United States
Environmental Protection
Agency

Office of
Solid Waste and
Emergency Response

Publication 9240.1-22
EPA/540/R/94/089
PB95-963520
December 1994

Superfund

EPA

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK FOR ANALYSIS OF

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

MULTI-MEDIA, MULTI-CONCENTRATION

DFLM 01.1

9240.1-22
PB95-963520
EPA540/R-94/089

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR ANALYSIS OF

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD)

AND POLYCHLORINATED DIBENZOFURANS (PCDF)

Multi-Media, Multi-Concentration

Document Number DFLM01.0

Including Revision DFLM01.1 (September 1991)

STATEMENT OF WORK

TABLE OF CONTENTS

EXHIBIT A

SUMMARY OF REQUIREMENTS

Table of Contents

SECTION I

GENERAL REQUIREMENTS

A. Purpose of the Statement of Work

Under the legislative authority granted to the U.S. Environmental Protection Agency (EPA) under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA), EPA develops standardized analytical methods for the measurement of various pollutants in environmental samples from known or suspected hazardous waste sites. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) are among the pollutants that are of concern to EPA at such sites. PCDDs/PCDFs are believed to be among the most toxic organic compounds ever released into the environment.

With the advent of the Superfund program in 1980, EPA required the analyses of many more environmental samples than could possibly be handled through its own laboratories. Therefore, EPA elected to procure analytical services through commercial laboratories and established the Contract Laboratory Program (CLP) as a means of obtaining standardized analyses on a long-term firm, fixed-price basis. This Statement of Work (SOW) provides a technical and contractual framework for laboratories to apply EPA analytical methods to the analysis of PCDDs/PCDFs in environmental samples. The SOW provides not only the analytical methods to be applied, but also the specific technical and contractual requirements by which EPA will evaluate the data.

B. General Requirements

This SOW provides an analytical method for the isolation, detection and quantitative measurement of PCDDs and PCDFs in water, soil, fly ash, and chemical waste samples such as oil, sludge, and stillbottoms. There are 210 possible PCDD/PCDF isomers, and the methods were developed for the analysis of the 17 PCDDs/PCDFs that bear chlorine atoms in the 2,3,7 and 8 positions of their respective structures. These 17 compounds, termed the "2,3,7,8-substituted PCDDs/PCDFs," are those PCDDs/PCDFs that, based on structure activity relationships, are believed to pose the greatest risks to human health and the environment. The SOW also requires determination of the total concentrations of all PCDDs or PCDFs in a given level of chlorination (i.e., Total TCDD, Total PecDD, etc.), although complete chromatographic separation of all 210 PCDDs/PCDFs is not possible under the instrumental conditions described in the method.

The SOW requires the calculation of the 2378-TCDD toxicity equivalence using the procedures described in the "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). To aid in the assessment

of risks associated with exposure to these compounds, a factor is assigned to each of the 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. The concentrations of any isomers that are detected in an environmental sample can then be adjusted by the toxicity equivalency factor (TEF) and summed, yielding a concentration of 2378-TCDD with an equivalent toxicity.

Because isomer specificity for all 17 2378-substituted PCDDs/PCDFs may not be achieved using a single gas chromatographic column, the SOW requires analysis of sample extracts on a second column when the TEF-adjusted concentration exceeds a specified level. This level varies by sample matrix.

The sample preparation procedures in the SOW use matrix-specific extraction techniques and a single set of cleanup techniques. The sensitivity of this method is dependent upon the level of interferents within a given sample. Interferents co-extracted from the sample may vary considerably from source to source, depending on the origin of the sample and the matrix type. PCDDs and PCDFs are often associated with other chlorinated compounds such as PCBs and polychlorinated diphenyl ethers which may occur at concentrations several orders of magnitude higher than that of the analytes of interest and may cause interference problems.

The samples to be analyzed by the Contractor are from known or suspected hazardous waste sites and may contain hazardous organic and/or inorganic materials at high concentration levels. The Contractor should be aware of the hazards associated with the handling and analysis of these samples. The Contractor is responsible for taking all necessary measures to ensure the health and safety of its employees.

The Contractor must be aware of the importance of maintaining the integrity of the data generated under the contract, as data may be used to make decisions regarding public health and environmental welfare. In addition, the data may be used in litigation against potentially responsible parties in the enforcement of Superfund legislation.

C. Applications and Limitations of the Statement of Work

This SOW is designed as part of the documentation for a contract between EPA and a commercial laboratory performing analyses in support of EPA Superfund programs. The resulting data may be used by EPA for a variety of purposes, such as determining the nature and extent of contamination at a hazardous waste site, assigning administrative priority to such sites based on the risk of exposure, determining appropriate cleanup actions, and determining when remedial actions are complete.

The methods described in this SOW are designed for the analysis of specific analytes in specific environmental matrices and over a limited concentration range. However, this SOW is not suitable for all analytical situations and should not be applied to matrices, analytes,

or concentration ranges for which it was not intended. Similarly, the contractual requirements embodied in the SOW apply only to those analyses performed by commercial laboratories through the CLP. Therefore, other organizations wishing to procure analytical services using the methods in this SOW are advised to develop a contracting mechanism that explicitly includes both the technical and contractual requirements contained in this SOW.

D. Organization of the Statement of Work

Exhibit A provides an overview of the SOW and its general requirements. Exhibit B contains a description of the reporting and deliverables requirements, in addition to the data reporting forms and the forms instructions. Exhibit C specifies the target compound list for this SOW with the contract-required quantitation limits for sample matrices. Exhibit D details the specific analytical procedures to be used with this SOW and resulting contracts. Exhibit E provides descriptions of required quality assurance/quality control (QA/QC) standard operating procedures and procedures used for the evaluation of analytical methodologies, QA/QC performance, and the reporting of data. Exhibit F contains chain-of-custody and sample documentation requirements which the Contractor shall follow. To ensure proper understanding of the terms utilized in this SOW, a glossary can be found in Exhibit G.

SECTION II

SPECIFIC REQUIREMENTS

A. Sample shipments to the Contractor's facility will be scheduled and coordinated by the EPA CLP Sample Management Office (SMO) acting on behalf of the Administrative Project Officer. The Contractor shall communicate with SMO personnel by telephone, as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed.

If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation/paperwork (e.g., Traffic Reports not with shipment, sample and Traffic Report numbers do not correspond), the Contractor shall immediately contact SMO for resolution. The Contractor shall immediately notify SMO regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall notify SMO in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

B. Sample analyses will be scheduled by groups of samples, each defined as a Case and identified by a unique EPA Case number assigned by SMO. A Case signifies a group of samples collected at one site or geographical area over a finite time period and includes one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.

A Case consists of one or more Sample Delivery Group(s). A Sample Delivery Group (SDG) is defined by the following, whichever is most frequent:

- Each Case of field samples received, OR
- Each 20 field samples within a Case, OR
- Each 14 calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

Samples may be assigned to SDGs by matrix (e.g., all soil samples in one SDG, all water samples a second SDG, and all fly ash samples in a third SDG), at the discretion of the laboratory. Such assignment must be made at the time the samples are received and may <u>not</u> be made retroactively.

All data for all samples in a SDG are due concurrently to all data recipients as stipulated in the Delivery Schedule in Exhibit B, Section I. Data for all samples in a SDG must be submitted together (in one package) in the order specified in Exhibit B. The SDG number 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 SDG number is reported on all data reporting forms.

The SDG receipt date is the day the last sample in the SDG is received. Data for all samples in the SDG are due as stipulated in the Delivery Schedule in Exhibit B.

The Contractor is responsible for identifying each SDG as samples are received, through proper sample documentation (see Exhibit B) and communication with SMO personnel.

C. Each sample received by the Contractor will be labeled with an EPA sample number and will be accompanied by a Traffic Report bearing the sample number and descriptive information regarding the sample. The Contractor shall complete and sign the Traffic Report, recording the date of sample receipt and sample condition for each sample container.

The Contractor shall submit signed copies of Traffic Reports for all samples in a SDG to SMO within three calendar days following receipt of the last sample in the SDG. Traffic Reports shall be submitted in SDG sets (i.e., all Traffic Reports for a SDG shall be clipped together) with a SDG Cover Sheet containing information regarding the SDG, as specified in Exhibit B.

D. The Contractor shall use EPA Case numbers (including SDG numbers) and EPA sample numbers to identify samples received under this contract both verbally and in reports/correspondence.

E. Samples will be shipped routinely to the Contractor through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Contractor's geographical area. The Contractor shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays.

F. The Contractor shall accept all samples scheduled by SMO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

G. The Contractor shall prepare, extract, cleanup extracts, and analyze samples according to the analytical procedures outlined in Exhibit D. The Contractor shall also adhere to the QA/QC requirements specified in Exhibit D, including the analyses of calibration standards, blanks, spiked samples, duplicate analyses, etc., as specified in the exhibit.

H. EPA has provided the Contractor with forms for the reporting of data (Exhibit B). The Contractor shall be responsible for completing and returning analysis data sheets in the format specified in the Contract Performance/Delivery Schedule.

Use of formats other than those designated by EPA will be deemed as noncompliance. Such data are unacceptable. Resubmission in the specified format will be required at no additional cost to the Government.

I. The Contractor shall have sufficient gas chromatograph/mass spectrometer/data system (GC/MS/DS) capability to meet all the terms and conditions of the EPA contract. The Contractor shall maintain, at a minimum, all analytical equipment allocated for this contract at the time of contract award. (See Section III for instrumentation requirements.)

J. Certain samples may require sample reruns (reextraction and/or reanalysis) due to either problems with the sample matrix or Contractor insufficiencies. Sample reruns may be considered either as billable or nonbillable as defined in Exhibit D. For the purposes of this contract, the term "automatic rerun" shall signify only billable rerun analyses.

K. EPA may provide standards for use in analyses performed under the contract, subject to availability. However, the SOW identifies specific solutions that must be purchased from commercial sources, and will not be provided by EPA. When provided, EPA-supplied materials are intended for use only on EPA samples, and the Contractor may be asked to demonstrate during EPA on-site evaluations that separate standards are maintained for non-EPA work. The Contractor will be instructed how and where to request EPA standards at time of contract award. The Contractor is responsible for ensuring that all required standards are available at the Contractor's facility before accepting any samples from EPA.

L. The Contractor shall respond within seven days to requests from data recipients for additional information or explanations that result from the Government's inspection activities.

M. The Contractor shall preserve all sample extracts after analysis in bottles/vials with Teflon-lined septa and shall maintain stored extracts in the dark at room temperature. The Contractor is required to retain the sample extracts for 365 days after data submission. During that time, the Contractor shall submit the extracts within seven days after request, as specified in the Contract Performance/Delivery Schedule.

N. The Contractor shall adhere to chain-of-custody procedures described in Exhibit F. Documentation, as described therein, shall show that all procedures are being strictly followed. This documentation shall be reported as the Complete SDG File (see Exhibit B).

SECTION III

DETAILED TECHNICAL AND MANAGEMENT REQUIREMENTS

The Contractor shall have the following technical and management capabilities. For those technical functions that require a minimum educational degree and experience, an advanced degree in chemistry or any scientific/engineering discipline (e.g., Master's or Doctorate) does not substitute for the minimum experience requirements.

The Contractor shall notify in writing the Technical Project Officer and the Administrative Project Officer of any changes affecting key personnel listed in this section within 14 days of the change. The Contractor shall provide a detailed resume to the Technical Project Officer, Administrative Project Officer, and EMSL-LV for the replacement personnel within 14 days of the Contractor's assignment of the personnel. The resume shall include position description of titles, education (pertinent to this contract), number of years of experience (pertinent to this contract), month and year hired, previous experience and publications.

A. TECHNICAL CAPABILITY

1. Technical Functions

a. GC/MS Laboratory Supervisor

(1) Responsible for all technical efforts of the GC/MS laboratory to meet all terms and conditions of the EPA contract.

(2) Qualifications:

(a) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience with dioxin and furan analyses, including at least one year of supervisory experience.

b. Sample Preparation Laboratory Supervisor

(1) Responsible for all technical efforts of sample preparations to meet all terms and conditions of the EPA contract.

(2) Qualifications:

(a) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience, including at least one year of supervisory experience.

c. Quality Assurance Officer

(1) Responsible for overseeing the QA aspects of data and reporting directly to upper management to meet all terms and conditions of the EPA contract.

(2) Qualifications:

(a) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience, including at least one year of applied experience with QA principles and practices in an analytical laboratory.

d. GC/MS Operator Qualifications

One year of experience in operating and maintaining GC/MS/DS used for selected ion monitoring (SIM) with a Bachelor's degree in chemistry or any scientific/engineering discipline, or in lieu of the Bachelor's degree, three years of experience in operating and maintaining the GC/MS and interpreting GC/MS SIM data.

e. Extract Cleanup Expert Qualifications

One year of experience in extract cleanup with a Bachelor's degree in chemistry or any scientific/engineering discipline, or in lieu of the Bachelor's degree, three years of experience in sample extraction and cleanup.

f. Extraction/Concentration Expert Qualifications

(1) Education:

Minimum of high school diploma and a college-level course in general chemistry.

(2) Experience:

Minimum of one year of experience in extraction/concentration.

g. Technical Staff Redundancy

The bidder shall have a minimum of one chemist available at any one time as a back-up technical person with the following qualifications to ensure continuous operations to accomplish the required work as specified by the EPA contract.

