" column. Flag any ion ratios that fall outside the ion ratio limits listed on the form by placing an asterisk (*) in the column under the number (#) symbol. There is no ion abundance ratio for the cleanup standard, as only one ion is monitored.

Report the percent recovery of the internal standards and the cleanup standard, calculated according to Exhibit D, under the "%REC" column. The quality control limits for recovery are listed on the form. Flag any recovery outside those limits by placing an asterisk (*) under the number (#) symbol in the recovery column. Requirements for reanalysis of samples due to poor recoveries are given in Exhibit D.

2. Form I PCDD-2, Toxicity Equivalence Summary

This page of Form I is used to report the results of the toxicity equivalence calculations for each sample analyzed. The concentration of each of the 2,3,7,8-substituted PCDD and PCDF isomers is multiplied by a toxicity equivalence factor (TEF), as described in Exhibit D, to arrive at a concentration of 2,3,7,8-TCDD with an equivalent toxicity. The total of all the toxic

equivalents determines whether or not the sample needs to be analyzed on a second GC column to more completely separate the 2378-TCDF from all other TCDD and TCDF isomers (see Exhibit D).

Complete the header information as above. The header of Form I PCDD-2 must match the header of Form I PCDD-1 for the same sample.

For each 2,3,7,8-substituted isomer positively identified in the sample, enter the concentration found in the column labeled "CONCENTRATION." If an isomer was not detected, i.e., flagged "U" on Form I PCDD-1, for the purposes of this calculation, enter 0.0 (zero) as the concentration. EMPC values are not included in the TEF calculations under this SOW.

Multiply each concentration times the TEF listed on the form for that isomer, and enter the product of the two in the column labeled "TEF-ADJUSTED CONCENTRATION." Add all 17 TEF-adjusted concentrations together, including any zeros, and enter the total on the line at the bottom of the form.

If the total TEF-adjusted concentration is greater than the values listed at the bottom of the form and in Exhibit D, then a second column confirmation analysis is required (see Exhibit D).

3. Form I PCDD-3, Second Column Confirmation Results

This page of Form I is used to report the results of all second column confirmation analyses performed. The requirements for second column confirmation are discussed above and in Exhibit D. Each time a second column confirmation is performed, the results are reported on Form I PCDD-3.

Complete the header information as above, except note that the fields for "GC Column" and "Date Analyzed" must correspond to the second column confirmation analysis, i.e., they must not match those fields in the header of Form I PCDD-1 or PCDD-2. Other fields such as "Instrument," "Dilution Factor," and "Lab File ID" may also differ and must correspond to the second column confirmation analysis.

Complete the information in the lower portion of the form in a fashion similar to that for Form I PCDD-1, but entering the results of the second column confirmation.

Enter the data on recovery of the internal standards and cleanup standard from the second column confirmation analysis in a fashion similar to that for the original analysis.

C. PCDD/PCDF Total Congener Concentration Summary (Form II)

This form is used to report the total concentration of all PCDD/PCDF isomers in a given homologue that are detected in the sample, including those isomers that do not represent the 2,3,7,8-substituted isomers of greatest toxicological concern. Because there are many isomers in each

homologue, it is necessary to indicate the number of peaks that represent isomers within the homologue. Enter the number of peaks detected in each homologue under "PEAKS." For instance, if three PeCDD peaks are detected and summed together, enter "3" under "PEAKS."

Enter the concentration of the total homologue, as calculated in Exhibit D, under "CONCENTRATION." Enter qualifiers under the "Q" column, as described above. If no isomers in a homologue were detected, enter "U" as the qualifier, and enter the lowest EDL of any of the 2,3,7,8-substituted isomers under the "EMPC/EDL" column.

If any of the peaks in a homologue meet all the identification criteria except the ion abundance ratio, then report the total concentration as an EMPC under the "EMPC/EDL" column.

D. PCDD/PCDF Spiked Sample and Duplicate Sample Results (Form III)

1. PCDD/PCDF Spiked Sample Summary (Form III PCDD-1)

This page of Form III is used to report the accuracy of the spiked sample analysis, measured as recovery of the 10 spiked analytes. Because some of the analytes may also be present in the unspiked aliquot of the sample, results for both the unspiked and spiked analyses are reported on Form III.

Complete the header information as in Part A. Enter the EPA sample number for the spiked sample aliquot in the box at the top of the form. Similarly, the lab sample ID and lab file ID must refer to the spiked sample analysis.

Enter the "Spike Added" of each of the 10 analytes in picograms (pg). In the column labeled "Spiked Sample Result," enter the concentration (or EMPC) of each analyte detected in the spiked sample aliquot. The concentration units must be those indicated at the top of the form and be appropriate to the sample matrix listed in the header. Enter the concentration (or EMPC) of each analyte detected in the original analysis of the unspiked sample aliquot. If an analyte was not detected in the unspiked aliquot, enter zero in place of the concentration, and use this value in the calculations described in Exhibit D. Calculate the recovery of each spiked analyte as described in Exhibit D, and enter this value to the nearest whole percentage point in the column labeled "%REC." Flag any recoveries outside the quality control limits listed on the form by placing an asterisk (*) in the column under the number (#) symbol.

In addition to Form III PCDD-1, a copy of Form I must be completed for the spiked sample analysis as well, following the procedures described above.

2. PCDD/PCDF Duplicate Sample Summary (Form III PCDD-2)

This page of Form III is used to report the precision of the duplicate sample analysis, measured as the relative percent

difference (RPD) between the results of the original and duplicate analyses of one sample of each matrix in each SDG. In order to allow direct comparison of the results of both the analyses, the concentration results from the original and duplicate analyses are reported on a single copy of Form III PCDD-2.

Complete the header information as described in Part A above, but enter the EPA sample number, lab sample ID, and lab file ID of the duplicate aliquot in these fields on Form III PCDD-2. Enter the concentration units.

For each target analyte, enter the results from both the analyses under the columns "Sample Concentration" and "Duplicate Concentration." These values must match those on Form I for these aliquots, <u>except</u> that undetected analytes (flagged "U" on Form I) are reported as zero on Form III PCDD-2. If either or both the analyses resulted in an EMPC for any analyte, enter the EMPC as the concentration, and use that value in the calculations.

Calculate the relative percent difference between the two concentrations or EMPCs, as described in Exhibit D, using zero for undetected analytes, and report this value to the nearest whole percentage point under "RPD." If the analyte was not detected in <u>either</u> aliquot, enter zero for both concentrations, and report the RPD as zero as well. Flag all values outside the quality control limits listed on the forms by entering an asterisk (*) under the number (#) symbol.

E. <u>PCDD/PCDF Method Blank Summary (Form IV)</u>

This form summarizes the samples associated with each method blank analysis. A copy of Form IV is required for each blank.

Complete the header information as described in Part A. The EPA sample number entered in the box at the top of the form shall be the number assigned to the method blank. The matrix entered on this form refers to the matrix of the associated samples, as one blank is required each time that samples of a similar matrix are extracted together. Therefore, samples of differing matrices cannot be mixed together on a single Form IV.

Summarize the samples associated with a given method blank in the box in the lower portion of the form, entering the EPA sample number, lab sample ID, lab file ID, and date of analysis of each sample. Include spiked samples and duplicate samples as well.

F. <u>PCDD/PCDF Window Defining Mix Summary, Chromatographic Resolution Summary, and Analytical Sequence (Form V)</u>

1. PCDD/PCDF Window Defining Mix Summary (Form V PCDD-1)

This page of Form V is used to report the results of the analysis of the window defining mixture that precedes each initial

calibration on each GC column and instrument used for analysis. The analysis of this mixture is used to document the retention time window for the PCDD/PCDF homologue.

Complete the header information as described in Part A, entering the EPA sample number of the window defining mixture injection in the box at the top of the form. The header information must correspond to the analysis of the window defining mixture.

In the box in the lower portion of the form, enter the absolute retention times of the first and last eluting isomers in each homologue. Enter the retention times in minutes and decimal minutes, not minutes and seconds, nor seconds.

NOTE: As there is only one possible octachlorinated dioxin and furan, the retention times of these analytes are not contained in the window defining mixture, and are not reported here.

2. PCDD/PCDF Chromatographic Resolution Summary (Form V PCDD-2)

This page of Form V is used to report the chromatographic resolution of selected analytes in one of two solutions, depending on the GC column. The chromatographic resolution of these analytes is crucial to evaluating the results for the PCDDs/PCDFs reported in the samples. This evaluation is made every 12 hours during which samples or standards are analyzed.

For the DB-5 (or equivalent) column, the chromatographic resolution is judged from the analysis of the CC3 standard during initial or continuing calibration. For the SP-2331 (or equivalent) column, the chromatographic resolution is judged from the analysis of the column performance solution that precedes the analysis of the CC3 standard on this column (see Exhibit D).

Complete one copy of Form V PCDD-2 for each GC column used for analysis. Complete the header information as described in Part A, entering the EPA sample number of the CC3 standard or the column performance solution in the box at the top of the form. Enter the date and time of analysis of the standard in the header.

Calculate the chromatographic resolution for the GC column identified in the header according to the procedures in Exhibit D. For the DB-5 (or equivalent) column, enter only the results from the CC3 analysis. For the SP-2331 (or equivalent) column, enter only the results from the column performance solution analysis.

The GC column chosen for the confirmation analysis must meet the resolution criteria for the other specified column. If the Contractor chooses a single column for analysis that is designed such that a second column confirmation analysis is not required, then the Contractor must demonstrate that the resolution criteria for both of the specified columns have been met (see Exhibit D).

3. PCDD/PCDF Analytical Sequence (Form V PCDD-3)

This page of Form V is used to report the sequence of analyses, including the analysis of the window defining mixture, the calibration standards, blanks, samples, duplicates, and spiked samples. One copy of Form V PCDD-2 is required for each 12-hour period during which samples, blanks, standards, etc. associated with the SDG are analyzed.

Complete the header information as described in Part A. Enter the inclusive dates and times of the analyses of the first and last initial calibration standards in the fields for "Init. Calib. Date(s)" and "Init. Calib. Times." Dates must be in the format MM/DD/YY, and all times are expressed as HHMM, in military time (i.e., a 24-hour clock).

In the box in the lower portion of the form, enter the EPA sample number, lab sample ID, lab file ID, and date and time of analysis of all standards, samples, blanks, duplicates, spiked samples, dilutions, reanalyses, etc. All analyses in the 12-hour period must be listed on Form V. If analysis is not associated with the SDG being reported, enter the EPA sample number as "ZZZZZ," as described in Part A. The 12-hour sequence must end with the analysis of the appropriate calibration standard, as described in Exhibit D. In order to meet the requirements of the 12-hour sequence, the standard must be injected within 12 hours of the injection of the standard that began the sequence (CC3 on the DB-5, and the column performance solution on the SP-2331).

If the analytical sequence includes the analysis of the initial calibration standards, these standards and the window defining mix must be included on that copy of Form V, identified by the EPA sample numbers described in Part A. A copy of the analytical sequence that includes these initial calibration standards and the window defining mix must be submitted with each data package to which the initial calibration applies, but the Case number and SAS number must match those of each data package in which these initial calibration data are reported.

G. PCDD/PCDF Initial Calibration Data Summary (Form VI)

1. PCDD/PCDF Initial Calibration Response Factor Summary (Form VI PCDD-1)

This form is used to summarize the response factors for each target analyte, internal standard and cleanup standard calculated from the initial calibration. Complete the header information as described in Part A. Enter the inclusive initial calibration date(s) and times, as described for Form V PCDD-2. One copy of Form VI PCDD-1 must be completed for each initial calibration, for each instrument and GC column used for analysis of samples, and must be accompanied by a corresponding Form VI PCDD-2.

Enter the relative response factors (RRF) determined from the analysis of each of the calibration standards (CC1 through CC5). Enter RRF values to three decimal places. Calculate the mean RRF, as described in Exhibit D, and enter in the column "MEAN RRF." Calculate the relative standard deviation as a percentage of the mean (%RSD), and enter under "%RSD." Note that seven of the native analytes and the cleanup standard occur only in the CC3 standard, and therefore, %RSD calculations are not possible and are not reported on this form. However, for these analytes, enter the single point RRF as the "MEAN RRF." Also note that as the recovery standards are used to determine the RRFs of the internal standards, no RRF values can be calculated for the recovery standards, and therefore, they do not appear on Form VI PCDD-1.

All initial calibrations must meet the quality control limits for %RSD listed on the form.

2. PCDD/PCDF Initial Calibration Ion Abundance Ratio Summary (Form VI PCDD-2)

This page of Form VI is used to report the ion abundance ratios for each of the initial calibration standards. Because the ratio of the abundances of the two ions monitored for each analyte is crucial to the identification of these analytes, the ion abundance ratios must meet the quality control limits.

For each native analyte, internal standard and recovery standard, the two ions monitored for each analyte are listed in the column labeled "Selected Ions." Calculate the ratio of the abundances of these two ions according to the procedures in Exhibit D, and enter the ion abundance ratio of each analyte in each of the initial calibration standards to two decimal places.

Compare the ion abundance ratios to the quality control limits shown on the form, and flag any analyte which did not meet these limits in one or more of the standards.

Note that the cleanup standard does not appear on Form VI PCDD-2, as only one ion is monitored for this analyte, and therefore, no ion abundance ratio can be calculated.

One copy of Form VI PCDD-2 must be completed for each initial calibration, for each instrument and GC column used for analysis of samples, and must accompany a corresponding copy of Form VI PCDD-1.

H. PCDD/PCDF Continuing Calibration Data Summary

1. PCDD/PCDF Continuing Calibration Summary (Form VII PCDD-1)

This page of Form VII is used to summarize the results of the continuing calibration that must occur in each 12-hour analytical sequence. The form is used to report the RRF values and ion abundance ratios of each analyte in the CC3 standard, and to compare these values to the initial calibration data reported on

Form VI. One copy of Form VII PCDD-1 must be completed for each continuing calibration performed, and must be accompanied by a corresponding copy of Form VII PCDD-2.

Complete the header information as described in Part A. The date and time of analysis and lab file ID in the header must correspond to the analysis of the CC3 standard. Enter the date of the associated initial calibration in the field for "Init. Calib. Date(s):" If the calendar date changed during the initial calibration, enter the inclusive dates of the first and last standards in the associated initial calibration in the fields for "Init. Calib. Date(s)."

For each of the native analytes, internal standards, and the cleanup standard, enter the relative response factor (RRF) determined from the analysis of the continuing calibration standard in the column labeled "RRF." Enter the mean RRF for each analyte from the associated initial calibration, in the column labeled "MEAN RRF." For the seven native analytes and the cleanup standard that undergo only a single-point calibration, enter the CC3 RRF from the initial calibration, which is also entered as the mean RRF on Form VI. The values reported in this column must match those reported on the Form VI for the associated initial calibration. Calculate the percent difference (%D) between the RRF and the mean RRF for each analyte, and report under "%D." If the percent difference exceeds the quality control limits shown on the form (±30%), flag that analyte by placing an asterisk (*) in the "RRF FLAG" column. Report the ion abundance ratio of each analyte under the "ION RATIO" column. Flag any ion ratio that fails outside the quality control limits shown on the form by placing as asterisk (*) in the "ION FLAG" column.

Note that because only one ion is monitored for the cleanup standard, no ion ratio is determined for this analyte. For the recovery standards, relative response factors are not calculated or reported on Form VII, but the ion abundance ratios for these standards must be reported on Form VII.

2. PCDD/PCDF Continuing Calibration Summary (Form VII PCDD-2)

This page of Form VII is used to summarize the absolute and relative retention times of the analytes in the continuing calibration standard that must be analyzed in each 12-hour analytical sequence. Absolute retention times and relative retention times are critical to the identification of PCDDs/PCDFs by this method. One copy of Form VII PCDD-2 must be completed for each continuing calibration performed and must be accompanied by a corresponding copy of Form VII PCDD-1.

Complete the header information as described in Part A. The date and time of analysis and lab file ID in the header must correspond to the analysis of the CC3 standard. Enter the date of the associated initial calibration in the field for "Init. Calib. Date(s):" If the calendar date changed during the initial

calibration, enter the inclusive dates of the analyses of the first and last standards in the associated initial calibration in the fields for "Init. Calib. Date(s)."

For each of the native analytes and the cleanup standard, enter the relative retention time (RRT) and absolute retention time (RT) of the analyte in the calibration standard. RRT is calculated according to the procedures in Exhibit D, as the RT of the native analyte divided by the RT of appropriate internal standard. For the internal standards and recovery standards, report the only the absolute retention times. Enter all RTs in minutes and decimal minutes. RRTs are reported to two decimal places.

SECTION IV

DATA REPORTING FORMS

1DFA
PCDD/PCDF SAMPLE DATA SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SELECTED IONS	PEAK RT	ION RATIO	#	CONCENTRATION	Q	EMPC/EDL
2378-TCDD	320/322						
2378-TCDF	304/306						
12378-PeCDF	340/342						
12378-PeCDD	356/358						
23478-PeCDF	340/342						
123478-HxCDF	374/376						
123678-HxCDF	374/376						
123478-HxCDD	390/392						
123678-HxCDD	390/392						
123789-HxCDD	390/392						
234678-HxCDF	374/376						
123789-HxCDF	374/376						
1234678-HpCDF	408/410						
1234678-HpCDD	424/426						
1234789-HpCDF	408/410						
OCDD	458/460						
OCDF	442/444						

NOTE: Concentrations, EMPCs, and EDLs are calculated on a wet weight basis.

INTERNAL STANDARD	SELECTED IONS	PEAK RT	ION RATIO	#	ION RATIO LIMITS	% REC	#	RECOVERY LIMITS
13C-2378-TCDF	316/318				0.65-0.89			25-150
13C-2378-TCDD	332/334				0.65-0.89			25-150
13C-123678-HxCDD	402/404				1.05-1.43			25-150
13C-1234678-HpCDF	420/422				0.88-1.20			25-150
13C-OCDD	470/472				0.76-1.01			25-150
37Cl-2378-TCDD	328/NA		NA		NA			25-150

Column to be used to flag values outside QC limits

1DFB
PCDD/PCDF TOXICITY EQUIVALENCE SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	CONCENTRATION	TEF	TEF-ADJUSTED CONCENTRATION
2378-TCDD		x 1.0 =	
2378-TCDF		x 0.1 =	
12378-PeCDF		x 0.05 =	
12378-PeCDD		x 0.5 =	
23478-PeCDF		x 0.05 =	
123478-HxCDF		x 0.1 =	
123678-HxCDF		x 0.1 =	
123478-HxCDD		x 0.1 =	
123678-HxCDD		x 0.1 =	
123789-HxCDD		x 0.1 =	
234678-HxCDF		x 0.1 =	
123789-HxCDF		x 0.1 =	
1234678-HpCDF		x 0.01 =	
1234678-HpCDD		x 0.01 =	
1234789-HpCDF		x 0.01 =	
OCDD		x 0.001 =	
OCDF		x 0.001 =	
		Total =	

NOTE: Do <u>not</u> include EMPC or EDL values in the TEF-adjusted Concentration.

If the Total Toxic Equivalent Concentration of the sample is greater than 7 ng/L for an aqueous sample, greater than 0.7 ug/Kg for any solid matrix, or greater than 7 ug/Kg for a chemical waste sample, then second column confirmation of the results may be required.

1DFC

PCDD/PCDF SECOND COLUMN CONFIRMATION SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SELECTED IONS	PEAK RT	ION RATIO #	CONCENTRATION	Q	EMPC/EDL
2378-TCDD	320/322					
2378-TCDF	304/306					
12378-PeCDF	340/342					
12378-PeCDD	356/358					
23478-PeCDF	340/342					
123478-HxCDF	374/376					
123678-HxCDF	374/376					
123478-HxCDD	390/392					
123678-HxCDD	390/392					
123789-HxCDD	390/392					
234678-HxCDF	374/376					
123789-HxCDF	374/376					
1234678-HpCDF	408/410					
1234678-HpCDD	424/426					
1234789-HpCDF	408/410					
OCDD	458/460					
OCDF	442/444					

NOTE: Concentrations, EMPCs, and EDLs are calculated on a wet weight basis.

INTERNAL STANDARD	SELECTED IONS	PEAK RT	ION RATIO #	ION RATIO LIMITS	% REC #	RECOVERY LIMITS
13C-2378-TCDF	316/318			0.65-0.89		25-150
13C-2378-TCDD	332/334			0.65-0.89		25-150
13C-123678-HxCDD	402/404			1.05-1.43		25-150
13C-1234678-HpCDF	420/422			0.88-1.20		25-150
13C-OCDD	470/472			0.76-1.01		25-150
37Cl-2378-TCDD	328/NA		NA	NA		25-150

Column to be used to flag values outside QC limits

2DF

PCDD/PCDF TOTAL HOMOLOGUE CONCENTRATION SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Received: _____

Concentrated Extract Volume: ____ (uL) Date Extracted: _____

Injection Volume: ___ (uL) % Solids: _____ Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

HOMOLOGUE	PEAKS	CONCENTRATION	Q	EMPC/EDL
DIOXINS				
Total TCDD_____	_____	_____	_____	_____
Total PeCDD_____	_____	_____	_____	_____
Total HxCDD_____	_____	_____	_____	_____
Total HpCDD_____	_____	_____	_____	_____
FURANS				
Total TCDF_____	_____	_____	_____	_____
Total PeCDF_____	_____	_____	_____	_____
Total HxCDF_____	_____	_____	_____	_____
Total HpCDF_____	_____	_____	_____	_____

NOTE: Concentrations, EMPCs, and EDLs are calculated on a wet weight basis. The total congener concentrations do not affect the TEF calculations.

3DFA
PCDD/PCDF SPIKED SAMPLE SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash)

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SPIKE ADDED (PG)	SPIKED SAMPLE CONCENTRATION	SAMPLE CONCENTRATION	% REC #	QC LIMITS
2378-TCDD					50-150
2378-TCDF					50-150
12378-PeCDF					50-150
12378-PeCDD					50-150
123678-HxCDF					50-150
123678-HxCDD					50-150
1234678-HpCDF					50-150
1234678-HpCDD					50-150
OCDD					50-150
OCDF					50-150

If an analyte is not detected in the unspiked sample, enter 0 (zero) as the "SAMPLE CONCENTRATION."

Column to be used to flag values outside QC limits.

QC limits are advisory.

3DFB
PCDD/PCDF DUPLICATE SAMPLE SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash)

CONCENTRATION UNITS: (ng/L or ug/Kg) _____

ANALYTE	SAMPLE CONCENTRATION	DUPLICATE CONCENTRATION	RPD	#	QC LIMITS
2378-TCDD					50
2378-TCDF					50
12378-PeCDF					50
12378-PeCDD					50
23478-PeCDF					50
123478-HxCDF					50
123678-HxCDF					50
123478-HxCDD					50
123678-HxCDD					50
123789-HxCDD					50
234678-HxCDF					50
123789-HxCDF					50
1234678-HpCDF					50
1234678-HpCDD					50
1234789-HpCDF					50
OCDD					50
OCDF					50

If an analyte is not detected in either analysis, enter 0 (zero) as the concentration.

Column to be used to flag values outside QC limits.

QC limits are advisory

4DF
PCDD/PCDF METHOD BLANK SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: _____ (Soil/Water/Waste/Ash) Lab Sample ID: _____

Sample wt/vol: _____(g/mL)____ Lab File ID: _____

Water Sample Prep.: _____ (Sepf/Cont) Date Extracted: _____

Date Analyzed: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, SPIKES, AND DUPLICATES:

EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED

5DFA
PCDD/PCDF WINDOW DEFINING MIX SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Lab File ID: _____

Instrument ID: _____ Date Analyzed: _____

Time Analyzed: _____

CONGENER	RT FIRST ELUTING	RT LAST ELUTING
TCDD_____	_____	_____
TCDF_____	_____	_____
PeCDD_____	_____	_____
PeCDF_____	_____	_____
HxCDD_____	_____	_____
HxCDF_____	_____	_____
HpCDD_____	_____	_____
HpCDF_____	_____	_____
_____	_____	_____

5DFB

PCDD/PCDF CHROMATOGRAPHIC RESOLUTION SUMMARY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Lab File ID: _____

Instrument ID: _____ Date Analyzed: _____

Time Analyzed: _____

Percent Valley determination for DB-5 (or equivalent) column -
For the CC3 standard beginning the 12-hour period:

13C-2378-TCDD/13C-1234-TCDD: _____

123478-HxCDD/123678-HxCDD: _____

QC LIMITS:

Percent Valley between the TCDD isomers must be less than or equal to 25%

Percent Valley between the HxCDD isomers must be less than or equal to 50%

Percent Valley Determination for SP-2331 (or equivalent) Column -
For the Column Performance Solution beginning the 12-hour period:

1478-TCDD/2378-TCDD: _____

2378-TCDD/(1237/1238)-TCDD: _____

QC LIMITS:

Percent Valley between the TCDD isomers must be less than or equal to 25%.

