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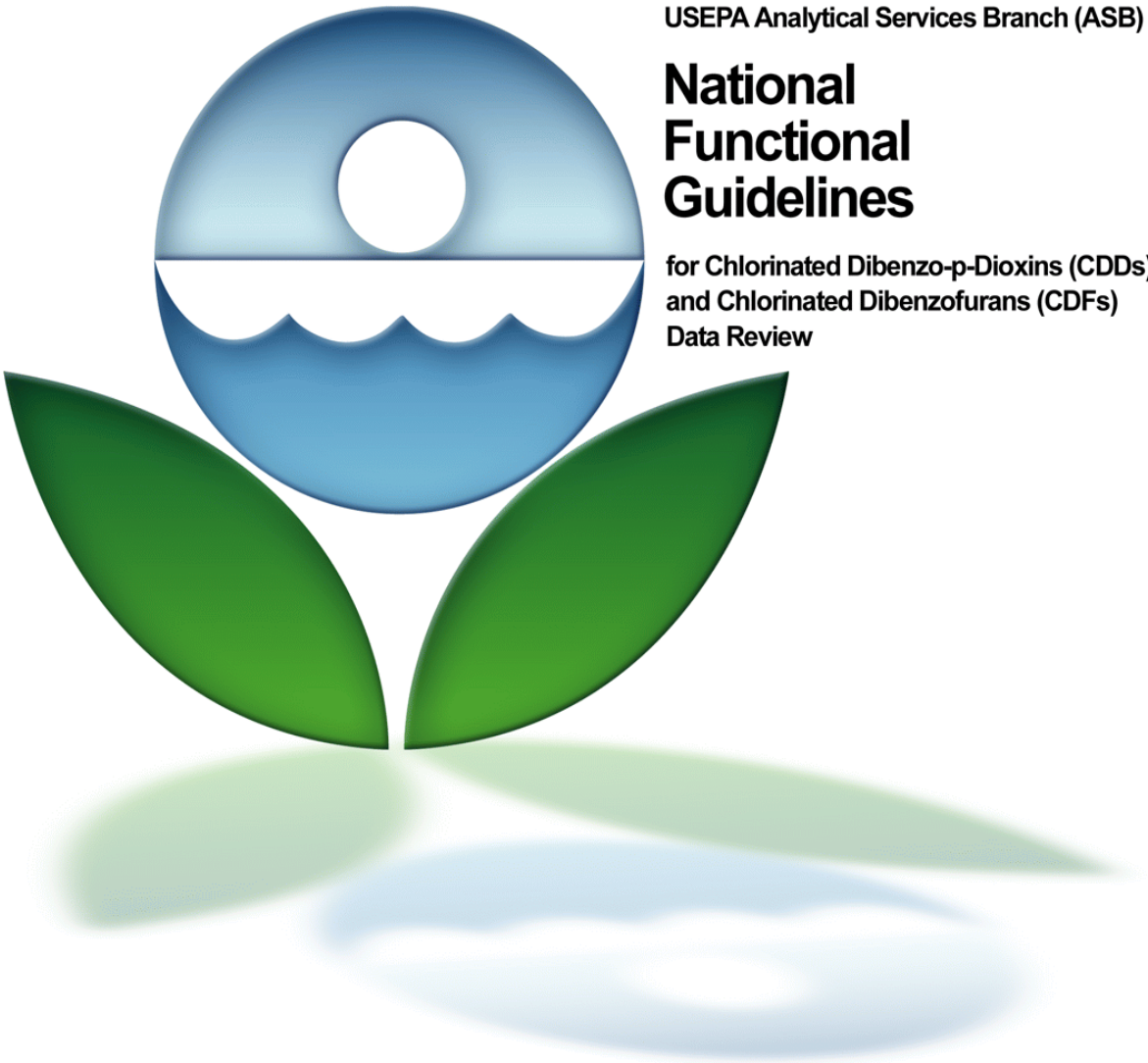

USEPA Analytical Services Branch (ASB)

National Functional Guidelines

for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review

Final

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NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by USEPA, and may not be relied upon to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

This document can be obtained from USEPA's Contract Laboratory Program (CLP) Web site at:

http://www.epa.gov/superfund/programs/clp/guidance.htm

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ACRONYMS

%D	Percent Difference
%Recovery	Percent Recovery
%RSD	Percent Relative Standard Deviation
%Solids	Percent Solids
%Valley	Percent Valley
CDD	Chlorinated Dibenzo-p-Dioxins
CDF	Chlorinated Dibenzofurans [also Polychlorinated Dibenzofuran (PCDF)]
CDWG	Chlorinated Dioxins Work Group
CLP	Contract Laboratory Program
CPS	Column Performance Solution
CRQL	Contract Required Quantitation Limits
CS	Calibration Standard
CWA	Clean Water Act
DQO	Data Quality Objective
EDL	Estimated Detection Limit
EMPC	Estimated Maximum Possible Concentration
GC	Gas Chromatography
HRGC	High Resolution Gas Chromatograph
HpCDD	Heptachlorinated Dibenzo-p-Dioxin
HpCDF	Heptachlorinated Dibenzofuran
HRMS	High Resolution Mass Spectrometer
HxCDD	Hexachlorinated Dibenzo-p-Dioxins
HxCDF	Hexachlorinated Dibenzofurans
ISC	Isomer Specificity Check
LCS	Laboratory Control Sample
Mean RR	Mean Relative Response
Mean RRF	Mean Relative Response Factor
NFG	National Functional Guidelines
OCDD	Octachlorinated Dibenzo-p-Dioxin
OCDF	Octachlorinated Dibenzofuran
PCDF	Polychlorinated Dibenzofuran
PCDPE	Polychlorinated Diphenyl Ether

PE	Performance Evaluation
PES	Performance Evaluation Sample
PeCDD	Pentachlorinated Dibenzo-p-Dioxin(s)
PeCDF	Pentachlorinated Dibenzofuran(s)
PFK	Perfluorokerosene
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support
QC	Quality Control
RR	Relative Response
RRF	Relative Response Factor
RSD	Relative Standard Deviation
RT	Retention Time
RRT	Relative Retention Time
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SDWA	Safe Drinking Water Act
SICP	Selected Ion Current Profile
SIM	Selected Ion Monitoring
S/N	Signal-to-Noise Ratio
SOP	Standard Operating Procedure
SOW	Statement of Work
TCL	Target Compound List
TCDD	Tetrachlorinated Dibenzo-p-Dioxin(s)
TCDF	Tetrachlorinated Dibenzofuran(s)
TEF	Toxicity Equivalency Factor
TICP	Total Ion Current Profile
TO	Task Order
TOPO	Task Order Project Officer
TR/COC	Traffic Report/Chain of Custody
VTSR	Validated Time of Sample Receipt
WDM	Window Defining Mixture
USEPA	United States Environmental Protection Agency

INTRODUCTION

The *USEPA Analytical Services Branch (ASB) National Functional Guidelines for Chlorinated Dioxin and Furan Data Review* (hereafter referred to as the NFG) is designed to offer guidance on USEPA chlorinated dibenzo-p-dioxin (CDD) and chlorinated dibenzofuran (CDF) data evaluation and review. In some applications, it may be used as a Standard Operating Procedure (SOP). In other, more subjective areas, only general guidance is offered due to the complexities and uniqueness of data relative to specific samples. For example, areas where the application of specific SOPs is possible are primarily those in which definitive performance criteria are established. These criteria are concerned with specifications that are not sample dependent; they specify performance requirements that should fully be under a laboratory's control. These specific areas include blanks, calibration standards, Performance Evaluation (PE) standard materials, and instrument performance checks.

These guidelines include the requirements for the *USEPA Analytical Services Branch Statement of Work for Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Multi-Media, Multi-Concentration (DLM02.X*) (hereafter referred to as DLM02.X SOW or DLM02.X). The DLM02.X SOW is based on USEPA Method 1613 (Revision B) and SW-846 Method 8290 (Revision 0) which use High Resolution Gas Chromatography and High Resolution Mass Spectrometry (HRGC/HRMS).

> USEPA Method 1613 (Revision B) can be obtained at:
> http://www.epa.gov/waterscience/methods/1613.pdf
>
> USEPA SW-846 Method 8290 (Revision 0) can be obtained at:
> http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8290a.pdf

The NFG is intended to assist in the technical review of analytical data generated through the DLM02.X SOW. Determining contract compliance is not the intended objective of these guidelines. The data review process provides information on analytical limitations of data, based on specific Quality Control (QC) criteria. To provide more specific usability statements, the reviewer must have a complete understanding of the intended use of the data. For this reason, it is recommended that whenever possible, the reviewer should obtain usability issues from the user prior to reviewing the data. When this is not possible, the user is encouraged to communicate any questions to the reviewer.

At times, there may be a need to use data which do not meet all contract requirements and technical criteria. Use of these data does not constitute either a new requirement standard or full acceptance of the data. Any decision to utilize data for which performance criteria have not been met is strictly to facilitate the progress of projects requiring the availability of the data. A contract laboratory submitting data which are out of specification may be required to rerun samples or resubmit data, even if the previously submitted data have been utilized due to program needs. Data which do not meet specified requirements are never fully acceptable. The only exception to this condition is in the area of the requirements for individual sample analysis; if the nature of the sample itself inhibits the attainment of specifications, appropriate allowances must be made.

Use professional judgment to determine the ultimate usability of the data.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the data qualifiers assigned to results in the data review process. If the data reviewer chooses to use additional qualifiers, a complete explanation of those qualifiers must accompany the data review.