(1) Education:

Minimum of a Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience: Minimum of one year in each of the following areas -

- o GC/MS operation and maintenance using selected ion monitoring.
- o Dioxin/furan analysis.
- o Sample extraction and cleanup.

2. Facilities

The adequacy of the facilities and equipment is of equal importance as the technical staff to accomplish the required work as specified by the EPA contract.

a. Sample Receipt Area

Adequate, contamination-free, well-ventilated work space provided with chemical resistant bench top for receipt and safe handling of EPA samples.

b. Storage Area

Sufficient space to maintain unused EPA sample volume for 60 days after data submission and sample extracts for 365 days after data submission. Samples must be stored in an atmosphere demonstrated to be free from all potential contaminants.

c. Sample Preparation Area

Adequate, contamination-free, well-ventilated work space provided with:

(1) Benches with chemical resistant tops, exhaust hoods.

NOTE: Standards must be prepared in a glove box or isolated area.

(2) Source of distilled or demineralized organic-free water.

(3) Analytical balance(s) located away from draft and rapid change in temperature.

3. Instrumentation

At a minimum, the Contractor shall have the following instruments operative and committed for the full duration of the contract.

a. Primary Instrument Requirements

(1) GC/MS equipped with GC to MS interface capable of extending a 60 meter by 0.32 mm ID, bonded DB-5 (or equivalent), fused silica capillary column into the MS ion source.

(2) GC/MS computer interfaced by hardware to the MS and capable of monitoring at least 18 selected ions for the duration of the chromatographic analysis.

(3) GC/MS computer equipped with mass storage device for saving all data from GC/MS analyses.

(4) GC/MS computer software capable of searching GC/MS analyses for specific ions and plotting the intensity of the ions with respect to time or scan run.

(5) Magnetic tape storage device capable of recording data for long-term, off-line storage.

b. Secondary Instrument Requirements

The Contractor shall have one back-up instrument, identical to the requirements above, in place and operational at any time. This instrument must be included in the bidder's inventory of equipment. In addition, the Contractor shall have an in-house stock of instrument parts and circuit boards to ensure continuous operation to meet contract-specified holding and turnaround times.

4. Data Handling and Packaging

The Contractor shall have reasonable capacity to submit reports and data packages as specified in Exhibit B. To complete this task, the Contractor shall be required to:

a. Provide space, tables and copy machines to meet the contract requirements.

b. Designate personnel.

B. LABORATORY MANAGEMENT CAPABILITY

The Contractor must have an organization with well-defined responsibilities for each individual in the management system to ensure sufficient resources for EPA contract(s) and to maintain a successful operation. To establish this capability, the Contractor shall designate personnel to carry out the following responsibilities for the EPA contract. Functions include, but are not limited to, the following:

1. Technical Staff

Responsible for all technical efforts for the EPA contract.

2. Project Manager

Responsible for overall aspects of EPA contract(s) (from sample receipt through data delivery) and the primary contact for the Administrative Project Officer and Technical Project Officer.

3. Sample Custodian

Responsible for receiving EPA samples (logging, handling and storage).

4. Quality Assurance Officer

Responsible for overseeing the QA aspects of the data and reporting directly to upper management.

5. Document Control Officer

Responsible for ensuring that all documents generated are placed in the Complete SDG File for inventory and are delivered to the appropriate EPA Region or other receiver as designated by EPA.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

Table of Contents

SECTION I

CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

The following table reiterates the contract reporting and deliverables requirements specified in the Contract Schedule and specifies the distribution that is required for each deliverable. NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Administrative Project Officer (APO) will notify the Contractor in writing of such changes when they occur.

Item	No. Copies	Delivery Schedule	Distribution (1)	(2)	(3)	(4)
A. Updated SOPs	3	60 days after contract award.		X	X	X
*B. Sample Traffic Reports (original)	1	3 days after receipt of last sample in Sample Delivery Group (SDG).**	X			
C. Sample Data Summary Package	1	45 days after receipt of last sample in SDG.	X			
***D. Sample Data Package	2	45 days after receipt of last sample in SDG.	X		X	
****E. Complete SDG File	1	45 days after receipt of last sample in SDG.	X			
*****F. Quality Assurance Plan	3	60 days after contract award and as required in Exhibit E.		As Directed		
G. GC/MS Tapes	Lot	Retain for 365 days after data submission, or submit within 7 days after receipt of written request by APO and/or EMSL-LV.		As Directed		

Item	No. Copies	Delivery Schedule	Distribution (1) (2) (3)
H. Extracts	Lot	Retain for 365 days after data submission, or submit within 7 days after receipt of written request by APO or SMO.	As Directed

Distribution:
(1) Sample Management Office (SMO)
(2) Region-Client (Technical Project Officer (TPO))
(3) Environmental Monitoring Systems Laboratory (EMSL-LV)
(4) National Enforcement Investigations Center (NEIC)

* Copy also required in the Sample Data Summary Package.

** Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 14 days or less and not exceeding 20 samples. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that all samples have been delivered. (See Exhibit A for further description.)

*** Concurrent delivery required. Delivery shall be made such that all designated recipients receive the item on the same calendar day.

**** Complete SDG File will contain the original sample data package plus all of the original documents described under Section II, Part E.

***** See Exhibit E for a more detailed description.

NOTE: As specified in the Contract Schedule (G.2 Government Furnished Supplies and Materials), unless otherwise instructed by SMO, the Contractor shall dispose of unused sample volume and used sample bottles/containers no earlier than 60 days following submission of analytical data.

Distribution Addresses:

(1) USEPA Contract Laboratory Program
Sample Management Office
P.O. Box 818
Alexandria, VA 22314

For overnight delivery service, use street address:
300 North Lee Street
Alexandria, VA 22314

(2) USEPA Regions:

SMO, acting on behalf of the APO, will provide the Contractor with the list of addressees for the 10 EPA Regions. SMO will provide the

Contractor with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

(3) USEPA Environmental Monitoring Systems Laboratory
P.O. Box 93478
Las Vegas, NV 89193-3478
ATTN: Data Audit Staff

For overnight delivery service, use street address:
944 E. Harmon, Executive Center
Las Vegas, NV 89109
ATTN: Data Audit Staff

(4) USEPA National Enforcement Investigations Center (NEIC)
Attn: CLP Audit Program
Denver Federal Center Building 53
P. O. Box 25227
Denver, CO 80225

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

The Contractor shall provide reports and other deliverables as specified in the Contract Schedule (Reporting Requirements and Deliverables, F.2). The required content and form of each deliverable are described in this exhibit.

All reports and documentation MUST BE:

- Legible.
- Clearly labeled and completed in accordance with instructions in this exhibit.
- Arranged in the order specified in this section.
- Paginated consecutively in ascending order starting from the SDG Narrative.

If submitted documentation does not conform to the above criteria, the Contractor shall be required to resubmit such documentation with deficiencies corrected, at no additional cost to the Government.

Whenever the Contractor is required to submit or resubmit data as a result of an onsite laboratory evaluation or through an APO/TPO action, the data must be clearly marked as ADDITIONAL DATA and must be sent to all three contractual data recipients (SMO, EMSL-LV and the Region). A cover letter shall be included which describes what data are being delivered, to which EPA Case(s) the data pertain, and who requested the data.

Whenever the Contractor is required to submit or resubmit data as a result of contract compliance screening by SMO, the data must be sent to all three contractual data recipients (SMO, EMSL-LV and the Region). In all three instances the data must be accompanied by a color-coded Cover Sheet (Laboratory Response To Results of Contract Compliance Screening) provided by SMO.

Section III of this exhibit contains forms instructions to assist the Contractor in accurately providing EPA with all required data. Section IV contains copies of the required data reporting forms in EPA-specified formats.

Descriptions of the requirements for each deliverable item cited in Reporting Requirements and Deliverables (Contract Schedule, Section F) are specified in this section. Items submitted concurrently MUST BE arranged in the order listed. Additionally, the components of each item MUST BE arranged in the order presented in this section when the item is submitted. Examples of specific data deliverables not included herein may be obtained by submitting a written request to the APO, stating the information requested and signed by the Laboratory Manager.

A. Quality Assurance Plan and Standard Operating Procedures

See Exhibits E and F for requirements.

B. Sample Traffic Reports

The original Sample Traffic Report (TR) page marked "Lab Copy for Return to SMO" shall be delivered with laboratory receipt information and signed in original Contractor signature, for each sample in the SDG. TRs shall be submitted in SDG sets (i.e., TRs for all samples in a SDG shall be clipped together) with a SDG Cover Sheet attached.

The SDG Cover Sheet shall contain the following items:

- Laboratory name.
- Contract number.
- Sample analysis price - full sample price from the EPA contract.
- Case number.
- List of EPA sample numbers of all samples in the SDG, identifying the first and last samples received and their dates of receipt (LRDs).

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the highest sample number (considering both alpha and numeric designations).

In addition, each TR must be clearly marked with the SDG number, the sample number of the first sample in the SDG (as described in the following paragraph). This information should be entered below the laboratory receipt date on the TR. In addition, the TR for the last sample received in the SDG must be clearly marked "SDG - FINAL SAMPLE."

The EPA sample number of the first sample received in the SDG is the SDG number. 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 SDG number is also reported on all data reporting form (see Section III, Form Instruction Guide).

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 and submit one copy with each SDG Cover Sheet.

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 pa[illegible] 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.

E. Complete SDG File

One Complete SDG File (CSF), including the original Sample Data Package, shall be delivered to the Region concurrently with delivery of the Sample Data Package to SMO and EMSL-LV. The contents of the CSF will be numbered according to the specifications described in Sections III and IV. The Document Inventory Sheet, Form DC-2, is contained in Section IV. The CSF will contain all original documents where possible. No copies will be placed in the CSF unless the originals are bound in a logbook which is maintained by the laboratory. The CSF will contain all original documents specified in Sections III and IV, and Form DC-2.

The CSF will consist of the following original documents in addition to the documents in the Sample Data Package:

1. Original Sample Data Package.

2. A completed and signed Document Inventory Sheet (Form DC-2).

3. All original shipping documents including, but not limited to, the following:

   a. EPA Chain-of-Custody Record.

   b. Airbills.

   c. EPA Traffic Reports.

   d. Sample tags (if present) sealed in plastic bags.

4. All original receiving documents including, but not limited to, the following:

   a. Form DC-1.

   b. Other receiving forms or copies of receiving logbooks.

   c. SDG Cover Sheet.

5. All original laboratory records, not already submitted in the Sample Data Package, of sample transfer, preparation and analysis including, but not limited to, the following:

   a. Original preparation and analysis forms or copies of preparation and analysis logbook pages.

   b. Internal sample and sample extract transfer chain-of-custody records.

   c. Screening records.

   d. All instrument output, including strip charts from screening activities.

6. All other original SDG-specific documents in the possession of the laboratory, including, but not limited to, the following:

   a. Telephone contact logs.

   b. Copies of personal logbook pages.

   c. All hand-written Case-specific notes.

   d. Any other Case-specific documents not covered by the above.

   NOTE: All Case-related documentation may be used or admitted as evidence in subsequent legal proceedings. Any other SDG-specific documents generated after the CSF is sent to EPA, as well as copies that are altered in any fashion, are also deliverables to EPA (original to the Region, and copies to SMO and EMSL-LV).

If the laboratory does submit SDG-specific documents to EPA after submission of the CSF, the documents should be numbered as an addendum to the CSF, and a revised DC-2 Form should be submitted, or the documents should be numbered as a new CSF, and a new DC-2 Form should be submitted to the Regions only.

F. GC/MS Tapes

The Contractor must store all raw and processed GC/MS data on magnetic tape in appropriate instrument manufacturer's format. This tape must include data for samples, blanks, initial calibrations and continuing calibrations, as well as all laboratory-generated quantitation reports and SICPs required to generate the data package. The Contractor shall maintain a written reference logbook of tape files to EPA sample number, calibration data, standards and blanks. The logbook should include EPA sample numbers and standard and blank IDs, identified by Case and SDG.

The Contractor is required to retain the GC/MS tapes for 365 days after data submission. During that time, the Contractor shall submit tapes and associated logbook pages within seven days after receipt of a written request from the APO or EMSL-LV.

When submitting GC/MS tapes to EPA, the following materials must be delivered in response to the request:

1. All associated raw data files for samples, blanks, matrix spikes, initial and continuing calibration standards, and window defining mix solutions.

2. All processed data files and quantitation output files associated with the raw data files described above.

3. All associated identifications and calculation files used to generate the data submitted in the data package.

4. A copy of the Contractor's written reference logbook relating tape files to EPA sample number, calibration data, standards, blanks and matrix spikes. The logbook must include EPA sample numbers and lab file identifiers for all samples, blanks and standards, identified by Case and SDG.

The laboratory must also provide a statement attesting to the completeness of the GC/MS data tape submission, signed and dated by the Laboratory Manager. This statement must be part of a cover sheet that includes the following information relevant to the data tape submission:

1. Laboratory name.

2. Date of submission.

3. Case number.

4. SDG number.

5. GC/MS make and model number.

6. Software version.

7. Disk drive type (e.g., CDC, PRIAM).

8. File transfer method (e.g., DSD, DTD, FTP, Aquarius).

9. Names and telephone numbers of two laboratory contacts for further information regarding the submission.

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.

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 and have additional SAS requirements, enter both "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 must 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 all 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 not associated with the SDG being reported.

For blanks and standards, the following identification scheme must 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." must be unique 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 any of the forms, or accompanying hardcopy data deliverables, it must be reported on all 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.

R 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.