5DFC
PCDD/PCDF ANALYTICAL SEQUENCE SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Init. Calib. Date(s): _____ _____

Init. Calib. Times: _____ _____

THE ANALYTICAL SEQUENCE OF STANDARDS, SAMPLES, BLANKS, SPIKES, AND DUPLICATES IS AS FOLLOWS:

EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED

6DFA

PCDD/PCDF INITIAL CALIBRATION RESPONSE FACTOR SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Init. Calib. Date(s): _____ _____

Init. Calib. Times: _____ _____

NATIVE ANALYTES VS. INTERNAL STDS.	RRF (N) CC1	CC2	CC3	CC4	CC5	MEAN RRF	%RSD
2378-TCDD							
2378-TCDF							
12378-PeCDF							
12378-PeCDD							
23478-PeCDF							
123478-HxCDF							
123678-HxCDF							
123478-HxCDD							
123678-HxCDD							
123789-HxCDD							
234678-HxCDF							
123789-HxCDF							
1234678-HpCDF							
1234678-HpCDD							
1234789-HpCDF							
OCDD							
OCDF							
INTERNAL STANDARDS VS. RECOVERY STDS.							
13C-2378-TCDD							
13C-2378-TCDF							
13C-123678-HxCDD							
13C-1234678-HpCDF							
13C-OCDD							
37Cl-2378-TCDD							

A single point calibration is performed for seven of the native analytes and the cleanup standard. Therefore, no %RSD is reported for these compounds.

QC Limits: %RSD must be less than or equal to 15.0%.

6DFB

PCDD/PCDF INITIAL CALIBRATION ION ABUNDANCE RATIO SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Init. Calib. Date(s): _____ _____

Init. Calib. Times: _____ _____

NATIVE ANALYTES	SELECTED IONS	ION ABUNDANCE RATIO					FLAG	QC LIMITS
		CC1	CC2	CC3	CC4	CC5		
2378-TCDD	320/322							0.65-0.89
2378-TCDF	304/306							0.65-0.89
12378-PeCDF	340/342							1.24-1.86
12378-PeCDD	356/358							1.24-1.86
23478-PeCDF	340/342							1.24-1.86
123478-HxCDF	374/376							1.05-1.43
123678-HxCDF	374/376							1.05-1.43
123478-HxCDD	390/392							1.05-1.43
123678-HxCDD	390/392							1.05-1.43
123789-HxCDD	390/392							1.05-1.43
234678-HxCDF	374/376							1.05-1.43
123789-HxCDF	374/376							1.05-1.43
1234678-HpCDF	408/410							0.88-1.20
1234678-HpCDD	424/426							0.88-1.20
1234789-HpCDF	408/410							0.88-1.20
OCDD	458/460							0.76-1.02
OCDF	442/444							0.76-1.02
INTERNAL STANDARDS								
13C-2378-TCDD	332/334							0.65-0.89
13C-2378-TCDF	316/318							0.65-0.89
13C-123678-HxCDD	402/404							1.05-1.43
13C-1234678-HpCDF	420/422							0.88-1.20
13C-OCDD	470/472							0.76-1.02
RECOVERY STANDARDS								
13C-1234-TCDD	332/334							0.65-0.89
13C-123789-HxCDD	402/404							1.05-1.43

QC limits represent ± 15% window around the theoretical ion abundance ratio.

A single point calibration is performed for seven of the native analytes and the cleanup standard.

The laboratory must flag any analyte in any calibration solution which does not meet the ion abundance ratio QC limit by placing an asterisk in the flag column.

7DFA
PCDD/PCDF CONTINUING CALIBRATION SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Date Analyzed: _____ Time Analyzed: _____

Lab File ID: _____ Init. Calib. Date(s): _____ _____

NATIVE ANALYTES	SELECTED IONS	RRF	MEAN RRF	%D	RRF FLAG	ION RATIO	ION FLAG	QC LIMITS
2378-TCDD	320/322							0.65-0.89
2378-TCDF	304/306							0.65-0.89
12378-PeCDF	340/342							1.24-1.86
12378-PeCDD	356/358							1.24-1.86
23478-PeCDF	340/342							1.24-1.86
123478-HxCDF	374/376							1.05-1.43
123678-HxCDF	374/376							1.05-1.43
123478-HxCDD	390/392							1.05-1.43
123678-HxCDD	390/392							1.05-1.43
123789-HxCDD	390/392							1.05-1.43
234678-HxCDF	374/376							1.05-1.43
123789-HxCDF	374/376							1.05-1.43
1234678-HpCDF	408/410							0.88-1.20
1234678-HpCDD	424/426							0.88-1.20
1234789-HpCDF	408/410							0.88-1.20
OCDD	458/460							0.76-1.02
OCDF	442/444							0.76-1.02
INTERNAL STANDARDS VS. RECOVERY STDS.								
13C-2378-TCDD	332/334							0.65-0.89
13C-2378-TCDF	316/318							0.65-0.89
13C-123678-HxCDD	402/404							1.05-1.43
13C-1234678-HpCDF	420/422							0.88-1.20
13C-OCDD	470/472							0.76-1.02
37Cl-2378-TCDD	328/NA					NA	NA	NA
RECOVERY STANDARDS								
13C-1234-TCDD	332/334	NA	NA	NA	NA			0.65-0.89
13C-123789-HxCDD	402/404	NA	NA	NA	NA			1.05-1.43

QC limits shown are for ion abundance ratios. Maximum %D for RRF is ± 30.0%
The laboratory must flag any analyte which does not meet criteria for %D or ion abundance ratio by placing an asterisk in the appropriate flag column.

7DFB

PCDD/PCDF CONTINUING CALIBRATION RETENTION TIME SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Instrument ID: _____

Date Analyzed: _____ Time Analyzed: _____

Lab File ID: _____ Init. Calib. Date(s): _____ _____

NATIVE ANALYTES	RRT	RT
2378-TCDD		
2378-TCDF		
12378-PeCDF		
12378-PeCDD		
23478-PeCDF		
123478-HxCDF		
123678-HxCDF		
123478-HxCDD		
123678-HxCDD		
123789-HxCDD		
234678-HxCDF		
123789-HxCDF		
1234678-HpCDF		
1234678-HpCDD		
1234789-HpCDF		
OCDD		
OCDF		
INTERNAL STANDARDS VS. RECOVERY STDS.		
13C-2378-TCDD	NA	
13C-2378-TCDF	NA	
13C-123678-HxCDD	NA	
13C-1234678-HpCDF	NA	
13C-OCDD	NA	
37Cl-2378-TCDD		
RECOVERY STANDARDS		
13C-1234-TCDD	NA	
13C-123789-HxCDD	NA	

RRT = (RT of analyte)/(RT of appropriate internal standard)

EXHIBIT C

TARGET COMPOUND LIST (TCL) AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQL)

NOTE: The values in these tables are quantitation limits, not absolute detection limits. The amount of material necessary to produce a detector response that can be identified and reliably quantified is greater than that needed to be simply detected above the background noise. The quantitation limits in these tables are set at the concentrations in the sample equivalent to the concentration of the lowest calibration standard analyzed for each analyte.

Specific quantitation limits are highly matrix-dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

The CRQL values listed on the following pages are based on the analysis of samples according the specifications given in Exhibit D. All CRQL values are reported on a wet weight basis, as are sample data produced using the specifications in Exhibit D.

TARGET COMPOUND LIST (TCL) AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQL)

PCDD/PCDF	CAS Number	Quantitation Limits[1] Water (ng/L)	Soil (ug/Kg)	Fly Ash (ug/Kg)	Chemical Waste[2] (ug/Kg)
2378-TCDD	1746-01-6	10	1.0	1.0	10
2378-TCDF	51207-31-9	10	1.0	1.0	10
12378-PeCDF	57117-41-6	25	2.5	2.5	25
12378-PeCDD	40321-76-4	25	2.5	2.5	25
23478-PeCDF	57117-31-4	25	2.5	2.5	25
123478-HxCDF	70648-26-9	25	2.5	2.5	25
123678-HxCDF	57117-44-9	25	2.5	2.5	25
123478-HxCDD	39227-28-6	25	2.5	2.5	25
123678-HxCDD	57653-85-7	25	2.5	2.5	25
123789-HxCDD	19408-74-3	25	2.5	2.5	25
234678-HxCDF	60851-34-5	25	2.5	2.5	25
123789-HxCDF	72918-21-9	25	2.5	2.5	25
1234678-HpCDF	67562-39-4	25	2.5	2.5	25
1234678-HpCDD	35822-46-9	25	2.5	2.5	25
1234789-HpCDF	55673-89-7	25	2.5	2.5	25
OCDD	3268-87-9	50	5.0	5.0	50
OCDF	39001-02-0	50	5.0	5.0	50

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.

In addition, data are reported for the total concentration of all detected PCDDs or PCDFs in the following homologues. However, because the number of non-2,3,7,8-substituted isomers that might be detected in a sample is unpredictable, it is not possible to assign CRQL values to the total homologue concentrations.

Homologue	CAS Number	Number of Possible Isomers	Number of 2,3,7,8-Substituted Isomers
Total TCDD	41903-57-5	22	1
Total TCDF	55722-27-5	38	1
Total PeCDD	36088-22-9	14	1
Total PeCDF	30402-15-4	28	2
Total HxCDD	34465-4608	10	3
Total HxCDF	55684-94-1	16	4
Total HpCDD	37871-00-4	2	1
Total HpCDF	38998-75-3	4	2

There is only one isomer in both the OCDD and OCDF homologues, hence the total concentration is the same as the 2,3,7,8-substituted concentration listed on the previous page.

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

EXHIBIT D

ANALYTICAL METHODS

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1. Scope and Application

1.1 This method is appropriate for the detection and quantitative measurement of 2378-tetrachlorinated dibenzo-p-dioxin (2378-TCDD), 2378-tetrachlorinated dibenzofuran (2378-TCDF), and the 2,3,7,8-substituted penta-, hexa-, hepta- and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soil, fly ash, and chemical waste samples including stillbottom, fuel oil, and sludge matrices. The analytical method requires the use of high resolution gas chromatography and low resolution mass spectrometry (HRGC/LRMS) on sample extracts that have been subjected to specified cleanup procedures. The calibration range is dependent on the compound and the sample size. The sample size varies by sample matrix. The Contract Required Quantitation Limits (CRQLs) for each matrix and compound are listed in Exhibit C. The upper limit of the calibration range for each compound is 20 times the CRQL. Samples in which any target compound is found above the calibration range must be diluted and reanalyzed.

1.2 The protocol requires the calculation of the 2378-TCDD toxicity equivalence according to the procedures given in the U.S. Environmental Protection Agency "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs)" March 1989 (EPA 625/3-89/016). This procedure recognized that structure-activity relationships exist between the chemical structure of a particular PCDD/PCDF "and its ability to elicit a biological/toxic response in various in vivo and in vitro test systems." Of the 210 possible chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans, the 17 isomers that bear chlorine atoms in the 2,3,7 and 8 positions of their respective structures are the compounds of greatest concern. To aid in the assessment of risks to human health and the environment, a factor is assigned to each of these 17 2,3,7,8-substituted PCDDs and PCDFs that relates the toxicity of that isomer to a concentration of the most toxic isomer, 2378-TCDD. These factors are called TEFs. The concentrations of any of the 17 isomers that are detected in an environmental sample can then be adjusted by the TEF and summed, yielding a concentration of 2378-TCDD with an equivalent toxicity.

1.3 If the toxicity equivalence is less than 0.7 parts per billion (ppb) for a soil or fly ash sample, less than 7 parts-per-trillion (ppt) for an aqueous sample, or less than 7 ppb for a chemical waste, no further analysis is required. If the toxicity equivalence is greater than or equal to 0.7 ppb (soil or fly ash), 7 ppt (aqueous), or 7 ppb (chemical waste), analysis on a column capable of resolving all 2,3,7,8-substituted PCDDs/PCDFs is required.

For any sample analyzed on a DB-5 (or equivalent) column in which either 2378-TCDD or 2378-TCDF is reported as an "Estimated Maximum Possible Concentration" (see Section 15.7), regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

1.4 This method is also capable of determining the total concentration of all PCDDs/PCDFs in a given level of chlorination (i.e., Total TCDD, Total PeCDF, etc.), although complete chromatographic separation of all 210 possible PCDDs/PCDFs is not possible under the instrumental conditions described here. The "Total" concentrations are not assigned TEF values in the February 1989 TEF procedure, and therefore are not included in the toxicity equivalence calculations.

1.5 The qualitative identification criteria (see Section 11) include requirements for retention times, simultaneous detection of three ions per compound, and limits on the ratio of the abundances of the two most intense ions produced by each compound. In instances where a signal is detected that meets all of the qualitative identification criteria except the ion abundance ratio, the method requires calculation of an "Estimated Maximum Possible Concentration" (EMPC). The presence of interferences that coelute with the compounds of interest may cause the ion abundance ratio to fall outside the limits for qualitative identification and would also affect the quantitative results. The EMPC is a worst case estimate of the sample concentration that the signal would represent if it did meet all the identification criteria (see Section 15.7). Because of the quantitative uncertainty associated with the EMPC values, they are not included in the TEF calculations performed in the method.

1.6 The data that result from these analyses are reported based on the wet weight of the sample. However, for solid matrices such as soil/sediments, the percent solid content of the sample is also reported, if needed by the data user. The percent solids content of fly ash samples is not reported because the fly ash is treated with an aqueous acid solution prior to extraction.

1.7 This method is designed for use only by analysts experienced with residue analysis and skilled in HRGC/LRMS.

1.8 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure of personnel to materials known or believed to contain PCDDs/PCDFs.

2. Summary of Method

2.1 Soil/Sediment Extraction

For the purposes of this method, a soil/sediment sample is defined as a portion of wet soil/sediment which does not contain oil, but which may contain other solids such as stones, vegetation, etc. The sample should not contain an obvious liquid phase (see Section 8.4). A 10 g aliquot of the soil/sediment sample is spiked with the internal standard solution and extracted with toluene in a combination of a Soxhlet extractor and a Dean Stark water separator (SDS).

2.2 Water Extraction

For the purposes of this method, a water sample is defined as a single phase system that is primarily clear water but may contain very small

amounts of floating, suspended and settled particulate matter. Multiple phases should not be present (see Section 8.4). Approximately 1 L of the water sample is spiked with the internal standard solution and filtered to separate the aqueous and particulate fractions. The filtered aqueous fraction is extracted with methylene chloride using a separatory funnel or continuous liquid-liquid extractor. The particulate fraction is extracted with toluene in a SDS extractor. The extracts of the two fractions are then combined for cleanup.

2.3 Fly Ash Extraction

For the purposes of this method, a fly ash sample is defined as a solid matrix from an incineration or other combustion process which may contain water and other solids. It should not contain an obvious liquid phase. A 10 g aliquot of the fly ash is washed with dilute hydrochloric acid, spiked with the internal standard solution, and extracted with toluene in a SDS extractor.

2.4 Chemical Waste Sample Extraction

For the purposes of this method, a chemical waste sample includes sample matrices of oils, stillbottoms, oily sludge, oil-laced soil, and surface water heavily contaminated with the matrices listed above (see Section 8.2). Internal standards are added in the concentrations listed in Table 4 to a 1 or 10 g aliquot of chemical waste. Wet fuel oil and oily sludge samples, showing signs of water, are spiked with the internal standard solution, fitted with a reflux condenser and a Dean Stark water separator to remove the water, and extracted with toluene. Stillbottom samples are spiked with the internal standard solution, refluxed with toluene, and filtered.

2.5 Cleanup and Analysis

Immediately prior to cleanup, all extracts are spiked with a ^{37}Cl-2378-TCDD standard. Because it is added after extraction, the recovery of this standard may be used to differentiate between losses of analytes or internal standards during extraction and losses that occur during the various cleanup procedures. The extracts are subjected to an acid-base washing treatment and dried. Following a solvent exchange step, the extract is cleaned up by column chromatographic procedures, including silica gel, acid alumina, and carbon on celite columns, to eliminate sample components that may interfere with the detection and measurement of PCDDs/PCDFs. The extracts are concentrated and the solvent is exchanged to tridecane. The recovery standards are added to an aliquot (50 uL) of the extract and the aliquot is reduced to the final volume of 50 uL. The remaining 50 uL of extract is retained in the event that dilutions or reanalyses are required. One or two uL of the concentrated aliquot containing the recovery standards are injected onto a fused silica capillary column in a gas chromatograph (GC) interfaced to a mass spectrometer (MS) (see Paragraph 4.1.1).

The identification of PCDD/PCDF isomers is based on the simultaneous detection of the two most abundant ions in the molecular ion regions and the M-COCl ion. In addition, the identification of OCDD and five

of the 2,3,7,8-substituted isomers, for which a ^{13}C-labeled standard is available in the internal standard and recovery standard solutions, is based on their exact retention time (-1 to 3 seconds from the respective internal or recovery standard signal). The 2,3,7,8-substituted isomers for which ^{13}C-labeled standards are not available in the sample extracts are identified by the relative retention times of the isomer in the daily standard as compared to the appropriate internal standard.

The identification of all other PCDD/PCDF isomers is based on their retention times falling within their respective PCDD/PCDF retention time windows as established by a window defining mix. Confirmation of all PCDDs/PCDFs is based on a comparison of the ratio of the integrated ion abundance of the molecular ion species to the theoretical ion abundance ratio.

The PCDDs/PCDFs are quantitated by comparing the MS response of the detected analyte relative to the MS response of the appropriate ^{13}C-labeled internal standard (Table 2). The responses of both the ions monitored for each analyte are used for quantitation. The labeled internal standards are added prior to sample extraction. Thus, the quantitative results for the native analytes are corrected for the recovery of the internal standards, based on the assumption that losses of the internal standards during sample preparation and analysis are equal to the losses of the unlabeled PCDDs/PCDFs.

2.6 The recovery of the internal standards is determined by comparing the MS response of the internal standard to the MS response of the appropriate recovery standard (Table 2). The recovery standards are also isotopically labeled compounds, and are added to each sample extract and blank aliquot just prior to injection.

Because the ability to quantify the concentrations of the unlabeled analytes and the precision of the measurements are related to the recovery of the internal standards, upper and lower limits are placed on the percent recovery of the internal standards (see Paragraphs 15.5.2 and 17.1.1).

2.7 If the concentration of any PCDD/PCDF exceeds the calibration range of the instrument, a dilution must be performed to bring that concentration within range. Additional recovery standard solution is added to the diluted sample extract immediately prior to reanalysis (see Section 10.4).

If the MS response of any internal standard in the diluted sample is less than 10% of its MS response in the continuing calibration standard, the unlabeled PCDD/PCDF concentrations in the sample are estimated using the MS responses of the recovery standards (see Paragraph 15.3). The purpose of this requirement is to ensure that there is an adequate MS response for quantitation.

2.8 In order to provide information on recovery of the analytes of interest from the sample matrix, the laboratory must prepare a second aliquot of one sample of each matrix in each Sample Delivery Group (SDG) and spike

it with the analytes at concentrations specified in Section 13. This aliquot is analyzed and the recovery of the spiked analytes is determined.

2.9 In order to provide information on the precision of the analysis in the sample matrix, the laboratory must perform a duplicate analysis on one sample of each matrix in each SDG. The samples to be analyzed in duplicate may be specified by the Region in advance; however, if no samples are so specified, the laboratory must select a sample of each matrix for duplicate analyses. The precision of the analysis is determined as the relative percent difference of the concentrations as specified in Section 14.

2.10 Due to a variety of situations that may occur during contract performance, the laboratory shall be required to reextract and reanalyze certain samples or groups of samples. As used hereafter, except in the case of dilutions, the term "rerun" shall indicate sample reextraction, cleanup and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed (see Section 10.4).

When the rerun is required due to matrix effects, interferences or other problems encountered, the Government will pay the Contractor for the reruns. Such reruns shall be billable and accountable under the specified contract allotment of automatic reruns. When the rerun is required due to Contractor materials, equipment or instrumentation problems or lack of Contractor adherence to specified contract procedures, the rerun shall not be billable nor accountable under the terms of this contract. The Contractor's failure to perform any of the sample reruns specified herein, either billable or nonbillable, shall be construed as Contractor nonperformance and may result in the termination of the contract for default. Specific requirements for reextraction and reanalysis are given in Section 17.

NOTE: A contaminated method blank is the only circumstance that may require more than one rerun per sample.

3. <u>Interferences</u>

3.1 Any compound that yields ions listed in Table 5 and also elutes within the retention time window of the corresponding homologue is a potential interference. PCDDs/PCDFs are often associated with other chlorinated compounds such as polychlorinated biphenyls (PCBs) and polychlorinated diphenyl ethers (PCDPEs). These compounds may be found at concentrations several orders of magnitude higher than that of the analytes of interest and may otherwise interfere with the analysis of PCDDs/PCDFs. Therefore, the retention time of the target analytes must be verified using reference standards and compared to retention time windows established during the calibration. While the cleanup procedures specified in this method are designed to minimize these interferences, some samples may ultimately require additional cleanup steps to achieve the detection limits.

3.2 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 these materials shall be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

NOTE: Because of the possibility of contamination, analysts should avoid using PVC gloves. However, latex gloves may be adequate.

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

3.4 High resolution capillary columns are used to resolve as many PCDD/PCDF isomers as possible. No single column is known to resolve all 210 of the isomers. The columns employed by the laboratory in these analyses must be capable of resolving the 17 2,3,7,8-substituted PCDDs/PCDFs sufficiently to meet the method specifications (see Section 7.1).

4. Apparatus and Equipment

Brand names and catalog numbers are for illustrative purposes only and do not imply an endorsement by EPA. Equivalency of materials from other suppliers may be demonstrated by performing analyses that meet the specifications of this method.

4.1 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

4.1.1 The GC shall be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port shall be designed for capillary columns; a splitless or an on-column injection technique is recommended. A 2 uL injection volume is assumed throughout this method; however, with some GC injection ports, other volumes may be more appropriate. A 1 uL injection volume may be used if adequate sensitivity and precision can be demonstrated.

NOTE: The injection volume for all sample extracts, blanks, quality control (QC) samples and calibration solutions shall be the same.

4.1.2 Mass spectral data shall be obtained using a low resolution instrument that utilizes 70 volts (nominal) electron energy in the electron impact mode. The system shall be capable of selected ion monitoring (SIM) for at least 18 ions per cycle, with a cycle time of 1 second or less. Minimum integration time for SIM is 25 milliseconds per m/z. The integration time used to analyze samples shall be identical to the time used to analyze the initial and continuing calibration solutions and QC samples. Total data acquisition time per cycle (18 ions) must not exceed 1 second.

4.1.3 An interfaced data system is required to acquire, store, reduce and output mass spectral data.

4.1.4 GC/MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.1.5 The Contractor shall use a magnetic media storage device capable of recording data suitable for long-term off-line storage. The Contractor shall record all raw GC/MS data acquired during the entire contract period on magnetic media in appropriate instrument manufacturer format.

4.2 GC Column

Fused silica capillary columns are required. The columns shall demonstrate the required separation of all 2378-specific isomers whether a dual column or a single column analysis is chosen. Column operating conditions shall be evaluated at the beginning and end of each 12-hour period during which samples or concentration calibration solutions are analyzed (see Section 7.4).

Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column. In order to determine the concentration of the individual 2,3,7,8-substituted isomers, if the toxicity equivalence is greater than 0.7 ppb (solids), 7 ppt (aqueous), or 7 ppb (chemical waste), the sample extract shall be reanalyzed on a 60 m SP-2330 or SP-2331 (or equivalent) GC column.