Data Qualifier	Qualifier Definitions
U	The analyte was analyzed for, but was not detected at a level greater than or equal to the level of the adjusted Contract Required Quantitation Limit (CRQL) for sample and method.
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample [due either to the quality of the data generated because certain Quality Control (QC) criteria were not met, or the concentration of the analyte was below the adjusted CRQL].
UJ	The analyte was not detected at a level greater than or equal to the adjusted CRQL or the reported adjusted CRQL is approximate and may be inaccurate or imprecise.
R	The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.

PRELIMINARY REVIEW

The NFG is used for the review of analytical data generated through the DLM02.X SOW. To use this document effectively, the reviewer must have an understanding of the analytical method and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analysis are essential information. Background information on the site is helpful, but often this information may be difficult to locate. If available, the field notes must be reviewed. The site manager is the best source for answers to questions, or for further direction.

Please note that individual Task Orders (TOs) may modify the DLM02.X SOW requirements, which will affect the generated data. For example, holding times, extraction procedures, compound analyses and calibration requirements, etc., may be affected by an individual TO depending on project requirements. Thus, the TO requirements must be taken into consideration, along with the requirements in the National Functional Guidelines (NFG) document, when reviewing the data.

The SDGs or Cases routinely have unique samples which require special attention by the reviewer. These samples include field blanks, field duplicates, and Performance Evaluation (PE) samples which need to be identified. The sampling records must provide:

1. The Region where the samples were taken; and

2. A complete list of samples with information on:
   a. Laboratories involved;
   b. Shipping dates;
   c. Preservatives;
   d. Sample matrix;
   e. Field blanks*;
   f. Field duplicates*;
   g. Field spikes*; and
   h. Quality Control (QC) audit samples*.

   * If applicable.

The Traffic Report/Chain of Custody (TR/COC) documentation includes sample descriptions, date(s) and time(s) of sampling, sample location, and sample matrix. The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, and unusual events should be listed in the SDG Narrative.

The SDG Narrative for the sample data package must include a Laboratory Certification Statement (exactly as stated in the DLM02.X SOW), signed by the Laboratory Manager or their designee. This statement authorizes the validation and release of sample data results. In addition, the laboratory must also provide comments in the SDG Narrative describing in detail any problems encountered in processing the samples associated with the data package.

DATA REVIEW NARRATIVE

A Data Review Narrative must accompany the laboratory data forwarded to the intended data recipient (client) or user to promote communications. A copy of the Data Review Narrative must also be submitted to the Task Order Project Officer (TOPO) assigned oversight responsibility for the laboratory producing the data.

The Data Review Narrative must include comments that clearly identify the problems associated with a Case or Sample Delivery Group (SDG) and state the limitations of the data. Documentation must include the sample number, analytical method or modification, extent of the problem, and assigned qualifiers.

CHLORINATED DIOXIN AND FURAN DATA REVIEW

The data requirements to be checked are listed below:

I. Holding Times, Storage, and Preservation

II. Performance Evaluation (PE) Samples

III. Mass Calibration and Mass Spectrometer Resolution

IV. Window Defining Mixture (WDM)

V. Chromatographic Resolution

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VII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Initial Calibration

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XVIII. Regional Quality Assurance and Quality Control (QA/QC)

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I. Holding Times, Storage, and Preservation

A. Review Items:

Form 1DFA, 1DFB, or 1DFC (Form I-HR CDD-1, CDD-2, or CDD-3), USEPA Sample Traffic Report/Chain of Custody (TR/COC) documentation, raw data, and sample extraction sheets.

B. Objective:

Ascertain the validity of sample results based on the contractual holding time, storage, and preservation of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

Aqueous and soil samples must be stored at 4°C (± 2°C) in the dark from the time of collection until extraction. If residual chlorine is present in aqueous samples, 80 mg of sodium thiosulfate per liter of sample must be added. If the sample pH is > 9, the sample pH must be adjusted to pH 7-9 with sulfuric acid.

NOTE: Aqueous samples subject to compliance with the Clean Water Act (CWA) or Safe Drinking Water Act (SDWA) (40CFR Part 136.3) may require extraction within 7 days from the time of collection to the day of extraction.

Fish and tissue samples must be received at the laboratory at a temperature of < 4°C and must be stored at the laboratory at < -10°C until prepared. Once thawed, tissue samples must be extracted within 24 hours.

- Analysis of sample extracts must be completed within 30 days of extraction.
- Sample extracts can be stored up to one year from the date of extraction in the event that reanalysis is required.
- Holding times for oily matrices have not been established. The aqueous holding times are recommended in this case. Holding times for fish and tissue samples have not been established, however, they must be extracted within one year of collection as recommended in USEPA Method 1613 (Revision B). As always, the professional judgment of the reviewer remains the final authority in issues such as these.

D. Evaluation:

1. Technical holding times for sample extraction are established by comparing the sampling dates on the TR/COC documentation with the dates of extraction on the sample extraction sheets and on Form I-HR CDD-1, CDD-2, or CDD-3. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I-HR CDD-1.

2. Verify that the TR/COC documentation indicates that the samples were received intact and iced at 4°C (± 2°C). Note in the Data Review Narrative if the samples were not iced, if there were any problems with the samples upon receipt, or if discrepancies in the sample condition could affect the data.

E. Action:

1. If holding times are exceeded, qualify all detects as estimated "J" and use professional judgment to qualify non-detects as estimated "UJ" or unusable "R". Document that holding times were exceeded (see Table 1).

2. If shipment and storage conditions are exceeded, either on the first analysis or upon reanalysis, use professional judgment to determine if the detects or non-detects are estimates and qualify with estimated "J" or "UJ", respectively.

3. If sodium thiosulfate preservative has not been added to aqueous samples, qualify all detects estimated "J" and non-detects estimated "UJ". If a residual chlorine test has been performed and found to be negative, do not qualify the data, due to lack of sodium thiosulfate preservative.

4. There is limited information concerning holding times for oily samples. Use professional judgment to evaluate the application of aqueous holding time criteria to oily samples.

5. Use professional judgment to evaluate holding times for fish and tissue samples.

6. For all sample extracts correctly stored and analyzed outside the 30-day holding time, but within the 1-year holding time, no qualification of the data is necessary.

7. For all sample extracts not correctly stored and analyzed outside the 30-day holding time but within the 1-year holding time, qualify detects estimated "J" and non-detects estimated "UJ".

8. For all sample extracts analyzed outside the 1-year holding time, qualify detects as estimated "J" and use professional judgment to qualify non-detects estimated "UJ" or unusable "R".

9. When holding times are exceeded, note in the Data Review Narrative the effect that the exceeded holding times will have on the resulting data and also note as an action item for the Task Order Project Officer (TOPO).

Table 1. Holding Times, Storage, and Preservation Evaluation Actions Data

Evaluation	Sample Type	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Contractual Holding Time	Aqueous	> 1 year	J	UJ or R
	Soil	> 1 year	J	UJ or R
	Fish, Tissue	> 1 year	Use professional judgment	
Storage Temperature	Aqueous	> 4°C shipment and storage	J	UJ
	Soil	> 4°C shipment and storage	J	UJ
	Fish, Tissue	> 4°C shipment and > -10°C storage	J	UJ
Preservation	Aqueous	Not added	J	UJ
Sample Extract Holding Time *	All types	> 30 days < 1 year	No qualification	
Sample Extract Holding Time **	All types	> 30 days < 1 year	J	UJ
Sample Extract Holding Time	All types	> 1 year	J	UJ or R

* If correctly stored
** If not correctly stored

II. Performance Evaluation (PE) Samples

A. Review Items:

Form 1DFA (Form I-HR CDD-1), Performance Evaluation (PE) sample score information from the Quality Assurance Technical Support (QATS) laboratory.

B. Objective:

Evaluate the laboratory's ability to achieve acceptable results through the analysis of PE samples.

C. Criteria:

1. The Region may provide the laboratory with a PE sample to be analyzed with each Sample Delivery Group (SDG). The laboratory must analyze PE samples when provided by the Region.

2. The Region may score the PE samples based on data provided by QATS.

D. Evaluation:

If PE samples are included in the SDG, verify that the PE sample results are within the action limits [99% (3σ) confidence interval] of the experimentally determined true values provided by QATS.

E. Action:

If a result is not within the action limits [99% (3σ) confidence interval] for any congener, evaluate the other Quality Control (QC) samples in the SDG [Laboratory Control Sample (LCS), calibration, labeled standard recovery, internal standard recovery, and clean-up standard recovery]. In such situations, the PE sample may not be representative of the field samples. PE samples are only one indicator of technical performance of the laboratory. In general, for PE sample analytes not within the 95% confidence intervals or action performance windows but within the 99% confidence interval, qualify associated sample detects as estimated "J" and non-detects as estimated "UJ". For data outside the 99% confidence interval, qualify the associated sample data as unusable "R" (see Table 2). Contact the Task Order Project Officer (TOPO) to determine if reanalysis of samples is required. Under certain circumstances, it may be necessary to utilize data that are not within the 99% confidence interval before reanalysis can take place. Use professional judgment to determine the usability of the data.

For Example: If hexachlorinated dibenzo-p-dioxin (HxCDD) is quantitated beyond the high-end of the action limit and all samples are non-detects for this compound, the usability of the data would not be affected.

NOTE: Qualify only those analytes that fail to meet criteria.

Table 2. PE Sample Data Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Results are not within the 95% confidence interval but inside the 99% interval (< 3σ)	J	UJ
Results are not within the 99% confidence interval (> 3σ)	R	R

III. Mass Calibration and Mass Spectrometer Resolution

A. Review Items:

Hardcopy of Mass Spectrometer resolution demonstration.