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

This form is used to document the receipt and inspection of sample containers and samples. One original of Form DC-1 is required for each sample shipping container. If the samples in a single sample shipping container must be assigned to more than one SDG, the original Form DC-1 shall be placed with the deliverables for the SDG of the lowest Arabic number, and a copy of Form DC-1 must be placed with the deliverables for the other SDG(s). The copies should be identified as "copy(ies)," and the location of the original should be noted on the copies.

Sign and date the airbill (if present). Examine the shipping container and record the presence/absence of custody seals and their condition (e.g., intact, broken) in item 1 of Form DC-1. Record the custody seal numbers in item 2.

Open the container, remove the enclosed sample documentation, and record the presence/absence of chain-of-custody record(s), SMO forms (e.g., Traffic Reports, Packing Lists), and airbills or airbill stickers in items 3-5. Specify if there is an airbill present or an airbill sticker in item 5. Record the airbill or sticker number in item 6.

Remove the samples from the shipping container(s), examine the samples and the sample tags (if present), and record the condition of the sample bottles (e.g., intact, broken, leaking) and presence of absence of sample tags in items 7 and 8.

Review the sample shipping documents and complete the header information described in Instruction A. Compare the information recorded on all the documents and samples and circle the appropriate answer in item 9.

If there are no problems observed during receipt, sign and date (include time) Form DC-1, the chain-of-custody record, and Traffic Report, and write the sample numbers on Form DC-1. Record the appropriate sample tags and assigned laboratory numbers if applicable. The log-in date should be recorded at the top of Form DC-1 and the date and time of cooler receipt at the laboratory should be recorded in items 10 and 11. Record the fraction designation (if appropriate) and the specific area designation (e.g., refrigerator number) in the Sample Transfer block located in the bottom left corner of Form DC-1. Sign and date the Sample Transfer block. Cross out unused columns and spaces.

If there are problems observed during receipt or an answer marked with an asterisk (e.g., "absent*") was circled, contact SMO and document the contact as well as resolution of the problem on a CLP Communication Log. Following resolution, sign and date the forms as specified in the preceding paragraph and note, where appropriate, the resolution of the problem.

J. CSF Inventory Sheet (Form DC-2)

This form is used to record the inventory of the CSF purge documents and count of documents in the original Sample Data Package that is sent to the Region.

Organize all EPA-CSF documents as described in Section II and Section III. Assemble the documents in the order specified on Form DC-2 and Section II and III, and stamp each page with a consecutive number. (Do not number the DC-2 form.) Inventory the CSF by reviewing the document numbers and recording page number ranges in the columns provided in the Form DC-2. If there are no documents for a specific document type, enter "NA" in the empty space.

Certain laboratory-specific documents related to the CSF may not fit into a clearly defined category. The laboratory should review Form DC-2 to determine if it is most appropriate to place them under item 5, 6, 7, or 8. Item 10 should be used if there is no appropriate previous item. These types of documents should be described or listed in the blanks under each appropriate item.

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 0.5 =	
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

EPA SAMPLE NO.

PCDD/PCDF SPIKED SAMPLE SUMMARY

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 CC1	CC2	CC3	CC4	CC5	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								
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)

SAMPLE LOG-IN SHEET

Lab Name	Page _____ of _____
Received By *(Print Name)*	Log-in Date
Received By *(Signature)*	
Case Number	Sample Delivery Group No. / SAS Number

Remarks:

1. Custody Seal(s) — Present/Absent* Intact/Broken
2. Custody Seal Nos.: _____ _____
3. Chain-of-Custody Records — Present/Absent*
4. Traffic Reports or Packing Lists — Present/Absent*
5. Airbill — Airbill/Sticker Present/Absent*
6. Airbill No.: _____ _____
7. Sample Tags — Present/Absent*
   Sample Tag Numbers — Listed/Not Listed on Chain-of-Custody
8. Sample Condition: — Intact/Broken*/Leaking
9. Does information on custody records, traffic reports, and sample tags agree? — Yes/No*
10. Date Received at Lab: _____
11. Time Received: _____

EPA Sample #	Corresponding Sample Tag #	Corresponding Assigned Lab #	Remarks: Condition of Sample Shipment, etc.

Sample Transfer

Fraction	Fraction
Area #	Area #
By	By
On	On

* Contact SMO and attach record of resolution.

Received By	Logbook No.
Date	Logbook Page No.

PCDD/PCDF COMPLETE SDG FILE (CSF) INVENTORY SHEET

LABORATORY NAME _____ CITY/STATE _____

CASE NO. _____ SDG NO. _____ SDG NOS. TO FOLLOW _____ _____ _____ SAS NO. _____

CONTRACT NO. _____

All documents delivered in the complete SDG file must be original documents where possible. (REFERENCE EXHIBIT B, SECTION II and SECTION III.)

		PAGE NOs FROM	TO	CHECK LAB	EPA
1.	Inventory Sheet (Form DC-2) (Do not number)	____	____	_____	_____
2.	SDG Narrative	____	____	_____	_____
3.	Traffic Report	____	____	_____	_____
4.	PCDD/PCDF Data				
	a. Sample Data				
	TCL Results (Form I PCDD-1)	____	____	_____	_____
	Calculation of the Toxicity Equivalence (Form I PCDD-2)	____	____	_____	_____
	Second Column Confirmation Summary (Form I PCDD-3)	____	____	_____	_____
	Selected Ion Current Profile (SICP) for each sample and each analysis of each sample	____	____	_____	_____
	Total Congener Concentration Results (Form II PCDD)	____	____	_____	_____
	b. Quality Control Data				
	Spiked Sample Results (Form III PCDD-1)	____	____	_____	_____
	Duplicate Sample Results (Form III PCDD-2)	____	____	_____	_____
	Method Blank Summary (Form IV PCDD)	____	____	_____	_____
	Window Defining Mix Summary (Form V PCDD-1)	____	____	_____	_____
	Chromatographic Resolution Summary (Form V PCDD-2)	____	____	_____	_____
	SICP for each QC analysis	____	____	_____	_____
	c. Calibration Data				
	Initial Calibration Data (Form VI PCDD-1 and Form VI PCDD-2) and PCDD/PCDF standard(s) SICPs for the initial (five-point) calibration	____	____	_____	_____
	Continuing Calibration Data (Form VII PCDD-1 and Form VII PCDD-2) and PCDD/PCDF standard(s) SICPs for all continuing calibrations	____	____	_____	_____
	d. Raw Quality Control Data				
	Blank Data and SICPs for each blank analyzed	____	____	_____	_____
	Spiked Sample Data and SICPs for each spiked sample analyzed	____	____	_____	_____

PCDD/PCDF COMPLETE SDG FILE (CSF) INVENTORY SHEET (Cont.)

CASE NO. _____ SDG NO. _____ SDG NOS. TO FOLLOW _____ _____ _____ SAS NO. _____

	PAGE NOs FROM	TO	CHECK LAB	EPA
5. Miscellaneous Data				
Original preparation and analysis forms or copies of preparation and analysis logbook pages	____	____	____	____
Internal sample and sample extract transfer chain-of-custody records	____	____	____	____
Screening records	____	____	____	____
All instrument output, including strip charts from screening activities (describe or list)				
_____	____	____	____	____
_____	____	____	____	____
6. EPA Shipping/Receiving Documents				
Airbills (No. of shipments ___)	____	____	____	____
Chain-of-Custody Records	____	____	____	____
Sample Tags	____	____	____	____
Sample Log-In Sheet (Lab & DCl)	____	____	____	____
SDG Cover Sheet	____	____	____	____
Miscellaneous Shipping/Receiving Records (describe or list)				
_____	____	____	____	____
_____	____	____	____	____
7. Internal Lab Sample Transfer Records and Tracking Sheets (describe or list)				
_____	____	____	____	____
_____	____	____	____	____
8. Other Records (describe or list)				
Telephone Communication Log	____	____	____	____
_____	____	____	____	____
_____	____	____	____	____

PCDD/PCDF COMPLETE SDG FILE (CSF) INVENTORY SHEET (Cont.)

CASE NO. _____	SDG NO. _____	SDG NOS. TO FOLLOW _____ _____ _____	SAS NO. _____

9. Comments: _____

Completed by:

(CLP Lab)	(Signature)	(Printed Name/Title)	(Date)
	_____	_____	_____

Audited by:

(EPA)	(Signature)	(Printed Name/Title)	(Date)
	_____	_____	_____

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 to 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

Table of Contents

LIST OF TABLES

LIST OF FIGURES

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. Interferences

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 $\leq$ 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 $\leq$ 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 all 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 must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all 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 not 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 $\pm$ 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 not 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, must 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 with 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:

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

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:

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

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. Calculations

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

$$EDL\ (ug/kg) = \frac{2.5 \times Q_{is} \times (H_x^1 + H_x^2) \times D}{W \times (H_{is}^1 + H_{is}^2) \times RRF_n}$$

WATER

$$EDL\ (ng/L) = \frac{2.5 \times Q_{is} \times (H_x^1 + H_x^2) \times D}{V \times (H_{is}^1 + H_{is}^2) \times RRF_n}$$

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 and met all of the qualitative identification criteria in Section 11. Do not 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. Isomer Specificity

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			
$^{37}C14$-2378-TCDD	328	(1)	263
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.

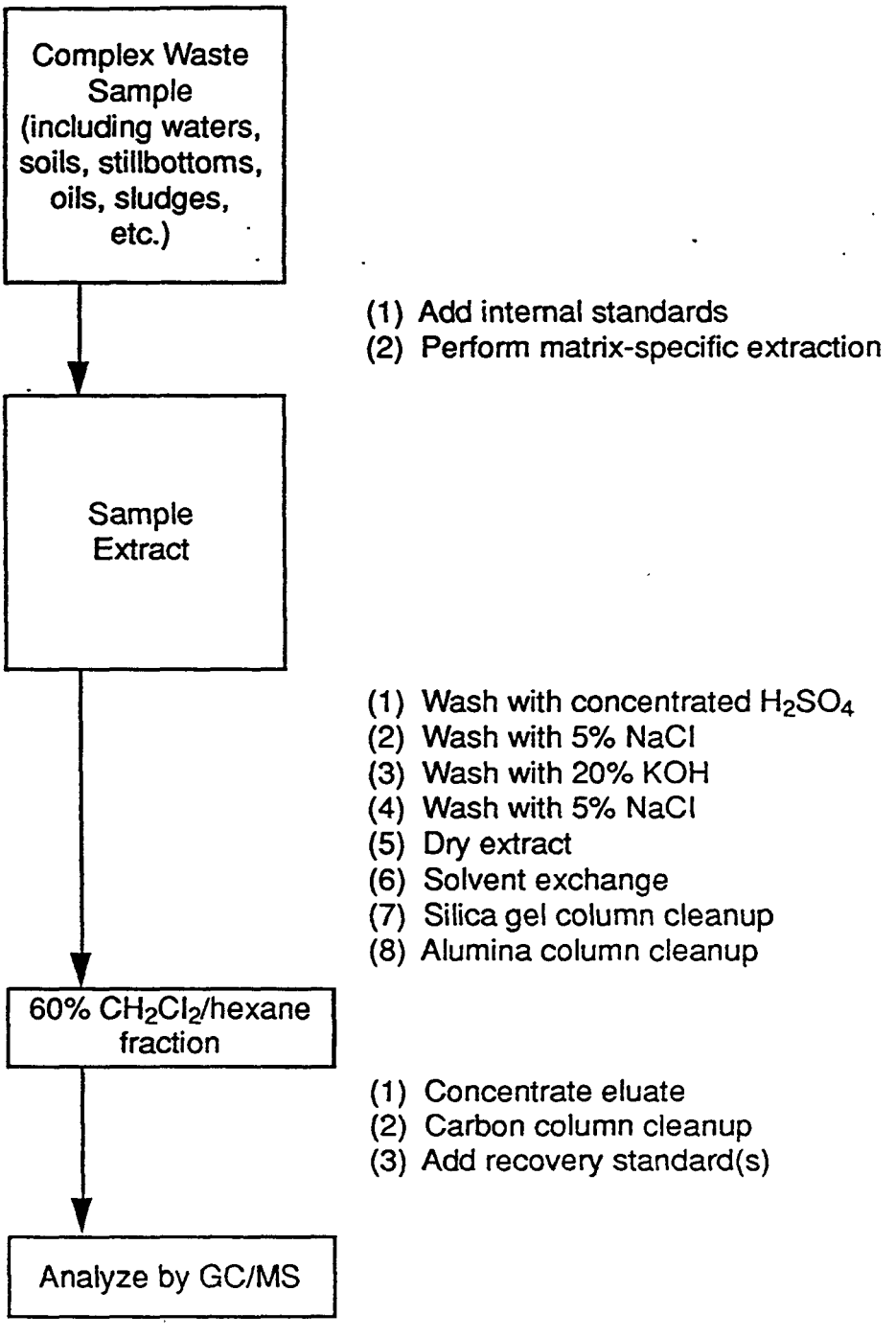
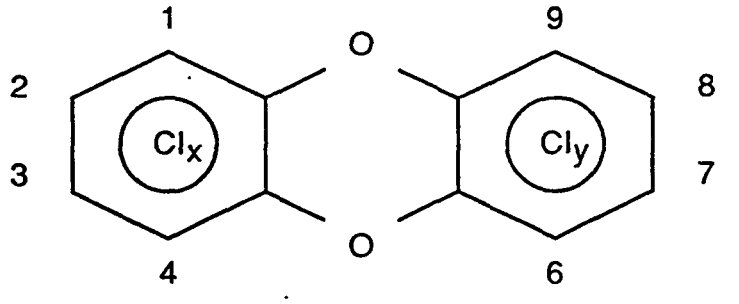
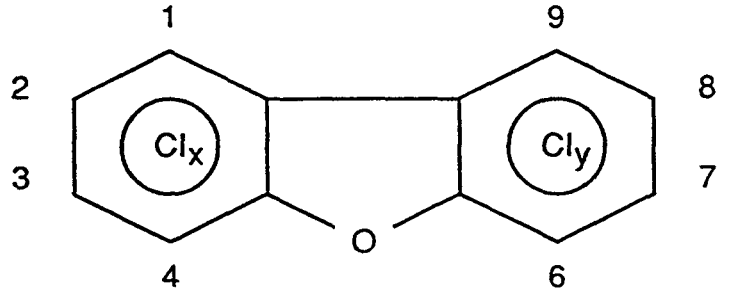