For any sample analyzed on a DB-5 (or equivalent) column in which either 2378-TCDD or 2378-TCDF is reported as an Estimated Maximum Possible Concentration (see Section 15.7), regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

Analysis on a single column is acceptable if the required separation of all the 2378-specific isomers is demonstrated and the minimum acceptance criteria outlined in Sections 7.1, 7.2 and 7.3 are met. See Section 11 for the specifications for the analysis of the 2378-specific isomers using both dual columns and single columns.

4.3 Miscellaneous Equipment

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

4.3.1 Nitrogen evaporation apparatus (N-Evap* Analytical Evaporator Model 111. Organomation Association Inc., Northborough, MA, or equivalent).

4.3.2 Balance capable of accurately weighing ± 0.01 g.

4.3.3 Water bath. Equipped with concentric ring cover and temperature controlled within ± 2°C.

4.3.4 Stainless steel (or glass) pan large enough to hold contents of 1-pint sample containers.

4.3.5 Glove box. For use in preparing standards from neat materials and in handling soil/sediment samples containing fine particulates that may pose a risk of exposure.

4.3.6 Rotary evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10 or equivalent.

4.3.7 Centrifuge. Capable of operating at 400 x G with a 250-300 mL capacity.

4.3.8 Drying oven.

4.3.9 Vacuum oven. Capable of drying solvent-washed solid reagents at 110°C.

4.3.10 Mechanical shaker. A magnetic stirrer, wrist-action or platform-type shaker, that produces vigorous agitation. Used for pre-treatment of fly ash samples.

4.4 Glassware

4.4.1 Extraction jars. Amber glass with Teflon-lined screw cap; minimum capacity of approximately 200 mL; must be compatible with mechanical shaker to be used.

4.4.2 Kuderna-Danish (KD) Apparatus. 500 mL evaporating flask, 10 mL graduated concentrator tubes with ground glass stoppers, three ball macro-Synder column.

4.4.3 Disposable Pasteur pipets, 150 mm long x 5 mm ID.

4.4.4 Disposable serological pipets, 10 mL for preparation of the carbon column specified in Section 9.10.

4.4.5 Vials. 0.3 mL and 2 mL amber borosilicate glass with conical shaped reservoir and screw caps lined with Teflon-faced silicone disks.

4.4.6 Funnels. Glass; appropriate size to accommodate filter paper (12.5 cm).

4.4.7 Chromatography Columns. 300 mm x 10.5 mm glass chromatographic column fitted with Teflon stopcock.

4.4.8 Soxhlet Apparatus, 500 mL flask, all glass. Complete with glass extractor body, condenser, glass extraction thimbles, heating mantle, and variable transformer for heat control.

NOTE: Extraction thimbles must be of sufficient size to hold 100 g of sand, 5 g of silica gel, and at least 10 g of solid sample, with room to mix the sand and sample in the thimble.

4.4.9 Dean Stark Water Separator Apparatus, with a Teflon stopcock. Must fit between Soxhlet extractor body and condenser.

4.4.10 Concentrator tubes. 15 mL conical centrifuge tubes.

4.4.11 Separatory funnels. 125 mL and 2 L separatory funnels with a Teflon stopcock.

4.4.12 Continuous Liquid-Liquid Extractor. 1 L sample capacity, suitable for use with heavier than water solvents.

4.4.13 Boiling chips. Teflon boiling chips washed with hexane prior to use.

4.4.14 Buchner funnel. 15 cm.

4.4.15 Filtration flask. For use with Buchner funnel, 1 L capacity.

4.5 Glassware Cleaning Procedures

Reuse of glassware should be minimized to avoid the risk of using contaminated glassware. All glassware that is reused shall be scrupulously cleaned as soon as possible after use, applying the following procedure.

4.5.1 Rinse glassware with the last solvent used in it.

4.5.2 Wash with hot water containing detergent.

4.5.3 Rinse with copious amounts of tap water and several portions of distilled water. Drain dry.

4.5.4 Rinse with high purity acetone and hexane.

4.5.5 After glassware is dry, store inverted or capped with aluminum foil in a clean environment.

Do <u>not</u> bake reusable glassware as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered, but should be minimized, as repeated baking may cause active sites on the glass surface that will irreversibly adsorb PCDDs/PCDFs.

CAUTION: The analysis for PCDDs/PCDFs in water samples is for much lower concentrations than in soil/sediment, fly ash, or chemical waste samples. Extreme care must be taken to prevent cross-contamination between soil/sediment, fly ash, chemical waste and water samples. Therefore, it is strongly recommended that separate glassware be reserved for analyzing water samples.

4.6 Preextraction of Glassware

It is required that all glassware be rinsed or preextracted with solvent immediately before use. The SDS apparatus and continuous liquid-liquid extractors must be preextracted for approximately three hours immediately prior to use. The pooled waste solvent for a set of extractions may be concentrated and analyzed as a method of demonstrating that the glassware was free of contamination.

It is recommended that each piece of reusable glassware be numbered in such a fashion that the laboratory can associate all reusable glassware with the processing of a particular sample. This procedure will assist the laboratory in tracking down possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

5. Reagents and Consumable Materials

Brand names and catalog numbers are for illustrative purposes only and do not imply an endorsement by EPA. Equivalency of materials from other suppliers may be demonstrated by performing analyses that meet the specifications of this method.

5.1 Solvents. High purity, distilled-in-glass: hexane, methanol, methylene chloride, toluene, isooctane, cyclohexane, acetone, tridecane (or nonane).

5.2 Filters

5.2.1 Filter paper. Whatman No. 1 or equivalent.

5.2.2 Glass fiber filter. 15 cm, for use with Buchner funnel.

5.2.3 0.45 micron, Millipore or equivalent, PTFE or other material compatible with toluene. Rinse with toluene.

5.3 White quartz sand. 60/70 mesh, for use in the SDS extractor. Bake at 450°C for 4 hours minimum.

5.4 Glass wool, silanized. Extract with methylene chloride and hexane before use.

5.5 Sodium Sulfate. Granular, anhydrous. Before use, heat to 400°C in a shallow tray for approximately 4 hours, cool in a desiccator, and store in a glass jar.

5.6 Potassium Hydroxide. ACS grade, prepare a 20% (w/v) solution in distilled water.

5.7 Sulfuric Acid, concentrated. ACS grade, specific gravity 1.84.

5.8 Sodium Chloride. ACS grade, prepare a 5% (w/v) solution in distilled water.

5.9 Hydrochloric Acid, concentrated. ACS grade, specific gravity 1.17. Prepare a 1N solution in distilled water for pretreatment of fly ash samples.

5.10 Column Chromatography Reagents

5.10.1 Alumina, acidic AG4, Bio Rad Laboratories (catalogue #132-1240) or equivalent. Soxhlet extract with methylene chloride for 21 hours and activate by heating in a foil-covered glass container for 24 hours at 190°C.

5.10.2 Charcoal Carbon. Active carbon AX-21 (Anderson Development Company, Adrian, MI, or equivalent), prewashed with methanol and dried in vacuo at 110°C.

5.10.3 Celite 545 (Supelco or equivalent).

5.10.4 Silica gel. High purity grade, type 60, 70-230 mesh; Soxhlet extract with methylene chloride for 21 hours and activate by heating in a foil-covered glass container for 24 hours at 190°C.

5.10.5 Silica gel impregnated with 2% (w/w) sodium hydroxide. Add 1 part by weight of 1 M NaOH solution to 2 parts silica gel (extracted and activated) in a screw-cap bottle and mix with a glass rod until free of lumps.

5.10.6 Silica gel impregnated with 40% (w/w) sulfuric acid. Add 2 parts by weight concentrated sulfuric acid to 3 parts silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw-cap glass bottle.

5.11 Calibration Solutions (Table 3)

Five tridecane (or nonane) solutions (CC1-CC5) containing 10 unlabeled and 7 carbon-labeled PCDDs/PCDFs at known concentrations which are used to calibrate the instrument. One of these five solutions (CC3) is used as the continuing calibration solution and contains 7 additional unlabeled 2,3,7,8-substituted isomers that are commercially supplied (see Paragraph 7.3.2.1). The concentration ranges are homologue-dependent with the lowest concentrations associated with tetra- and pentachlorinated dioxins and furans (0.1-2.0 ng/uL), and the higher concentrations associated with the hexa- through octachlorinated homologues (0.5-10.0 ng/uL). Depending on the availability of materials, the Environmental Monitoring Systems Laboratory (EMSL-LV) will provide these solutions, with the exception of the additional 2,3,7,8-substituted isomers for the CC3 solution.

5.12 Internal Standard Solution (Table 4)

The solution contains the five internal standards in tridecane (or nonane) at the nominal concentrations listed in Table 4. Depending on the availability of materials, EMSL-LV will provide the solution. Mix 10 uL with 1.0 mL of acetone before adding to each sample and blank.

5.13 Recovery Standard Solution

The hexane solution contains the recovery standards, $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD, at concentrations of 5.0 ng/uL, in a solvent other than tridecane or nonane (see Section 10.2). Depending upon the availability of materials, EMSL-LV will provide the solution.

5.14 Continuing Calibration Solution

This solution contains standards to be used for identification and quantitation of target analytes. In order to have all 2,3,7,8-substituted isomers and the cleanup standard present for quantitation purposes, a commercially supplied supplemental standard and the cleanup standard solution are combined with the EPA-supplied CC4 solution to produce the CC3 solution (see Paragraph 7.4.1). This solution is identified in Table 3.

5.15 Window Defining Mix

This solution is to be obtained by the laboratory through commercial vendors. The solution contains the first and last eluting isomer of each homologue (see Table 9) and is used to verify that the switching times between the descriptors have been appropriately set.

The window defining mix need not contain any of the labeled internal or recovery standards, as no quantitative measurements are based on this mixture. However, these standards and other isomers may be added to the mixture listed in Table 7 at the discretion of the laboratory, so long as the additional contents of the mixture are clearly specified in every SDG Narrative.

If the laboratory employs a GC column that has a different elution order than those specified here, the laboratory must ensure that the first and last eluting isomers in each homologue are represented in the window defining mix used to evaluate that column. The concentrations of any additional isomers should be approximately the same as those listed in Table 9.

EMSL-LV does not supply the window defining mix (see Table 9).

5.16 Supplemental Calibration Solution

This solution contains seven 2,3,7,8-substituted PCDD/PCDF isomers to be added to the CC4 solution to produce the CC3 solution that is used for identification and quantitation of target analytes. EMSL-LV does not supply this solution (see Table 10).

5.17 Cleanup Standard

This solution contains $^{37}Cl_4$-2378-TCDD at a concentration of 5 ng/uL (5 ug/mL) in tridecane (or nonane) and is added to all sample extracts prior to cleanup. The solution may be added at this concentration or

diluted into a larger volume of solvent (see Paragraph 9.7.1). The recovery of this compound is used to judge the efficiency of the cleanup procedures.

5.18 Matrix Spiking Standard

This solution contains 10 of the 2,3,7,8-substituted isomers, at the concentrations listed in Table 11 in tridecane (or nonane), and is used to prepare the spiked sample aliquot (see Section 13). Dilute 10 uL of this standard to 1.0 mL with acetone and add to the aliquot chosen for spiking.

5.19 Column Performance Solution

The laboratory must obtain this solution through commercial vendors. The solution contains 2378-TCDD and the other TCDD isomers (1478-TCDD and the 1237/1238-TCDD pair) that elute closest to 2378-TCDD on the SP-2331 (or equivalent) column. The solution is used to verify the chromatographic resolution of the SP-2331 (or equivalent) GC column. The concentrations of these isomers should be approximately 0.5 ng/uL in tridecane (or nonane).

If the laboratory employs a GC column that has a different elution order than those specified here, the laboratory must ensure that the isomers eluting closest to 2378-TCDD are represented in the column performance solution.

EMSL-LV does <u>not</u> supply the column performance solution.

6. <u>Mass Calibration</u>

Mass calibration of the MS is recommended prior to analyzing the calibration solutions, blanks, samples and QC samples. It is recommended that the instrument be tuned to greater sensitivity in the high mass range in order to achieve better response for the later eluting compounds. Optimum results using FC-43 for mass calibration may be achieved by scanning from 222-510 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 30-50% of m/z 264 (base peak).

7. <u>Retention Time Windows and Calibration of Target Analytes</u>

Prior to the calibration of the GC/MS system, it is necessary to establish the appropriate switching times for the SIM descriptors (see Table 7) and to verify the chromatographic resolution. The switching times are determined by the analysis of the window defining mix, containing the first and last eluting isomers in each homologue (see Table 9). Chromatographic resolution is verified by the analysis of one of two solutions, depending on the GC column used for analysis.

Two types of calibration procedures, initial and continuing, are required. The initial calibration is required before any samples are analyzed for PCDDs/PCDFs, and intermittently throughout sample

analysis, as dictated by the results of the continuing calibration (see Section 7.4). The continuing calibration is required at the beginning of each 12-hour time period during which samples are analyzed.

Samples shall not be analyzed until acceptable descriptor switching times, chromatographic resolution, and calibrations, as described in Sections 7.1, 7.2, 7.3 and 7.4, are achieved and documented. The sequence of analyses is shown in Table 13.

7.1 Window Defining Mix

The window defining mix shall be analyzed before any calibration standards in order to evaluate the descriptor switching times. The commercially available mix (see Section 5.15) contains the first and last eluting isomers in each homologue. Mixes are available for various columns. The mix for the DB-5 (or equivalent) column may not be appropriate for the SP-2331 or other columns.

The ions in each of the four recommended descriptors are arranged so that there is overlap between the descriptors. The ions for the TCDD, TCDF, PeCDD and PeCDF isomers are in the first descriptor, the ions for the PeCDD, PeCDF, HxCDD and HxCDF isomers are in the second descriptor, the ions for the HxCDD, HxCDF, HpCDD and HpCDF isomers are in the third descriptor, and the ions for the HpCDD, HpCDF, OCDD and OCDF isomers are in the fourth descriptor.

The descriptor switching times are set such that the isomers that elute from the GC during a given retention time window will also be those isomers for which the ions are monitored. For the homologues that overlap between descriptors, the laboratory may use discretion in setting the switching times. However, do not set descriptor switching times such that a change in descriptors occurs at or near the expected retention time of any of the 2,3,7,8-substituted isomers.

The window defining mix need not contain any of the labeled internal or recovery standards, as no quantitative measurements are based on this mixture. However, these standards and other isomers may be added to the mixture listed in Table 7 at the discretion of the laboratory, so long as the additional contents of the mixture are clearly specified in every SDG Narrative.

7.1.1 Analyze a 2 uL aliquot of the window defining mix, using the GC column conditions in Table 1.

7.1.2 Adjust the descriptor switching times and the GC column conditions as needed to ensure that the isomers elute in the appropriate ion descriptors (see Table 7).

7.1.3 The window defining mix must be analyzed at the following frequency:

7.1.3.1 Before initial calibration on each instrument and GC column used for analysis.

7.1.3.2 Each time a new initial calibration is performed, regardless of reason.

7.1.3.3 Each time adjustments or instrument maintenance activities are performed that may affect retention times.

7.1.3.4 Any time the retention time of either the $^{13}C_{12}$-1234-TCDD or $^{13}C_{12}$-123789-HxCDD recovery standards in <u>any</u> analysis varies by more than 10 seconds from its retention time in the most recent continuing calibration standard (see Paragraphs 7.3.2.3, 7.5.2.1 and 11.1.4)

7.1.4 If the laboratory employs a GC column that has a different elution order than those columns specified here, the laboratory must ensure that the first and last eluting isomers in each homologue are represented in the window defining mix used to evaluate that column. The concentrations of any additional isomers should be approximately the same as those listed in Table 9.

7.1.5 Analysis on a single GC column (as opposed to situations requiring a second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for <u>both</u> the DB-5 and SP-2331 (or equivalent) columns are met (see Paragraphs 7.3.2.1 and 7.2.3).

7.2 Chromatographic Resolution

7.2.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the CC3 standard during both the initial and continuing calibration procedures (see Paragraphs 7.3.2.1 and 7.4.2).

7.2.2 For analyses on a SP-2331 (or equivalent) GC column, the chromatographic resolution is evaluated <u>before</u> the analysis of any calibration standards by the analysis of a commercially available column performance mixture (see Section 5.19) that contains the TCDD isomers that elute most closely with 2378-TCDD on this GC column (1478-TCDD and the 1237/1238-TCDD pair).

Analyze a 2 uL aliquot of this solution, using the column operating conditions and descriptor switching times previously established.

Note: The column performance mixture may be combined with the window defining mix into a single solution, provided that the combined solution contains the isomers needed to determine that the criteria for both analyses can be met.

7.2.3 GC Resolution Criteria for SP-2331 or Equivalent Column. The chromatographic peak separation between unlabeled 2378-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of ≤ 25 percent, where:

Valley = (x/y)(100).
y = the peak height of any TCDD isomer.
x = the distinction from the baseline to the bottom of the valley between adjacent peaks, measured as shown in Figure 5.

The resolution criteria must be evaluated using measurements made on the selected ion current profile (SICP) for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

Further analyses may not proceed until the GC resolution criteria have been met.

7.2.4 If the laboratory uses a GC column other than those specified here, the laboratory must ensure that the isomers eluting closest to 2378-TCDD on that column are used to evaluate GC column resolution. The chromatographic peak separation between unlabeled 2378-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of ≤ 25 percent.

7.2.5 Analysis on a single GC column (as opposed to situations requiring a second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for <u>both</u> the DB-5 and SP-2331 (or equivalent) columns are met (see Paragraphs 7.3.2.1 and 7.2.3).

7.3 Initial Calibration

Once the window defining mix has been analyzed and the descriptor switching times have been verified (and after the analysis of the column performance solution if using a GC column other than DB-5), the five concentration calibration solutions (CC1-CC5), described in Table 3, shall be analyzed prior to any sample analysis. The CC1, CC2, CC4 and CC5 solutions shall be used as provided by EPA. The CC3 solution is prepared by combining CC4 solution, the supplemental calibration solution, and the internal, cleanup, and recovery standard solutions as described in Paragraph 7.4.1.

7.3.1 Analyze a 2 uL (see Paragraph 4.1.1) aliquot of each of the five concentration calibration solutions, beginning with CC3 solution (see Paragraph 7.4.1). The following MS/DS conditions shall be used:

7.3.1.1 Acquire SIM data for each of the ions listed in Table 5 including the ions to monitor interfering compounds. See Table 7 for the recommended MS descriptors.

7.3.1.2 The total cycle time for data acquisition must be less than one second. Acquire at least five data points for each ion during the elution of the GC peak.

7.3.2 The Contractor shall not proceed with the sample analysis until an acceptable initial calibration has been performed and documented according to the following criteria: GC resolution, ion abundance ratios, retention times, and instrument sensitivity.

7.3.2.1 GC Resolution Criteria for DB-5 or Equivalent Column. The chromatographic peak separation between the $^{13}C_{12}$-2378-TCDD peak and $^{13}C_{12}$-1234-TCDD isomers shall be resolved with a valley of $\leq$ 25 percent, in <u>all</u> calibration standards, where:

Valley = (x/y)(100).
y = the peak height of $^{13}C_{12}$-2378-TCDD.
x = measured using the $^{13}C_{12}$-1234-TCDD peak as shown in Figure 5.

In addition, the chromatographic peak separation between the 123478-HxCDD and 123678-HxCDD in the CC3 solution shall be resolved with a valley of $\leq$ 50 percent, calculated in a similar fashion as above.

The resolution criteria must be evaluated using measurements made on the SICP for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

7.3.2.2 The relative ion abundance criteria for PCDDs/PCDFs listed in Table 6 <u>must</u> be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in <u>all</u> solutions. The lower and upper limits of the ion abundance ratios represent a $\pm$ 15 percent window around the theoretical abundance ratio for each pair of selected ions. The ^{37}Cl-2378-TCDD cleanup standard contains no ^{35}Cl, thus the ion abundance ratio criterion does <u>not</u> apply to this compound.

7.3.2.3 For all calibration solutions, the retention times of the isomers must fall within the appropriate retention time windows established by the window defining mix analysis. In addition, the absolute retention times of the recovery standards, $^{13}C_{12}$-

1234-TCDD and $^{13}C_{12}$-123678-HxCDD, shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard.

7.3.2.4 MS Sensitivity. For all calibration solutions, including the CC1 solution, 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.

7.3.3 Calculate the relative response factors (RRFs) for the 17 unlabeled target analytes relative to their appropriate internal standards (RRF_n) (see Table 8), according to the formulae below. For the seven unlabeled analytes and the $^{37}Cl_4$-2378-TCDD cleanup standard that are found only in the CC3 solution, only one RRF is calculated for each analyte. For the other 10 unlabeled analytes, calculate the RRF of each analyte in each calibration standard.

Calculate the RRFs for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RRF_{is}) (see Table 8), in each calibration standard, according to the following formulae:

$$RRF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

where:

A_n^1 and A_n^2 = integrated areas of the two quantitation ions of the isomer of interest (Table 5).

A_{is}^1 and A_{is}^2 = integrated areas of the two quantitation ions of the appropriate internal standard (Table 5).

A_{rs}^1 and A_{rs}^2 = integrated areas of the two quantitation ions of the appropriate recovery standard (Table 5).

Q_n = quantity of unlabeled PCDD/PCDF analyte injected (ng).

Q_{is} = quantity of appropriate internal standard injected (ng).

Q_{rs} = quantity of appropriate recovery standard injected (ng).

For quantitations involving the use of peak heights instead of peak areas, see Section 11.4.

There is only one quantitation ion for the ^{37}Cl cleanup standard. Calculate the relative response factor as described for RRF_{is}, using one area for the cleanup standard and the sum of the areas of the ions from the recovery standard.

The RRF_n and RRF_{is} are dimensionless quantities; therefore, the units used to express the Q_n, Q_{is} and Q_{rs} must be the same.

NOTE: This protocol is based on the assumption that if the 10 unlabeled 2,3,7,8-substituted isomers provided in the EPA standard solutions meet linearity criteria, then the seven additional 2,3,7,8-substituted isomers and the cleanup standard in the CC3 solution may be assumed to have a sufficiently linear response to be used for quantitation. These eight RRFs cannot be used to determine percent relative standard deviation, but <u>are</u> used for percent difference determinations (as described in Paragraph 7.4.6.4) and quantitation of target analytes.

7.3.4 Calculate the relative response factors for the native PCDDs/PCDFs relative to the recovery standards (RRF_{rs}) where:

$$RRF_{rs} = RRF_n \times RRF_{is}$$

This relative response factor is necessary when the sample is diluted to the extent that the MS response of the internal standard is less than 10 percent of its MS response in the continuing calibration standard (see Section 15.3).

7.3.5 Relative Response Factor Criteria. Calculate the mean RRF and percent relative standard deviation (%RSD) of the five RRFs (CC1-CC5) for each unlabeled PCDD/PCDF and labeled internal standards present in all five concentration calibration solutions.

No mean RRF or %RSD calculations are possible for the 2,3,7,8-substituted isomers or the cleanup standard found only in the CC3 solution.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean RRF}} \times 100$$

The %RSD of the five RRFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards must not exceed 15.0 percent.

7.3.6 The response factors to be used for determining the total homologue concentrations are described in Section 15.2.

7.3.7 If any of the requirements listed in Paragraphs 7.3.2 or 7.3.5 are not met, the Contractor is responsible for taking corrective action before sample analyses are performed. The following suggestions may be useful.

7.3.7.1 Check and adjust the GC and/or MS operating conditions.

7.3.7.2 Replace the GC column.

7.3.7.3 Adjust the MS for greater or lesser resolution using FC-43 (see Section 6).

7.3.7.4 Recalibrate the mass scale.

Once the corrective actions have been completed, the Contractor must perform a new initial calibration that does meet all the QC requirements, beginning with analysis of the window defining mix, before sample analyses may proceed.

7.4 Continuing Calibration

The continuing calibration consists of two parts: evaluation of the chromatographic resolution and verification of the RRF values to be used for quantitation. At the beginning of each 12-hour period, the chromatographic resolution is verified in the same fashion as in the initial calibration: through the analysis of the CC3 solution on the DB-5 (or equivalent) column or through the analysis of the column performance solution on the SP-2331 (or equivalent) column.

NOTE: The 12-hour time period is defined as beginning with the injection of the CC3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12-hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be <u>injected</u> within 12:00 hours of the CC3 solution or the column performance solution.