B. Objective:

Perform mass calibration and Mass Spectrometer resolution ≥ 10,000 with perfluorokerosene (PFK) calibrant. This is a fundamental requirement for any laboratory using DLM02.X and other High Resolution Mass Spectrometry (HRMS) methods [e.g., Method 1613 (Revision B), SW-846 Method 8290 (Revision 0)]. If mass calibration and resolution tuning is not correctly performed, interferences may degrade chlorinated dibenzo-p-dioxin and chlorinated dibenzofuran (CDD/CDF) identification and quantitation. Mass calibration and resolution is the first part of the three fundamental High Resolution Gas Chromatography/HRMS (HRGC/HRMS) system performance checks. The second fundamental performance check is the Mass Spectrometer Selected Ion Monitoring (SIM) scan descriptor switching times. The third fundamental performance check is Gas Chromatograph (GC) resolution.

C. Criteria:

Laboratories are required to provide evidence of Mass Spectrometer resolution ≥ 10,000 at the beginning and end of each 12-hour analytical sequence. Documentation of Mass Spectrometer resolving power must include a hardcopy peak profile of a high-mass reference signal from PFK (e.g., m/z 380.9760) obtained during peak matching with another high-mass ion (e.g., m/z 304.9824). The selection of the low- and high-mass ions must be such that they provide the largest voltage jump in any of the five mass descriptors. The format of the peak profile representation must allow manual determination of Mass Spectrometer resolution [i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division)]. The result of the peak width measurement must appear on the hardcopy. The deviation between the exact m/z and the theoretical m/z monitored must be < 5 ppm.

D. Evaluation:

Verify that the Mass Spectrometer has been tuned to a resolution of ≥ 10,000. A demonstration of Mass Spectrometer resolving power is provided within USEPA SW-846 Method 8290 (Revision 0).

E. Action:

Mass Spectrometer resolution is critical to the success of this method of CDD/CDF analysis. In the event that Mass Spectrometer resolution is < 10,000 or is not demonstrated, qualify all associated data as unusable "R".

IV. Window Defining Mixture (WDM)

A. Review Items:

Form 5DFA (Form V-HR CDD-1).

B. Objective:

Prior to the calibration of the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system, establish the appropriate switching times for the Selected Ion Monitoring (SIM) descriptors (see Table A.1) and verify the chromatographic resolution. The switching times are determined by the analysis of the Window Defining Mixture (WDM) which contains the first and last eluting isomers in each homologue (see Table A.2). Chromatographic resolution is verified by analyzing one of two Isomer Specificity Check (ISC) solutions, depending on the Gas Chromatograph (GC) column used for analysis. The WDM and ISC can be combined in a single Column Performance Solution (CPS) analysis at the discretion of the analyst.

The 12-hour time period begins with the injection of the WDM or CPS.

C. Criteria:

1. To evaluate the Mass Spectrometer SIM scan descriptor switching times, the WDM must be analyzed after the perfluorokerosene (PFK) tune and before any calibration standards on each instrument and GC column used for analysis, once at the beginning of each 12-hour period during which standards or samples are analyzed and whenever adjustments or instrument maintenance activities are performed that may affect Retention Times (RTS). This commercially available, 16-component mixture contains the first and last eluting isomers in each homologue. Mixtures are available for various columns. The mixture for the DB-5 (or equivalent) column may not be appropriate for the DB-225 or other columns.

2. The ions in each of the five recommended descriptors are arranged for minimal overlap between the descriptors. The ions for the tetrachlorinated dibenzo-p-dioxin (TCDD) and tetrachlorinated dibenzofuran (TCDF) isomers are in the first descriptor, the ions for the pentachlorinated dibenzo-p-dioxin (PeCDD) and pentachlorinated dibenzofuran (PeCDF) isomers are in the second descriptor, the ions for the hexachlorinated dibenzo-p-dioxin (HxCDD) and hexachlorinated dibenzofuran (HxCDF) isomers are in the third descriptor, the ions for the heptachlorinated dibenzo-p-dioxin (HpCDD) and heptachlorinated dibenzofuran (HpCDF) isomers are in the fourth descriptor, and the ions for the octachlorinated dibenzo-p-dioxin (OCDD) and octachlorinated dibenzofuran (OCDF) isomers are in the fifth descriptor. In some cases, the tetrachlorinated and pentachlorinated dioxins and furans are combined in a single descriptor.

3. The descriptor switching times are set such that the isomers that elute from the GC during a given RT window will also be those isomers for which the ions are monitored. If homologue overlap between descriptors occur, the laboratory may use professional judgment in setting the switching times. The switching times are **not** to be set such that a change in descriptors occurs at or near the expected RT of any 2,3,7,8-substituted isomers.

4. The WDM must be analyzed at the following frequency:

   - Before initial calibration on each instrument and GC column used for analysis;
   - Each time a new initial calibration is performed, regardless of reason;
   - Each time adjustments or instrument maintenance activities are performed that may affect RTS; and
   - During each 12-hour sample analysis period prior to the calibration verification.

5. If the laboratory uses a GC column that has a different elution order than the columns specified, the laboratory must ensure that the first and last eluting isomers in each homologue are represented in the WDM used to evaluate that column. The concentrations of any additional isomers should be approximately the same as those in WDM solutions intended for use with conventional chlorinated-p-dioxin/chlorinated dibenzofuran (CDD/CDF) GC columns.

6. Analysis on a single GC column (as opposed to situations requiring 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 both the DB-5 and DB-225 (or equivalent) columns are met (see Section V).

D. Evaluation:

1. Verify that the WDM is analyzed at the required frequency.

2. Examine the WDM chromatograms to determine when descriptor switching times are turned on and off.

3. Note the RT of each first and last eluting isomer in each homologue for identification of switching times.

4. Each positive dioxin and furan result (tetra- through hepta-) must have an RT within the limits established by the WDM for the corresponding homologue. The 2,3,7,8-substituted dioxins and furans must also meet the Relative Retention Time (RRT) limits in Table A.3.

E. Action:

1. If the WDM was not analyzed at the required frequency or correct adjustments in descriptor switching times are not evident, but the calibration standards met specifications the individual 2,3,7,8-substituted target analyte, results may be usable without qualification. Qualify total homologue results as estimated "J" since one or more CDDs/CDFs may not have been detected.

2. If the chromatography for the calibration standards indicate a significant problem with descriptor switching times, qualify all associated data as unusable "R". Notify the Task Order Project Officer (TOPO) to decide if sample reanalysis is necessary.

V. Chromatographic Resolution

A. Review Items:

Form 5DFB (Form V-HR CDD-2), and the corresponding Selected Ion Current Profile (SICP) of each isomer and each of the analyses reported on Form 5DFB.

B. Objective:

Evaluate the ability of the Gas Chromatograph (GC) column to resolve the closely eluting dioxin and furan isomers. An evaluation must be made for each column used in the analysis of samples.

C. Criteria:

The resolution criteria must be evaluated using measurements made on the SICPs for the appropriate ions for each isomer. Measurements are **not** to be performed on Total Ion Current Profiles (TICPs).

1. For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the commercially available, 4-component DB-5 Isomer Specificity Check (ISC) standard prior to both the initial and calibration verification procedures for each instrument and GC column used for analysis. Use professional judgment to combine the ISC and Window Defining Mixture (WDM) in a single Column Performance Solution (CPS) analysis.

    a. GC resolution criteria for DB-5 (or equivalent) column: The chromatographic peak separation between the 2,3,7,8-TCDD peak and the 1,2,3,8-TCDD peak shall be resolved with a valley of ≤ 25% using the following equation:

$$\text{Valley} = \frac{x}{y} \times 100$$

Where,

x = The measurement from the baseline to the deepest part of the valley between 2,3,7,8-TCDD and 1,2,3,8-TCDD

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

    b. For the DB-5 (or equivalent) column, the 12-hour sample analysis period begins by analyzing the WDM or CPS solution. The identical HRGC/HRMS conditions used for the analysis of the WDM, ISC, and CPS solutions must also be used for the analysis of the initial calibration and calibration verification solutions. Evaluate the chromatographic resolution using the Quality Control (QC) criteria listed above.

2. Evaluate the chromatographic resolution for analyses on a DB-225 (or equivalent) GC column, then analyze the calibration standards. To evaluate the chromatographic resolution, use a commercially available, 3-component DB-225 ISC containing the tetrachlorinated dibenzofuran (TCDF) isomers that elute most closely with 2,3,7,8-TCDF on the GC column (1,2,3,9-TCDF and 2,3,4,7-TCDF).

   a. GC resolution criteria for DB-225 (or equivalent) column: The chromatographic peak separation between the 2,3,7,8-TCDF peak and the 2,3,4,7-TCDF peak must be resolved with a valley of ≤ 25% using the following equation:

$$\text{Valley} = \frac{x}{y} \times 100$$

   Where,

   x = The measurement from the baseline to the deepest part of the valley between 2,3,7,8-TCDF and 2,3,4,7-TCDF

   y = The peak height of 2,3,7,8-TCDF

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

3. If the laboratory uses a GC column other than the columns specified here, the laboratory must ensure that the isomers eluting closest to 2,3,7,8-TCDD on that column are used to evaluate GC column resolution. The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing all other tetrachlorinated dibenzo-p-dioxin (TCDD) isomers shall be resolved with a valley of ≤ 25%.

4. Analysis on a single GC column (as opposed to situations requiring 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 both the DB-5 and DB-225 (or equivalent) columns are met, as stated above.

D. Evaluation:

Verify from the SICPs that the ≤ 25% valley criteria are met. Examples of GC resolution can be found in USEPA Method 1613 (Revision B) and SW-846 Method 8290 (Revision 0).