Figure 1: Flow Chart for Sample Extraction and Cleanup for the Analysis of PCDDs and PCDFs in Complex Waste Samples



Polychlorinated Dibenzo-*p*-Dioxin

where $x + y \leq 8$



Polychlorinated Dibenzofuran

Figure 2: General Structures of PCDDs and PCDFs

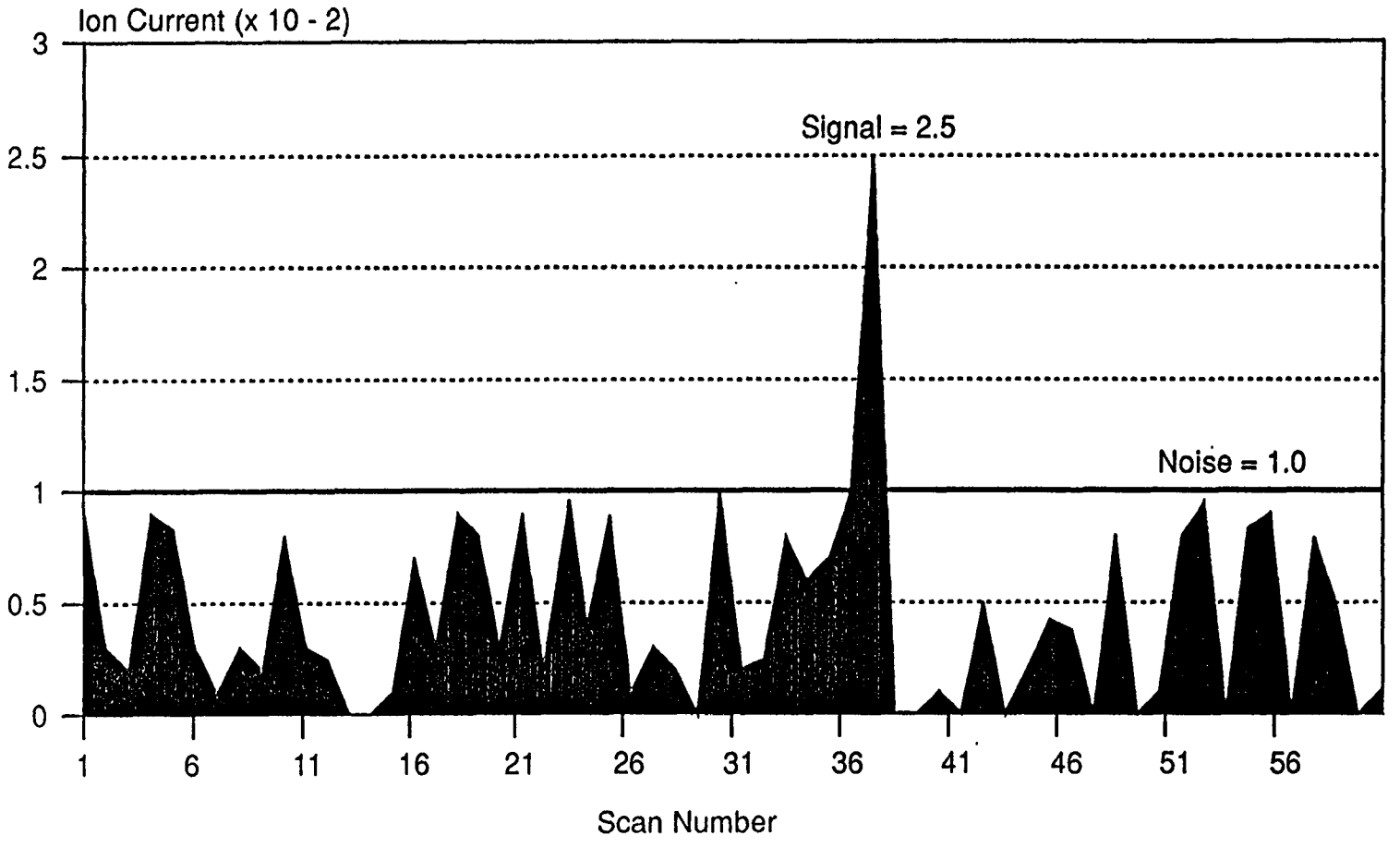


Figure 3: Measurement of Signal-To-Noise Ratio

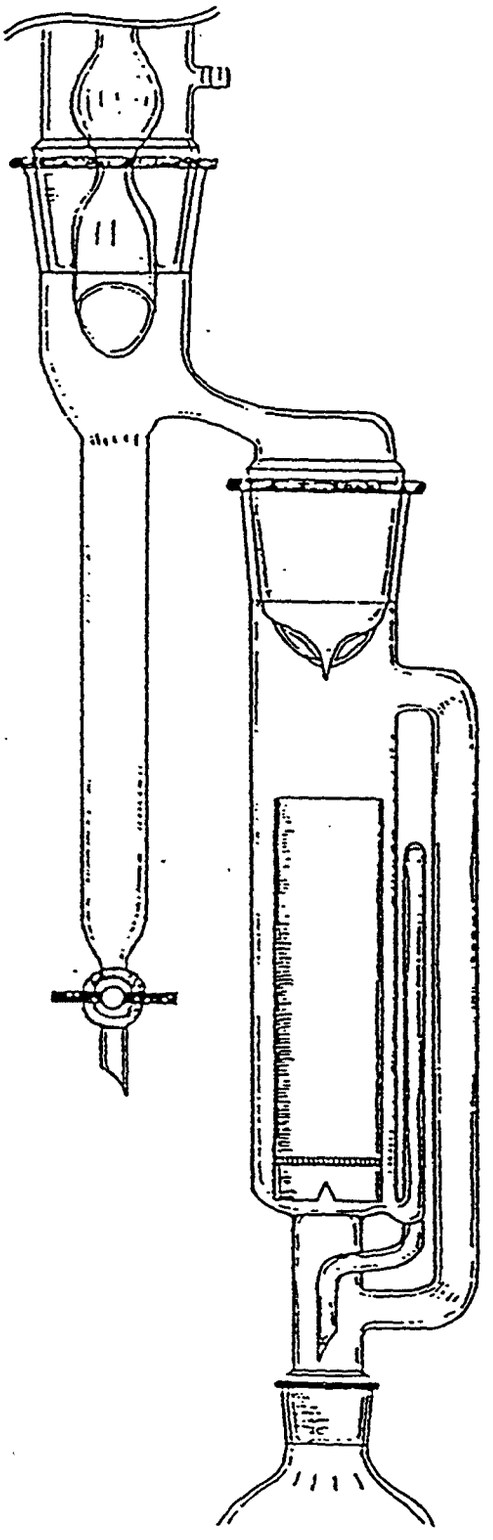


Figure 4: Soxhlet/Dean-Stark Extractor

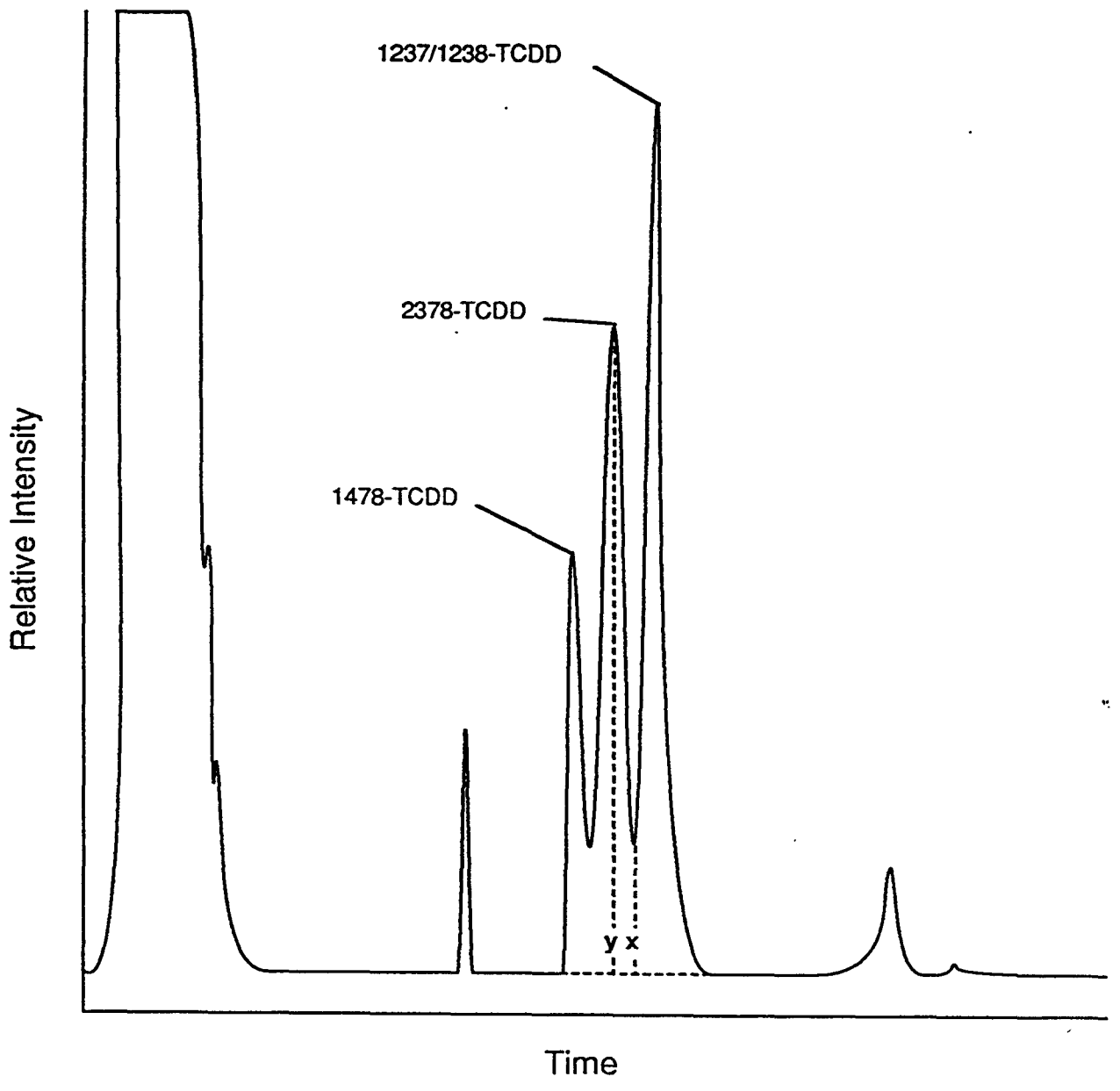


Figure 5: Valley Between 2378-TCDD and Other Closely Eluting Isomers on an SP-2331 (or Equivalent) Column

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

Table of Contents

OVERVIEW

Quality assurance (QA) and quality control (QC) are integral parts of the CLP.[1,2,4,5,6] The QA process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity to ensure that data provided are of the quality required. The QC process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.[1]

During the planning of an environmental data collection program, QA activities focus on defining data quality criteria and designing a QC system to measure the quality of data being generated. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively, and that the deficiencies uncovered by the QC system are corrected. After environmental data are collected, QA activities focus on assessing the quality of data obtained to determine its suitability to support enforcement or remedial decisions.[1,2,3]

This exhibit describes the overall QA/QC operations and the processes by which the CLP meets the QA/QC objective defined above. This contract requires a variety of QA/QC activities. These contract requirements are the minimum QC operations necessary to satisfy the analytical requirements associated with the determination of the different method analytes. These QC operations are designed to facilitate laboratory comparison by providing the EPA with comparable data from all Contractors. These requirements do not release the analytical Contractor from maintaining their own QC checks on method and instrument performance.

SECTION I

INTRODUCTION

Appropriate use of data generated under the great range of analytical conditions encountered in environmental analyses requires reliance on the QC procedures and criteria incorporated into the methods. The methods in this contract have been validated on samples typical of those received by the laboratories in the CLP. However, the validation of these methods does not guarantee that the methods perform equally well for all sample matrices encountered. Inaccuracies can also result from causes other than unanticipated matrix effects, such as sampling artifacts, equipment malfunctions, and operator error. Therefore, the QC component of each method is indispensable.

The data acquired from QC procedures are used to estimate and evaluate the information content of analytical results and to determine the necessity for or the effect of corrective action procedures. The means used to estimate information content include precision, accuracy, detection limit, and other quantitative and qualitative indicators. In addition, the QC component gives an overview of the activities required in an integrated program to generate data of known and documented quality required to meet defined objectives.