7.4.1 Prepare the CC3 solution by combining the following volumes of the solutions listed in Section 5:

500 uL	CC4 Solution
125 uL	Supplemental Calibration Solution
50 uL	Internal Standard Solution
50 uL	Recovery Standard Solution
50 uL	Cleanup Standard Solution
225 uL	Tridecane (or nonane)

to yield a final volume of 1.0 mL at the concentrations specified for the CC3 solution in Table 3.

7.4.2 For the DB-5 (or equivalent) column, begin the 12-hour period by analyzing the CC3 solution. Inject a 2 uL aliquot of the continuing calibration solution (CC3) into the GC/MS. The identical GC/MS/DS conditions used for the analysis of the initial calibration solutions must be used for the continuing calibration solution (see Paragraph 7.3.1). Evaluate the chromatographic resolution using the QC criteria in Paragraph 7.3.2.1.

7.4.3 For the SP-2331 (or equivalent) column, or other columns with different elution orders, begin the 12-hour period by analyzing a 2 uL aliquot of the appropriate column performance solution. Evaluate the chromatographic resolution using the QC criteria in Paragraph 7.2.3 or 7.2.4. If this solution meets the QC criteria, proceed with the analysis of a 2 uL aliquot of the CC3 solution. The identical GC/MS/DS conditions used for the analysis of the initial calibration solutions must be used for the continuing calibration solution (see Paragraph 7.3.1).

7.4.4 Calculate the RRFs for the 17 unlabeled target analytes relative to their appropriate internal standards (RRF_n) and the response factors for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RRF_{is}), according to the following formulae:

$$RRF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

A_n^1, A_n^2, A_{is}^1, A_{is}^2, A_{rs}^1, A_{rs}^2, Q_n, Q_{is} and Q_{rs} are defined in Paragraph 7.3.3.

There is only one quantitation ion for the ^{37}Cl cleanup standard. Calculate the relative response factor as described for RRF_{is}, using one area for the cleanup standard and the sum of the areas of the ions from the recovery standard.

The RRF_n and RRF_{is} are dimensionless quantities; therefore, the units used to express the Q_n, Q_{is} and Q_{rs} must be the same.

7.4.5 Calculate the RRFs for the native PCDDs/PCDFs relative to the recovery standards (RRF_{rs}), where $RRF_{rs} = RRF_n \times RRF_{is}$. This relative response factor is necessary for calculations when the sample is diluted (see Section 15.3).

7.4.6 Continuing Calibration Criteria. The Contractor shall not proceed with sample analysis until an acceptable continuing

calibration has been performed and documented according to the following criteria: GC resolution, ion abundance ratios, retention times, instrument sensitivity, and response factors.

7.4.6.1 GC Column Resolution Criteria. The chromatographic resolution on the DB-5 (or equivalent) column must meet the QC criteria in Paragraph 7.3.2.1. The chromatographic resolution on the SP-2331 (or equivalent) column must meet the QC criteria in Paragraph 7.2.3. In addition, the chromatographic peak separation between the 123478-HxCDD and the 123678-HxCDD in the CC3 solution shall be resolved with a valley of $\leq$ 50 percent.

7.4.6.2 Ion Abundance Criteria. The relative ion abundances listed in Table 6 shall be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.

7.4.6.3 Instrument Sensitivity Criteria. For the CC3 solution, the S/N ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.

7.4.6.4 Response Factor Criteria. The measured RRFs of each analyte and internal standard in the CC3 solution must be within $\pm$ 30.0 percent of the mean RRFs established during initial calibration for the EPA-supplied standards and within $\pm$ 30.0 percent of the single point RRFs established during initial calibration for the supplemental calibration standards and the cleanup standards.

$$\% \text{ Difference} = \frac{(RRF_i - RRF_c)}{RRF_i} \times 100$$

where:

RRF_i = Relative response factor established during initial calibration.

RRF_c = Relative response factor established during continuing calibration.

7.4.7 If any of the criteria listed in Paragraph 7.4.6 are not met, the Contractor must take corrective actions and reanalyze the continuing calibration standard (CC3). If the criteria in Paragraph 7.4.6 <u>are</u> met after the corrective action, then sample analysis may begin, as described in Section 10.

If the criteria in Paragraph 7.4.6 are <u>not</u> met after the corrective action, then the Contractor must perform a new initial calibration, beginning with the analysis of the window

defining mix. This new initial calibration must meet all of the QC criteria in Sections 7.1, 7.2 and 7.3 before sample analysis may begin.

7.5 Instrument Sensitivity Check

In order to demonstrate that the GC/MS/DS system has retained adequate sensitivity during the course of sample analyses, the Contractor must analyze the lowest of the standards (CC1) at the end of each 12-hour period during which samples and standards are analyzed.

7.5.1 Analyze a 2 uL aliquot of the CC1 solution, using the identical instrumental conditions used for analysis of samples and standards.

7.5.2 The CC1 solution analyzed at the end of the 12-hour period must meet the following QC criteria:

7.5.2.1 Retention Time Criteria. The absolute retention time of the recovery standards, $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123678-HxCDD, shall not change by more than 10 seconds between the initial CC3 analysis and the ending CC1 analysis. If the retention times of either of these standards changes by more than ± 10 seconds, the Contractor must adjust the switching times of the descriptors and analyze the window defining mix before proceeding with further analyses.

7.5.2.2 All the analytes in the CC1 solution must meet the ion abundance ratio criteria in Table 6.

7.5.2.3 Instrument Sensitivity Criteria. For the CC1 solution, the S/N ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10.0 for the labeled internal and recovery standards.

7.5.3 If the analysis of the CC1 solution at the end of the 12-hour period fails <u>either</u> the ion abundance ratio or S/N criteria above, the Contractor must:

7.5.3.1 Take corrective action.

7.5.3.2 Perform a new initial calibration, beginning with the analysis of the window defining mix.

7.5.3.3 Start a new analytical sequence (see Table 13).

7.5.3.4 Reanalyze all samples originally analyzed in the preceding 12-hour time period in which:

7.5.3.4.1 No PCDDs/PCDFs were detected.

7.5.4.3.2 Neither 2378-TCDD or 2378-TCDF were detected, even if other PCDDs or PCDFs were detected.

7.5.4.3.3 Any 2,3,7,8-substituted PCDD or PCDF is reported as an Estimated Maximum Possible Concentration (see Section 15.7).

These reanalyses are necessary because poor S/N ratios indicate a loss of sensitivity that could lead to false negative results, underestimation of concentrations, or could cause ion abundance ratios to fall outside the QC limits.

8. Sample Homogenization, Preservation and Handling

8.1 Homogenization

Although sampling personnel will attempt to collect homogeneous samples, the Contractor shall examine each sample and determine if the sample needs phase separation or mixing. The extent to which phase separation or mixing is required will depend on the sample type.

The Contractor is responsible for taking a representative sample aliquot from the phase or phases to be analyzed. This responsibility entails efforts to make the sample phase as homogeneous as possible. Stirring is recommended when possible.

8.2 Sample Types

8.2.1 For the purpose of this method, a chemical waste sample includes the sample matrices of oils, oily sludge, stillbottom, oil-laced soil, and surface water heavily contaminated with any of the above matrices. The sample may contain particulates and an obvious non-aqueous liquid phase.

8.2.2 For the purpose of this method, a soil/sediment sample is defined as a single phase solid system composed of soil or sediment. The sample may contain stones and vegetation, but should not contain an obvious aqueous or non-aqueous liquid phase.

CAUTION: Finely divided soils contaminated with PCDDs/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing the analytes. Such samples should be handled in a confined environment (e.g., a closed hood or a glove box).

8.2.3 For the purpose of this method, a water sample is defined as a single phase system, the primary component of which is water.

The sample may include floating, suspended and settled particulate matter in quantities that do not cause severe problems with filtration or extraction.

8.3 Sample Preservation

8.3.1 Water Samples. Each water sample received will consist of at least two 1-liter (or quart) amber glass bottles. Store at 4 ± 2°C from collection until extraction. Do not freeze. After a portion of the sample is removed for analysis, the unused portion of the sample is stored at 4 ± 2°C in a locked, limited access area for at least 60 days from the date of data submission.

8.3.2 Soil/Fly Ash/Chemical Waste Samples. Each soil/fly ash/chemical waste sample received will be contained in a 1-pint glass jar surrounded by vermiculite in a sealed metal paint can. Until a portion is removed for analysis, the sealed sample must be stored in a locked, limited access area at room temperature. Do not freeze. After a portion is removed for analysis, the unused portion of the sample is returned to its original container and stored at room temperature for at least 60 days from the date of data submission.

8.3.3 To minimize the potential for photodecomposition, all samples must be protected from light from the time of receipt until extraction.

8.4 Sample Handling and Preextraction Treatment

8.4.1 If a soil/sediment sample contains an obvious aqueous liquid phase, decant or centrifuge the sample to separate the phases (see Paragraph 8.4.7).

8.4.2 If a soil/sediment sample does not contain an obvious liquid phase, homogenize the sample by careful stirring with a clean glass rod or spatula.

8.4.3 If a soil/sediment sample contains an obvious non-aqueous liquid phase, or contains more than two phases (i.e. non-aqueous liquid/aqueous liquid/solid), contact the Sample Management Office (SMO) in order to determine which phase(s) should be analyzed.

8.4.4 All water samples are filtered prior to extraction, and the filtered liquid and the particulates are extracted separately (see Section 9.5). If a water sample contains significant amounts of suspended particulates, centrifuge the sample and decant the water from the particulates before filtering (Paragraph 8.4.7).

8.4.5 If a water sample contains an obvious non-aqueous liquid phase or a non-particulate solid phase, contact SMO in order to determine which phase(s) should be analyzed.

8.4.6 If a water sample does not contain significant amounts of suspended particulates, homogenize the sample by carefully shaking the capped sample bottle.

8.4.7 Centrifugation. If centrifugation of a sample is necessary, place the entire sample in a suitable centrifuge bottle(s) with a 250-300 mL capacity, and centrifuge for 30 minutes at 400 x G. Decant the liquid phase into a clean container. Remove the solid phase by careful pouring or using a clean spatula or glass rod. Proceed with the analysis of the appropriate phase or phases.

CAUTION: A phase that is not analyzed may contain PCDDs/PCDFs and should be handled and disposed of appropriately.

9. Extraction Procedures

Four types of extraction procedures are employed in these analyses depending on the sample matrix. Chemical waste samples are extracted by refluxing with a Dean Stark water separator. Fly ash samples and soil/sediment samples are extracted in a combination of a Soxhlet extractor and a Dean Stark water separator. Water samples are filtered and then the filtrate is extracted using either a separatory funnel procedure or a continuous liquid-liquid extraction procedure. The filtered particulates are extracted in a combination of a Soxhlet extractor and a Dean Stark water separator.

9.1 Chemical Waste Sample Extraction

9.1.1 Assemble a flask (50 mL or 125 mL, see below), a Dean Stark trap, and a condenser, and preextract with toluene for three hours. Preextraction will ensure that the glassware is as clean as possible and minimize cross-contamination problems. Discard the used toluene, or pool it for later analysis to verify the cleanliness of the glassware.

9.1.2 Oily Sludge/Wet Fuel Oil. Weigh about 1 g of sample to two decimal places into a tared preextracted 125-mL flask. Add 1 mL of the acetone-diluted internal standard solution (see Section 5.12) to the sample in the flask. Attach the preextracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours.

Continue refluxing the sample until all the water has been removed. Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 9.6.

9.1.3 Stillbottom/Oil. Weigh about 1 g of sample to two decimal places into a tared preextracted 50-mL flask. Add 1 mL of the

acetone-diluted internal standard solution (see Section 5.12) to the sample in the flask. Attach the preextracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours.

Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 9.6.

9.1.4 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.2 Soxhlet-Dean Stark (SDS) Apparatus

The combination of a Soxhlet extractor and a Dean Stark moisture trap is used for the removal of water and extraction of PCDDs/PCDFs from samples of fly ash, soil/sediment, and the particulate fraction of water samples. The combination consists of a Soxhlet extractor body with a Dean Stark moisture trap fitted between the extractor and the condenser (see Figure 4).

Procedures for the use of this apparatus were developed by the Dow Chemical Company and have been tested by the EPA Industrial Technology Division, Office of Water Regulations and Standards. Those tests indicate that based on the recovery of labeled analytes, the extraction by SDS apparatus is as good, or better, than extraction by Soxhlet alone.

For soil/sediment samples, the results of these analyses are reported based on the <u>wet weight</u> of the sample. However, use of the SDS apparatus allows the water content of a sample to be determined from the same aliquot of sample that is also extracted for analysis. The amount of water evolved from the sample during extraction is used to approximate the percent solids content of the sample. The percent solids data may be employed by the data user to approximate the dry weight concentrations. The percent solids determination does <u>not</u> apply to the extraction of particulates from the filtration of water samples or to the extraction of fly ash samples which are treated with an HCl solution prior to extraction.

Further, as described here, the SDS apparatus allows the extraction of sample matrices containing water <u>without</u> the addition of drying agents such as sodium sulfate. The use of sodium sulfate during extraction may be responsible for the loss of analytes, through adsorption onto carbon particles produced by baking this reagent at high temperatures in order to remove organic contaminants, and by trapping analytes in pores in the sodium sulfate as moisture is adsorbed.

The following procedures apply to all uses of the SDS apparatus for extracting matrices covered by this protocol.

NOTE: It may be necessary to wrap portions of the SDS apparatus with aluminum foil or glass wool to obtain proper operation.

9.2.1 Refer to Section 4.5 for detailed instructions on cleaning glassware such as the SDS apparatus. In particular, do <u>not</u> bake the components of the SDS apparatus as part of routine cleaning, as repeated baking of glassware can cause active sites on the glass surface that will adsorb PCDDs/PCDFs and other analytes. All glass parts of the SDS apparatus, including the thimbles, <u>must</u> be preextracted with toluene for approximately three hours immediately prior to use. Preextraction will ensure that the glassware is as clean as possible and minimize cross-contamination problems. Discard the used toluene, or pool it for later analysis to verify the cleanliness of the glassware.

9.2.2 The extraction of soil/sediment, fly ash, and particulates from water samples will require the use of a Soxhlet thimble. Prior to preextraction, prepare the thimble by adding 5 g of 70/230 mesh silica gel to the thimble to produce a thin layer in the bottom of the thimble. This layer will trap fine particles in the thimble. Add 80-100 g of quartz sand on top of the silica gel, and place the thimble in the extractor.

9.2.3 After preextraction for three hours, allow the apparatus to cool and remove the thimble. Mix the appropriate weight of sample with the sand in the thimble, being careful not to disturb the silica gel layer.

If the sample aliquot to be extracted contains large lumps or is otherwise not easily mixed in the thimble, the sand and sample may be mixed in another container. Transfer approximately 2/3 of the sand from the thimble to a clean container, being careful not to disturb the silica gel layer when transferring the sand. Thoroughly mix the sand and the sample and a clean spatula, and transfer the sand/sample mixture to the thimble.

If a sample with particularly high moisture content is to be extracted, it may be helpful to leave a small conical depression in the material in the thimble. This procedure will allow the water to drain through the thimble more quickly during the early hours of the extraction. As the moisture is removed during the first few hours of extraction, the depression will collapse, and the sample will be uniformly extracted.

9.3 Fly Ash Sample Extraction

9.3.1 Weigh about 10 g of the fly ash to two decimal places, and transfer to an extraction jar (Paragraph 4.4.1). Add 1 mL of the acetone-diluted internal standard solution (Section 5.12) to the sample.

9.3.2 Add 150 mL of 1 N HCl to the fly ash sample in the jar. Seal the jar with the Teflon-lined screw cap, place on a mechanical shaker, and shake for three hours at room temperature.

9.3.3 Rinse a Whatman #1 (or equivalent) filter paper with toluene, and then filter the sample through the filter paper in a Buchner funnel into a 1 L receiving flask. Wash the fly ash with approximately 500 mL distilled water.

9.3.4 Mix the fly ash with the sand in a preextracted thimble, and place the filter paper on top of the sand. Place the thimble in a SDS extractor, add 200 mL toluene, and extract for 16 hours.

The solvent must cycle completely through the system 5-10 times per hour. Cool and filter the toluene extract through a rinsed glass fiber filter into a 500 mL round-bottom flask. Rinse the filter with 10 mL of toluene. Concentrate the extract as described in Section 9.6.

NOTE: A blank must be analyzed using a piece of filter paper handled in the same manner as the fly ash sample.

9.3.5 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.4 Soil/Sediment Sample Extraction

NOTE: Extremely wet samples may require centrifugation to remove standing water before extraction (see Paragraph 8.4.7).

9.4.1 Weigh about 10 grams of the soil to two decimal places and transfer to a preextracted thimble (see Paragraph 9.2.2). Mix the sample with the quartz sand, and add 1 mL of the acetone-diluted internal standard solution (see Section 5.12) to the sample/sand mixture. Add small portions of the solution at several sites on the surface of the sample/sand mixture.

9.4.2 Place the thimble in the SDS apparatus. Add 200 to 250 mL toluene to the SDS apparatus, and reflux for 16 hours. The solvent must cycle completely through the system 5-10 times per hour.

9.4.3 Estimate the percent solids content of the soil/sediment sample by measuring the volume of water evolved during the SDS

extraction procedure. For extremely wet samples, the Dean Stark trap may need to be drained one or more times during the 16-hour extraction. Collect the water from the trap, and measure its volume to the nearest 0.1 mL. Assume a density of 1.0 g/mL, and calculate the percent solids content according to the formula below:

$$\text{Percent Solids} = \frac{(\text{Wet weight of sample} - \text{Weight of water})}{\text{Wet weight of sample}} \times 100$$

9.4.4 Concentrate this extract as described in Section 9.6.

9.4.5 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.5 Water Sample Extraction

9.5.1 Allow the sample to come to ambient temperature, then mark the water meniscus on the side of the 1-L sample bottle for determination of the exact sample volume. Add 1 mL of the acetone-diluted internal standard solution (see Section 5.12) to the sample bottle. Cap the bottle, and mix the sample by gently shaking for 30 seconds. Filter the sample through a 0.45 micron filter that has been rinsed with toluene.

NOTE: Reagent water used as a blank must also be filtered in a similar fashion and subjected to the same cleanup and analysis as the water samples.

If the total dissolved and suspended solids contents are too much to filter through the 0.45 micron filter, centrifuge the sample, decant, and then filter the aqueous phase (see Paragraph 8.4.7). Combine the solids from the centrifuge bottle(s), the particulate on the filter and the filter itself, and proceed with the SDS extraction in Paragraph 9.5.4.

9.5.2 The filtered aqueous sample is poured into a 2-L separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the Contractor shall employ mechanical techniques to complete the phase separation (i.e., glass stirring rod). Drain the methylene chloride extract into a 500-mL KD concentrator (mounted with a 10-mL concentrator tube) by passing the extract through a funnel packed with a glass wool plug and half-filled with anhydrous sodium sulfate. Extract the water sample two more times using 60 mL of fresh methylene

chloride each time. Drain each extract through the funnel into the KD concentrator. After the third extraction, rinse the sodium sulfate with at least 30 mL of fresh methylene chloride. Concentrate this extract as described in Section 9.6.

9.5.3 A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. The following procedure is used for a continuous liquid-liquid extractor.

Preextract the continuous liquid-liquid extractor for three hours with methylene chloride and reagent water. Filter the sample as in Paragraph 9.5.1. Allow the extractor to cool, discard the methylene chloride, and add the filtered aqueous sample to the continuous liquid-liquid extractor. Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds.

Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL methylene chloride to the distilling flask and sufficient reagent water to ensure proper operation. Extract for 16 hours. Allow to cool, then detach the flask and dry the sample by running it through a rinsed funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate into a 500 mL KD flask. Proceed to Section 9.6.

9.5.4 Combine the filtered particulate portion of the sample with the quartz sand in the extraction thimble. Add the filter on top of the particulate/sand mixture, and place the thimble into a preextracted SDS apparatus.

Add 200 to 250 mL of toluene to the SDS apparatus and reflux for 16 hours. The solvent must cycle completely through the system 5-10 times per hour. Concentrate this extract as described in Section 9.6.

9.5.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1-L graduated cylinder. Record the sample volume to the nearest 5 mL.

9.5.6 Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis, using the procedures in Sections 13 and 14 and at the frequency given in those sections.

9.6 Macro-Concentration Procedures (All Matrices)

Prior to cleanup, extracts from all matrices must be concentrated to approximately 10 mL. In addition, the concentrated extracts from the

aqueous filtrate and the filtered particulates must be combined prior to cleanup. Two procedures may be used for macro-concentration, Kuderna-Danish (K-D) or rotary evaporator. Concentration of toluene by K-D requires the use of a heating mantle, as toluene boils above the temperature of a water bath. The two procedures are described in general terms below.

9.6.1 Concentration by K-D

9.6.1.1 Add one or two clean boiling chips to the round bottom flask from the SDS extractor or the reflux flask. Attach a three-ball macro Snyder column.

9.6.1.2 Pre-wet the column by adding approximately 1 mL of toluene through the top. Place the round bottom flask in a heating mantle and apply heat as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

9.6.2 Concentration by Rotary Evaporator

9.6.2.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for contamination check if necessary. Between samples, three 2-3 mL aliquots of toluene should be rinsed down the feed tube into a waste beaker.

9.6.2.2 Attach the round bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

9.6.2.3 Lower the flask into the water bath and adjust the speed of rotation and the temperature as required to complete the concentration in 15-20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

NOTE: If the rate of concentration is too fast, analyte loss may occur.

9.6.2.4 When the liquid in the concentration flask has reached an apparent volume of 2 mL, remove the flask from the water bath, and stop the rotation. Slowly and carefully, admit air into the system. Be sure

not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of hexane.

9.6.3 Extracts of Chemical Waste, Fly Ash, and Soil/Sediment Samples

9.6.3.1 For chemical waste, fly ash, and soil/sediment samples, the extract must be concentrated to approximately 10 mL prior to acid-base washing treatment. Concentrate the extract by either of the two procedures listed above.

9.6.3.2 Transfer the concentrated extract to a 125 mL separatory funnel. Rinse the flask with toluene and add the rinse to the separatory funnel. Proceed with acid-base washing treatment per Section 9.7.

9.6.4 Extracts of Aqueous Filtrates

9.6.4.1 Extracts of the aqueous filtrate of water samples are in methylene chloride which is concentrated to approximately 10 mL by K-D or rotary evaporator prior to combining with the toluene extract of the particulates. If using K-D, the methylene chloride can be concentrated in a water bath instead of a heating mantle.

9.6.4.2 Combine the extract of the filtrate with the extract of the particulates as described in Section 9.6.

9.6.5 Extracts of Particulates from Aqueous Samples

9.6.5.1 If the extract is from the particulates from an aqueous sample, it must be concentrated to approximately 10 mL by either K-D or rotary evaporator, and combined with the concentrated extract of the filtrate (Paragraph 9.6.4.1) prior to acid-base washing treatment.

9.6.5.2 Assemble a glass funnel filled approximately one-half full with sodium sulfate such that the funnel will drain into the K-D concentrator or round bottom flask from Paragraph 9.6.4.1 containing the concentrated methylene chloride extract of the filtrate. (You may use the same funnel from Paragraph 9.5.2 or 9.5.3.) Pour the concentrated toluene extract of the particulates through the sodium sulfate into the K-D concentrator or round bottom flask. Rinse the flask from the particulate extract with three 15-20 mL volumes of hexane, and pour each rinse through the sodium sulfate into the K-D concentrator or round bottom flask.

9.6.5.3 Concentrate the combined extract to approximately 10 mL (the volume of the toluene) by either K-D or rotary evaporator.

9.6.5.4 Transfer the concentrated combined extract to a 125 mL separatory funnel. Rinse the concentrator with three 5 mL volumes of hexane, and add each rinse to the separatory funnel. Proceed with acid-base washing treatment per Section 9.7.

9.7 Extract Cleanup Procedures (All Matrices)

9.7.1 Prior to cleanup, all extracts are spiked with the $^{37}Cl_4$-2378-TCDD cleanup standard (Section 5.17). The recovery of this standard is used to monitor the efficiency of the cleanup procedures. Spike 5 uL of the cleanup standard (or a larger volume of diluted solution containing 25 ng of $^{37}Cl_4$-2378-TCDD) into each separatory funnel containing an extract, resulting in a concentration of 0.25 ng/uL in the final extract analyzed by GC/MS.