E. Action:

If the GC resolution does not meet the specifications, qualify all detects and non-detects for 2,3,7,8-TCDD and/or 2,3,7,8-TCDF, whichever failed, as estimated "J" (see Table 3) and notify the Task Order Project Officer (TOPO) to decide on sample reanalysis.

Table 3. System Performance Checks

Criteria	Action
Mass Spectrometer resolution of ≥ 10,000 is not demonstrated	R
WDM fails, or WDM adjustments are not made, or WDM is not reported	J
WDM fails, and WDM adjustments are not made, and Calibration standards indicate a problem in detecting 2,3,7,8-substituted congeners because of gross errors in the scan descriptor times	R
CPS fails or is not reported	J

VI. Instrument Stability

A. Review Items:

Raw data for the midpoint (CS3) standard at the beginning of the 12-hour sample analysis period.

B. Objective:

Demonstrate that the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system has retained adequate stability, the CS3 standard is analyzed at the beginning and end of each 12-hour period or analytical sequence during which samples and standards were analyzed. The end analysis may also serve as the beginning analysis of the subsequent 12-hour period. The use of the CS3 standard as a measure of instrument stability includes the evaluation of Gas Chromatograph (GC) Retention Times (RTS), relative ion abundance criteria, sensitivity, and calibration criteria.

C. Criteria:

The CS3 solution must meet the following Quality Control (QC) criteria:

1. Absolute RT criteria: The absolute RT of the first internal standard $^{13}C_{12}$-1,2,3,4-TCDD must be within ± 15 seconds of the absolute RTS of the identical compound obtained during initial calibration. If the RT of the first internal standard changes by more than ± 15 seconds, the laboratory must adjust the switching times of the descriptors and analyze the Window Defining Mixture (WDM) before proceeding with further analyses. Additionally, the absolute RT of the aforementioned first internal standard must exceed 25.0 minutes on the DB-5 column, and 15.0 minutes on the DB-225 column.

2. Relative Retention Time (RRT) criteria: The RRTs of the native and labeled chlorinated dibenzo-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) shall be within the limits described in Section VII and Table A.3.

3. Ion abundance ratio criteria: All native and labeled CDDs/CDFs in the CS3 standard must be within their respective ion abundance ratios (see Table A.4).

4. Instrument sensitivity criteria: The peaks representing both native and labeled analytes in the CS3 standard must have signal-to-noise (S/N) ratios ≥ 10:1.

5. Response criteria: The %D of the Relative Response (RR) must be within ± 25% of the RR of the initial calibration. The %D of the Relative Response Factor (RRF) must be within ± 35% of the initial calibration. Use the following equation to calculate the Percent Difference (%D):

$$\%D = \frac{Response_{ver} - Response_{INT}}{Response_{INT}} \times 100$$

Where,

$Response_{ver}$	=	Response (RR or RRF) established during calibration verification
$Response_{INT}$	=	Mean response ($\overline{RR}$ or $\overline{RRF}$) established during initial calibration according to DLM02.X, Exhibit D

D. Evaluation:

Verify that the CS3 standard meets the criteria for both RT and RRT, ion abundance ratio, S/N ratio, and response (%D associated with RR and RRF). An example of the measurement of S/N can be found in USEPA SW-846 Method 8290A (Revision 0) and can be obtained at: http://www.epa.gov/sw-846/pdfs/8290a.pdf

E. Action:

1. The RTS and RRTs of the CS3 internal standards will tell the reviewer much about the stability of the instrument. If the RT changes by more than ± 15 seconds when compared to previous calibration standards, the reviewer should carefully examine subsequent samples to determine if the change is an isolated occurrence or if the RT of the internal standard is consistent in the 12-hour period. The reviewer should use professional judgment to qualify the sample data if the CS3 internal standard RT changes by more than ± 15 seconds from subsequent sample internal standards (see Table 4). No qualification of sample data is necessary if the sample internal standard RTS are consistent.

2. The ion abundance, sensitivity, and calibration criteria are all critical indicators of instrument stability (see Table 4). Failure to satisfy the ion abundance criteria, S/N ratio 10:1 criteria, or the %D RR and RRF criteria each indicate significant problems with the instrument. Qualify detects as estimated "J" if any of these criteria fail. The S/N criteria are especially indicative of severely degraded instrument performance. For all affected analytes, qualify non-detects in associated samples as unusable "R" if the S/N ratio < 10:1 in the CS3 calibration verification standard.

Table 4. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Instrument Stability

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RT changes > 15 seconds or RRT changes not within the values in Table A.3	Use professional judgment	
Relative ion abundance criteria is not within windows in CS3 (12-hour) standard	J	No qualification
S/N ratio < 10:1 in CS3 standard	J	R
%D greater than criteria in CS3 standard	J	No qualification

VII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Initial Calibration

A. Review Items:

Form 6DFA (Form VI-HR CDD-1), Form 6DFB (Form VI-HR CDD-2), and raw data for all standards.

B. Objective:

Establish compliance requirements for satisfactory instrument calibration to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the compounds on the Target Compound List (TCL).

The objective of the initial calibration is to establish a linear range and Mean Relative Responses ($\overline{RR}$s) and the Mean Relative Response Factors ($\overline{RRF}$s) for the instrumentation. The initial calibration is to be used for routine quantitation of samples using the $\overline{RR}$s and $\overline{RRF}$s established from the five Calibration Standards (CS1, CS2, CS3, CS4, and CS5). Subsequent calibration verifications occurring every 12 hours thereafter are not to be used for quantitation of samples, nor is the initial midpoint (CS3) solution to be used for this purpose.

C. Criteria:

The initial calibration criteria are strict because of their use in quantitation of sample data and the infrequency of initial calibration. Thus, the initial calibration affects the quality of the data based on it for an extended period of time.

Initial Calibration

Once the perfluorokerosene (PFK), Window Defining Mixture (WDM), Isomer Specificity Check (ISC), and Column Performance Solution (CPS) solutions have all been analyzed, and once the descriptor switching times have all been verified, the five CSs described in Table A.5 must be analyzed prior to any sample analysis.

The following criteria must be met for the initial calibration to be acceptable: Gas Chromatograph (GC) resolution; ion abundance ratio; Retention Time (RT); Relative Retention Time (RRT); instrument sensitivity [signal-to-noise (S/N)]; linearity of analyte response associated with Relative Response (RR) and Relative Response Factor (RRF); analyte concentration (ng/mL); and calibration frequency.

1. GC resolution criteria: Use DB-5, DB-225, or equivalent columns (see Section V).

2. Ion abundance criteria: The relative ion abundance criteria for chlorinated dibenzo-p-dioxins/ chlorinated dibenzofurans (CDDs/CDFs) listed in Table A.4, must be met for all CDD/CDF peaks, including the isotope-labeled peaks, in all solutions. The lower and upper limits of the ion abundance ratios represent a ± 15% window around the theoretical abundance ratio for each pair of selected ions (see Table A.1, for m/z types and exact m/z

ratios). The $^{37}Cl_4$-2,3,7,8-TCDD clean-up standard contains no ^{35}Cl, therefore the ion abundance ratio criteria do not apply to this compound.

3. Retention Time (RT) criteria: For all calibration solutions, the RTS of the isomers must fall within the appropriate RT windows established by the WDM analysis. In addition, the absolute RT of the internal standard $^{13}C_{12}$-1,2,3,4-TCDD must exceed 25 minutes on the DB-5 (or equivalent) column and 15 minutes on the DB-225 (or equivalent) column.

4. Mass Spectrometer sensitivity criteria: For all calibration solutions, including the CS1 solution, the S/N ratio must be $\geq$ 10:1.

5. Linearity criteria: The $\overline{RRF}$s and Percent Relative Standard Deviation (%RSD) of the five RRFs (CS1-CS5) for each compound applicable to RRF (internal standard) treatment is calculated. The %RSD of the five RRFs (CS1-CS5) must not exceed 35% for these compounds. Likewise, the $\overline{RR}$ and %RSD of the five RRs (CS1-CS5) for each compound applicable to RR (isotope dilution) treatment is calculated. The %RSD of the five RRs (CS1-CS5) must not exceed 20% for these compounds.

6. Concentration criteria: All initial Calibration Standards (CSs) must be analyzed at the correct concentration levels (see Table A.5).

7. Frequency criteria: Each HRGC/HRMS system must be initially calibrated to meet the terms of the contract whenever:

   - The laboratory takes corrective action which may change or affect the initial calibration criteria.

   - The calibration verification (CS3 calibration verification) acceptance criteria cannot be met even after corrective action (see Sections VI and VIII).

D. Evaluation:

1. Verify that the PFK, WDM, ISC, and CPS solutions were analyzed before the calibration standards.

2. Verify that all analytes in all calibration solutions are present at the correct concentrations (see Table A.5).

3. Verify that the requirements for frequency of initial calibration were observed.

4. Verify that the five RRF %RSDs are $\leq$ 35%.

5. Verify that the five RR %RSDs are $\leq$ 20%.

6. Verify that the ion abundance ratios in each CS are within $\pm$ 15% of the limits listed in Table A.4.

7. Verify that the GC resolution criteria are met [Percent Valley (% Valley) ≤ 25%].

8. Verify that the instrument sensitivity criteria are met (S/N ≥ 10) in all Selected Ion Current Profiles (SICPs).

9. Verify that the RT criteria involving the WDM and the internal standards are met.

E. Action:

1. Concentrations and Frequency

   All initial calibration standards must be analyzed at the concentrations described in the DLM02.X SOW. Initial calibrations must be performed when the contract is awarded, whenever significant instrument maintenance is performed (e.g., ion source cleaning, GC column replacement, etc.), or if calibration verification criteria are not met (see Table 5).