The necessary components of a complete QA/QC program include internal QC criteria that demonstrate acceptable levels of performance, as determined by QA review. External review of data and procedures is accomplished by the monitoring activities of the National Program Office (NPO), Regional data users, the Sample Management Office (SMO), the National Enforcement Investigations Center (NEIC), and the Environmental Monitoring Systems Laboratory (EMSL-LV). Each external review accomplishes a different purpose. These reviews are described in specific sections of this exhibit. Performance evaluation (PE) samples and magnetic tape audits provide an external QA reference for the program. A laboratory on-site evaluation system is also part of the external QA monitoring. A feedback loop provides the results of the various review functions to the contract laboratories through direct communications with the Administrative Project Officer (APO) and Technical Project Officer (TPO).

This exhibit is not a guide to constructing QA project plans, QC systems, or a QA organization. However, the exhibit does explain the QA/QC requirements of the program, outlines some minimum standards for QA/QC programs, and includes specific items that are required in a QA Plan and QA/QC documentation detailed in this contract. Delivery of this documentation provides EPA with a complete data package which will stand alone, and limits the need for contact with the Contractor or with an analyst, at a later date, if some aspect of the analysis is questioned.

In order to assure that the product delivered by the Contractor meets the requirements of the contract, and to improve interlaboratory data comparison, EPA requires the following from the Contractor:

- A written QA Plan, the elements of which are designated in Section II.
- Written preparation of and adherence to QA/QC standard operating procedures (SOPs) as described in Section III.
- Adherence to the analytical methods and associated QC requirements specified in the contract.
- Verification of an analytical standard and documentation of the purity of neat materials and the purity and accuracy of solutions obtained from private chemical supply houses.
- Submission of all raw data and pertinent documentation for Regional review.
- Participation in the analysis of laboratory evaluation samples, including adherence to corrective action procedures.
- Submission, upon request, of GC/MS tapes and applicable documentation for tape audits.
- Participation in on-site laboratory evaluations, including adherence to corrective action procedures.
- Submission of all original documentation generated during sample analyses for EPA review.

SECTION II

QUALITY ASSURANCE PLAN

The Contractor shall establish a QA program with the objective of providing sound analytical chemical measurements. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

As evidence of such a program, the Contractor shall prepare a written QA Plan (QAP) which describes the procedures that are implemented to achieve the following:

- o Maintain data integrity, validity, and usability.
- o Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility.
- o Detect problems through data assessment and establish corrective action procedures which keep the analytical process reliable.
- o Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

The QAP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA and QC activities designed to achieve the data quality requirements in this contract. Where applicable, SOPs pertaining to each element shall be included or referenced as part of the QAP. The QAP must be available during an on-site laboratory evaluation. Additional information relevant to the preparation of a QAP can be found in EPA and ASTM publications. [2,4]

The elements of a QAP are as follows:

A. Organization and Personnel
   1. QA Policy and Objectives
   2. QA Management
      a. Organization
      b. Assignment of QC and QA Responsibilities
      c. Reporting Relationships
      d. QA Document Control Procedures
      e. QA Program Assessment Procedures
   3. Personnel
      a. Resumes
      b. Education and Experience Pertinent to this Contract
      c. Training Progress

B. Facilities and Equipment

1. Instrumentation and Backup Alternatives
2. Maintenance Activities and Schedules

C. Document Control

1. Laboratory Notebook Policy
2. Samples Tracking/Custody Procedures
3. Logbook Maintenance and Archiving Procedures
4. Case File Organization, Preparation and Review Procedures
5. Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs
6. Process for Revision of Technical or Documentation Procedures

D. Analytical Methodology

1. Calibration Procedures and Frequency
2. Sample Preparation/Extraction Procedures
3. Sample Analysis Procedures
4. Standards Preparation Procedures
5. Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

E. Data Generation

1. Data Collection Procedures
2. Data Reduction Procedures
3. Data Validation Procedures
4. Data Reporting and Authorization Procedures

F. Quality Control

1. Solvent, Reagent and Adsorbent Check Analysis
2. Reference Material Analysis
3. Internal Quality Control Checks
4. Corrective Action and Determination of QC Limit Procedures
5. Responsibility Designation

G. Quality Assurance

1. Data Quality Assurance
2. Systems/Internal Audits
3. Performance/External Audits
4. Corrective Action Procedures
5. Quality Assurance Reporting Procedures
6. Responsibility Designation

Updating and Submission of the QAP:

Within 60 days of contract award:

During the contract solicitation process, the Contractor was required to submit their QAP to EMSL-LV and NEIC. Within sixty (60) days after contract award, the Contractor shall send a revised QAP, fully compliant with the requirements of this contract, to the TPO, EMSL-LV and NEIC. The revised QAP will become the official QAP under the contract. The revised QAP must include:

1. Changes resulting from the Contractor's internal review of their organization, personnel, facility, equipment, policy and procedures and the Contractor's implementation of the requirements of the contract; and

2. Changes resulting from the Agency's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the preaward laboratory site evaluation.

Subsequent submissions:

During the term of contract, the Contractor shall amend the QAP when the following circumstances occur:

1. The Agency modifies the contract,

2. The Agency notifies the Contractor of deficiencies in the QAP,

3. The Agency notifies the Contractor of deficiencies resulting from the Agency's review of the Contractor's performance,

4. The Contractor identifies deficiencies resulting from the internal review of the QAP,

5. The Contractor's organization, personnel, facility, equipment, policy or procedures change, or

6. The Contractor identifies deficiencies resulting from the internal review of their organization, personnel, facility, equipment, policy or procedures.

The Contractor shall amend the QAP within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the QAP and what is presently occurring at the Contractor's facility. When the QAP is amended, all changes in the QAP must be clearly marked (i.e., indicating where the change is in the document with a bar in the margin, underlining the change, printing the change in bold, or using a different print font). The amended pages must have the date on which the changes were implemented.

The Contractor shall incorporate all amendments to the current QAP. The Contractor shall archive all amendments to the QAP for future reference by the Agency. The Contractor shall send a copy of the current QAP within 14 days of a request by the TPO or APO to the designated recipients.

Corrective action:

If the Contractor fails to adhere to these requirements, the Contractor may expect, but the Agency is not limited to, the following actions: reduction of numbers of samples sent under this contract, suspension of sample shipment to the Contractor, GC/MS tape audit, data package audit, on-site laboratory evaluation, remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

SECTION III

STANDARD OPERATING PROCEDURES

In order to obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of SOPs. As defined by EPA, a SOP is a written document which provides directions for the step-by-step execution of an operation, analysis or action which is commonly accepted as the method for performing certain routine or repetitive tasks.[2]

SOPs prepared by the Contractor must be functional, i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts. All SOPs, as presented to EPA, must reflect activities as they are currently performed in the laboratory. In addition, all SOPs must meet the following criteria:

- Be consistent with current EPA regulations, guidelines, and the contract's requirements.[3,4,5,6,7]
- Be consistent with instrument manufacturers' specific instruction manuals.
- Be available to the EPA during an on-site laboratory evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During on-site evaluations, laboratory personnel may be asked to demonstrate the application of the SOPs.
- Provide for the development of documentation that is sufficiently complete to record the performance of all tasks required by the protocol.
- Demonstrate the validity of data reported by the Contractor and explain the cause of missing or inconsistent results.
- Describe the corrective measures and feedback mechanism utilized when analytical results do not meet protocol requirements.
- Be reviewed regularly and updated as necessary when contract, facility or Contractor procedural modifications are made.
- Be archived for future reference in usability or evidentiary situations.
- Be available at specific work stations as appropriate
- Be subject to a document control procedure which precludes the use of outdated or inappropriate SOPs.

A. SOP Format

The format for SOPs may vary depending upon the kind of activity for which they are prepared; however, at a minimum, the following sections must be included:

- o Title page.
- o Scope and application.
- o Definitions.
- o Procedures.
- o QC limits.
- o Corrective action procedures, including procedures for secondary review of information being generated.
- o Documentation description and example forms.
- o Miscellaneous notes and precautions.
- o References.

B. Required SOPs

The following SOPs are required by EPA:

1. Evidentiary SOPs (see Exhibit F).
2. Sample receipt and storage.
3. Sample preparation.
4. Calibration.
5. Standards purity/preparation.
6. Maintaining instrument records and logbooks.
7. Sample analysis and data control systems.
8. Glassware cleaning.
9. Technical and managerial review of laboratory operation and data package preparation.
10. Internal review of contractually required QA/QC data for each individual data package.
11. Chain-of-custody procedures and document control including Complete Sample Delivery Group (SDG) File preparation.
12. Laboratory data validation/laboratory self-inspection.
    a. Data flow and chain-of-command for data review.
    b. Procedures for measuring precision and accuracy.
    c. Evaluation parameters for identifying systematic errors.[9]
    d. Procedures to assure that hardcopy deliverables are complete and compliant with the requirements in Exhibit B.

e. Demonstration of internal QA inspection procedures (demonstrated by supervisory sign-off on personal notebooks, internal PE samples, etc.).

f. Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas).

g. Demonstration of problem identification-corrective actions and resumption of analytical processing and sequence resulting from internal audit (i.e., QA feedback).

h. Documentation of audit reports (internal and external), response, corrective action, etc.

13. Data management and handling.

a. Procedures for controlling and estimating data entry errors.

b. Procedures for reviewing changes to data and deliverables and ensuring traceability of updates.

c. Lifecycle management procedures for testing, modifying and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems.

d. Database security, backup and archival procedures including recovery from system failures.

e. System maintenance procedures and response time.

f. Individuals(s) responsible for system operation, maintenance, data integrity and security.

g. Specifications for staff training procedures.

C. SOP Delivery Requirements

Updating and submission of SOPs:

During the contract solicitation process, the Contractor was required to submit their SOPs to EMSL-LV and NEIC. Within sixty (60) days after contract award, the Contractor shall send a complete revised set of SOPs, fully compliant with the requirements of this contract, to the TPO, EMSL-LV and NEIC. The revised SOPs will become the official SOPs under the contract. The revised SOPs must include:

1. Changes resulting from the Contractor's internal review of their procedures and the Contractor's implementation of the requirements of the contract;

2. Changes resulting from the Agency's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the preaward laboratory site evaluation.

Subsequent submissions:

During the term of contract, the Contractor shall amend the SOPs when the following circumstances occur:

1. The Agency modifies the contract,

2. The Agency notifies the Contractor of deficiencies in their SOPs documentation,

3. The Agency notifies the Contractor of deficiencies resulting from the Agency's review of the Contractor's performance,

4. The Contractor's procedures change,

5. The Contractor identifies deficiencies resulting from the internal review of their SOPs, or

6. The Contractor identifies deficiencies resulting from the internal review of their procedures.

The SOPs must be amended or new SOPs must be written within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Contractor's facility. All changes in the SOPs must be clearly marked (i.e, indicating where the change is in the document with a bar in the margin, underlining the change, printing the change in bold, or using a different print font). The amended/new SOPs must have the date on which the changes were implemented.

When the SOPs are amended or new SOPs are written, the Contractor shall document in a letter the reasons for the changes, and submit the amended SOPs or new SOPs to the TPO, EMSL-LV (quality assurance/technical SOPs) and NEIC (evidentiary SOPs). The Contractor shall send the letter and the amended sections of the SOPs or new SOPs within 14 days of the change. An alternate delivery schedule for the submittal of the letter and amended/new SOPs may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the TPO or APO, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the TPO, APO, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The TPO/APO will not grant an extension for greater than 30 days for amending/writing new SOPs. The TPO/APO will not grant an extension for greater than 14 days for submission of the letter documenting the reasons for the changes and for submitting amended/new SOPs. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPO and/or APO.

The Contractor shall send a complete set of current SOPs within 14 days of a request by the TPO or APO to the recipients he/she designates.

Corrective action:

If the Contractor fails to adhere to these requirements, the Contractor may expect, but the Agency is not limited to, the following action: reduction of number of samples sent under this contract, suspension of sample shipment to the Contractor, GC/MS tape audit, data package audit, on-site laboratory evaluation, remedial laboratory evaluation sample, and/or contract sanction, such as a Cure Notice.

SECTION IV

QA/QC REQUIREMENTS

This section outlines the minimum QC operations necessary to satisfy the analytical requirements associated with the detection and quantitative measurement of 2378-tetrachlorinated dibenzo-*p*-dioxin and total tetra-, penta-, hexa-, hepta- and octachlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), by using the procedures outlined in Exhibit D. This section is not intended as a comprehensive QC document, but rather as a guide to the specific QC operations that must be considered for PCDD/PCDF analysis.

The QC operations that must be considered include the following:

- o Mass Calibration.
- o Window Defining Mix.
- o Chromatographic Resolution.
- o GC/MS Initial Calibration.
- o GC/MS Continuing Calibration.
- o Instrument Sensitivity.
- o Identification Criteria.
- o Method Blank Analysis.
- o Spiked Sample Analysis.
- o Duplicate Sample Analysis.
- o Toxicity Equivalency Factor and Isomer Specificity.
- o Dilutions.
- o Reanalyses.

1. Mass Calibration

1.1 Mass calibration of the mass spectrometer 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.

1.2 Optimum results using FC-43 for mass calibration can be achieved by scanning from 222-510 amu every one second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode (see Exhibit D, Section 6).

1.3 m/z 414 and m/z 502 should be 30-50 percent of m/z 264 base peak (see Exhibit D, Section 6).

2. Window Defining Mix

2.1 The window defining mix is analyzed to verify that the switching times between the descriptors have been appropriately set.

2.2 The window defining mix is obtained from commercial sources and must contain the first and last eluting isomers in each homologue on the GC column chosen for analyses (see Exhibit D, Section 5.12 and Table 9).