9.7.2 Partition the concentrated extract against 40 mL of concentrated sulfuric acid. Shake for two minutes. Remove and discard the acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

CAUTION: Concentrated sulfuric acid is hazardous and should be handled with care.

9.7.3 Partition the concentrated extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

9.7.4 Partition the concentrated extract against 40 mL of 20 percent (w/v) potassium hydroxide (KOH). Shake for two minutes. Remove and discard the base layer (bottom). Repeat the base washes until color is not visible in the bottom layer (perform base washes a maximum of four times). Strong base (KOH) is known to degrade certain PCDDs/PCDFs; therefore, contact time should be minimized.

9.7.5 Partition the concentrated extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring it through a funnel containing a rinsed filter half-filled with anhydrous sodium sulfate. Collect the extract in an appropriate size (100-250 mL) round bottom flask. Wash the separatory funnel with two 15-mL portions of hexane, pour through the funnel and combine the extracts. Concentrate the extracts to 1.0 mL using the procedures described in Section 9.8.

9.8 Micro-Concentration of Extracts

Prior to column chromatographic cleanup procedures, the extracts from all matrices must be concentrated to approximately 1.0 mL. This concentration may be accomplished using either K-D or rotary evaporator, followed by nitrogen evaporation.

9.8.1 Concentrate the extracts to approximately 1 mL, using the procedures in Paragraph 9.6.1 or 9.6.2.

9.8.2 When the liquid in the concentration flask has reached an apparent volume of 1 mL, transfer the extract to a conical centrifuge tube using three 2-3 mL rinses of hexane.

9.8.3 Transfer the centrifuge tube containing the sample extract to a nitrogen evaporation device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

NOTE: A large vortex in the solvent may cause analyte loss.

9.8.4 Lower the tube into a 45°C water bath and continue concentrating. When the volume of the liquid is approximately 100 uL, add 2-3 mL of the hexane and continue concentration to a final volume of 1.0 mL. Proceed with column chromatography as described in Section 9.9.

9.9 Silica Gel and Alumina Column Chromatographic Procedure

9.9.1 Column 1. Insert a glass wool plug onto the bottom of a gravity column (1 cm x 30 cm glass column) fitted with a Teflon stopcock. Add 1 g silica gel and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 1 g silica gel, 4 g sulfuric acid-impregnated silica gel, and 2 g silica gel (see Section 5.10). Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed.

9.9.2 Column 2. Insert a glass wool plug onto the bottom of a gravity column (1 cm x 30 cm glass column) fitted with a Teflon stopcock. Add 6 g of the activated acid alumina (see Paragraph 5.10.1). Tap the top of the column gently.

Check each new batch of silica gel and alumina and maintain the results of the analyses on file for examination during EPA on-site evaluations. To accomplish this, combine 50 uL of the continuing calibration solution (CC3) with 950 uL of hexane. Process this solution through both columns in the same manner as a sample extract (Paragraphs 9.9.3 through 9.9.9). Concentrate the continuing calibration solution to a final volume of 50 uL. Proceed to Section 10. If the recovery of any of the analytes is less than 80%, the batch of alumina or silica gel must not be used.

9.9.3 Add hexane to each column until the packing is free of air bubbles. A small positive pressure (5 psi) of clean dry nitrogen may be used if needed. Check the columns for channeling. If channeling is present, discard the column.

CAUTION: Do not tap a wetted column.

9.9.4 Assemble the two columns such that the eluate from Column 1 (silica gel) drains directly into Column 2 (alumina).

9.9.5 Apply the hexane solution from Paragraph 9.8.4 to the top of the silica gel column. Rinse the vial with enough hexane (1-2 mL) to complete the quantitative transfer of the sample to the surface of the silica.

9.9.6 Using 90 mL of hexane, elute the extract from Column 1 directly onto Column 2 which contains the alumina.

CAUTION: Do not allow the alumina column to run dry.

9.9.7 Add 20 mL of hexane to Column 2, and elute until the hexane level is just below the top of the alumina. Do not discard the eluted hexane, but collect in a separate flask and store it for later use, as it may be useful in determining where the labeled analytes are being lost if recoveries are less than 50 percent.

9.9.8 Add 20 mL of 20% methylene chloride/80% hexane (v/v) to Column 2 and collect the eluate.

9.9.9 Concentrate the extract to approximately 2 to 3 mL using the procedures in Section 9.8.

CAUTION: Do not concentrate the eluate to dryness. The sample is now ready to be transferred to the carbon column.

9.10 Carbon Column Chromatographic Procedure

9.10.1 Thoroughly mix 5.35 g active carbon AX-21 and 62.0 g Celite 545 to produce a 7.9% w/w mixture. Activate the mixture at 130°C for six hours, and store in a desiccator.

Check each new batch of the Carbon/Celite and maintain the results from the analyses for examination during EPA on-site evaluations. To accomplish this, add 50 uL of the continuing calibration solution to 950 uL of hexane. Process the spiked solution in the same manner as a sample extract (Paragraphs 9.10.2 through 9.10.6). Concentrate the continuing calibration solution to 50 uL and proceed with Section 9.10. If the recovery of any of the analytes is less than 80%, this batch of Carbon/Celite mixture may not be used.

9.10.2 Prepare a 4-inch glass column by cutting off each end of a 10-mL disposable serological pipet. Fire polish both ends and

flare if desired. Insert a glass wool plug at one end of the column, and pack it with 1 g of the Carbon/Celite mixture. Insert an additional glass wool plug in the other end.

CAUTION: It is very important that the column be packed properly to ensure that carbon fines are not carried into the eluate. PCDDs/PCDFs will adhere to the carbon fines and greatly reduce recovery. If carbon fines are carried into the eluate in Paragraph 9.10.5, filter the eluate using a 0.45 micron filter (pre-rinsed with toluene), then proceed to Section 9.11.

9.10.3 Rinse the column with:

9.10.3.1 4 mL Toluene.

9.10.3.2 2 mL of Methylene Chloride/Methanol/Toluene (75:20:5 v/v).

9.10.3.3 4 mL of Cyclohexane/Methylene Chloride (50:50 v/v).

Discard all the column rinsates.

9.10.4 While the column is still wet, transfer the concentrated eluate from Paragraph 9.9.9 to the prepared carbon column. Rinse the eluate container with two 0.5 mL portions of hexane and transfer the rinses to the AX-21 carbon column. Elute the column with the following sequence of solvents.

9.10.4.1 10 mL of Cyclohexane/Methylene Chloride (50:50 v/v).

9.10.4.2 5 mL of Methylene Chloride/Methanol/Toluene (75:20:5 v/v).

NOTE: The above two eluates may be collected, combined and used as a check on column efficiency.

9.10.5 Once the solvents have eluted through the column, turn the column over, elute the PCDD/PCDF fraction with 20 mL of toluene, and collect the eluate.

9.11 Final Concentration

9.11.1 Evaporate the toluene fraction from Paragraph 9.10.5 to approximately 1.0 mL in a rotary evaporator (see Section 9.8). Transfer the extract to a 2.0 mL conical vial using a toluene rinse.

CAUTION: Do <u>not</u> evaporate the sample extract to dryness.

9.11.2 Add 100 uL tridecane (or nonane) to the extract and reduce the volume to 100 uL using a gentle stream of clean dry nitrogen.

The final extract volume should be 100 uL of tridecane (or nonane). Seal the vial and store the sample extract in the dark at ambient temperature until just prior to GC/MS analysis.

10. GC/MS Analysis

10.1 Remove the extract of the sample or blank from storage. Gently swirl the solvent on the lower portion of the vial to ensure complete dissolution of the PCDDs/PCDFs.

10.2 Transfer a 50 uL aliquot of the extract to a 0.3 mL vial, and add sufficient recovery standard solution to yield a concentration of 0.5 ng/uL in a 50 uL volume. Reduce the volume of the extract back down to 50 uL using a gentle stream of dry nitrogen.

Inject a 2 uL aliquot of the extract into the GC/MS instrument (see Paragraph 4.1.1). Reseal the vial from Paragraph 9.11.2, containing the original concentrated extract.

10.3 Analyze the extract by GC/MS, and monitor all of the ions listed in Table 7. The same MS parameters used to analyze the calibration solutions shall be used for the sample extracts.

10.4 Dilutions

10.4.1 If the concentration of any PCDD/PCDF in the sample has exceeded the calibration range or the detector has been saturated, a dilution shall be performed.

An appropriate dilution will result in the largest peak in the diluted sample falling between the mid-point and high-point of the calibration range.

10.4.2 Dilutions are performed using an aliquot of the original extract, of which approximately 50 uL remain from Paragraph 9.11.2. Remove an appropriate size aliquot from the vial and add it to a sufficient volume of tridecane (or nonane) in a clean 0.3 mL conical vial. Add sufficient recovery standard solution to yield a concentration of 0.5 ng/uL (1.0 ng/uL ^{13}C-OCDD). Reduce the volume of the extract back down to 50 uL using a gentle stream of dry nitrogen.

10.4.3 The dilution factor is defined as the total volume of the sample aliquot and clean solvent divided by the volume of the sample aliquot that was diluted.

10.4.4 Inject 2 uL of the diluted sample extract into the GC/MS, and analyze according to Section 10.3.

10.4.5 Diluted samples in which the MS response of any internal standard is $\geq$ 10% of the MS response of that internal standard in the most recent continuing calibration standard are quantified using the internal standards.

Diluted samples in which the MS response of any internal standard is < 10% of the MS response of that internal standard in the most recent continuing calibration standard are quantified using the recovery standards (see Section 15.3).

11. Identification Criteria

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

11.1 Retention Times

Retention times are required for all chromatograms; scan numbers are optional. Retention times shall either be printed at the apex of each peak on the chromatogram, or each peak shall be unambiguously labeled with an identifier that refers to the quantitation report. The chromatogram, the quantitation report, or a combination of both shall contain the retention time of each peak and its area.

11.1.1 In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time (RT) at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

11.1.2 In order to make a positive identification of the 2,3,7,8-substituted isomers for which a labeled standard is not available, the relative retention time (RRT) of the analyte must be within 0.05 RRT units of the RRT established by the continuing calibration. The RRT is calculated as follows:

$$RRT = \frac{\text{retention time of analyte}}{\text{retention time of corresponding internal standard}}$$

11.1.3 For non-2,3,7,8-substituted compounds (tetra through hepta), the retention time must be within the retention time windows established by the window defining mix for the corresponding homologue (see Section 7.1).

11.1.4 In order to assure that retention time shifts do not adversely affect the identification of PCDDs/PCDFs, the absolute retention times of the two recovery standards added to every sample extract immediately prior to analysis may not shift by more than ± 10 seconds from their retention times in the continuing calibration standard (see Paragraph 17.1.4).

11.2 Peak Identification

All of the specified ions listed in Table 5 for each PCDD/PCDF homologue and labeled standards must be present in the SICP. The ion current response for the two quantitation ions and the M-[COCl]+ ions

for the analytes must maximize simultaneously (± 2 seconds). This requirement also applies to the internal standards and recovery standards. For the cleanup standard, only one ion is monitored.

11.3 Signal-To-Noise Ratio

The integrated ion current for each analyte ion listed in Table 5 must be at least 2.5 times background noise and must not have saturated the detector. The internal standard ions must be at least 10.0 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 meets all the other criteria listed in Section 11 and, in the judgement of the GC/MS Interpretation Specialist the peak is a PCDD/PCDF, the peak may be reported as positive and the data flagged on Form I. See the instructions in Exhibit B for Form I.

11.4 Ion Abundance Ratios

The relative ion abundance criteria listed in Table 6 for native analytes and internal standards must be met using peak areas to calculate ratios.

11.4.1 If interferences are present and ion abundance ratios are not met using peaks areas, but all other qualitative identification criteria <u>are</u> met (RT, S/N, presence of all three ions), then the Contractor may use peak heights to evaluate the ion ratio.

11.4.2 If, in the judgement of the GC/MS Interpretation Specialist the peak is a PCDD/PCDF, then report the ion abundance ratios determined using peak heights, <u>quantitate</u> the peaks using peak heights rather than areas for both the target analyte and the internal standard, and flag the data on Form I.

11.5 Polychlorinated Diphenyl Ether (PCDPE) Interferences

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 5). If a PCDPE is detected, it shall be documented in the SDG Narrative, and an Estimated Maximum Possible Concentration (EMPC) shall be calculated for this GC peak according to Section 15.7, regardless of the ion abundance ratio, and reported on Form I.

12. <u>Method Blanks</u>

12.1 A minimum of one blank per matrix shall be analyzed with each SDG. If samples of the same matrix are extracted in different episodes (i.e., different shifts or days), one blank per matrix must be prepared for each episode. When water samples in a SDG are extracted using both the separatory funnel and continuous liquid-liquid extraction procedures, at least one blank must be prepared by each procedure.

12.2 Method Blank Criteria

12.2.1 Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions that is greater than 5 percent of the signal of the appropriate internal standard quantitation ion.

12.2.2 A peak that meets identification criteria as a PCDD/PCDF in the method blank must not exceed 2 percent of the signal of the appropriate internal standard.

12.2.3 If the method blank extracted along with a group of samples is contaminated per Paragraph 12.2.1 or 12.2.2, then the associated positive samples and any samples containing peaks that do not meet all of the identification criteria in Section 11 must be rerun.

12.2.4 If all the criteria listed above are not met, check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any more samples are extracted and before any positive samples are reextracted.

12.2.5 Test each new lot of reagents or solvents by using them to prepare a method blank and analyze it according the procedures in this exhibit. If new lots of reagents or solvents contain interfering contaminants, purify or discard them. Maintain records of all such blanks on file for examination during EPA on-site evaluations.

13. Spiked Sample Analysis

In order to provide data on the accuracy of the analytical method, the laboratory is required to prepare and analyze a spiked sample for each matrix being analyzed. For each SDG, the laboratory must prepare a spiked sample for all of the following matrix types that occur in the SDG:

- Water
- Soil/Sediment
- Chemical Waste
- Fly Ash

If a matrix is not represented in a SDG, then no spiked sample is required for that matrix. If the Region or samplers have identified a particular sample to be used for the spike, the laboratory must use an aliquot of that sample. If the Region or samplers have not identified a specific sample for spiking, then the laboratory may choose a sample from the SDG; however, the sample chosen must not be a sample identified by the Region as a field or trip blank.

13.1 Prepare the spiked sample aliquot by taking the same weight (or volume) of the representative matrix as is indicated in Sections 9.1 to 9.5 and placing it in a clean container of suitable size.

13.2 Add 1.0 mL of the spiking solution in Section 5.18 and Table 11 to the aliquot. Manually mix the sample to distribute the spiking solution, and let the aliquot equilibrate for one hour.

13.3 Prepare and extract the spiked sample aliquot in the same fashion as is used for field samples, and carry the aliquot through the entire analytical procedure including cleanup.

13.4 Calculate the concentration of each analyte according to the procedures in Section 15.

13.5 Calculate the recovery of each spiked analyte, using the following equation:

$$R_{spike} = \frac{\text{Amount found - Amount in unspiked sample}}{\text{Amount spiked}} \times 100$$

where the recovery (R) is expressed as a percentage

13.6 The recovery of each spiked analyte must be in the range of 50-150 percent. If the recovery of any analyte falls outside this range, the laboratory must recheck all calculations, and confirm that the spiking solutions were added and were at the correct concentrations, but no further action is necessary by the laboratory at this time. Recovery limits for these analytes will be developed at a later date.

14. Duplicate Sample Analysis

In order to provide data on the precision of the analytical method, the laboratory is required to prepare and analyze a duplicate of one sample for each matrix being analyzed. For each SDG, the laboratory must prepare a duplicate sample for all of the following matrix types that occur in the SDG:

- Water
- Soil/Sediment
- Chemical Waste
- Fly Ash

If a matrix is not represented in a SDG, then no duplicate sample is required for that matrix. If the Region or samplers have identified a particular sample to be used for the duplicate, the laboratory must use an aliquot of that sample. If the Region or samplers have not identified a specific sample for use as the duplicate, then the laboratory may choose a sample from the SDG; however, the sample chosen must not be a sample identified by the Region as a field or trip blank.

14.1 Prepare the duplicate sample aliquot by taking the same weight (or volume) of the representative matrix as is indicated in Sections 9.1 to 9.5 and carrying it through the entire analytical procedure including extraction, cleanup and analysis.

14.2 Calculate the concentration of each analyte detected in the duplicate sample according the procedures in Section 15.

14.3 Calculate the precision of each detected analyte in the original and duplicate analyses, expressed as the Relative Percent Difference (RPD), according to the following equation:

$$RPD = \frac{|\text{Sample Result} - \text{Duplicate Result}|}{(\text{Sample Result} + \text{Duplicate Result})/2} \times 100$$

14.4 The RPD of any detected analyte must be less than or equal to 50 percent. If the RPD of any detected analyte falls above this limit, the laboratory must recheck all calculations, but no further action is necessary by the laboratory at this time. RPD limits for these analytes will be developed at a later date.

15. <u>Calculations</u>

15.1 For GC peaks that have met all the identification criteria outlined in Section 11, calculate the concentration of the individual PCDD or PCDF isomers using the following formulae:

ALL MATRICES OTHER THAN WATER

$$C_n \text{ (ug/kg)} = \frac{Q_{is} \times (A_n^1 + A_n^2)}{W \times (A_{is}^1 + A_{is}^2) \times RRF_n}$$

WATER

$$C_n \text{ (ng/L)} = \frac{Q_{is} \times (A_n^1 + A_n^2)}{V \times (A_{is}^1 + A_{is}^2) \times RRF_n}$$

Where:

A_n^1 and A_n^2 = integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest (Table 5).

A_{is}^1 and A_{is}^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard (Table 5).

NOTE: In instances where peak heights are used to evaluate ion abundance ratios due to interferences (see Section 11.4), substitute peak heights for areas in the formulae above.

W - weight of sample extracted, in grams.

V - volume of sample extracted, in liters.

Q_{is} - quantity (ng) of the appropriate internal standard added to the sample prior to extraction.

RRF_n - calculated relative response factor from continuing calibration (see Section 7.3).

For solids matrices, the units of ng/g that result from the formula above are equivalent to ug/Kg. Using isotope dilution techniques for quantitation, the concentration data are recovery corrected, and therefore, the volume of the final extract and the injection volume are implicit in the value of Q_{is}.

15.1.1 For homologues that contain only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD and TCDF), the RRF of the 2,3,7,8-substituted isomer from the continuing calibration (see Paragraph 7.3.2.3) will be used to quantitate both the 2,3,7,8-substituted isomers and the non-2,3,7,8-substituted isomers.

15.1.2 For homologues that contain more than one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF and HpCDF), the RRF used to calculate the concentration of each 2,3,7,8-substituted isomers will be the RRF determined for that isomer during the continuing calibration (see Paragraph 7.3.2.3).

15.1.3 For homologues that contain one or more <u>non</u>-2,3,7,8-substituted isomers, the RRF used to calculate the concentration of these isomers will be the <u>lowest</u> of the RRFs determined during the continuing calibration (see Paragraph 7.3.2.3) for the 2,3,7,8-substituted isomers in that homologue. This RRF will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

NOTE: The relative response factors of given isomers within any homologue may be different. However, for the purposes of these calculations, it will be assumed that every non-2,3,7,8-substituted isomer for a given homologue has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, the 2,3,7,8-substituted isomer with the lowest RRF was chosen as representative of each homologue. All relative response factor calculations for the non-2378-substituted isomers in a given homologue are based on that isomer.

15.2 In addition to the concentrations of specific isomers, the total homologue concentrations are also reported. Calculate the total concentration of each homologue of PCDDs/PCDFs as follows:

Total concentration = sum of the concentrations of every positively identified isomer of each PCDD/PCDF homologue.

The total must include the non-2,3,7,8-substituted isomers as well as the 2,3,7,8-substituted isomers that are also reported separately. The total number of GC peaks included in the total homologue concentration must be specified (see Exhibit B).

15.3 If the area of any internal standard in a diluted sample is less than 10 percent of the area of that internal standard in the continuing calibration standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the recovery standard, using the formulae that follow. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. While use of a smaller aliquot of the sample might require smaller dilutions and therefore yield a larger area for the internal standard in the diluted extract, this practice leads to other concerns about the homogeneity of the sample and the representativeness of the aliquot taken for extraction.

ALL MATRICES OTHER THAN WATER

$$C_n \text{ (ug/kg)} = \frac{Q_{rs} \times (A_n^1 + A_n^2) \times D}{W \times (A_{rs}^1 + A_{rs}^2) \times RRF_{rs}}$$

WATER

$$C_n \text{ (ng/L)} = \frac{Q_{rs} \times (A_n^1 + A_n^2) \times D}{V \times (A_{rs}^1 + A_{rs}^2) \times RRF_{rs}}$$

D = dilution factor (see Paragraph 10.4.3).

A_n^1, A_n^2, A_{rs}^1, A_{rs}^2, Q_{rs}, RRF_{rs}, W and V are defined in Paragraphs 7.3.3 and 7.3.4 and Section 15.1.

15.4 Report results for soil/sediment, fly ash, and chemical waste samples in micrograms per kilograms (ug/kg) and water samples in nanograms per liter (ng/L), as described in Exhibit B.

15.5 Calculate the percent recovery for each internal standard and the cleanup standard in the sample extract, R_{is}, using the formula:

$$R_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times RRF_{is} \times Q_{is}} \times 100\%$$

A_{is}^1, A_{is}^2, A_{rs}^1, A_{rs}^2, Q_{is}, Q_{rs} and RRF_{is} are defined in Paragraph 7.3.3 and Section 15.1.

NOTE: When calculating the recovery of the $^{37}Cl_4$-2378-TCDD cleanup standard, only one m/z is monitored for this standard;

therefore, only one peak area will be used in the numerator of this formula. Use both peak areas of the $^{13}C_{12}$-1234-TCDD recovery standard in the denominator.

15.5.1 The $^{13}C_{12}$-1234-TCDD is used to quantitate the tetra internal standards and the cleanup standard, and $^{13}C_{12}$-123789-HxCDD is used to quantitate the HxCDD, HpCDF and OCDD internal standards (see Table 8).

15.5.2 If the original sample, prior to any dilutions, has any internal standard with a percent recovery of less than 25% or greater than 150%, reextraction and reanalysis of that sample is required (see Section 17).

15.6 Sample Specific Estimated Detection Limit

The sample specific Estimated Detection Limit (EDL) is the estimate made by the laboratory of 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. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc.

An EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for 2,3,7,8-substituted isomers giving responses for both the quantitation ions that are less than 2.5 times the background level.

Use the formulae below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level (H_x) is determined by measuring the height of the noise at the expected retention times of both the quantitation ions of the particular 2,3,7,8-substituted isomer. The expected retention time is determined from the most recent analysis of the CC3 standard on the same GC/MS system.

ALL MATRICES OTHER THAN WATER

$$\text{EDL (ug/kg)} = \frac{2.5 \times Q_{is} \times (H_x^1 + H_x^2) \times D}{W \times (H_{is}^1 + H_{is}^2) \times RRF_n}$$

WATER

$$\text{EDL (ng/L)} = \frac{2.5 \times Q_{is} \times (H_x^1 + H_x^2) \times D}{V \times (H_{is}^1 + H_{is}^2) \times RRF_n}$$

Where:

H_x^1 and H_x^2 = Peak heights of the noise for both of the quantitation ions of the 2,3,7,8-substituted isomer of interest.

H_{is}^1 and H_{is}^2 = Peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor (see Paragraph 10.4.3).

Q_{is}, RRF_n, W and V are defined in Paragraph 7.3.3 and Section 15.1.

15.7 Estimated Maximum Possible Concentration

An estimated maximum possible concentration (EMPC) is calculated for 2,3,7,8-substituted isomers that are characterized by a response with a S/N of at least 2.5 for both the quantitation ions, but that do not meet all the identification criteria in Section 11.

Calculate the EMPC according to the following formulae:

ALL MATRICES OTHER THAN WATER

$$\text{EMPC (ug/L)} = \frac{(A_x^1 + A_x^2) \times Q_{is} \times D}{(A_{is}^1 + A_{is}^2) \times RRF_n \times W}$$

WATER

$$\text{EMPC (ng/L)} = \frac{(A_x^1 + A_x^2) \times Q_{is} \times D}{(A_{is}^1 + A_{is}^2) \times RRF_n \times V}$$

Where:

A_x^1 and A_x^2 = areas of both quantitation ions.