2. Ion Abundance Ratios

   If an analyte in a calibration standard failed the ion abundance ratio criteria, qualify sample results analyzed immediately after that initial calibration using the $\overline{\text{RRF}}$s or $\overline{\text{RR}}$ values for quantitation as unusable "R" for that analyte, because both the RRF and RR values depend on the areas used in the ion abundance ratio. Failed ion abundance ratio criteria for any analyte is a cause for concern, and may indicate that the Mass Spectrometer is not tuned correctly, the zero point is not correctly adjusted, or other problems.

   Use professional judgment for a more in-depth review to minimize the qualification of data which may be accomplished by considering the following hypothetical examples:

   - If the ion abundance ratio is not within the limits for an analyte in the CS1 solution (see Table A.4), qualify the low-end results for that analyte (below the CS2 concentration from Table A.5) as unusable "R".

   - If the ion abundance ratio is not within the limits for an analyte in the CS5 solution (see Table A.4), qualify the high-end results for that analyte (above the CS4 concentration from Table A.5) as unusable "R".

3. GC Resolution

   If failed resolution criteria involves tetrachlorinated dibenzo-p-dioxin (TCDD) isomers, qualify only those isomers as estimated "J". Request a reanalysis for all samples following a failed resolution to ensure the quantity of isomers present. When GC resolution capability is lacking, assume that 2,3,7,8-TCDD is the only isomer present.

4. Analyte Response

   If the %RSD is not within ± 20% and ± 35% for the RR and RRF, respectively, qualify the detects as estimated "J". The reviewer may discard either the CS1 or CS5 values for the initial calibration and recalculate the %RSD. If discarding either of these points brings the %RSD within the specified limits, qualify either the low- or high-end hits, depending on which point was discarded. Use professional judgment to perform reanalysis if either of these scenarios affect a majority of the data.

5. Sensitivity

   If the S/N ratio 10:1 sensitivity requirements are not met, qualify any detects as estimated "J" and non-detects as unusable "R" for all associated samples.

6. Retention Time

   Qualify all failed RT criteria from the initial calibration associated with the failed analyte(s) and reanalysis of all affected samples as unusable "R". No action is taken for non-detects. Systematic RT problems affecting all data require complete rejection of the entire data package, followed by reanalysis of all the samples.

Table 5. Initial Calibration

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
Initial calibrations are not performed at the prescribed concentration and frequency	R	R
Ion Abundance Ratios is not within ± 15% of theoretical values, as described in Table A.4	R	R
GC Resolution (% Valley) of > 25%	J	No qualification
Linearity: RRF %RSDs is not within ± 35%; RR %RSDs is not within ± 20%	J	UJ
Sensitivity < 10:1 S/N ratio for all SICPs	J	R
RTs: Not within appropriate windows and absolute RT of internal standard $^{13}C_{12}$-1,2,3,4-TCDD or, > 25 minutes on DB-5 (or equivalent) column, or > 15 minutes on DB-225 (or equivalent) column	R	No qualification

VIII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Calibration Verification

A. Review Items:

Form 7DFA (Form VII-HR CDD-1), Form 7DFB (Form VII-HR CDD-2), and raw data from the midpoint (CS3) standard.

B. Objective:

Establish compliance requirements for satisfactory calibration to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Calibration verification is used to validate the Relative Responses (RRs) and Relative Response Factors (RRFs) of the initial calibration on which quantitations are based, and to check for satisfactory performance of the instrument on a day-to-day basis.

C. Criteria:

Calibration verification criteria: The laboratory must not proceed with sample analysis until an acceptable calibration verification has been performed and documented according to the following criteria: ion abundance ratios; Retention Times (RTS); Relative Retention Times (RRTs); instrument sensitivity [signal-to-noise (S/N)]; and analyte response [Percent Difference (%D) associated with the RR and RRF].

1. Ion abundance criteria: The ion abundance ratio criteria listed in Table A.4, must be met for all chlorinated dibenzo-p-dioxin/chlorinated dibenzofuran (CDD/CDF) peaks, including the labeled versions of native compounds and the internal standards.

2. Absolute Retention Time (RT) criteria: The RT of the first-eluting internal standard ($^{13}C_{12}$-1,2,3,4-TCDD) on the DB-5 (or equivalent) column and the DB-225 (or equivalent) column must meet the absolute RT criteria (see Section VI). In addition, the absolute RT of the internal standards must be within ± 15 seconds of the RTS obtained during the initial calibration.

3. Relative Retention Time (RRT) criteria: The RRTs of the native and labeled chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans (CDDs/CDFs) must be within the defined limits (see Section VII).

4. Instrument sensitivity criteria: For the CS3 solution, the signal-to-noise (S/N) ratio must be ≥ 10:1 for all CDD/CDF peaks, including the labeled versions of native compounds and the internal standards.

5. Analyte response criteria: The measured RRFs and RRs of each analyte and standard (labeled and internal) must be within ± 20% (RR) and ± 35% (RRF) of the mean values established during initial calibration:

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

Where,

RRF_c = RRF established during calibration verification

RRF_i = RRF established during initial calibration

And:

$$\% \text{ Difference} = \frac{[(RR_c - RR_i) \times 100]}{RR_i}$$

Where,

RR_c = RR established during calibration verification

RR_i = RR established during initial calibration

D. Evaluation:

1. Verify that the calibration verification was run at the required frequency [following the Window Defining Mixture (WDM) or Column Performance Solution (CPS) in each 12-hour period] and that the calibration verification was compared to the correct initial calibration.

2. Verify from the raw data that the ion abundance ratios listed in Table A.4, were all met.

3. Verify from the raw data that the absolute RT criteria for the compound $^{13}C_{12}$-1,2,3,4-TCDD were met.

4. Verify from the raw data that the RRT criteria for the native and labeled CDDs/CDFs were met.

5. Verify from the raw Selected Ion Current Profile (SICP) data that the S/N ratio is ≥ 10:1 for the unlabeled CDD/CDF ions, labeled compounds, and internal standards.

6. Verify from the raw data that the measured RRs and RRFs of each analyte, labeled and otherwise, in the CS3 solution are within ± 25% (RRs) and within ± 35% (RRFs) of the mean values established during initial calibration.

E. Action:

If the calibration verification was not analyzed at the required frequency, contact the Task Order Project Officer (TOPO) to initiate sample reanalysis.

1. Use professional judgment to qualify any analyte in samples associated with a calibration verification not meeting the RT and/or RRT criteria (see Table 6).

2. Any detect in samples associated with a calibration verification not meeting the ion abundance criteria listed in Table A.4, is to be estimated "J" and non-detects estimated "UJ". The High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGS/HRMS) must be re-calibrated and the affected samples must be re-analyzed.

3. If the S/N ratio ≥ 10:1 limit is not met in a calibration verification, qualify all detects as estimated "J" and all non-detects as unusable "R".

4. Since the initial calibration is used to generate the RR and RRF values used for quantitation, the %D relative to the initial calibration's Mean RR ($\overline{RR}$) or Mean RRF ($\overline{RRF}$) is a crucial criterion for review. Qualify data associated with an analyte with a %D not within ± 20% (RR) and not within ± 35% (RRF) as estimated "J". Re-calibrate the HRGS/HRMS and re-analyze the affected samples.

Table 6. Calibration Verification Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Ion abundance ratios not within ± 15% window	J	UJ
Absolute RT of internal standard $^{13}C_{12}$-1,2,3,4-TCDD > 25 minutes on DB-5 (or equivalent) column, or > 15 minutes on DB-225 (or equivalent) column	Use professional judgment	
Internal standards in the calibration verification not within 15 seconds of the RTS in the initial calibration	Use professional judgment	
RRTs in the calibration verification not within the limits defined in Table A.3	Use professional judgment	
Sensitivity: S/N < 10 for all compounds	J	R
%D for RRs not within ± 20% %D for RRFs not within ± 35%	J	No qualification

IX. Identification Criteria

A. Review Items:

Form 1DFA (Form I-HR CDD-1), Form 2DF (Form II-HR CDD), and raw data.

B. Objective:

Unambiguously identify a Gas Chromatographic (GC) peak as a chlorinated dibenzo-p-dioxin (CDD) or a chlorinated dibenzofuran (CDF).

C. Criteria:

For a GC peak to be unambiguously identified as a CDD or CDF, it must meet all of the following criteria:

1. Retention Times (RTS) and Relative Retention Times (RRTs)

   Retention Times (RTS) are required for all chromatograms; scan numbers are optional. For positive identifications, RTS for the two quantitation ions must maximize within 2 seconds. RTS must either be printed at the apex of each peak on the chromatogram, or each peak must be unambiguously labeled with an identifier that refers to the quantitation report. The chromatogram, the quantitation report, or a combination of both must contain the RT of each peak and its area.

   - To make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled counterpart or internal standard is present in the sample extract, the Relative Retention Time (RRT) at the maximum peak height of the analyte must be within the RRT window in Table A.3. The RRT is calculated as follows:

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

   - To make a positive identification of the non-2,3,7,8-substituted isomers (tetra- through hepta-) for which a labeled standard is not available, the RT must be within the RT window established by the Window Defining Mixture (WDM) for the corresponding homologue.

2. Peak Identification

   Both of the specified ions listed in Table A.1, and on Forms I for each CDD/CDF homologue, must be present in the Selected Ion Current Profile (SICP). The ion current response for the two quantitation ions for the analyte in question must maximize simultaneously within the same 2 seconds. This requirement also applies to the labeled

versions of the native and internal standards. For the clean-up standard, only one ion is monitored.