2.3 The window defining mix must be analyzed before the initial calibration on each instrument and GC column used for analysis and at the frequency found in Exhibit D, Paragraph 7.1.3.

3. Chromatographic Resolution

3.1 Chromatographic resolution is evaluated using one of two standard solutions, depending on the GC column chosen for analyses.

3.2 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 Exhibit D, Paragraphs 7.3.2.1 and 7.4.2).

3.3 For analyses on a SP-2331 (or equivalent) GC column, the chromatographic resolution is evaluated before the analysis of any calibration standard by the analysis of a commercially available column performance mixture (see Exhibit D, 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) (see Exhibit D, Paragraph 7.2.2).

3.4 The chromatographic resolution criteria are found in Exhibit D, Paragraphs 7.3.2.1 and 7.2.3.

4. GC/MS Initial Calibration

4.1 Prior to analysis of samples and blanks, the GC/MS system must be initially calibrated at a minimum of five concentrations to verify linearity of response.

4.2 The calibration solutions containing the labeled and unlabeled analogs must be analyzed at five concentrations as described in Exhibit D, Section 5.11 and Table 3.

4.3 The CC1, CC2, CC4 and CC5 solutions shall be used as provided by EPA (see Exhibit D, Section 7.3). The CC3 solution must be prepared as explained in Exhibit D, Paragraph 7.4.1.

4.4 The calibration standard must be analyzed using the MS/DS conditions as described in Exhibit D, Paragraph 7.3.1.

4.5 The chromatographic resolution between the $^{13}C_{12}$ 2378-TCDD and $^{13}C_{12}$ 1234-TCDD isomers must be resolved with a valley of < 25 percent, and

the chromatographic peak separation between the 123478-HxCDD and 123678-HxCDD in the CC3 solution must be resolved with a valley of ≤ 50 percent (see Exhibit D, Paragraph 7.3.2.1).

4.6 The relative ion abundance criteria for PCDDs/PCDFs must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all solutions (see Exhibit D, Table 6).

4.7 For all calibration solutions, the retention times of the isomers must fall within the appropriate retention time windows established by the window defining mix (see Exhibit D, Section 7.1).

4.8 For all calibration solutions, the signal-to-noise ratio must meet the criteria specified in Exhibit D, Paragraph 7.3.2.4.

4.9 The relative response factors for the 17 unlabeled target analytes relative to their appropriate internal standards, and the relative response of the five labeled internal standard standards relative to the appropriate recovery standard are determined according to the procedures in Exhibit D, Paragraph 7.3.3.

4.10 Calculate the mean RRF and percent relative standard deviation (%RSD) of the five RRFs (CC1 to CC5) for each unlabeled PCDD/PCDF, and labeled internal and recovery standards, present in all five concentration calibration solutions as described in Exhibit D, Paragraph 7.3.5. As indicated in the referenced paragraph, no %RSD calculation is possible for the 2,3,7,8-substituted isomers in the CC3 supplemental calibration solution, because they are only present in the one solution.

4.11 The %RSD is calculated for the EPA-supplied unlabeled and labeled analytes only. To establish linearity, the %RSD of the five RRFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards must not exceed 15.0% (see Exhibit D, Paragraph 7.3.5).

4.12 If the initial calibration criteria for GC resolution, ion abundance ratios, retention times, instrument sensitivity and relative response factors are not met, the Contractor must take the corrective actions as explained in Exhibit D, Paragraph 7.3.7.

4.13 The response factors to be used for determining the total homologue concentrations are described in Exhibit D, Section 15.2.

5. GC/MS Continuing Calibration

5.1 Once the GC/MS system has been calibrated, the calibration must be verified for each 12-hour time period for each GC/MS system.

5.2 The continuing calibration standard is prepared by mixing the commercially supplied supplemental standard with the EPA supplied CC4 solution (see Exhibit D, Paragraph 7.4.1).

5.3 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 (see Exhibit D, Section 7.4).

5.4 The continuing calibration standard must be analyzed according to the procedures given in Exhibit D, Section 7.4, and at the frequency in that section.

5.5 Calculate the relative response factors for the 17 unlabeled target analytes relative to their appropriate internal standards and the response factor for the five labeled internal standard relative to the appropriate recovery standard, according to the procedure described in Exhibit D, Paragraph 7.4.4.

5.6 The GC resolution criteria for DB-5 or SP-2331 (or equivalent) column, as specified in Exhibit D, Paragraph 7.3.2.1 or 7.4.3, must be met before the analysis of samples may begin. If the separation criteria for both DB-5 and SP-2331 (or equivalent) column analysis are met, a single column analysis may be used.

5.7 The relative ion abundance for all PCDD/PCDF peaks, including the labeled internal and recovery standards, for both beginning and ending analyses must meet the criteria listed in Exhibit D, Table 6.

5.8 The signal-to-noise ratio for the CC3 and CC1 solutions must meet the criteria specified in Exhibit D, Paragraph 7.4.6.3.

5.9 The percent difference for the RRFs must be calculated as explained in Exhibit D, Paragraph 7.4.6.4 and must meet the criteria specified in that paragraph.

5.10 If the criteria specified in Exhibit D, Paragraph 7.4.6 are not met, the Contractor must take the corrective actions outlined in Exhibit D, Paragraph 7.4.7.

6. Instrument Sensitivity

6.1 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 calibration standards (CC1) at the end of each 12-hour period during which samples and standards are analyzed.

6.2 Analyze the CC1 solution according to Exhibit D, Paragraph 7.5.1.

6.3 This analysis must meet the retention time criteria in Exhibit D, Paragraph 7.5.2.1.

6.4 This analysis must meet the ion abundance ratio criteria in Exhibit D, Table 6.

6.5 For this analysis, the signal-to-noise 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. Identification Criteria

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

7.2 The identification of the PCDD/PCDF isomers is based on simultaneous detection of the two most abundant ions in the molecular ion regions and the M-COCl ion. In order to make a positive identification, the relative retention time criteria specified in Exhibit D, Section 11.1 must be met.

7.3 All of the ions specified for each PCDD/PCDF homologue and labeled standards must be present in the selected ion current profile. The ion current response for the analytes and labeled standards must meet the QC criteria (see Exhibit D, Section 11.2).

7.4 The integrated ion current for each analyte ion listed in Exhibit D, 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 times background noise and must not have saturated the detector (see Exhibit D, Section 11.3).

7.5 The relative ion abundance criteria for the native analytes and internal standard must be met (see Exhibit D, Table 6).

7.6 The identification of a GC peak as a PCDF cannot be made if a signal having a signal-to-noise ratio greater than 2.5 is detected in the corresponding PCDPE channel (see Exhibit D, Section 11.5).

8. Method Blank Analysis

8.1 A method blank is a volume of clean reference matrix that is carried through the entire analytical sequence.

8.2 A minimum of one blank per matrix must be analyzed with each SDG at a frequency described in Exhibit D, Section 12.1.

8.3 An acceptable method blank must not contain any chemical interferences or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions which is greater than 5 percent of the signal of the appropriate internal standard, or any peak that meets the identifications criteria as a PCDD/PCDF which is greater than 2 percent of the appropriate internal standard (see Exhibit D, Section 15.2).

8.4 If the blank is contaminated, the associated positive samples and any samples containing peaks that do not meet all the identification criteria must be rerun (see Exhibit D, Paragraph 12.2.3).

9. Spiked Sample Analysis

9.1 In order to provide data on the accuracy of the analytical method, the Contractor is required to prepare and analyze a spiked sample for each matrix being analyzed. For each SDG, the Contractor must prepare a spiked sample for all of the matrix types that occur in the SDG (see Exhibit D, Section 13).

9.2 Prepare a spiked sample according to the procedures in Exhibit D, Sections 13.1 and 13.2.

9.3 Extract and analyze the spiked sample according to the procedures in Exhibit D, Sections 9 and 10.

9.4 Calculate the recovery of the spiked analytes according to the procedures in Exhibit D, Section 13.5.

10. Duplicate Sample Analysis

10.1 In order to provide data on the precision of the analytical method, the Contractor is required to prepare and analyze a duplicate of one sample for each matrix being analyzed. For each group of samples, the laboratory must prepare a duplicate sample for all of the following matrix types that occur in the SDG (see Exhibit D, Section 14).

10.2 Prepare a duplicate sample according to the procedures in Exhibit D, Section 14.1.

10.3 Extract and analyze the spiked sample according to the procedures in Exhibit D, Sections 9 and 10.

10.4 Calculate the relative percent difference between the results of the original analysis and the duplicate analysis according to the procedures in Exhibit D, Section 14.3.

11. Toxicity Equivalency Factor and Isomer Specificity

11.1 The 2378-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample must be calculated according to procedures outlined in Exhibit D, Section 15.8.

11.2 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 the 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 in Exhibit D, Section 16.

11.3 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 in Exhibit D, Paragraphs 16.1.1 or 16.1.2 to achieve adequate isomer specificity.

12. Dilutions

If the concentration of any PCDD/PCDF in the sample exceeds the calibration range or the detector is saturated, a dilution must be performed using the procedures given in Exhibit D, Section 10.4.

13. Reanalyses

The requirements for reextraction and for reanalysis of samples are given in Exhibit D, Section 17.

SECTION V

ANALYTICAL STANDARDS REQUIREMENTS

A. Overview

EPA will not supply all the analytical reference standards required for performance of this contract. See Exhibit D, Section 5 for the standards that may be provided by EPA, subject to availability. Contractors will be required to prepare from neat materials or purchase from private chemical supply houses the standards not supplied by EPA but necessary to successfully and accurately perform the analyses required in this contract.

B. Preparation of Chemical Standards from the Neat High Purity Bulk Material

The Contractor may prepare chemical standards from neat materials. Commercial sources for neat chemical standards pertaining to compounds listed on the Target Compound List are given in Appendix C of the "Quality Assurance Materials Bank: Analytical Reference Standards," Seventh Edition, January 1988. Laboratories should obtain the highest purity possible when purchasing neat chemical standards; standards purchased at less than 97% purity must be documented as to why a higher purity could not be obtained.

1. Neat chemical standards must be kept refrigerated when not being used in the preparation of standard solutions. Proper storage of neat chemicals is essential in order to safeguard them from decomposition.

2. The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration of solute in a solution standard, the Contractor is responsible for having analytical documentation ascertaining that the purity of each compound is correctly stated. Purity confirmation, when performed, should use either differential scanning calorimetry, gas chromatography with flame ionization detection, high performance liquid chromatography, infrared spectrometry, or other appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

   Equation 1

$$\text{weight of impure compound} = \frac{\text{weight of pure compound}}{(\text{percent purity}/100)}$$

   where "weight of pure compound" is that required to prepare a specific volume of a solution standard of a specified concentration.

3. Mis-identification of compounds occasionally occurs and it is possible that a mislabeled compound may be received from a chemical supply house. The Contractor is responsible for having analytical documentation ascertaining that all compounds used in the preparation of solution standards are correctly identified. Identification confirmation, when performed, should use gas chromatographic/mass spectrometry analysis on at least two different analytical columns, or other appropriate techniques.

4. Calculate the weight of material to be weighed out for a specified volume taking into account the purity of the compound and the desired concentration. A second person must verify the accuracy of the calculations. Check balances for accuracy with a set of standard weights. All weighing should be performed on an analytical balance to the nearest 0.1 mg and verified by a second person. The solvent used to dissolve the solute should be compatible with the protocol in which the standard is to be used; the solute should be soluble, stable, and nonreactive with the solvent. In the case of a multicomponent solution, the components must not react with each other.

5. Transfer the solute to a volumetric flask, and dilute to the specified solution volume with solvent after ensuring dissolution of the solute in the solvent. Sonication or warming may be performed to promote dissolution of the solute. This solution is to be called the primary standard, and all subsequent dilutions must be traceable back to the primary standard.

6. Log notebooks are to be kept for all weighing and dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be recorded and verified by a second person. All solution standards are to be refrigerated when not in use. All solution standards are to be clearly labeled as to the identity of the compound(s), concentration, date prepared, solvent, and initials of the preparer.

C. Purchase of Chemical Standards Already in Solution

Solutions of analytical reference standards can be purchased by the Contractor provided they meet the following criteria:

1. Laboratories must maintain the following documentation to verify the integrity of the standard solutions they purchase:

   a. Mass spectral identification confirmation of the neat material.

   b. Purity confirmation of the neat material.

   c. Chromatographic and quantitative documentation that the solution standard was QC-checked according to the following section.

2. The Contractor must purchase standards for which the quality is demonstrated statistically and analytically by a method of the supplier's choice. One way quality can be demonstrated is to prepare and analyze three solutions; a high standard, a low

standard, and a standard at the target concentration (see parts a and b below). The supplier must then demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations by using the Student's t-test in part d. If this consistency is achieved, the supplier must then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards by using the Student's t-test in part e. Thus, the standard is certified to be within 10 percent of the target concentration.

If the above procedure is used, the supplier must document that the following have been achieved:

a. Two solutions of identical concentration must be prepared independently from neat materials. An aliquot of the first solution must be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration 10 percent greater than the target standard. This aliquot is called the "high standard." One further aliquot is taken from the second solution and diluted to a concentration 10 percent less that the target standard. This aliquot is called the "low standard."

b. Six replicate analyses of each standard (a total of 18 analyses) must be performed in the following sequence: low standard, target standard, high standard, low standard, target standard, high standard, ...

c. The mean and variance of the six results for each solution must be calculated.