A_{is}^1, A_{is}^2, Q_{is}, RRF, D, W, and V are defined in Paragraph 7.3.3 and 10.4.3 and Section 15.1.

15.8 Toxicity Equivalency Factor (TEF) Calculation

The 2378-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample is calculated according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Centers for Disease Control (CDC). This method assigns a 2378-TCDD toxicity equivalency factor (TEF) to each of the 17 2,3,7,8-substituted PCDDs/PCDFs shown in Table 11 ("Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs)" March 1989 (EPA 625/3-89/016)). The 2378-TCDD toxicity equivalence of the PCDDs/PCDFs present in the sample is calculated by summing the product of the TEF and the concentration for each of the compounds listed in Table 11.

The exclusion of homologues such as mono-, di-, tri- and the non-2,3,7,8-substituted isomers in the higher homologues does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less than the toxicity of the compounds listed in Table 11. Hence, only the 2,3,7,8-substituted isomers are included in the TEF calculations. The procedure for calculating the 2378-TCDD toxic equivalence cited above is not claimed by the CDWG to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

When calculating the 2378-TCDD toxicity equivalence of a sample, the Contractor shall include only those 2,3,7,8-substituted isomers that were detected in the sample <u>and</u> met all of the qualitative identification criteria in Section 11. Do <u>not</u> include EMPC or EDL values in the TEF calculations. Further instructions regarding the calculation of the 2378-TCDD toxicity equivalence may be found in Exhibit B.

The 2378-TCDD toxicity equivalence of a sample is used in Sections 16 and 17 of this procedure to determine when second column confirmation or reextractions and reanalyses may be required.

16. <u>Isomer Specificity</u>

Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column alone. Historically, problems have been associated with the separation of 2378-TCDD from 1237-TCDD and 1268-TCDD, and separation of 2378-TCDF from 2347-TCDF. Because of the toxicologic concern associated with 2378-TCDD and 2378-TCDF, additional analyses may be required for some samples, as described below.

16.1 If the toxicity equivalence calculated in Section 15 is greater than 0.7 ppb (soil/sediment or fly ash), 7 ppb (chemical waste), or 7 ppt (aqueous), better isomer specificity is required than can be achieved on the DB-5 column. The Contractor may utilize either of the two options listed below to achieve adequate isomer specificity.

16.1.1 The sample extract may be reanalyzed on a 60 m SP-2330 or SP-2331 (or equivalent) GC column in order to achieve better GC resolution, and therefore, better identification and quantitation of the individual 2,3,7,8-substituted isomers.

16.1.2 The sample extract may be analyzed on a single GC column capable of resolving all 2,3,7,8-substituted PCDDs/PCDFs from other isomers, but not necessarily resolving all the non-2,3,7,8-substituted isomers from one another.

Regardless of GC column used, for a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF isomer, it must meet the ion abundance, signal-to-noise, and retention time criteria listed in Section 11. In addition, when using any GC column other than those specified here (DB-5, SP-2330 or SP-2331), the Contractor shall clearly document, in the SDG Narrative, the elution order of all the analytes of interest on any such column.

16.2 For any sample analyzed on a DB-5 (or equivalent) column in which either 2378-TCDD or 2378-TCDF is reported as an EMPC, regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

17. Required Sample Reruns

Due to a variety of situations that may occur during contract performance, the laboratory shall be required to reextract and reanalyze certain samples or groups of samples. Except in the case of dilutions, the term "rerun" shall indicate sample reextraction, cleanup and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed.

When the rerun is required due to matrix effects, interferences, or other problems encountered, the Government will pay the Contractor for the reruns. Such reruns shall be billable and accountable under the specified contract allotment of automatic reruns. When the rerun is required due to Contractor materials, equipment or instrumentation problems, or lack of Contractor adherence to specified contract procedures, the rerun shall not be billable nor accountable under the terms of this contract.

17.1 The following sample reruns may be billable as such under the contract, as defined below.

17.1.1 If the original sample has a percent recovery of any internal standard or the cleanup standard outside of the range of 25-150 percent, then reextraction and reanalysis are required.

NOTE: This rerun is billable only if the Contractor can demonstrate that the internal standards or cleanup standard were added to the original sample in accordance with contract specifications, and that the same standards are out of criteria in the reextraction and reanalysis.

17.1.2 If the internal standards are not present with at least a 10/1 S/N ratio at their respective m/z's (316, 318, 332, 334, 402, 404, 420, 422, 470 and 472), then reextraction and reanalysis are required. If the $^{37}Cl_4$-2378-TCDD is not present with at least a 10/1 S/N ratio at m/z 328, then reextraction and reanalysis are required.

NOTE: This rerun is billable only if the Contractor can demonstrate that the internal standards or cleanup standard were added to the original sample in accordance with contract specifications, and that the same standards are out of criteria in the reextraction and reanalysis.

17.1.3 If any of the internal standard ion abundance ratios as specified in Table 6 are outside the contract specified control

limits, the Contractor must reanalyze the sample extract on a second GC column with different elution characteristics, as discussed in Section 16. No reextraction is required for such an analysis. This reanalysis is only billable if the same internal standard ion abundance ratios are outside the control limits on the second column, indicating matrix effects may have occurred.

17.1.4 If the absolute retention time of either the $^{13}C_{12}$-1234-TCDD or $^{13}C_{12}$-123789-HxCDD recovery standard in a sample extract shifts by greater than 10 seconds from the retention time of that standard in the continuing calibration standard, then the sample extract must be reanalyzed after the Contractor has investigated the cause of the retention time shift and taken corrective action. No reextraction is required for such an analysis. This reanalysis is only billable if the same recovery standard retention time shifts by greater than 10 seconds in the second analysis, indicating matrix effects may have occurred.

17.2 If the calculated concentration of the unlabeled PCDDs/PCDFs exceeded the initial calibration range, the sample extract shall be diluted and reanalyzed (see Section 10.4). Such sample dilutions are billable under the contract.

NOTE: Only one dilution shall be billable per sample and <u>only</u> as an additional analysis with no extraction.

17.3 The following sample reruns shall be performed at the Contractor's expense and shall <u>not</u> be billable under the terms of the contract.

17.3.1 All positive samples associated with a contaminated method blank <u>and</u> any samples which contain peaks that do not meet all of the qualitative identification criteria in Section 11 associated with a contaminated method blank must be reextracted and reanalyzed. Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions that is greater than five percent of the signal of the appropriate internal standard quantitation ion. A peak that meets identification criteria in the method blank must not exceed two percent of the signal of the appropriate internal standard.

17.3.2 If the chromatographic peak separation between $^{13}C_{12}$-2378-TCDD and $^{13}C_{12}$-1234-TCDD is <u>not</u> resolved with a valley of $\leq$ 25% on the DB-5 (or equivalent) column, or 2378-TCDD is <u>not</u> resolved from the closest eluting isomer with a valley of $\leq$ 25% on the SP-2331 (or equivalent) column, then the Contractor shall adjust the GC/MS operating conditions and rerun the affected sample. This criterion applies to sample analyses. If this criterion is not met for a <u>calibration standard</u>, all associated samples must be rerun.

17.3.3 If a false positive is reported for a blind QC sample submitted by the Region, the Contractor shall reextract and reanalyze the entire SDG upon notification by SMO.

17.3.4 If the analysis results for a blind QC sample do not fall within the acceptance windows established by EPA, the Contractor shall reextract and reanalyze the entire SDG upon notification by SMO.

17.4 A native spike and duplicate shall be performed for each group of samples reextracted and reanalyzed under Section 17.3.

17.4.1 If a concurrent PCDD/PCDF SDG is being processed, the native spike and duplicate from that SDG may be shared with the rerun samples if the total number of samples does not exceed 20. The native spike and duplicate data shall be reported in the data packages for both SDGs, but are only billable once, under the original SDG for which they were prepared. If the total number of samples exceeds 20, an additional native spike and duplicate must be analyzed.

17.4.2 If no other PCDD/PCDF SDG is being processed at the time of reanalysis, the native spike and duplicate shall be chosen from the SDG for which the rerun samples are required. The native spike and duplicate analyses are only billable in instances where one or more of the associated rerun samples are also billable.

TABLE 1. SUGGESTED OPERATING CONDITIONS FOR A DB-5 (OR EQUIVALENT) COLUMN

Stationary Phase	DB-5 (or equivalent)
Film Thickness	0.25 um
Column Dimensions	60 m x 0.32 mm
Helium Linear Velocity	35 - 40 cm/sec at 240°C
Initial Temperature	170°C
Initial Time	10 minutes
Temperature Program	increase to 320°C at 8°/minute
Hold Time	until OCDF elutes
Total Time	40-45 minutes

TABLE 2. 2378-TCDD TOXICITY EQUIVALENCY FACTORS (TEFs) FOR PCDDs/PCDFs

Analyte	TEF
2378-TCDD	1.00
2378-TCDF	0.10
12378-PeCDF	0.05
12378-PeCDD	0.50
23478-PeCDF	0.50
123478-HxCDF	0.10
123678-HxCDF	0.10
123478-HxCDD	0.10
123678-HxCDD	0.10
123789-HxCDD	0.10
234678-HxCDF	0.10
1234678-HpCDF	0.01
1234678-HpCDD	0.01
1234789-HpCDF	0.01
OCDD	0.001
OCDF	0.001

Reference: "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs)," March 1989, (EPA 625/3-89/016)

TABLE 3. CONCENTRATION CALIBRATION SOLUTIONS

Analyte	CC1	CC2	CC3	CC4	CC5
2378-TCDD	0.1	0.25	0.5	1.0	2.0
2378-TCDF	0.1	0.25	0.5	1.0	2.0
12378-PeCDF	0.1	0.25	0.5	1.0	2.0
12378-PeCDD	0.1	0.25	0.5	1.0	2.0
*23478-PeCDF	---	---	0.5	---	---
*123478-HxCDF	---	---	1.25	---	---
123678-HxCDF	0.25	0.625	1.25	2.5	5.0
*123478-HxCDD	---	---	1.25	---	---
123678-HxCDD	0.25	0.625	1.25	2.5	5.0
*123789-HxCDD	---	---	1.25	---	---
*234678-HxCDF	---	---	1.25	---	---
*123789-HxCDF	---	---	1.25	---	---
*1234789-HpCDF	---	---	1.25	---	---
1234678-HpCDF	0.25	0.625	1.25	2.5	5.0
1234678-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
$^{13}C_{12}$-2378-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-2378-TCDF	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-123678-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1234678-HpCDF	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-OCDD	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-1234-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-123789-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{37}Cl_4$-2378-TCDD	---	---	0.25	---	---

All concentrations are in ng/uL.

*Supplemental commercial standard. Do not perform %RSD calculations on these analytes. (See Paragraph 7.4.1 for CC3 standard preparation.)

TABLE 4. INTERNAL STANDARD, RECOVERY STANDARD, AND CLEANUP STANDARD SOLUTIONS

INTERNAL STANDARD SOLUTION

Internal Standards	Concentration
$^{13}C_{12}$-2378-TCDD	5 ng/uL
$^{13}C_{12}$-2378-TCDF	5 ng/uL
$^{13}C_{12}$-123678-HxCDD	5 ng/uL
$^{13}C_{12}$-1234678-HpCDF	10 ng/uL
$^{13}C_{12}$-OCDD	10 ng/uL

RECOVERY STANDARD SOLUTION

Recovery Standards	Concentration
$^{13}C_{12}$-1234-TCDD	5 ng/uL
$^{13}C_{12}$-123789-HxCDD	5 ng/uL

CLEANUP STANDARD SOLUTION

Cleanup Standards	Concentration
$^{37}Cl_4$-2378-TCDD	5 ng/uL

TABLE 5. IONS SPECIFIED FOR SELECTED ION MONITORING FOR PCDDs/PCDFs

Analyte	Quantitation Ions		$M-[COCl]^+$
TCDD	320	322	259
PeCDD	356	358	293
HxCDD	390	392	327
HpCDD	424	426	361
OCDD	458	460	395
TCDF	304	306	243
PeCDF	340	342	277
HxCDF	374	376	311
HpCDF	408	410	345
OCDF	442	444	379
Internal Standards			
$^{13}C_{12}$-2378-TCDD	332	334	---
$^{13}C_{12}$-123678-HxCDD	402	404	---
$^{13}C_{12}$-OCDD	470	472	---
$^{13}C_{12}$-2378-TCDF	316	318	---
$^{13}C_{12}$-1234678-HPCDF	420	422	---
Recovery Standards			
$^{13}C_{12}$-1234-TCDD	332	334	---
$^{13}C_{12}$-123789-HxCDD	402	404	---
Cleanup Standard			
^{37}Cl4-2378-TCDD	328	(1)	265
Polychlorinated diphenyl ethers			
HxCDPE	376	---	---
HpCDPE	410	---	---
OCDPE	446	---	---
NCDPE	480	---	---
DCDPE	514	---	---

(1) There is only one quantitation ion monitored for the cleanup standard.

TABLE 6. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDDs/PCDFs

Analyte	Selected Ions	Theoretical Ion Abundance	Control Limits
TCDD	320/322	0.77	0.65 - 0.89
PeCDD	356/358	1.55	1.24 - 1.86
HxCDD	390/392	1.24	1.05 - 1.43
HpCDD	424/426	1.04	0.88 - 1.20
OCDD	458/460	0.89	0.76 - 1.02
TCDF	304/306	0.77	0.65 - 0.89
PeCDF	340/342	1.55	1.24 - 1.86
HxCDF	374/376	1.24	1.05 - 1.43
HpCDF	408/410	1.04	0.88 - 1.20
OCDF	442/444	0.89	0.76 - 1.02
Internal Standards			
$^{13}C_{12}$-1234-TCDD	332/334	0.77	0.65 - 0.89
$^{13}C_{12}$-123678-HxCDD	402/404	1.24	1.05 - 1.43
$^{13}C_{12}$-OCDD	470/472	0.89	0.76 - 1.01
$^{13}C_{12}$-2378-TCDF	316/318	0.77	0.65 - 0.89
$^{13}C_{12}$-1234678-HPCDF	420/422	1.04	0.88 - 1.20
Recovery Standards			
$^{13}C_{12}$-1234-TCDD	332/334	0.77	0.65 - 0.89
$^{13}C_{12}$-123789-HxCDD	402/404	1.24	1.05 - 1.43

TABLE 7. RECOMMENDED SELECTED ION MONITORING DESCRIPTORS

Descriptor 1	Descriptor 2	Descriptor 3	Descriptor 4
243	277	311	345
259	293	327	361
277	311	345	379
293	327	361	395
304	338	374	408
306	340	376	410
316	342	390	420
318	354	392	422
320	356	402	424
322	358	404	426
328	374	408	442
332	376	410	444
334	390	420	458
340	392	422	460
342	402	424	470
356	404	426	472
358	410	446	480
376	446	480	514

The ions at m/z 376 (HxCDPE), 410 (HpCDPE), 446 (OCDPE), 480 (NCDPE) and 514 (DCDPE) represent the polychlorinated diphenyl ethers.

The ions in each of the four recommended descriptors are arranged so that there is overlap between the descriptors. The ions for the TCDD, TCDF, PeCDD and PeCDF isomers are in the first descriptor, the ions for the PeCDD, PeCDF, HxCDD and HxCDF isomers are in the second descriptor, the ions for the HxCDD, HxCDF, HpCDD and HpCDF isomers are in the third descriptor, and the ions for the HpCDD, HpCDF, OCDD and OCDF isomers are in the fourth descriptor.

NOTE: The descriptors used by the laboratory must be documented, and this information must be available for examination during the EPA on-site evaluations.

TABLE 8. RELATIONSHIP OF INTERNAL STANDARDS TO ANALYTES, AND RELATIONSHIP OF RECOVERY STANDARDS TO ANALYTES, INTERNAL STANDARDS AND CLEANUP STANDARD

INTERNAL STANDARDS VS. ANALYTES

$^{13}C_{12}$-TCDD	$^{13}C_{12}$-HxCDD	$^{13}C_{12}$-OCDD	$^{13}C_{12}$-TCDF	$^{13}C_{12}$-HpCDF
TCDD	HxCDD	OCDD	TCDF	HxCDF
PeCDD	HpCDD	OCDF	PeCDF	HpCDF

RECOVERY STANDARDS VS. ANALYTES, INTERNAL STANDARDS AND CLEANUP STANDARD

$^{13}C_{12}$-1234-TCDD	$^{13}C_{12}$-123789-HxCDD
TCDD	HxCDD
TCDF	HxCDF
PeCDD	HpCDD
PeCDF	HpCDF
	OCDD
	OCDF
$^{13}C_{12}$-2378-TCDD	$^{13}C_{12}$-123678-HxCDD
$^{13}C_{12}$-2378-TCDF	$^{13}C_{12}$-1234678-HpCDF
$^{37}Cl_4$-2378-TCDD	$^{13}C_{12}$-OCDD

TABLE 9. PCDD/PCDF ISOMERS IN THE WINDOW DEFINING MIX FOR A 60 M DB-5 (OR EQUIVALENT) COLUMN

Homologue	First Eluted	Last Eluted	Approximate Concentration
TCDD	1368-	1289-	0.5
TCDF	1368-	1289-	0.5
PeCDD	12479-	12389-	0.5
PeCDF	13468-	12389-	0.5
HxCDD	124679-	123467-	1.25
HxCDF	123468-	123489-	1.25
HpCDD	1234679-	1234678-	1.25
HpCDF	1234678-	1234789-	1.25

TABLE 10. SUPPLEMENTAL CALIBRATION SOLUTION

Analyte	Concentration (ng/uL)
23478-PeCDF	4
123789-HxCDD	10
123478-HxCDD	10
123478-HxCDF	10
123789-HxCDF	10
234678-HxCDF	10
1234789-HpCDF	10

The supplemental calibration solution is commercially supplied and is used for preparation of the CC3 solution. (See Paragraph 7.4.1 for CC3 preparation.)

TABLE 11. MATRIX SPIKING SOLUTION

Analyte	Concentration (ng/uL)
2378-TCDD	2.5
2378-TCDF	2.5
12378-PeCDF	6.25
12378-PeCDD	6.25
123678-HxCDF	6.25
123678-HxCDD	6.25
1234678-HpCDF	6.25
1234678-HpCDD	6.25
OCDD	12.5
OCDF	12.5

This solution is prepared in tridecane (or nonane) and diluted with acetone prior to use (see Section 5.18).

TABLE 12. COLUMN PERFORMANCE SOLUTION FOR A SP-2331 (OR EQUIVALENT) COLUMN

Isomer	Approximate Concentrations (ng/uL)
1478-TCDD	0.5
2378-TCDD	0.5
1237/1238-TCDD	0.5

The commercially supplied column performance solution may be combined with the window defining mix, provided that the combined soultion contains the isomers needed to determine that the criteria for both analyses can be met (see Paragraph 7.2.2).

TABLE 13. EXAMPLE ANALYTICAL SEQUENCES

Time	Analysis
	Window Defining Mix
	Column Performance Solution (SP-2331)
Hour 0	CC3
	CC1 (Initial Calibration)
	CC2
	CC4
	CC5
	Blanks and Samples
	o
	o
	o
	o
Hour 12	CC1
	Column Performance Solution (SP-2331)
Hour 0	CC3
	Blanks and Samples
	o
	o
	o
	o
Hour 12	CC1
	Column Performance Solution (SP-2331)
Hour 0	CC3
	Blanks and Samples
	o
	o
	o
	etc.
	CC1 (whenever the sequence does end)

NOTE: Matrix spike and duplicate samples may be analyzed in place of any "sample" listed above.

EXHIBIT G

GLOSSARY

GLOSSARY

ALIQUOT - a measured portion of a sample taken for analysis.

ANALYSIS DATE/TIME - the date and military time of the injection of the sample, standard or blank into the GC/MS or GC system.

BLANK - see Method Blank.

CASE - a finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office. A Case consists of one or more Sample Delivery Groups.

CONCENTRATION CALIBRATION SOLUTION (Table 3) - solutions (tridecane) containing known amounts of selected analytes, five internal standards and two recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CONTINUING CALIBRATION SOLUTION - a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time windows for each homologue. The same solution is used for the mid-level concentration calibration solution, CCB.

DAY - unless otherwise specified, day shall refer to calendar day.

ESTIMATED DETECTION LIMIT (EDL) - the concentration of a analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8-substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level.

ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC) - the concentration of a given analyte that would produce a signal with a given peak area. The EMPC is calculated for 2,3,7,8-substituted isomers for which the quantitation and/or the confirmation ion(s) has signal-to-noise in excess of 2.5 but does not meet identification criteria.

FIELD BLANK - a portion of chemical waste, soil or water that is not contaminated with PCDDs/PCDFs and is submitted with the samples. The field blank is used to check for contamination from the time of sample collection through the time of sample analysis.

HOMOLOGUE - a member or members of a particular homologous series that has the same molecular weight but not necessarily the same structural arrangement. For example, the 28 pentachlorinated dibenzofurans are homologues.

HOMOLOGOUS SERIES - a series of organic compounds in which each successive member has one more atom or group of atoms than the preceding member. The straight chain hydrocarbons and the polychlorinated dibenzo-p-dioxins are examples of a homologous series.

IN-HOUSE - at the Contractor's facility.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations. The initial calibration used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS (Tables 2 and 4) - $^{13}C_{12}$-2378-TCDD, $^{13}C_{12}$-123678-HxCDD, $^{13}C_{12}$-OCDD, $^{13}C_{12}$-2378-TCDF and $^{13}C_{12}$-1234678-HpCDF (in isooctane) are added to every sample and are present at the same concentration in every blank, quality control sample, and concentration calibration solution. The internal standards are added to the sample before extraction and are used to measure the concentrations of the analytes.

ISOMER - chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1234-TCDD and 2378-TCDD are structural isomers.

LABORATORY - synonymous with the term Contractor.

LOW RESOLUTION MASS SPECTROMETRY - a mass spectrometric technique capable of achieving unit mass (i.e., 1 amu) resolution between compounds introduced into the instrument.

MATRIX - the predominant material that comprises the sample to be analyzed. For the purpose of this contract, a sample matrix may be water, soil or chemical waste (including stillbottoms, fuel oil, sludge and fly ash). Matrix is not synonymous with phase (liquid or solid).

METHOD BLANK (previously termed reagent blank) - an analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background contamination.

NARRATIVE (SDG Narrative) - the portion of the data package which includes laboratory, contract, Case and sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete SDG Narrative specifications are included in Exhibit B.

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at 105°C, including water. Percent moisture is determined from decanted samples and from samples that are not decanted.

PERFORMANCE EVALUATION (PE) SAMPLE - a chemical waste, soil or water sample containing known amounts of unlabeled PCDDs/PCDFs.

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) - compounds (Figure 2) that contain from one to eight chlorine atoms. The 15 2,3,7,8-substituted PCDDs (total PCDDs is 75) and PCDFs (total PCDFs is 135) are shown in Table 13. The number of isomers at different chlorination levels is shown in Table 12.

PROTOCOL - describes the exact procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Synonymous with Statement of Work (SOW).

REAGENT WATER - water in which an interferent is not observed at or above the minimum quantitation limit of the parameters of interest.

RECOVERY - a determination of the accuracy of the analytical procedure made by comparing measured values for a fortified (spiked) sample against the known spike values. Recovery is determined by the following equation:

$$\%\text{Recovery} = \frac{\text{measured value}}{\text{known value}} \times 100\%$$

RECOVERY STANDARD (Table 9) - $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD are added to every blank, quality control sample, and sample extract aliquot just prior to analysis and are present in all solutions except the internal standards solutions. Recovery standards are used to measure the recovery of the internal standards. When a dilution is required (see Exhibit D, Paragraph 13.2.5), recovery standards are used to quantitate the native PCDDs/PCDFs; the TCDD recovery standard is used to quantitate the tetra- and penta- isomers and the HxCDD recovery standard is used to quantitate the hexa- through octa- isomers.

RELATIVE RESPONSE FACTOR (RRF) - 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. The RRF is used to determine instrument performance and is used in the quantitation calculations.

RESOLUTION (also termed separation) - the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multipled by 100.