3. Signal-to-Noise (S/N) Ratio

   The integrated ion current for each native analyte ion listed in Table A.1, must be at least 2.5 times (2.5x) the background noise and must not have saturated the detector (applies to sample extracts only). The labeled and internal standard ions, however, must be at least 10.0x the background noise and must also not have saturated the detector (applies to sample extracts only). In the case of the various calibration standard solutions, the S/N ratio must be ≥ 10:1 for all of the CDD/CDF compounds, whether or not they are labeled.

4. Ion Abundance Ratios

   The ion abundance ratio criteria listed in Table A.4, for native and labeled analytes and for internal standards must be met using peak areas to calculate ratios.

   If interferences are present and ion abundance ratios are not met using peak areas, but all other qualitative identification criteria are met (RT, S/N, presence of both ions), the laboratory may use peak heights to evaluate the ion ratio. If the peak is a CDD/CDF, the ion abundance ratios may be determined using peak heights instead of areas. Quantitate the peaks as "H" using peak heights rather than areas for both the target analyte and the labeled compound or internal standard.

5. Polychlorinated Diphenyl Ether (PCDPE) Interferences

   If PCDPE interferences are detected above the 2.5:1 S/N ratio limit, as indicated by the presence of peaks at the exact m/z(s) monitored for these interferents (see Table A.1), qualify all CDF sample results with a coeluting PCDPE interference as estimated "J".

D. Evaluation:

1. Verify that the RRTs for the 2,3,7,8-substituted compounds are within the RRT windows listed in Table A.3.

2. Verify that the RTS for the non-2,3,7,8-substituted compounds are within the RT windows established by the WDM for the corresponding homologues (Form 5DFA).

3. Verify from the SICPs that the ion current responses for the two quantitation ions for each analyte maximize simultaneously (within the same 2 seconds).

4. Verify from the SICPs that for each analyte ion listed in Table A.1, the S/N ratio is ≥ 2.5:1 and that the detector has not been saturated. Use professional judgment to verify the presence of the CDD/CDF if an analyte is flagged with an asterisk (*).

5. Verify from the Forms I that the ion abundance ratios are within the criteria listed in Table A.4.

6. Verify that no PCDPE interferences exist.

E. Action:

1. If a peak falls outside of the Table A.3 and/or the WDM windows, qualify the results as unusable "R" (see Table 7).

2. If ion current responses for the two quantitation ions for an analyte fail to maximize simultaneously (within 2 seconds), qualify the data as unusable "R".

3. If ion abundance criteria are not satisfied, qualify the detects as unusable "R" and use professional judgment to qualify non-detects.

4. If S/N criteria are not satisfied, qualify the detects as estimated "J" and non-detects as estimated "UJ".

5. If PCDPE interferences exist above the 2.5:1 S/N ratio limit, qualify associated CDFs as estimated "J" and non-detects as estimated "UJ".

Table 7. Identification Criteria Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Signals do not maximize within 2 seconds	R	R
S/N < 2.5	J	UJ
Ion abundance ratios not within the limits in Table A.4, or not within 10% of the ratio in the most recent CS3 standard	R	R
RRTs for 2,3,7,8-substituted CDD and CDF not within the limits in Table A.3 The RT of non-substituted CDDs/CDFs not within the RTS established by the WDM	R	R
PCDPE ion S/N > 2.5	J	UJ

NOTE: Use professional judgment to determine the correct identification of analytes.

X. Method Blank Analysis

A. Review Items:

Form 4DF (Form IV-HR CDD) and raw data.

B. Objective:

Determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any method blank associated with samples. If problems with a blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at or above the Contract Required Quantitation Limit (CRQL) at the m/z of the specified unlabeled chlorinated dibenzo-p-dioxin/chlorinated dibenzofuran (CDD/CDF) ions. There must be at least one laboratory method blank for each batch of samples extracted.

2. A peak that meets identification criteria as a CDD/CDF in the method blank must not exceed the CRQL for that analyte except in the case of octachlorinated dibenzo-p-dioxin/octachlorinated dibenzofuran (OCDD/OCDF), where the maximum allowable amount is less than three times (< 3x) the CRQL.

3. If a group of samples and the method blank are contaminated, rerun the associated detects and any samples containing peaks that do not meet all of the qualitative identification criteria for a contaminated method blank.

   NOTE: Report results for all peaks with signal-to-noise (S/N) ratio > 2.5:1, even if they are < CRQL (see DLM02.X, Exhibit C for CDD/CDF CRQLs).

4. The method blank, like any other sample in the Sample Delivery Group (SDG), must meet the technical acceptance criteria for sample analysis (see DLM02.X, Exhibit D).

D. Evaluation:

1. Verify that at least one method blank is analyzed with each matrix-specific extraction procedure, including separatory funnel and continuous liquid-liquid extraction procedures.

2. Verify that, with the exception of OCDD and OCDF, the method blank(s) are free from contamination ≤ CRQL for the native compounds. The concentration of OCDD/OCDF in the method blank must be < 3x the CRQL.

E. Action:

1. If the method blank is contaminated with a CDD/CDF greater than or equal to the CRQLs listed in the DLM02.X SOW, or are greater than three times (> 3x) the CRQLs for OCDD/OCDF, qualify all detects as estimated "J" and non-detects for those analytes as estimated "UJ" (see Table 8).

2. Use professional judgment to qualify detects as unusable "R" that are below method blank contaminant concentrations and a sample/sample set with results at levels similar to the levels reported in the method blank.

Table 8. Method Blank Evaluation Actions

Method Blank Result	Sample Result	Action
< CRQL	Not detected	No qualification
	< CRQL	U
	≥ CRQL	Use professional judgment
> CRQL (> 3x CRQL for OCDD/OCDF)	Not detected	UJ
	< CRQL	U
	≥ CRQL and < Blank Result	U or J
	> CRQL and ≥ Blank Result	Use professional judgment
=CRQL	Not detected	UJ
	< CRQL	U
	≥ CRQL	Use professional judgment
Gross contamination	Positive	R

XI. Laboratory Control Sample (LCS) Analysis

A. Review Items:

Form 3DFA (Form III-HR CDD-1) and raw data.

B. Objective:

Provide data on the accuracy of the analytical method, and prepare and analyze a sample of spiked reference matrix [the Laboratory Control Sample (LCS)] for each matrix analyzed. If a matrix is not represented in a Sample Delivery Group (SDG), no spiked LCS is required for that matrix. USEPA has identified a number of reference matrices to be used for the spiked LCS, and the laboratory must use an aliquot of that matrix for its own LCS work (see DLM02.X, Exhibit D). When a reference matrix that simulates the sample matrix under test is not readily available, USEPA retains the option to supply the laboratory with a reference matrix containing the expected interferences for a particular project.

C. Criteria:

1. For each sample Delivery Group (SDG), the laboratory must prepare a spiked LCS for all of the matrix types that occur in that SDG (see DLM02.X, Exhibit D).

2. The recovery of each spiked analyte must be in the range in Table A.6.

3. The LCS must meet the technical acceptance criteria for sample analysis (see DLM02.X, Exhibit D).

D. Evaluation:

Confirm that the spiking solution was added to the LCS, and that the chlorinated-p-dioxin/chlorinated dibenzofuran (CDD/CDF) analytes were at their correct concentrations. Verify that calculations, and transcriptions from raw data, were performed correctly.

E. Action:

1. If LCS recovery results are greater than the upper acceptance limits, qualify all associated sample data for those analytes which fail in the LCS as estimated "J" (see Table 9). No qualification of the data is necessary if the laboratory failed to prepare and analyze the LCS at the required frequency. Note this in the Data Review Narrative and notify the Task Order Project Officer (TOPO).

2. If LCS results are < 10%, qualify those analytes and non-detects as unusable "R" in all of the associated samples. Notify the TOPO concerning samples associated with a non-compliant LCS to decide on re-extraction and reanalysis.

Table 9. Laboratory Control Sample (LCS) Recovery Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
10% < %R < Lower Acceptance Limit	J	R
10% > %R	R	R

XII. Toxicity Equivalency Factor (TEF) and Isomer Specificity

A. Review Items:

Form 1DFB (Form I-HR CDD-2) and raw data.

B. Objective:

Isomer specificity for all 2,3,7,8-substituted chlorinated dibenzo-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) cannot be achieved on the 60 meter DB-5 column alone. Historically, problems have been associated with the separation of 2,3,7,8-TCDD from 1,2,3,7-/1,2,3,8-TCDD and 1,2,3,9-TCDD, and separation of 2,3,7,8-TCDF from 1,2,3,9-TCDF and 2,3,4,7-TCDF. There is toxicological concern associated with 2,3,7,8-TCDD and 2,3,7,8-TCDF; therefore additional analyses may be required for some samples, as described below.

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 native 2,3,7,8-substituted isomers listed in Table A.6. Hence, only the 2,3,7,8-substituted tetra- through octa- isomers are included in the Toxicity Equivalency Factor (TEF) calculations. The procedure for calculating the 2,3,7,8-TCDD TEFs for the Target Compound List (TCL) analytes is not claimed by the Chlorinated Dioxins Workgroup (CDWG) to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

The 2,3,7,8-TCDD TEF-adjusted concentration of a sample is used by the laboratory as an aid in determining when second column confirmation or re-extractions and re-analyses are required.

C. Criteria:

1. When calculating the 2,3,7,8-TCDD TEF-adjusted concentration of a sample, the laboratory must include only those 2,3,7,8-substituted isomers that were detected in the sample and that met all of the qualitative identification criteria. The laboratory does not include Estimated Maximum Possible Concentration (EMPC) or Estimated Detection Limit (EDL) values in the TEF calculations.