Equation 2

$$\text{MEAN} = (Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6)/6$$

Equation 3

$$\text{VARIANCE} = (Y_1^2 + Y_2^2 + Y_3^2 + Y_4^2 + Y_5^2 + Y_6^2 - (6*\text{MEAN})^2)/5$$

The values Y_1, Y_2, Y_3, ..., represent the results of the six analyses of each standard. The means of the low, target and high standards are designated M_1, M_2 and M_3, respectively. The variances of the low, target and high standards are designated V_1, V_2 and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

Equation 4

$$V_p = (V_1/(0.81) + V_2 + V_3/(1.21))/3$$

If the square root of V_p is less than one percent of M_2, then $M_2^2/10{,}000$ is to be used as the value of V_p in all subsequent calculations.

d. The test statistic must be calculated:

Equation 5
$$\text{TEST STATISTIC} = |(M_3 / 1.1) - (M_1 / 0.9)| / (V_p / 3)^{0.5}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate a twenty percent difference between the high and low standards. In such a case, the standards are not acceptable.

e. The test statistic must be calculated:

Equation 6
$$\text{TEST STATISTIC} = |M_2 - (M_1 / 1.8) - (M_3 / 2.2)| / (V_p / 4)^{0.5}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate that the target standard concentration is midway between the high and low standards. In such a case, the standards are not acceptable.

f. The 95 percent confidence intervals for the mean result of each standard must be calculated:

Equation 7
$$\text{Interval for Low Standard} = M_1 \pm (2.13)(V_p / 6)^{0.5}$$

Equation 8
$$\text{Interval for Target Standard} = M_2 \pm (2.13)(V_p / 6)^{0.5}$$

Equation 9
$$\text{Interval for High Standard} = M_3 \pm (2.13)(V_p / 6)^{0.5}$$

These intervals must not overlap. If overlap is observed, the supplier has failed to demonstrate the ability to discriminate the 10 percent difference in concentrations. In such a case, the standards are not acceptable.

In any event, the Contractor is responsible for the quality of the standards employed for analyses under this contract.

D. Requesting Standards From the EPA Standards Repository

Solutions of analytical reference materials can be ordered from the U.S. EPA Chemical Standards Repository, depending on availability. The Contractor can place an order for standards only after demonstrating that these standards are not available from commercial vendors either in solution or as a neat material.

E. Documentation of the Verification and Preparation of Chemical Standards

Each laboratory is responsible for maintaining the necessary documentation to show that the chemical standards they have used in the performance of CLP analysis conform to the requirements previously listed. Weighing logbooks, calculations, chromatograms, mass spectra,

etc, whether produced by the laboratory or purchased from chemical supply houses, must be maintained by the laboratory and may be subject to review during on-site inspections. Documentation of standards preparation may be required to be sent to EPA for verification of contract compliance. In those cases where the documentation is supportive of the analytical results of data packages sent to EPA, such documentation is to be kept on file by the laboratory for a period of one year.

SECTION VI

CONTRACT COMPLIANCE SCREENING

Contract Compliance Screening (CCS) is one aspect of the Government's contractual right of inspection of analytical data. CCS examines the Contractor's adherence to the contract requirements based on the sample data package delivered to EPA.

CCS is performed by SMO under the direction of the EPA. To assure a uniform review, a set of standardized procedures have been developed to evaluate the sample data package submitted by a Contractor against the technical and completeness requirements of the contract.

CCS results are mailed to the Contractor and all other data recipients. The Contractor has a period of time to correct deficiencies. The Contractor must send all corrections to the Regional client, EMSL-LV and SMO.

CCS results are used in conjunction with other information to measure overall Contractor performance and to take appropriate actions to correct deficiencies in performance.

SECTION VII

REGIONAL DATA REVIEW

Contract laboratory data are generated to meet the specific needs of the Regions. In order to verify the usability of data for the intended purpose, each Region reviews data from the perspective of end-user, based upon functional aspects of data quality. General guidelines for data review have been developed jointly by the Region and the NPO. Each Region uses these guidelines as the basis for data evaluation. Individual Regions may augment the basic guideline review process with additional review based on Region-specific or site-specific concerns. Regional reviews, like the sites under investigation, vary based on the nature of the problems under investigation and the Regional response appropriate to the specific circumstances.

Regional data reviews, relating usability of the data to a specific site, are part of the collective assessment process. They complement the review done at SMO, which is designed to identify contractual discrepancies, and the review done at EMSL-LV which is designed to evaluate Contractor and method performance. These individual evaluations are integrated into a collective review that is necessary for program and laboratory administration and management and may be used to take appropriate action to correct deficiencies in the Contractor's performance.

SECTION VIII

LABORATORY EVALUATION SAMPLES

Although intralaboratory QC may demonstrate Contractor and method performance that can be tracked over time, an external performance evaluation program is an essential feature of a QA program. As a means of measuring Contractor and method performance, Contractors participate in interlaboratory comparison studies conducted by the EPA. Results from the analysis of laboratory evaluation samples will be used by the EPA to verify the Contractor's continuing ability to produce acceptable analytical data. The results are also used to assess the precision and accuracy of the analytical methods for specific analytes.

Sample sets may be provided to participating Contractors as frequently as on a SDG-by-SDG basis as a recognizable QC sample of known composition, as a recognizable QC sample of unknown composition, or not recognizable as a QC material. Laboratory evaluation samples may be sent either by the Regional client or the NPO and may be used for contract action.

Contractors are required to analyze the samples and return the data package and all raw data within the contract required turnaround time.

At a minimum, the results are evaluated for compound identification, quantification, and sample contamination. Confidence intervals for the quantification of target compounds are based on reported values using population statistics. EPA may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract.

A Contractor's results on the laboratory evaluation samples will determine the Contractor's performance as follows:

1. Acceptable, No Response Required (Score greater than or equal to 90 percent):

   Data meets most or all of the scoring criteria. No response is required.

2. Acceptable, Response Explaining Deficiency(ies) Required (Score greater than or equal to 75 percent but less than 90 percent):

   Deficiencies exist in the Contractor's performance.

   Within 14 days of receipt of notification from EPA, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the APO, the TPO and EMSL-LV.

3. Unacceptable Performance, Response Explaining Deficiency(ies) Required (Score less than 75 percent):

Deficiencies exist in the Contractor's performance to the extent that the NPO has determined that the Contractor has not demonstrated the capability to meet the contract requirements.

Within 14 days of receipt of notification from EPA, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the APO, the TPO and EMSL-LV.

The Contractor shall be notified by the APO or TPO concerning the remedy for their unacceptable performance. A Contractor may expect, but EPA is not limited to, the following actions: reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, an on-site audit, a full data audit, analysis of remedial PE samples, and/or a contract sanction, such as a Cure Notice.

NOTE: A Contractor's prompt response demonstrating that corrective actions have been taken to ensure the Contractor's capability to meet contract requirements will facilitate continuation of full sample delivery.

SECTION IX

GC/MS TAPE AUDITS

Periodically, EPA requests from Contractors the GC/MS magnetic tapes corresponding to a specific Case in order to accomplish tape audits. Generally, tape submissions and audits are requested for the following reasons:

- o Program overview.
- o Indication of data quality problems from EMSL-LV, SMO, or Regional data reviews.
- o Support for on-site audits.
- o Specific Regional requests.

Depending upon the reason for an audit, the tapes from a recent Case, a specific Case, or a laboratory evaluation sample may be requested. Tape audits provide a mechanism to assess adherence to contractual requirements and ensure the consistency of data reported on the hardcopy forms with that generated on the GC/MS tapes. This function provides external monitoring of CLP QC requirements and checks adherence of the Contractor to internal QA procedures. In addition, tape audits enable EPA to evaluate the utility, precision and accuracy of the analytical methods.

The GC/MS tape shall include raw data and quantitation reports for samples, blanks, laboratory evaluation samples, initial calibrations, and continuing calibrations associated with the SDG requested. The specific requirements for submissions of GC/MS tapes are discussed in Exhibit B.

Upon request of the APO or EMSL-LV, the required tapes and all necessary documentation shall be submitted to EPA within seven days of notification.

SECTION X

ON-SITE LABORATORY EVALUATIONS

At a frequency dictated by a Contractor's performance, the APO, TPO or their authorized representative will conduct an on-site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Contractor's ability to meet selected terms and conditions specified in the contract. The evaluation process incorporates two separate categories: a QA evaluation and an evidentiary audit.

A. Quality Assurance Evaluation

QA evaluators inspect the Contractor's facilities to verify the adequacy and maintenance of instrumentation, the continuity of personnel meeting experience or education requirements, and the acceptable performance of analytical and QC procedures. The Contractor should expect that items to be monitored will include, but not be limited to, the following items:

- Size and appearance of the facility.
- Quantity, age, availability, scheduled maintenance and performance of instrumentation.
- Availability, appropriateness, and utilization of SOPs.
- Staff qualifications, experience, and personnel training programs.
- Reagents, standards, and sample storage facilities.
- Standard preparation logbooks and raw data.
- Bench sheets and analytical logbook maintenance and review.
- Review of the Contractor's sample analysis/data package inspection procedures.

Prior to an on-site evaluation, various documentation pertaining to performance of the specific Contractor is integrated in a profile package for discussion during the evaluation. Items that may be included are previous on-site reports, laboratory evaluation sample scores, Regional review of data, Regional QA materials, GC/MS tape audit reports, results of CCS, and date trend reports.

B. Evidentiary Audit

Evidence auditors conduct an on-site laboratory evaluation to determine if laboratory policies and procedures are in place to satisfy evidence handling requirements as stated in Exhibit F. The evidence audit is comprised of the following three activities:

1. Procedural Audit

The procedural audit consists of review and examination of actual SOPs and accompanying documentation for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis), and analytical project file organization and assembly.

2. Written SOPs Audit

The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis), and analytical project file organization and assembly.

3. Analytical Project File Evidence Audit

The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

- o Accuracy of the document inventory.
- o Completeness of the file.
- o Adequacy and accuracy of the document numbering system.
- o Traceability of sample activity.
- o Identification of activity recorded on the documents.
- o Error correction methods.

C. Discussion of the On-Site Team's Findings

The QA and evidentiary auditors discuss their findings with the APO/TPO prior to debriefing the Contractor. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Contractor personnel.

D. Corrective Action Reports For Follow-Through to Quality Assurance and Evidentiary Audit Reports

Following an on-site evaluation, QA and evidentiary audit reports which discuss deficiencies found during the on-site evaluation will be forwarded to the Contractor. The Contractor must discuss the corrective actions taken to resolve the deficiencies discussed during the on-site visit and discussed in the on-site reports in a letter to the APO, TPO, EMSL-LV (response to the QA report) and NEIC (response to the evidentiary report) within 14 days of receipt of the finding or within the time agreed upon between the APO/TPO and the Contractor. If SOPs are required to be written or amended, the Contractor must provide

the SOPs to the TPO, EMSL-LV (QA/technical SOPs) and NEIC (evidentiary SOPs) within 30 days of receipt of the finding or within the time agreed upon between the APO/TPO and the Contractor.

If the Contractor fails to take appropriate corrective action to resolve the deficiencies discussed in the on-site reports, a Contractor may expect, but the Government is not limited to, the following actions: reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, a follow-up site visit, a full data audit, analysis of remedial PE samples and/or contract sanction, such as a Cure Notice.

SECTION XI

QUALITY ASSURANCE AND DATA TREND ANALYSIS

Data submitted by laboratories are subject to review from several aspects: compliance with contract-required QC, usability, and full data package evaluation. Problems resulting from any of these reviews may determine the need for a GC/MS tape audit, an on-site laboratory evaluation and/or a remedial laboratory evaluation sample. In addition, QC prescribed in the methods provides information that is continually used by EPA to assess sample data quality, Contractor data quality and CLP data quality via data trend analysis. Trend analysis is accomplished by entering data into a computerized database. Statistical reports that evaluate specific anomalies or disclose trends in many areas, including the following, are generated from this database:

- Internal standard recovery.
- Laboratory evaluation sample.
- Blanks.
- Gas chromatographic resolution of analytes.
- Initial and continuing calibration data.
- Other QC and method parameters.

Program-wide statistical results are used to rank laboratories in order to observe the relative performance of each Contractor using a given protocol against its peers. The reports are also used to identify trends within laboratories. The results of many of these trends analyses are included in overall evaluation of a Contractor's performance, and are reviewed to determine if corrective action or an on-site laboratory evaluation is indicated in order to meet the QA/QC requirements of the contract.

Contractor performance over time is monitored using these trend analysis techniques to detect departures of Contractor output from required or desired levels of QC, and to provide an early warning of Contractor QA/QC problems which may not be apparent from the results of an individual case.

As a further benefit to the CLP, the database provides the information needed to establish performance-based criteria in updated analytical protocols, where advisory criteria has been previously used. The vast empirical data set produced by contract laboratories is carefully analyzed, with the results augmenting theoretical and research-based performance criteria. The result is a continuously monitored set of QC and performance criteria specifications of what is routinely achievable and expected of environmental chemistry laboratories in mass production analysis of environmental samples. This information, in turn, assists EPA in meeting its objectives of obtaining data of known and documented quality.

SECTION XII

DATA MANAGEMENT

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage and security of computer-readable data and files. These procedures should be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security), documentation operations, traceability and QC.

Data manually entered from hardcopy must be quality controlled and the error rates estimated. Systems should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates must be estimated and recorded on a monthly basis by reentering a statistical sample of the data entered and calculating discrepancy rates by data element.