RINSATE - a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

SAMPLE DELIVERY GROUP (SDG) - a unit within a single Case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer samples within a Case, received over a period of up to 14 calendar days. Data from all samples in a SDG are due concurrently. A SDG is defined by one of the following, whichever occurs first:

- o Case; or
- o Each 20 samples within a Case; or
- o Each 14-day calendar period during which samples in a Case are received, beginning with receipt of the first sample in the Case or SDG.

Samples may be assigned to SDGs by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory.

SAMPLE NUMBER (EPA Sample Number) - a unique identification number designated by EPA for each sample. The EPA sample number appears on the sample Traffic Report which documents information on that sample.

SELECTED ION MONITORING - a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SIGNAL-TO-NOISE (S/N) RATIO - the ratio of analyte signal to random background signal. To determine the ratio, display each characteristic ion using a window 100 scans wide, and draw a base line from the lowest point in the 100 scan window. The noise is defined as the height of the largest signal (excluding signal due to PCDDs/PCDFs or other chemicals) within the 100 scan window. The signal is defined as the height of the PCDD/PCDF peak. If the data system determines the ratio, the Contractor shall demonstrate comparability between the above criteria and the automated S/N determination. Chemical noise is left to the judgement of the analyst.

SOIL - synonymous with soil/sediment and sediment.

STANDARD ANALYSIS - an analytical determination made with known quantities of target compounds. The standard analysis is used to determine response factors.

SURROGATES (Surrogate Standard) - the compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard. Surrogates are used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labelled compounds not expected to be detected in environmental media.

TIME - when recording time on any deliverable item, time shall be expressed as military time, (i.e., a 24-hour clock).

TOXICITY EQUIVALENCY FACTOR (TEF) - a method of converting concentrations of PCDDs/PCDFs to an equivalent concentration of 2378-TCDD to obtain an estimation of the toxicity of the entire sample. (Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (CDDs/CDFs), March 1989, (EPA 625/3-89/016).

TRAFFIC REPORT (TR) - an EPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and documents sample condition and receipt by the laboratory.

TWELVE-HOUR TIME PERIOD - the 12-hour time period begins with the injection of the CC3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12-hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be injected within 12:00 hours of the CC3 solution or the column performance solution.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR) - the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Traffic Report.

ABSTRACTED PROCEDURES

PROCEDURES FOR FAST TURNAROUND OF SOILS

1. Always check the sample's chain-of-custody records for special instructions.

2. Weigh out approximately 5 grams of sample to 3 significant figures into a 40 ml vial. Record weight on extraction sheet.

3. Include the 4 laboratory performance samples: 5 grams of Anhydrous Sodium Sulfate, 5 grams of soil blank (OCL34...), 5 grams of soil spike (OCL35...), and a PE sample. Include 1 set of performance samples for each set of 24 or fewer samples.

4. Add 50 ul of Spike I to the soil spike performance sample, then set this sample aside.

5. Add 50 ul of Spike II to all the other samples (excluding soil spike).

6. Add some anhydrous sodium sulfate to all samples.

7. Add 6 ml of 2:1 acetonitrile / methylene chloride extracting solution to all samples. (Additional extracting solution may be added if necessary.)

8. Shake vials well on vortex mixer.

9. Allow sample to extract at least 1 hour, shake samples 3 to 4 more times on mixer during this time.

10. Centrifuge samples at 1500 RPM's for 2 minutes.

11. Pipet off extracting solution into a clean 40 ml vial.

12. Discard original vial with soil into the holding box.

13. Add 10 ml of water to extract, mix and immediately centrifuge for 1 minute.

14. If an emulsion occurs, add approximately 1 to 2 pipets full of methylene chloride and centrifuge without mixing for approximately 5 minutes.

15. Pull off methylene chloride bubble (bottom layer) with a clean syringe and place in a clean 20 ml vial.

16. Evaporate off solvent on the hot plate with N2, just to dryness. (If there is water in the sample, add a few ml of Acetone and dry down.) Add approximately 1 ml of cyclohexane to sample.

17. Proceed to Option A cleanup.

PROCEDURES FOR FAST TURNAROUND OF WATERS

1. Prepare method blank and native spike each using 1 liter of distilled -water. Spike the method blank with 50 ul of Spike II and the native spike with 50 ul Spike II and 3 ng of native.

2. About 1 liter of sample is necessary to obtain good results. Measure out the sample in a clean 1 liter graduated cylinder. Record exact amount on extraction sheet.

3. Pour the sample into a clean 2 liter separatory funnel and place in the ringstand.

4. Spike the sample with 50 ul of Spike II.

5. Measure out 100 ml of methylene chloride, rinse it through the original sample bottle and the 1 liter graduated cylinder, then pour it into the separatory funnel.

6. Shake separatory funnel under the hood, venting frequently to release built up gas.

7. Allow the layers to separate.

8. Drain off methylene chloride extract layer (bottom layer) into a clean 500 ml flask.

9. Repeat steps 5 through 7 two more times so a total of 300 ml of methylene xhloride is used.

10. Rotovap the methylene chloride extract (with water bath set at 50 degrees Celcius and RPM's to 90) until approximately 1 ml of extract is left in the flask.

11. Transfer the sample to a clean 40 ml vial, using 5 ml of methlyene chloride per rinse. Rinse the flask thoroughly, at least 3 times.

12. Dry sample down just to dryness on the hot plate under a stream of N2, then add approximately 1 ml of cyclohexane.

13. Proceed to Option A cleanup.

PROCEDURES FOR FAST TURNAROUND OF WIPES

1. With each set of 24 or fewer wipes, include a blank (Spike II only) and a wipe spike (Spike II and 3 ng of native TCDD, using piece of filter paper.) Always check the sample's chain-of-custody / release form for special instructions. (i.e., they may request a sample to be spiked to certain level with native TCDD, in this case a spike of TMS may not be needed).

2. Extract wipes in their original sample vials if possible, otherwise, place the wipe in a clean, appropriate size vial.

3. Add 50 ul of spike II to each sample.

4. Add enough hexane to just about cover the wipe (but try not to add any more than necessary)

5. Allow samples to extract for at least 1 hour.

6. Pull about 35 ml of the hexane off of the sample and place in a clean 40 ml vial. Dry down hexane on hot plate with N2. If more than 35 ml of hexane were used to extract the sample, continue pulling off the extract, adding to the previous 40 ml vial. Evaporate until dryness. (If more than 100 ml of hexane was used, you may consider filtering the hexane through a Watman 41 filter into a 500 ml flask, then evaporating the hexane on the rotovap to save time.)

7. Add approximately 1 ml of cyclohexane, after evaporating the hexane.

8. Proceed to option A cleanup.

PROCEDURES FOR FAST TURNAROUND OF SWEEPER BAGS

1. With each set of 24 or fewer sweeper bags, include 1 method blank (Spike II only) and one sweeper bag spike (Spike II and 3 ng native TCDD). Use a clean piece of filter paper as the matrix. Be sure to check the sample's chain-of-custody/release form for special instructions. (i.e., if the client sends a sweeper bag to be spiked by TMS, we may not need to do another spike.)

2. Choose an appropriate sized sample vial (a qorpak jar may be needed to hold the entire sweeper bag).

3. Record the weight of each sweeper bag, in case it may be needed later.

4. Add 50 ul of Spike II to each sample.

5. Add enough hexane to the sample to extract it well.

6. If the volume of hexane used to extract the sample is small enough (approximately 100 ml or less), pull off the hexane and dry it down in a 40 ml vial following the same procedure as for wipes. (If the sample is very dirty, you may want to water wash it.)

7. If the volume of hexane is large, filter the sample into a 500 ml flask through a Watman 41 paper filter. Rinse the filter and funnel with clean hexane after all the sample has gone through.

8. Evaporate the solvent on the rotovap (set water bath temperature to 50 degrees Celcius and RPM's to 90) until approximately 1 ml of solvent is left in the flask.

9. Transfer the sample to a clean 40 ml vial doing at least 3 rinses with approximately 5 ml of hexane each.

10. Dry samples to just dryness on the hot plate under a stream of N2.

11. Proceed to Option A cleanup.

PROCEDURES FOR FAST TURNAROUND OF AIR SAMPLES

1. With each set of 24 or fewer air samples, include one method blank (Spike II only) and one air spike (Spike II and 3 ng native TCDD) on foam puffs.

2. For each sample, record the cartridge number printed or etched on the glass cartridge holding the foam puff.

3. Add 50 ul of Spike II to the foam puff (sample).

4. Place the sample (includes glass cartridge, foam puff and filter paper, if present) upside down into a large, clean soxhlet extractor.

5. Place the extractor on top of a clean 1 liter flask.

6. Add 500 ml of methylene chloride to each sample, pouring it into the top of the large extractor and allow it to cycle into the flask.

7. Place the extractor and flask on the hot plate extraction apparatus, fitting the large condenser on top of the extractor and making sure the chiller is turned on. Set the hot plate to six (6).

8. Allow the airs to cycle and extract for at least 4 hours (16 cycles minimum).

9. Shut off the hot plate and allow the flask to cool.

10. Remove the flask and soxhlet with air puff from the hot plate.

11. Cycle as much of the solvent as possible into the flask.

12. Place soxhlet and extracted air puff under a hood.

13. Evaporate off the solvent on the rotovap (set to 50 degrees Celcius and RPM's to 90) until approximately 1 ml of solvent is left in the flask.

14. Transfer the sample to a clean 40 ml vial, with at least 3 flask rinses, approximately 5 ml of methylene chloride with each rinse.

15. Evaporate the solvent on the hot plate under a stream of N2, just to dryness.

16. Proceed to Option A.

PROCEDURES FOR FAST TURNAROUND OF OPTION A CLEANUP

1. Pack silica and alumina columns according to procedure.
2. Place columns in rack, with silica column on top draining into the alumina column.
3. Wet the columns with about 1 ml of clean cyclohexane.
4. As soon as the liquid reaches the surface of the silica column, add the sample in about 1/2 ml of cyclohexane.
5. Wash the columns with 3 x 1 ml portions of clean cyclohexane straight from the cyclohexane stock.
6. Remove the silica column, then wash the alumina column with an additional 1/2 ml portion of clean cyclohexane.
7. Replace the waste vial container with a clean 3.7-ml vial, then elute the dioxin with 3 ml of the methylene chloride in cyclohexane mix. (Place the expended columns and prewashes in reserve, discarding only after the analysis has successfully been performed.)
8. Evaporate the eluate under a stream of nitrogen on the blowdown apparatus, being very careful to take the solution just nearly to dryness, and being careful that the vial is not heated in the dry state.
9. Cap the labeled vial, and put it aside for mass spec analysis.
10. Return to vial rack and replace silica and alumina columns above prewash vial.
11. Elute columns with 4 to 5 ml of CH_2Cl_2 into prewash vial.
12. Discard columns into cold trash and save prewash.

PROCEDURES FOR OPTION D

Column prep:

1. File off pipet (leaving just pipette barrel).
2. Stuff glass wool into nonfiled end of tube and place 1 and 1/2 inches from other end.
3. Add about 3/4 of an inch celite and 3/4 of an inch special carbon (AX-21).
4. Stuff glass wool to keep celite and carbon from moving.
5. If not using columns immediately, place in hexane jar for storage.

Chemical prep:

1. Set up column and prewash vial. Celite side up, carbon down.
2. Add 1 ml benzene wait until it is adsorbed on column.
3. Add 1 ml tertiary solvent mix and wait until it is adsorbed on column.
4. Add 1 ml binary solvent mix and wait until it is adsorbed on column.
5. Add sample and 3 vial rinses of cyclohexane.
6. Add 2 ml binary mix and wait until it is adsorbed on column.
7. Add 1 ml tertiary mix and wait until it is adsorbed on column.
8. Flip column and reverse elute with approximately 7 ml of toluene or until 10 ml vial is two-thirds full.
9. Evaporate just to dryness and transfer to a small 3.7 ml vial with 4 to 5 washes of cyclohexane.
10. Evaporate just to dryness, and place vial aside for GC/MS analysis.

PROCEDURES FOR METHOD #8280 - COLUMN CHROMATOGRAPHY

1. Use large columns for method #8280.
2. Place glass wool into the bottom of each column.
3. For each sample, pack column with 5.0 grams of silica gel and top with sodium sulfate.
4. For each sample, add small amount of sodium sulfate and pack column with 5.0 grams of alumina, top with sodium sulfate.
5. Place silica column on top of alumina column under hood.
6. Elute columns with 20 ml hexane.
7. Add sample followed by 3 washes of sample vial in hexane.
8. Flush columns with 4 - 20 ml portions of hexane.
9. Remove silica column and flush alumina column with 10 ml hexane.
10. Strip alumina with methylene chloride and hexane
    a. 15 ml 25% CH2CL2 in hexane
    b. 15 ml 60% CH2CL2 in hexane
       or (20 ml 60%) only
11. Evaporate samples and blank down to approximately 1 ml.
12. Transfer volume to 3.7 ml vials and wash 40 ml vials with CH2Cl2 2 to 3 times.
13. Evaporate CH2CL2 down to about 0.5 ml (bearly visible)
14. Add recovery standards (25 ul of R.S.)
15. Transfer volume with hexane to autosampler vial.

PROCEDURES FOR ACID-BASE WASH

1. This procedure is performed on any sample which appears to be extremely dirty or oily (black).
2. Weigh out approximately 1.0 g of sample into a 40 ml vial.
3. Spike with appropriate internal standard.
4. Add 20 ml hexane to vial and mix.
5. Allow mixture to shake at least 2 to 3 hours on shaker.
6. Retrieve sample from shaker and add 3 or 4 ml of 20% KOH, shake while venting.
7. KOH should settle to the bottom of vial in a visible layer.
8. Pipet out KOH layer and discard into acid/base waste.
9. Repeat the KOH wash, not to exceed 4 times until KOH layer appears "relatively" clear. (May not need to repeat KOH wash, if first wash is clear.)
10. Wash sample mixture with 5% NaCL approximately 3 or 4 ml.
11. NaCl wash procedure is the same as KOH, only wash once with NaCL, discard pipeted NaCl into acid/base waste.
12. Wash sample with concentrated H2SO4 using 3 or 4 ml.
13. Sample may need centifuging to separate the H2SO4 layer to the bottom of the vial.
14. Pull off H2SO4 layer and discard into acid/base waste. Repeat H2SO4 wash not to exceed 4 times until a clear layer of H2SO4 is reached.
15. Add 3 to 4 ml 7.7 buffer. Shake, let settle and pull off.
16. Clear layer may not be reached after 4 washes, if so, add some Na2SO4 into sample vial and mix.
17. Proceed to option A, using the "big" columns and option D, if needed.

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TMS ANALYTICAL SERVICES STANDARD OPERATING PROCEDURE
EPA CONTRACT LABORATORY PROGRAM

1.0 SAMPLE CUSTODY PROCEDURE - RECEPTION AND LOGGING

1.1 Purpose: to describe procedures for sample reception and logging that will ensure integrity and continuous custody of samples.

1.1.1 Management will notify the Sample Custodians when to expect the arrival of samples. Samples are accepted daily between 9:00 a.m. to 5:00 p.m. If the Project Manager has agreed in advance to accept a shipment of samples from EPA at other times, management will make arrangements to have the Sample Custodians or a designated alternate present to receive the samples.

The Sample Custodians will receive all samples, sign and date all shipping manifests, record date and time of sample receipt, examine all samples and documentation, record all data on the appropriate forms, initiate the preparation of the case file, be responsible for appropriate sample storage, and control access to the samples.

1.2 Upon receipt of a sample shipment, the Sample Custodians shall:

1.2.1 Receive the samples from the carrier in the sample receiving area.

1.2.2 Sign and date the carrier's shipping documents (airbill).

1.2.3 Start a Sample Receipt/Condition Documentation Form for the shipment, recording all required data as it comes available.

1.2.4 Inspect outer shipping container for presence/absence and condition of:

1.2.4.1 custody seals, locks, "evidence tape", etc.
1.2.4.2 container breakage and/or container integrity.

1.2.5 Open the outer shipping container and remove paperwork not attached to individual samples (chain-of-custody, traffic reports, etc.). Sign and date each document as appropriate.

1.2.6 Individual samples will be observed for apparent completeness, damage (intact, broken, leaking, properly iced, etc.).

1.2.7 Presence of sample tags. If present:

1.2.7.1 Record sample tag numbers on the Sample Receipt/Condition Documentation form. A single sample may arrive in more than one container (water samples, in particular, may have more than one container for one sample). All tag numbers for a single sample must be grouped together and recorded with the appropriate SMO number. Samples will be recorded in increasing SMO number order.

1.2.7.2 Compare chain-of-custody records with sample tags. Note if tag numbers are listed on the chain-of-custody. If so, record these numbers in the space provided. Document whether these numbers agree or if there is a discrepancy between chain-of-custody. Check other information (samples preservative, etc.) recorded on the chain-of-custody for agreement with sample tags.

1.2.8 A bound master sample log-in book is maintained for the project. Information contained will include, at a minumum, case number, number of samples received, data and time receive, and notation of any special problems. Record receipt of shipment in EPA/CLP logbook.

1.2.9 Verify and record agreement or non-agreement of information on sample documents (i.e., sample tags, chain-of-custody records, SMO traffic reports, airbills, shipping manifests, etc.). If there is non-agreement, record the problems/inconsistencies for the case file, and inform the document control officer or management who will contact SMO for direction/clarification. Minimum documentation of sample condition will include the following items. (If additional space is needed to document problems, inconsistencies, or observations, this information will be recorded in the CLP-logbook and referenced on the Sample Receipt/Condition Documentation form with the book number and page number of the entry.)

1.2.10 Start a case file by numbering a folder with the case number and placing in the folder the completed sample receipt/condition documentation form, the chain-of-custody records, the SMO traffic reports, sample tags, and all other paperwork relating to receipt of this shipment (Items such as sample tags which might easily fall out of the folder shall be placed in an envelope marked with the case number and placed in the file). If the tag is suspected of being contaminated, is wet, or cannot be removed, place

a memorandum in the file indicating where the tag can be found and why it is not in the file. All tags must be accounted for.

2.0 SAMPLE STORAGE PROCEDURE

2.1 Purpose: to establish procedures for storage of samples and extracts to ensure adequate maintenance of sample integrity.

2.2 Samples will be maintained in the sample storage room. The samples will be stored in the containers in which they arrived. Solid samples not requiring refrigeration will be stored accordingly, while water samples or other samples that may require refrigeration will be stored as required by documentation received with the samples.

2.2.1 Integrity of the sample storage room will be maintained at all times. The Sample Custodian will ensure controlled access to the room. Whenever samples are removed from the sample storage room, all transfers of samples will be accounted for in the appropriate file or analytical record.

2.2.2 Sample extracts will be stored in a sample storage room.

2.2.3 After analysis, sample extracts will be preserved in bottles/vials with teflon-lined septa, and segregated by case number.

2.2.3.1 Within 180 days after data submission, management will authorize the disposal of sample extracts, or

2.2.3.2 Management will provide the sample extracts to the USEPA within seven (7) days after a request by the Sample Management Office (SMO).

3.0 STANDARD OPERATING PROCEDURES FOR DATA ASSEMBLY

3.1 A procedure for organization and assembly of all documents relating to each EPA case will be implemented.

3.2 This procedure will ensure that all documents are compiled in one location for submission to EPA, preferably in single case files in case number order, and are arranged by SMO sample number.

Prepare case file folders:

3.2.1 Using appropriate file folders, assign one folder to each case according to SMO case number.
3.2.2 Place all documents, sample tags, SMO forms, and laboratory-generated data, pertaining to one case in the folder.
3.2.3 Documents should be arranged by document type within the case folders, i.e., all sample tags together, all traffic reports together, all hard-copy Mass Spectra together and in order by SMO number, etc.
3.2.4 These document case files will be filed in one location and stored in a secure area.
3.2.5 The kinds of documents that will be contained in case and sample files are described in Tables I.

3.3 The system may include a document numbering and inventory procedure.

3.3.1 Assignment of accountable numbers to laboratory-generated data.

3.3.1.1 Each document of a case may be inventoried and assigned a serialized number (an identifier) associating it with a particular case and region. For example:

SMO Case #	-	Region #	-	Serialized Document #
232		2		0240

3.3.1.2 All documents pertaining to each case including, but not limited to, the following may be numbered and inventoried:

3.3.1.2.1 Sample traffic records, weekly reports.
3.3.1.2.2 Custody records, sample tags, airbills, internal custody records.
3.3.1.2.3 Laboratory logbooks, personal logbooks, instrument logbooks, benchsheets.
3.3.1.2.4 Laboratory data (sorted by

sample), calibration and quality control results.

3.3.1.2.5 Data summaries and reports.

3.3.1.2.6 All other documents, forms, or records referencing the samples. [The laboratory's name and/or logo should appear on all forms.]

3.3.2 Preparation of a document inventory

3.3.2.1 A document inventory list provides a record of <u>all</u> documents, and their corresponding document numbers, that are included in the completed case file.

3.3.2.2 A separate document inventory list is prepared for each case.

3.3.2.3 The laboratory will retain copies of the document inventory lists for case files purged to NEIC.

3.3.2.4 If case documents are not individually numbered, the number of documents for each document type must be recorded.

4.0 STANDARD OPERATING PROCEDURES FOR TRACKING SAMPLE ANALYSES

4.1 Both the preparation and the analysis of samples will be documented.

4.2 All notebook pages, bench sheets, graphs, computer printouts, chromatograms, GC/MS spectra and other laboratory case related documents will contain the EPA case/sample number, date, signature (initials) of the analyst and other pertinent information.

4.3 Upon completion of analysis, data will be filed in the appropriate case or sample files.

4.4. Copies of QA/QC data will be placed in the appropriate case files.

4.5 Instrument logs will be maintained for each gas chromatograph-mass apectrometer (GC/MS), gas chromatograph (GC).

4.6 Copies of the instrument logs will be placed in the appropriate case files.

4.7 Organic sample preparation and analysis records should be completed on a per case basis, as each step of sample preparation and analysis is completed. All sample preparation information will be documented in laboratory notebook or other appropriate form. All sample analysis data will be documented using instrument logbooks, computer printouts, chromatograph tracings, analyst's laboratory notebooks, and/or other laboratory documents. When sample preparation or analysis is finished, the completed documents should be placed in the appropriate sample and/or case files.

4.8 If for any reason the original data cannot be placed in a sample/case file, this shall be documented and the location of the original data noted on the case file inventory.

4.9 All notes, comments and calculations made on or added to case related data/documents will be signed and dated by the author/analyst/reviewer.

4.10 Corrections made to any documents placed in the case files shall be made as follows:

4.10.1 Draw a single line through the incorrect data.
4.10.2 Initial and date the line.
4.10.3 Write in the correct data.

4.11 All data will be recorded in ink.

5.0 STANDARD OPERATING PROCEDURES FOR HANDLING CONFIDENTIAL DOCUMENTS

5.1 All documents received with a group of samples and/or generated in the course of their analysis shall be kept confidential. Standard Business Records Confidentiality practices shall apply.

5.2 Documents specifically marked CONFIDENTIAL that may accompany the samples, are to be treated separately from other case-related documents.

5.3 Procedures for handling documents marked CONFIDENTIAL:

5.3.1 Contact SMO to assure that receipt of these document(s) is correct and necessary for analysis of the samples. If not required for analysis, return as directed by SMO.

5.3.2 If the document(s) are necessary to execute the sample analyses, place the document(s) in a secure file separate from the regular files and under the control of a designated individual. This individual keeps this file of confidential document(s) secure at all times and only allow authorized personnel access on an as needed basis.

5.3.3 Receipt of confidential documentation, its use, duplication, and ultimate disposition shall be documented in a Confidential Document Log. Duplication of confidential documents shall be kept to a minimum and done with the concurrence of the Project Officer or his deputy.

5.3.4 Management shall remove and retain for one year the cover sheet of any confidential material disposed of and note the disposition in the Confidential Document Log. Disposal of confidential documents should only be done at the direction of the EPA Project Manager and/or the EPA Contracting Officer.

6.0 STANDARD OPERATING PROCEDURES FOR DOCUMENT/DATA PACKAGE SHIPPING

6.1 The delivery schedule of data/documents will be as described in Exhibit B of the Statement of Work.

6.2 The shipping of data/documents will be documented. The information documented will include the following:

6.2.1 Date shipped
6.2.2 Addressee
6.2.3 What was sent, including case number, if appropriate
6.2.4 Method of shipment (Federal Express, UPS Overnight, First Class Mail, etc.)
6.2.5 Airbill or invoice number, if applicable
6.2.6 By whom sent

6.3 All data/documents shipped shall have custody seals placed so that opening the package will cause the seals to be broken.