2. For each 2,3,7,8-substituted isomer positively identified in the sample, the TEF from 1DFB (Form I-HR CDD-2) is multiplied by the concentration from 1DFA (Form I-HR CDD-1) to give the TEF-adjusted concentration. The sum of the TEF-adjusted concentrations serves as an aid in determining when second column confirmation or re-extractions and re-analyses are required. Include the octachlorinated dibenzo-p-dioxin (OCDD) data in the TEF calculations only if the OCDD concentration in the sample is greater than the OCDD concentration in the blank.

D. Evaluation:

Verify that the TEF calculations were correctly performed.

NOTE: The *reviewer* may be required to recalculate the TEFs using EMPCs and EDLs. The *laboratory*, however, is not required to perform such calculations.

E. Action:

If calculations were not correctly performed by the laboratory, notify the Task Order Project Officer (TOPO) of the deficiency.

XIII. Dilution by Addition of Solvent

A. Review Items:

Raw data (quantitation reports and chromatograms).

B. Objective:

A calibrated range is defined by the initial calibration. All sample results must be within the calibrated range judged to be acceptable.

C. Criteria:

If the Selected Ion Current Profile (SICP) area at either quantitation m/z for any compound exceeds the calibration range of the system, a solvent dilution of the extract can be performed. The sample extract is diluted by a factor of up to 20 times (20x) with n-nonane, the instrument internal standard in the extract is adjusted to 100 pg/uL, and an aliquot of this diluted extract is analyzed by the internal standard method. If more than a dilution of 20 times (20x) is required, contact the Task Order Project Officer (TOPO).

D. Evaluation:

1. Verify that all reported sample values are within the calibration range.

2. Verify that the internal standard calculations used to determine analyte concentrations in the diluted sample were performed correctly.

3. Verify that a dilution factor of $\leq$ 20x was used and correctly documented.

4. Verify that the laboratory contacted the TOPO prior to diluting the sample by a factor of $>$ 20x.

E. Action:

1. Compare the original and diluted analyses of the sample. Use professional judgment to qualify results if substantial differences are noted.

2. Qualify all of the sample detects which are out of range as estimated "J" if a sample value is not within the calibration range, and appropriate dilution was not performed.

XIV. Dilution by Re-extraction and Reanalysis

A. Review Items:

Raw data (quantitation reports and chromatograms).

B. Objective:

A calibrated range is defined by the initial calibration. All sample results must be within the calibrated range to be acceptable.

C. Criteria:

If the Selected Ion Current Profile (SICP) area at either quantitation m/z for any compound exceeds the calibration range of the system, re-extract and re-analyze a smaller sample aliquot.

D. Evaluation:

1. Verify that all reported sample values are within the calibration range.

2. Verify that the internal standard and/or isotope dilution calculations used to determine analyte concentrations in the diluted sample were performed correctly.

3. Verify that a smaller sample size was used and correctly documented.

4. Verify that the Percent Solids (% Solids) procedure in DLM02.X, Exhibit D, was carried out for soil/sediment samples, even if no dilutions were subsequently required.

E. Action:

Qualify out-of-range sample data as estimated "J" if a sample value is not within the calibration range, and re-extraction with dilution was not performed.

XV. Second Column Confirmation

A. Review Items:

Form 1DFC (Form I-HR CDD-3) and raw data.

B. Objective:

Isomer specificity for all 2,3,7,8-substituted chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) cannot be achieved on the 60-meter DB-5 column alone. Historically, problems have been associated with the separation of 2,3,7,8-TCDF from 1,2,3,9-TCDF and 2,3,4,7-TCDF. There is toxicological concern associated with 2,3,7,8-TCDF; therefore, a second column confirmation is used and additional analyses may be required for some samples.

C. Criteria:

1. Second column confirmation is required for any sample analyzed on a DB-5 (or equivalent) column in which 2,3,7,8-TCDF is reported, or where 2,3,7,8-TCDF is reported as an Estimated Maximum Possible Concentration (EMPC) at or above the Contract Required Quantitation Limit (CRQL). The laboratory may utilize one of the following options to achieve better isomer specificity than can be obtained on the DB-5 column alone.

    - The sample extract may be re-analyzed on a DB-225 (or equivalent) Gas Chromatograph (GC) column to achieve better GC resolution and, therefore, better identification and quantitation of the individual 2,3,7,8-substituted isomers.

    - The sample extract may be analyzed on a GC column capable of resolving all of the 2,3,7,8-substituted CDDs/CDFs from other isomers, but not necessarily capable of resolving all of the non-2,3,7,8-substituted isomers from one another.

2. Regardless of the GC column used, for a GC peak to be identified as a 2,3,7,8-substituted CDD/CDF isomer, it must meet all of the criteria listed in DLM02.X, Exhibit D, [ion abundance ratio, signal-to-noise (S/N) ratio, Retention Time (RT), etc.]. If using any GC column other than those specified (DB-5, DB-225), the laboratory shall clearly document in the Data Review Narrative, the elution order of all analytes of interest on any such column.

3. For any sample analyzed on a DB-5 (or equivalent) column in which 2,3,7,8-TCDF is reported as an EMPC, regardless of Toxicity Equivalency Factor (TEF)-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

D. Evaluation:

1. Verify that second column confirmation is used whenever 2,3,7,8-TCDF is detected in any sample at any level (S/N ratio for the peak must be ≥ 2.5:1).

2. Verify that quantitation is performed on both columns and reported on the appropriate page of
   Form I. The two concentrations should not be combined or averaged, especially if the second column confirmation analysis is performed on a different instrument.

3. Verify that second column confirmation analysis meets all criteria previously discussed in this document (initial calibration requirements, linearity specifications, etc.).

   NOTE: Second column confirmation analysis is usually performed on a different instrument than that used for primary analysis.

E. Action:

If second-column confirmation is required but was not performed, qualify the 2,3,7,8-TCDF detects as unusable "R".

XVI. Estimated Detection Limit (EDL) and Estimated Maximum Possible Concentration (EMPC)

A. Review Items:

Form 1DFA (Form I-HR CDD-1) and raw data.

B. Objective:

For each analyte that is not detected, calculate an Estimated Detection Limit (EDL). The sample-specific EDL is an estimate made by the laboratory of the concentration of a given analyte that must be present to produce a signal with a peak height of at least 2.5 times (2.5x) the background noise signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc. There is toxicological significance of chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs); therefore, the EDL value is reported for non-detected analytes rather than simply reporting the respective Contract Required Quantitation Limit (CRQL).

The Estimated Maximum Possible Concentration (EMPC) value is applied to a sample when the signal-to-noise (S/N) ratio is at least 2.5:1 for both quantitation ions, but the ion abundance ratio criteria are not met.

C. Criteria:

1. EDL

The EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not any non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for those 2,3,7,8-substituted isomers where responses for both of the quantitation ions are less than 2.5 times (< 2.5x) the background level, and therefore do not meet the identification criteria.

The formulas below are used to calculate an EDL for each absent 2,3,7,8-substituted CDD/CDF. The background level (H_x) is determined by measuring the height of the noise at the expected Retention Times (RTS) of both of the quantitation ions of the particular 2,3,7,8-substituted isomer. The expected RT is determined from the most recent analysis of the midpoint standard (CS3) performed on the same High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system that was used for the analysis of the samples that are associated with the EDL calculations.

All Matrices Other than Aqueous:

$$\text{Soil EDL (ng/kg)} = \frac{2.5 \times Q_{IS} \times (H_{x1}+H_{x2}) \times D}{W \times (H_{IS1}+H_{IS2}) \times \overline{RR}}$$

Where,

EDL = Estimated Detection Limit for 2,3,7,8-substituted CDDs/CDFs

Q_{IS} = Quantity (pg) of appropriate internal standard added prior to sample extraction

H_{x1},H_{x2} = Peak heights of the noise for both quantitation ions of the CDD/CDF

H_{IS1},H_{IS2} = Peak heights of the internal standard ions

D = Dilution Factor

W = Weight extracted in grams

$\overline{RR}$ = The Mean Relative Response for the isomer of interest from the initial calibration (see DLM02.X, Exhibit D)

Aqueous:

$$\text{Aqueous EDL (pg/L)} = \frac{2.5 \times Q_{IS} \times (H_{x1}+H_{x2}) \times D}{V \times (H_{IS1}+H_{IS2}) \times \overline{RR}}$$

Where,

EDL = Estimated Detection Limit for 2,3,7,8-substituted CDDs/CDFs

Q_{IS} = Quantity (pg) of appropriate internal standard added prior to sample extraction

H_{x1},H_{x2} = Peak heights of the noise for both quantitation ions of the CDD/CDF

H_{IS1},H_{IS2} = Peak heights of the internal standard ions

D = Dilution Factor

V = Volume extracted in liters

$\overline{RR}$ = The Mean Relative Response for the isomer of interest from the initial calibration (see DLM02.X, Exhibit D)

2. Estimated Maximum Possible Concentration

An EMPC is calculated for 2,3,7,8-substituted isomers that are characterized by a response with a S/N ratio of at least 2.5:1 for both of the quantitation ions, but that do not meet the ion abundance ratio criteria outlined in Section IX.