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted must be documented to allow traceability of updates. Documentation must include the following for each change:

- Justification or rationale for the change.
- Initials of the person making the change or changes. Data changes must be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Change documentation must be retained according to the schedule of the original deliverable.
- Resubmitted deliverables must be reinspected as a part of the laboratory's internal inspection process prior to resubmission. The entire deliverable, not just the changes, must be inspected.
- The Laboratory Manager must approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by laboratory auditors.

Life cycle management procedures must be applied to computer software systems developed by the laboratory to be used to generate and edit contract deliverables. Such systems must be thoroughly tested and documented prior to utilization.

- A software test and acceptance plan including test requirements, test results and acceptance criteria must be developed, followed, and available in written form.
- System changes must not be made directly to production systems generating deliverables. Changes must be made first to a development system and tested prior to implementation.

- Each version of the production system will be given an identification number, a date of installation, and a date of last operation, and will be archived.
- System and operations documentation must be developed and maintained for each system. Documentation must include a user's manual and an operations and maintenance manual.

Individual(s) responsible for the following functions must be identified:

- System operation and maintenance including documentation and training.
- Database integrity, including data entry, data updating and quality control.
- Data and system security, backup and archiving.

REFERENCES

1. Fisk, J.F. and Manzo, S.M. "Quality Assurance/Quality Control in Organics Analysis," Proceedings from the Water Pollution Control Federation Meeting, May 1986.

2. Office of Monitoring Systems and Quality Assurance, U.S. Environmental Protection Agency, "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80, December 1980.

3. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Third Edition, SW-846, November 1986.

4. Laidlaw, R.H., "Document Control and Chain of Custody Considerations for the National Contract Laboratory Program," Quality Control in Remedial Site Investigations: Hazardous and Industrial Solid Waste Testing, Fifth Volume, ASTM STP 925, C.L. Perket, ed., American Society for Testing and Materials, Philadelphia, 1986.

5. Health Effects Research Laboratory, U.S. Environmental Protection Agency, Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples, EPA-600/8-80-036, June 1980.

6. Environmental Protection Agency, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," 40 CFR Part 136, Federal Register, Vol. 49, No. 209, pp. 43234-43442, October 26, 1984.

7. Health Effects Research Laboratory, U.S. Environmental Protection Agency, Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples-Second Revision, EPA-600/2-81-059, April 1981.

8. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Analytical Reference Standards and Supplemental Data: The Pesticides and Industrial Chemicals Repository, EPA-600/4-84-082, October 1984.

9. American Chemical Society Committee on Environmental Improvement, and Subcommittee on Environmental Analytical Chemistry, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," Analytical Chemistry, Volume 52, Number 14, December 1980.

10. Moore, J.M. and Pearson, J.G. "Quality Assurance Support for the Superfund Contract Laboratory Program," Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Fifth Volume, ASTM STP 925, C.L. Perket, ed., American Society for Testing and Materials, Philadelphia, 1986.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND STANDARD OPERATING PROCEDURES

Table of Contents

1. Sample Chain-of-Custody

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To accomplish this task, Contractors are required to develop and implement the following sample identification, chain-of-custody, sample receiving, and sample tracking procedures.

1.1 Sample Identification

To assure traceability of the samples while in the possession of the Contractor, the Contractor shall have a specified method for maintaining identification of samples throughout the laboratory. Each sample and sample preparation container shall be labeled with the EPA number or a unique laboratory identifier. If a unique laboratory identifier is used, it shall be cross-referenced to the EPA number.

1.2 Chain-of-Custody Procedures

Because of the nature of the data being collected, the custody of EPA samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. The Contractor shall have procedures ensuring that EPA sample custody is maintained and documented. A sample is under custody if:

- It is in your possession, or
- It is in your view after being in your possession, or
- It was in your possession and you locked it up, or
- It is in a designated secure area. (Secure areas shall be accessible only to authorized personnel.)

1.3 Sample Receiving Procedures

1.3.1 The Contractor shall designate a sample custodian responsible for receiving all samples.

1.3.2 The Contractor shall designate a representative to receive samples in the event that the sample custodian is not available.

1.3.3 The condition of the shipping containers and sample bottles shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.4 The condition of the custody seals (intact/not intact) shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.5 The sample custodian or his/her representative shall check for the presence or absence of the following documents accompanying the sample shipment:

- o Airbills or airbill stickers
- o Custody seals
- o EPA custody records
- o Sample Traffic Reports or SAS Packing Lists
- o Sample tags

1.3.6 The sample custodian or his/her representative shall sign and date all forms (e.g., custody records, Traffic Reports or Packing Lists, and airbills) accompanying the samples at the time of sample receipt.

1.3.7 The Contractor shall contact the Sample Management Office (SMO) to resolve discrepancies and problems such as absent documents, conflicting information, broken custody seals, and unsatisfactory sample condition (e.g., leaking sample bottle).

1.3.8 The Contractor shall record the resolution of discrepancies and problems on Telephone Contact Logs.

1.3.9 The following information shall be recorded on Form DC-1 (see Exhibit B) by the sample custodian or his/her representative as samples are received and inspected:

- o Condition of the shipping container.
- o Presence or absence and condition of custody seals on shipping and/or sample containers.
- o Custody seal numbers, when present.
- o Condition of the sample bottles.
- o Presence or absence of airbills or airbill stickers.
- o Airbill or airbill sticker numbers.
- o Presence or absence of EPA custody records.
- o Presence or absence of Traffic Reports or SAS Packing Lists.
- o Presence or absence of sample tags.
- o Sample tag identification numbers cross-referenced to the EPA sample numbers.
- o Verification of agreement or non-agreement of information recorded on shipping documents and sample containers.
- o Problems or discrepancies.

1.4 Sample Tracking Procedures

The Contractor shall maintain records documenting all phases of sample handling from receipt to final analysis.

2. Document Control Procedures

The goal of the laboratory document control program is to assure that all documents for a specified Sample Delivery Group (SDG) will be accounted for when the project is completed. Accountable documents used by contract laboratories shall include, but not be limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analysis. The following document control procedures have been established to ensure that all laboratory records are assembled and stored for delivery to EPA or are available upon request from EPA prior to the delivery schedule.

2.1 Preprinted Laboratory Forms and Logbooks

2.1.1 All documents produced by the Contractor that are directly related to the preparation and analysis of EPA samples shall become the property of EPA and shall be placed in the Complete SDG File (CSF). All observations and results recorded by the laboratory but not on preprinted laboratory forms shall be entered into permanent laboratory logbooks. When all data from a SDG are compiled, all original laboratory forms and copies of all SDG-related logbook entries shall be included in the documentation package.

2.1.2 The Contractor shall identify the activity recorded on all laboratory documents that are directly related to the preparation and analysis of EPA samples.

2.1.3 Pre-printed laboratory forms shall contain the name of the laboratory and be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.4 Logbook entries shall be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.5 Logbook entries shall be in chronological order. Entries in logbooks, with the exception of instrument run logs and extraction logs, shall include only one SDG per page.

2.1.6 Pages in both bound and unbound logbooks shall be sequentially numbered.

2.1.7 Instrument run logs shall be maintained so as to enable a reconstruction of the run sequence of individual instruments. Because the laboratory must provide copies of the instrument run logs to EPA, the laboratory may exercise the option of using only laboratory or EPA sample identification numbers in the logs for sample ID rather than government agency or commercial client names to preserve the confidentiality of commercial clients.

2.1.8 Corrections to supporting documents and raw data shall be made by drawing a single line through the error and entering the correct information. Corrections and additions to supporting documents and raw data shall be dated and initialed. No information shall be obliterated or rendered unreadable.

All notations shall be recorded in ink. Unused portions of documents shall be "z'd" out.

2.2 Consistency of Documentation

The Contractor shall assign a Document Control Officer (DCO) responsible for the organization and assembly of the CSF. All copies of laboratory documents shall be complete and legible.

Original documents which include information relating to more than one SDG shall be filed in the CSF of the lowest SDG number. The copy(ies) shall be placed in the other CSF(s), and the Contractor shall record the following information on the copy(ies) in red ink:

"COPY - ORIGINAL IS FILED IN CSF _____"

The Contractor shall sign and date this addition to the copy(ies).

Before releasing analytical results, the DCO shall assemble and cross-check the information on samples tags, custody records, lab bench sheets, personal and instrument logs, and other relevant deliverables to ensure that data pertaining to each particular sample or SDG are consistent throughout the CSF.

2.3 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in the CSF shall be inventoried and assigned a serialized number as described in Exhibit B.

All documents relevant to each SDG, including logbook pages, bench sheets, mass spectra, chromatograms, screening records, re-preparation records, reanalysis records, records of failed or attempted analysis, custody records, library research results, etc., shall be inventoried.

The DCO shall be responsible for ensuring that all documents generated are placed in the CSF for inventory and are delivered to the appropriate EPA Region or other receiver as designated by EPA. The DCO shall place the sample tags in plastic bags in the file.

2.4 Storage of EPA Files

The Contractor shall maintain EPA laboratory documents in a secure location.

2.5 Shipment of Deliverables

The Contractor shall document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that the containers cannot be opened without damaging or breaking the seal. The Contractor shall document what was sent, to whom, the date, and the method (carrier) used. A copy of the transmittal letter for the CSF shall be sent to the National Enforcement Investigations Center and SMO.

3. Specifications for Written Standard Operating Procedures

The Contractor shall have written standard operating procedures (SOPs) for receipt of samples, maintenance of custody, sample identification, sample storage, sample tracking, and assembly of completed data. A SOP is defined as a written narrative stepwise description of laboratory operating procedures including examples of laboratory documents. The SOPs shall accurately describe the actual procedures used in the laboratory, and copies of the written SOPs shall be available to the appropriate laboratory personnel. These procedures are necessary to ensure that analytical data produced under this contract are acceptable for use in EPA enforcement case preparation and litigation. The Contractor's SOPs shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA as the basis for laboratory evidence audits.

3.1 The Contractor shall have written SOPs describing the sample custodian's duties and responsibilities.

3.2 The Contractor shall have written SOPs for receiving and logging in of the samples. The procedures shall include, but not be limited to, documenting the following information:

3.2.1 Presence or absence of EPA chain-of-custody forms.

3.2.2 Presence or absence of airbills or airbill stickers.

3.2.3 Presence or absence of Traffic Reports or SAS Packing Lists.

3.2.4 Presence or absence of custody seals on shipping and/or sample containers and their condition.

3.2.5 Custody seal numbers, when present.

3.2.6 Airbill or airbill sticker numbers.

3.2.7 Presence or absence of sample tags.

3.2.8 Sample tag ID numbers.

3.2.9 Condition of the shipping container.

3.2.10 Condition of the sample bottles.

3.2.11 Verification of agreement or non-agreement of information on receiving documents and sample containers.

3.2.12 Resolution of problems or discrepancies with SMO.

3.2.13 An explanation of any terms used by the laboratory to describe sample condition upon receipt (e.g., good, fine, OK).

3.3 The Contractor shall have written SOPs for maintaining identification of EPA samples throughout the laboratory. If the Contractor assigns unique laboratory identifiers, written SOPs shall include a description of the method used to assign the unique laboratory identifier and shall include a description of the document used to cross-reference the unique laboratory identifier to the EPA sample number. If the Contractor uses prefixes or suffixes in addition to sample identification numbers, the written SOPs shall include their definitions.

3.4 The Contractor shall have written SOPs describing all storage areas for samples in the laboratory. The SOPs shall include a list of authorized personnel who have access or keys to secure storage areas.

3.5 The Contractor shall have written SOPs describing the method by which the laboratory maintains samples under custody.

3.6 The Contractor shall have written SOPs describing the method by which the laboratory maintains the security of any areas identified as secure.

3.7 The Contractor shall have written SOPs for tracking the work performed on any particular samples. The tracking SOP shall include:

- o A description of the documents used to record sample receipt, sample storage, sample transfers, sample preparations, and sample analyses.
- o A description of the documents used to record calibration and QA/QC laboratory work.
- o Examples of document formats and laboratory documents used in the sample receipt, sample storage, sample transfer, and sample analyses.
- o A narrative step-wise description of how documents are used to track samples.

3.8 The Contractor shall have written SOPs for organization and assembly of all documents relating to each SDG. Documents shall be filed on a SDG-specific basis. The procedures shall ensure that all documents including logbook pages, sample tracking records, chromatographic charts, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the SDG are compiled in one location for submission to EPA. The written SOPs shall include:

- o A description of the numbering and inventory method.

- o A description of the method used by the laboratory to verify consistency and completeness of the CSF.
- o Procedures for the shipment of deliverables packages using custody seals.

4. Handling of Confidential Information

A Contractor conducting work under this contract may receive confidential information from EPA. Confidential information must be handled separately from other documentation developed under this contract. To accomplish this, the following procedures for the handling of confidential information have been established.

4.1 All confidential documents shall be under the supervision of a designated DCO.

4.2 Any samples or information received with a request of confidentiality shall be handled as "confidential." A separate locked file shall be maintained to store this information and shall be segregated from other nonconfidential information. Data generated from confidential samples shall be treated as confidential. Upon receipt of confidential information, the DCO will log these documents into a Confidential Inventory Log. The information will then be available to authorized personnel but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by the Technical Project Officer and Administrative Project Officer. The DCO will enter all copies into the document control system described above. In addition, this information may not be disposed of except upon approval by the Technical Project Officer and Administrative Project Officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record on the disposition in the Confidential Inventory Log.

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, CC3.

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.