6.4 The method used must assure delivery to each user (the Region, SMO, and EMSL) at the same time. In the event the packages cannot be shipped at the same time, priority shipping shall be given to the Region's data package.

6.5 A list of data/documents shipped should be retained.

6.6 The case files shall be purged in accordance with the schedule in Exhibit B of the Statement of Work and these documents will be shipped as stated above.

7.0 SAFE HANDLING AND DISPOSITION OF HAZARDOUS MATERIALS

7.1 Purpose: to provide general procedures and guidelines for the safe handling and disposition of hazardous materials.

7.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined: therefore, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory shall maintain a file of material safety data sheets regarding the safe handling of the chemicals specified in this method.

7.2.1 The following precautions for safe handling of 2,3,7,8-TCDD in the laboratory are presented as guidelines only, and are based on safe handling practices included in USEPA Method 613.(4). The precautions for safe handling and use are necessarily general in nature because detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual usage. Although 2,3,7,8-TCDD is extremely toxic to laboratory animals, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

7.2.1.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.

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

7.2.1.3 Personal Hygiene: Thorough washing of hands and forearems after each manipulation and before breaks (coffee, lunch, and shift) with any mild soap and plenty of scrubbing action.

7.2.1.4 Confinement: Isolated work area, posted with signs; segregated glassware and tools; and plastic-backed absorbent paper on benchtops.

7.2.1.5 Waste: Good technique includes

minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors should not handle wastes.

7.2.1.6 Disposal of Wastes: 2,3,7,8 - TCDD decomposes above 800 degrees Celcius. Waste should be packaged securely and disposed through commercial or governmental channels that are capable of handling high-level or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container; residues may then be handled as above. Metal containers, lined with plastic bags shall be available in the laboratory areas so that any contaminated glassware can be immediately placed in the container. When the container is full, the lid will be crimped shut and then labeled as contaminated glassware.

7.2.1.7 Glassware, Tools and Surfaces: Satisfactory cleaning may be accomplished by rinsing with 1,1,1-trichloroethane, then washing with any detergent and water. Dishwater may be disposed to the sewer. Organic rinses should be disposed of as mentioned above.

7.2.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under Section 7.2.1.6. Lab coats or other clothing worn in 2,3,7,8-TCDD work may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing. Disposable garments may be used to avoid a laundry problem, but they must be properly disposed or incinerated.

7.2.1.9 Wipe Test: A useful method to determine cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, which is extracted and analyzed by gas chromatography (limit of sensitivity of approximately 0.1 ug per wipe). Less than 4 pg/cm2 2,3,7,8-TCDD indicates acceptable cleanliness; anything higher warrants further cleaning. More than 400 pg/cm2 indicates

an acute hazard that requires prompt cleaning before further use of the equipment or work space and indicates that unacceptable work practices have been employed in the past.

7.2.1.10 Inhalation: Any procedure that may produce airborne contamination should be performed with good ventilation. Gross losses to a ventilation system are not allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident. Finely divided soils contaminated with 2,3,7,8-TCDD are hazardous because of the potential for inhalation. Such samples should be handled in a confined environment, such as a hood or glove box, or laboratory personnel should wear masks fitted with a particulate filter and charcoal sorbent.

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

TMS ANALYTICAL SERVICES STANDARD OPERATING PROCEDURE
EPA CONTRACT LABORATORY PROGRAM

8.0 GLASSWARE CLEANING PROCEDURES

8.1 Purpose: to establish a procedure for cleaning analytical glassware to ensure that sample integrity is not violated by contaiminated glassware.

8.2 Procedures are as follows:

8.2.1 Wash with Hexane once, draining the washings into the contaminated solvent storage containers.

8.2.2 Wash with Acetone once, draining the washings into the contaminated solvent storage containers.

8.2.3 Wash glassware with phosphate-free detergent (e.g., Alcanox). Rinse thoroughly with tap water.

8.2.4 Rinse with acetone and hang on glassware rack to dry.

8.2.5 After glassware is dry, store inverted in appropriate clean environment.

NOTE: Disposition of potentially contaminated organic solvents used to rinse glassware should follow procedure

Laboratory: TMS ANALYTICAL SERVICES, INC.

SIGNATURE LIST

NAME	INITIALS	SIGNATURE	INITIALS	EMPLOYMENT DATES	TYPE OF WORK
Stephen A. Barnett	SAB		SAB	10 / 24 / 88 -	Vice President of Operations
Dawn Beck	DB	Dawn Beck	DB	2 / 21 / 90 -	Scientist
Helen A Benningfield	HAB	Helen Ann Benningfield	HAB	1 / 8 / 90 -	Assistant Scientist
Diana M. Daniels				1 / 23 / 89 -	Administrative Assistant
Dan W. Delinger				4 / 14 / 86 -	Client Services
Kevin L. Dice	KLD	Kevin L Dice	KLD	1 / 22 / 90 -	Laboratory Technician
Melony G. Dolletzki	MGD	Melony G. Dolletzki	MGD	5 / 22 / 89 -	Laboratory Technician
Don G. Eickhoff	DGE		DGE	2 / 20 / 89 -	Environmental Analyst
Diane M. Ely	DME		DME	2 / 5 / 90 -	Receptionist
Dennis L. Heuring	DLH	Dennis L. Heuring	DLH	4 / 2 / 82 -	President
Kelly E. Mills	KEM	Kelly E. Mills	KEM	5 / 27 / 86 -	Senior Scientist
Michelle Y. Morgenstern	MYM	Michelle Y. Morgenstern	MYM	9 / 25 / 89 -	Scientist
Julie K. Noble	JKN	Julie K. Noble	JKN	3 / 2 / 87 -	Asst. Taga Operator
Jane E. Stevenson	JES	Jane E. Stevenson	JES	9 / 11 / 89 -	Office Manager
John L. Wagner	JLW	John Loren Wagner	JLW	10 / 23 / 89 -	Laboratory Technician

Laboratory: TMS Analytical Services, Inc.

SIGNATURE LIST

NAME	INITIALS	SIGNATURE	INITIALS	EMPLOYMENT DATES	TYPE OF WORK
Rita M. Bahner	RMB	Rita M. Bahner	RMB	4 / 2 / 90 - / /	VP of Marketing and Public Relations
John S. Murray	JSM	John S. Murray	JSM	4 / 23 / 90 - / /	Manager of Inorganics and Organics
				/ / - / /	
				/ / - / /	
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				/ / - / /	

Laboratory: TMS ANALYTICAL SERVICES INC
Part -Time Employees

SIGNATURE LIST

NAME	INITIALS	SIGNATURE	INITIALS	EMPLOYMENT DATES	TYPE OF WORK
Bruce McGathey	BLM	Bruce L. McGathey	BLM	1/31/89 -	Laboratory Technician
Roland L. Hodges				10/25/88 -	Scientist
James Swarting				10/25/89 -	Laboratory Technician
Tonya Pohl				1/9/89 -	Laboratory Technician
Jason Ty Sibbitt	JTS	Jason Ty Sibbitt	JTS	4/6/89 -	Laboratory Technician
				/ / -	
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10.0 BALANCE CHECK PROCEDURE

10.1 The toploading balances will be checked as follows:

10.1.1 After cleaning the pan thoroughly, the tare bar will be pressed to set the balance to zero.

10.1.2 The 10 g weight will be placed on the balance and the weight observed. If the balance reads within 0.01 g of the nominal weight, record the balance as calibrated. If this is not met, adjust the balance until this criterion is met and record accordingly.

10.1.3 The 10 g weight will be verified on a quarterly basis againast the set of NBS traceable class S weights.

11.0 SAMPLE IDENTIFICATION PROCEDURES

11.1 PURPOSE: Establish procedures to create and maintain sample identity.

11.1.1 In order to maintain sample identity, each sample received must have a unique sample identification (sample ID) number. Two methods of numbering are discussed below:

11.1.2 SMO Sample Number

Sample containers are typically labeled with SMO sample numbers with the following format:

XXYYYY

where "XX" represents a letter prefix, and "YYYY" represents a four (4) digit number.

These numbers may be used by the laboratory for continuous identification of the sample from receipt to completion of analysis. Each fraction can be identifiedby using the SMO number and a suffix. For example, a BNA extract could be identified as XXYYYY-BNA.

11.1.3 Laboratory Assigned Number

The laboratory may assign any unique number to each sample received. However, adequate cross-reference between the laboratory number and the SMO number should be monitored in the sample receipt and data summary documentation.

11.2 Sample containers (ie, bottles and extract vials) should be clearly identified with the appropriate sample numbers. Suggested guidelines for numbering sample containers are listed below:

11.2.1 During the sample receiving process, the sample custodian or other appropriate personnel will assure that each sample container is identified with a unique sample ID number and that this number is recorded in the sample receipt documentation. If a laboratory ID number is to be used, the number will be reco*rded on label and the label attached to the sample container for written on the container label.

11.2.2 The sample custodian will then remove the sample tag and place it in the appropriate case file. If stick- on labels are used instead of tie-on sample tags, this fact should be noted in the comment section of the log-in sheet. If tags are disposed of due to suspected contamination, this disposal should be noted on the sample receipt documentation.

11.2.3 Extract vial numbers should correspond to the sample numbers they originated from. These numbers should be recorded on the sample tracking documentation. Extract vials will have the sample ID numbers affixed in a manner to assure that the identities of the extracts are maintained.

12.0 CASE FILE PURGE

12.1 PURPOSE: To define procedures for CLP Contract Case File Purge.

12.1.2 Submit case file 180 days after EDS or within 7 days after receipt of written request by PO or SMO.

EPA case file purging will be monitored and maintained on a monthly basis. The Document Control Officer will be responsible for the identification and disposition of case files.

12.2 The Sample Log Book will be the reference point to be used in identifying case files for purging.

12.2.1 Identify all cases with a six month old or older completion date.

12.2.2 Note in log book the month the case file is being purged.

12.2.3 Pull case file.

12.2.4 Copy Document Inventory form from case file.

12.3 All files to be purged are to documented on the **Sample Management Office Case File Purge Inventory Log** (exhibit 1).

12.3.1 Record case number.

12.3.2 Record purge date.

12.3.3 Record original case file date of receipt.

12.3.4 File case in shipping carton.

12.4 Once shipping carton is filled, prepare for distribution.

12.4.1 Copy **Sample Management Office Case File Purge Inventory Log** form.

12.4.2 Prepare case file purge cover letter (exhibit 2).

12.4.3 Place inventory and letter in sealed envelop inside shipping carton.

12.4.4 Seal carton.

12.4.5 Prepare address label to the following address:

Mr. Jeff Worthington
TECH LAW
12600 W. Colfax Avenue
Suite C310
Lakewood, CO 80215

12.4.6 Place label on carton and protect with shipping tape.

12.4.7 Prepare appropriate UPS materials for ground shipping.

12.5 File Case File Inventory and Document Inventory forms in the EPA Case Purge file.

STATEMENT OF QUALIFICATIONS FOR DIOXINS

TMS ANALYTICAL SERVICES, INC.

7726 Moller Road Indianapolis, Indiana 46268 317-875-5894 FAX 317-872-[illegible]

STATEMENT OF QUALIFICATIONS FOR DIOXINS

1. **Name, address, and telephone number of laboratory:**

   TMS Analytical Services, Inc.
   7726 Moller Road
   Indianapolis, IN 46268

   Phone Number 317-875-5894
   FAX Number 317-872-6189

2. **Contact persons:**

   Primary contact: Janet Sachs
   Secondary contact: Jay Shearard

3. **Description of analytical procedures:**

   CLP Method for Isomer Specific Analysis of 2,3,7,8-TCDD/TCDF

   EPA Region VII "Protocol for Analysis of Soils and Sediments for 2,3,7,8-TCDD by Tandem Mass Spectrometry" as outlined in the RFP WA87-J060.

   EPA Method 8280, latest revision by EPA HQ Staff

   EPA Method 1613, latest revision by EPA HQ Staff

NOTE: All procedures are performed to CLP laboratory standards wherever applicable. All sample extraction procedures, sample cleanup procedure, computational procedures, report formats, methods cited above. Clients may specify specific sample cleanup procedures from the literature if desired. If it is necessary to use a procedure from another source, such as a literature reference or a procedure desired by EPA, these requirements are applied to that procedure to the extent that they are applicable.

4. **Instrumentation description:**

   VG AutoSpec EBE geometry computer controlled double focusing mass spectrometer with OPUS data analysis and chemical information system

   Sciex TAGA 6000E Tandem Mass Spectrometer

   Hewlett-Packard 5970 MSD with RTE-A Computer Data System

   Hewlett-Packard 5985 Mass Spectrometer with RTE Data System

5. **Detection limits:**

For GC/MS Analysis:

Soil/Sediment:	20-50 ppt for 2,3,7,8-TCDD
	10-25 ppt for 2,3,7,8-TCDF
	~100 ppt for PeCDD/PeCDF
	~100 ppt for HxCDD/HxCDF
	~200 ppt for HpCDD/HpCDF
	~500 ppt for OCDD/OCDF
Water:	0.1-0.5 ppt for 2,3,7,8-TCDD
	0.1-0.5 ppt for 2,3,7,8-TCDF
	~1 ppt for PeCDD/PeCDF
	~1 ppt for HxCDD/HxCDF
	~2 ppt for HpCDD/HpCDF
	~2 ppt for OCDD/OCDF

For GC/MS/MS Analysis:

Soil, Sediment, and Other Solids:

1.0-5.0 ppt for 2,3,7,8-TCDD or TCDF

Water: 0.2-0.5 ppt for 2,3,7,8-TCDD or TCDF

Detection limits are highly dependent upon the sample matrix and must be calculated for each analysis. In general, if the samples are normal type samples that are relatively clean, these detection limits can be routinely met. If, however, soil samples come from chemical waste disposal sites, or include asphalt, oils, tar, etc. then detection limits can rise sharply. The instrumental sensitivity is rarely the limiting factor. Both the HRMS and GC/MS/MS techniques offer more certainty for achieving the desired detection limits because of their selectivety, but only the tandem option is suitable for rapid sample screening at low cost.

6. **Sample capacity:**

The laboratory is currently capable of processing approximately 100 samples per week for total PCDD's and PCDF's by Method 8280, depending on the sample matrix. An additional 250-300 samples per week can be processed for GC/MS and/or GC/MS/MS analysis of samples for 2,3,7,8-TCDD.

7. **Sample turn-around:**

Sample turn-around is normally three weeks from date of receipt. Other turn-around times are available with special arrangement.

The laboratory has been a very high volume, quick turn-around support laboratory for EPA and can process on a one-day turn-around basis as many as 300 TCDD samples per week for analysis by tandem mass spectrometry according to EPA protocol. In addition, for two years the laboratory was the sole support for quick turn-around dioxin analysis for EPA Region VII in the Times Beach, MO area, amassing a record of better than 99% on-time delivery for 16-hour data turn-around. The broad range of instrumentation, methodology, and personnel ensure that client needs are achieved promptly without sacrificing accuracy or precision.

FACILITY DESCRIPTION

TMS Analytical Services, Inc. occupies a 17,000 square foot facility located in Indianapolis, IN, approximately 15 minutes from the airport. The facility contains separate dedicated laboratory preparation rooms with state of the art air handling and exhaust systems, three dedicated mass spectrometry laboratories, an inorganic laboratory, dedicated glassware cleaning area, and document control areas.

TMS has the capability to perform standard GC/MS and GC/HRMS methods as well as a variety of specialized MS/MS methods. The laboratory staff includes low resolution, high resolution, and tandem mass spectrometer operators, along with staff experienced in sample preparation. The laboratory holds national EPA contracts for the analysis of samples for dioxin, and is one of the few laboratories in the CLP program for such analysis.

Laboratory equipment available includes gas chromatographs, liquid chromatographs, assorted spectrophotometers, and support equipment. The principle laboratory instrumentation includes a sophisticated tandem quadrapole mass spectrometer, an EBE geometry computer controlled double focusing mass spectrometer, as well as conventional Hewlett-Packard GC/MS systems.

The tandem quadrapole mass spectrometer is a top-of-the-line SCIEX TAGA 6000E. The instrument is equipped with extended mass range to 1500 amu, and all available interfaces including GC, APCI, LPCI, LC, probes, and gas sampling. The instrument is computer controlled and is capable of all forms of MS/MS operation, including SIM, parent/daughter SIM, parent scans, daughter scans, and neutral loss scans. The instrument is cryopumped and capable of handling continuous gas loads directly into the source as high as 40 ml/min. The low pressure CI source is a bright Townsend discharge that generates an extremely high ion density.

The high resolution mass spectrometer is a VG AutoSpec hybridized magnetic sector with OPUS data analysis and chemical information system. The present configuration includes, EI, CI, and probe sources. Due to the great sensitivity of this instrument, an injection of 1 picogram of 2,3,7,8-TCDD shows a signal-to-noise ratio greater than 500:1.

The conventional Hewlett-Packard GC/MS systems are capillary gas chromatographs coupled with mass selective detectors. The data system supporting the three GC/MSD units is an HP 1000 A-Series computer, Real-Time Executive (RTE-A) operating system, HP mass spectrometer applications/data reduction software and HP peripheral hardware (scanning interface, disc drives, terminals, printers, etc.) It controls or assists in instrument tuning, data acquisition, data reduction, report production and automation.

PAST PERFORMANCE

TMS Analytical Services has been performing rapid turn-around Dioxin analysis since 1984. The following is a partial listing of Government contracts that TMS has received during the past few years:

Contract #	Agency	Type of Contract	Type of Work
2142G	VIAR/EPA	SAS	Rapid Turnaround Dioxin Analysis
4948C	VIAR/EPA	SAS	Method 8280 PCDD/PCDF Analysis
2212G	VIAR/EPA	SAS	Rapid Turnaround Dioxin Analysis
2204G	VIAR/EPA	SAS	Rapid Turnaround Dioxin Analysis
4761B	VIAR/EPA	SAS	Method 8280 PCDD/PCDF Analysis
2205G	VIAR/EPA	SAS	Rapid Turnaround Dioxin Analysis
2691X	VIAR/EPA	SAS	Rapid Turnaround Dioxin Analysis
4761B	VIAR/EPA	SAS	Method 8280 PCDD/PCDF Analysis
2843G	VIAR/EPA	SAS	Rapid Turnaround Dioxin Analysis
4246A	VIAR/EPA	SAS	Method 8280 PCDD/PCDF Analysis
4470C	VIAR/EPA	SAS	Method 8280 PCDD/PCDF Analysis
4430G	VIAR/EPA	SAS	Method Develop. Dioxin Analysis
68-01-7390	VIAR/EPA	CLP	Rapid & RAS Dioxin Analysis
5615-G	VIAR/EPA	SAS	Method 8290 PCDD/PCDF Analysis

In addition to performing CLP government contract work, TMS has performed dioxin analysis for a wide variety of private clients. References from both EPA and private clients are available upon request.

SAMPLING AND DATA REPORTING INFORMATION

QA/QC procedures:

TMS Analytical Services was one of the few laboratories in the U.S.EPA Contract Laboratory Program designated for the analysis of dioxin, and routinely analyzes samples from various EPA regions. TMS follows U.S.EPA guidelines regarding sample preparation, reporting, and QA/QC requirements. Brief descriptions of these guidelines can be provided upon request. Specific QA/QC descriptions are also given in the methodology for Rapid Analysis of TCDD by Tandem Mass Spectrometry; Isomer Specific Analysis of 2,3,7,8-TCDD; Analysis of Polychlorinated Dibenzodioxin and Polychlorinated Dibenzofurans by Analysis of Polychlorinated Dibenzodioxin and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (Method 8290).

The prices for analyses include the final summary report and all laboratory QA/QC requirements. EPA procedures require that a laboratory method blank be run with each set of samples, as well as daily calibration checks and, in some cases, column performance checks. These samples are supplied by TMS at no cost. However, EPA programs also usually include a requirement to duplicate one or more samples in each shipment, and also frequently require that duplicate samples be spiked with known quantities of the PCDD/PCDF's. Requirements for this type of sample are at the discretion of the client and are billable at the quoted prices.

If no samples are designated for QA/QC purposes, the laboratory shall include the minimum number of QA/QC samples required to fulfill EPA requirements. These samples are billable at the quoted price and serve to ensure the reliability of the data.

Sampling procedures:

Samples may be submitted in any of the recommended standard EPA packaging. For solid samples, either wide-mouth bottles (such as Qorpak bottles available from American Scientific Products or specially cleaned containers available from I-Chem) should be used. A minimum of 10 grams for a single attempt is required; however, a sample size of 50-100g is recommended be sent to allow for any necessary repeat analysis. For water samples, two one-liter bottles are required, one for analysis and one for any necessary reanalysis. Adsorptive materials must not be used for sampling water. Please consult EPA procedures before sampling. EPA requires water samples be maintained at 0-4 degrees C., and all samples should be protected from light. It is the client's responsibility to ship the sample in compliance with DOT regulations.

Please note that all samples will be returned after analysis. Final disposal of these samples is the responsibility of the submitting laboratory. This is necessary since even if samples are negative for dioxins and furans, they may contain other hazardous materials. If found to be hazardous, these samples can usually be returned to the original site, provided agreement is obtained with the appropriate agencies.

Turn-around times:

Turn-around times from receipt of sample at TMS are as follows:

Rapid Analysis of TCDD/TCDF	48 Hours
Method 8280 (Congeners)	30 Days
Method 1613 (High Resolution)	45 Days

Faster turn-around may be available with special arrangement. If such is the case, verbal results will be given within the specified time period, with written copy following seven (7) days after verbal notification. Turn-around times listed are for soil, sediment, still bottoms, sludges, fly ash, water, air filters, wipe samples, etc., which are amenable to cleanup by standard EPA cleanup procedures. For complex matrices that are not adequately cleaned up by standard EPA procedures (such as asphalt, tar, etc.), or for requirements for unusually low detection limits (such as 1 ppt in paper sludge, 1 ppt in fish tissue, etc.), turn-around times guarantee the completion of one attempt by standard EPA cleanup procedures, as outlined in the appropriate methodology, on or before the due date.

Limits of detection:

Limits of detection are calculated for each sample based on signal-to-noise ratios for the carbon-13 labeled internal standards used. This limit of detection is somewhat matrix dependent, but for 2,3,7,8-TCDD in normal samples, limits of detection below 300 ppt are readily achieved for soils, sediments, and similar samples; limits of detection below 1 ppt are readily achieved for most water samples. Guidelines for the limits of detection to be expected for other congener groups in other matrices are given in the appropriate methodology. Results comparable to these are guaranteed. If lower detection limits are needed, requests must be made in advance. For most solid matrices, detection limits at or below 10 ppt can be reached.

Quantitation range:

The quantitation range is generally set to give maximum accuracy close to the action levels for dioxins and furans, i.e., close to 1 ppb for solids and 1 ppt for water. Values above 20 times this level are outside the calibration range, but are reported as extrapolated values. If a sample is known to be heavily contaminated and an accurate number at that high level is needed, the analysis can be adjusted accordingly with advance notice.

Transmission of results:

Results are transmitted first either by telephone, by FAX, or directly to the client's computer. This initial notification of results is then followed by hard copy of the final analytical report showing sample identification and results.

Billing policy:

Although the large majority of samples are cleaned up and successfully analyzed by standard EPA cleanup procedures, some samples do not yield results on the first analysis attempt. If this occurs, the client is notified that a repeat analysis is underway. If the client does not wish to pursue the analysis further and does not wish that analysis repeated, there is no charge for the first attempt. If the client does wish to proceed, and the sample yields valid results upon re-analysis, the client is charged only for the valid result. However, if the sample again does not yield valid results and QA/QC criteria are met for the method controls and related sample groups, the EPA cleanup methods are assumed to be inadequate to handle that sample matrix and the client is charged the billable price. If the client desires, further method development work can be done at a mutually agreed upon rate.

Certain classes of complex matrix samples are known to give serious problems with every known cleanup method, particularly when coupled with a need for low limits of detection. For this type of sample, the client will be informed in advance that the billable price will be applied to all analysis attempts.

Invoicing will be itemized, completed, and mailed the same day as the final hard copy report. Payment is due upon receipt.