The EMPC is calculated according to one of the following formulas:

All Matrices Other than Aqueous:

$$\text{EMPC (ng/kg)} = \frac{(C_{EX} \times D)}{W_S}$$

Where,

D = Dilution Factor

W_S = Sample dry weight in kg

C_{EX} = The concentration of the native compound in the extract

Aqueous:

$$\text{EMPC (pg/L)} = \frac{(C_{EX} \times D)}{V_S}$$

Where,

D = Dilution Factor

V_S = Sample volume in liters

C_{EX} = The concentration of the native compound in the extract

D. Evaluation:

1. Verify that EDLs and EMPCs are correctly calculated.

2. An EDL must be reported for each undetected analyte. The EDL must be < CRQL, except when increased due to dilution of the extract.

3. Analytes reported as EMPCs must meet all of the identification criteria, except for ion abundance ratios, as outlined in Section IX.

E. Action:

Qualify all EDLs and EMPCs that were not correctly calculated as unusable "R".

XVII. Labeled Compound Recoveries

A. Review Items:

Form 1DFA (Form I-HR CDD-1) and raw data.

B. Objective:

The 15 labeled chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) serve as the isotopic dilution quantitative mechanism in this method. The recovery of these compounds, along with the recovery of the clean-up standard, is a critical measure of the effectiveness of the laboratory and method to extract the compounds of interest.

C. Criteria:

1. If the original sample, prior to any dilutions, has any labeled compound or internal standard with a Percent Recovery (% Recovery) not within the limits specified in Table A.7, re-extract and re-analyze that sample.

   Values below 100% indicate loss of labeled and unlabeled compounds during the analytical process. Values over 100% indicate errors in the quantitation of the labeled compounds, or problems with the addition of the internal standards to the sample extracts. Within the limits, the use of isotope dilution or internal standard quantitation (depending on the analyte) will produce acceptable results for the target compounds. Outside the limits, the quantitation accuracy or precision of the results will be affected.

2. Re-extract and re-analyze if the labeled compounds are not present with at least a 10:1 signal-to-noise ratio (S/N) at their respective m/z(s).

3. If any of the labeled compound ion abundance ratios specified in Table A.4 are not within the contract-specified control limits, re-analyze the sample extract on the same Gas Chromatograph (GC) column and Mass Spectrometer used for the original analysis. If the problem corrects itself, use the data from the second analysis and disregard the data from the first analysis. No additional re-extraction and reanalysis are required. Re-extract and re-analyze if the failed ion abundance ratios persist through the second analysis.

4. If the absolute Retention Time (RT) of $^{13}C_{12}$-1,2,3,4-TCDD shifts by more than ± 15 seconds from the RTS of that standard in the initial calibration, re-analyze the sample extract after the laboratory has investigated the cause of the RT shift and taken corrective action. No re-extraction is required for such an analysis.

5. If $^{13}C_{12}$-2,3,7,8-TCDD is not resolved from $^{13}C_{12}$-1,2,3,4-TCDD with a valley of ≤ 25% on the DB-5 (or equivalent) column, or $^{13}C_{12}$-2,3,7,8-TCDD is not resolved from $^{13}C_{12}$-1,2,3,4-TCDD with a valley of ≤ 25% on the DB-225 (or equivalent) column, adjust the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) operating conditions, re-calibrate the instrument, and re-analyze the

affected sample. This criterion applies to sample analysis; no re-extraction and reanalysis are required if the second analysis resolves the problem. If this criterion is not met for a calibration standard, re-analyze associated samples after instrument re-calibration. Re-extraction is not ordinarily required unless the resolution difficulties reappear after re-calibration.

D. Evaluation:

1. Verify that the labeled compound and the internal standard recoveries fall within the required limits.

2. Verify that the S/N ratio of the labeled compound is ≥ 10:1.

3. Verify that the ion abundance ratios of the labeled compounds are within the required limits.

E. Action:

1. If the recovery of the labeled compounds are not within the limits in Table A.7, qualify all associated sample results as estimated "J". If no reanalysis is found, contact the Task Order Project Officer (TOPO) to initiate reanalysis.

2. The ^{37}Cl-labeled clean-up standard is used to monitor the efficiency of the clean-up; it is added to the sample extracts after extraction and before any clean-up steps. Low recoveries of the labeled compounds and the clean-up standard suggest that losses may be due to the performance of the clean-up steps. Thus, re-extraction and reanalysis of the sample may yield better results. If the labeled compound recoveries are low (< 40%), and the clean-up standard recovery is not, the recovery problems may be associated with the extraction procedures or related to a particularly difficult matrix. In this case, reanalysis may only serve to confirm a "matrix effect".

XVIII. Regional Quality Assurance and Quality Control (QA/QC)

A. Review Items:

Form 1DFA (Form I-HR CDD-1), chromatograms, quantitation reports, Traffic Report/Chain of Custody (TR/COC) documentation, and raw data for Regional Quality Control (QC) samples.

B. Objective:

Evaluate the results of any Regional Quality Assurance (QA) and QC samples initiated by the Region, including field duplicates, Regional Performance Evaluation (PE) samples, blind spikes, and blind blanks. (It is highly recommended to adopt the use of these QA/QC samples.)

C. Criteria:

Criteria are determined by each Region.

1. The PE sample frequency may vary. A PE sample may be included as frequently as once per Sample Delivery Group (SDG).

2. The analytes present in the PE sample must be correctly identified and quantitated.

D. Evaluation:

Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. If available, compare results for PE samples to the acceptance criteria for the specific PE samples.

E. Action:

Any action must be in accordance with Regional specifications and criteria for acceptable PE sample results. Note in the Data Review Narrative for Task Order Project Officer (TOPO) action any unacceptable PE sample results.

XIX. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, Quality Assurance Project Plan (QAPP), if available, and the Sampling and Analysis Plan (SAP), if available.

B. Objective:

Assess the overall quality of the data.

C. Criteria:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses their comments, concerns, and opinions about the quality and usability of the data.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.

2. Remember that analytical problems are often additive in nature.

3. Review all available information including, but not limited to, the QAPP [specifically, the Data Quality Objectives (DQOs)], the SAP, and any communications from the data user that concern the intended use and desired quality of the data.

4. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate application of the data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not already qualified based on the Quality Control (QC) criteria previously discussed.

2. Write a brief narrative to give the data user an indication of the analytical limitations of the data. Note for Task Order Project Officer (TOPO) action any inconsistencies between data and the Data Review Narrative. If sufficient information on the intended use and required quality of the data is available, include an assessment of the data usability within the given context.

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Appendix A: Tables

Extracted From:

USEPA Statement of Work (SOW) for Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs), Multi-Media, Multi-Concentration, DLM02.X, Dated May 2005

Table A.1. Descriptors, Exact Mass-to-Charge (m/z) Ratios, m/z Types, and Elemental Compositions of the CDDs/CDFs

Descriptor	Exact m/z[1]	m/z Type	Elemental Composition	Substance[2]
1	292.9825	Lock	$C_7 F_{11}$	PFK
	303.9016	M	$C_{12} H_4 {}^{35}Cl_4 O$	TCDF
	305.8987	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF
	315.9419	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O$	TCDF[3]
	317.9389	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF[3]
	319.8965	M	$C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD
	321.8936	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD
	327.8847	M	$C_{12} H_4 {}^{37}Cl_4 O_2$	TCDD[4]
	330.9792	QC	$C_7 F_{13}$	PFK
	331.9368	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD[3]
	333.9339	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD[3]
	375.8364	M+2	$C_{12} H_4 {}^{35}Cl_5 {}^{37}Cl O$	HxCDPE
2	339.8597	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF
	341.8567	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF
	351.9000	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF
	353.8970	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF[3]
	354.9792	Lock	$C_9 F_{13}$	PFK
	355.8546	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD
	357.8516	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD[3]
	369.8919	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD[3]
	409.7974	M+2	$C_{12} H_3 {}^{35}Cl_6 {}^{37}Cl O$	HpCDPE
3	373.8208	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF
	375.8178	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O$	HxCDF
	383.8639	M	$^{13}C_{12} H_2 {}^{35}Cl_6 O$	HxCDF[3]
	385.8610	M+2	$^{13}C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF[3]
	389.8157	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O_2$	HxCDD
	391.8127	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O_2$	HxCDD
	392.9760	Lock	$C_9 F_{15}$	PFK
	401.8559	M+2	$^{13}C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O_2$	HxCDD[3]
	403.8529	M+4	$^{13}C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O_2$	HxCDD[3]
	430.9729	QC	$C_9 F_{17}$	PFK

Table A.1. Descriptors, Exact Mass-to-Charge (m/z) Ratios, m/z Types, and Elemental Compositions of the CDDs/CDFs (con't)

Descriptor	Exact m/z[1]	m/z Type	Elemental Composition	Substance[2]
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF[3]
	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF[3]
	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	430.9729	Lock	C_9F_{17}	PFK
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD[3]
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD[3]
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCDPE
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	442.9728	Lock	$C_{10}F_{17}$	PFK
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD[3]
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD[3]
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE

[1]Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F= 18.9984

O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

[2]TCDD = Tetrachlorodibenzo-p-dioxin
TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-p-dioxin
PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-p-dioxin
HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-p-dioxin
HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-p-dioxin
OCDF = Octachlorodibenzofuran
HxCDPE = Hexachlorodiphenyl ether
HpCDPE = Heptachlorodiphenyl ether

OCDPE = Octachlorodiphenyl ether
NCDPE = Nonachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether
PFK = Perfluorokerosene

[3]Labeled compound.

[4]There is only one m/z for $^{37}Cl_4$-2,3,7,8,-TCDD (cleanup standard).

Table A.2. Gas Chromatography (GC) RT Window Defining Mixture (WDM) and Isomer Specificity Check Standard

CDD/CDF	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 Column TCDD Isomer Specificity Check Standard

1,2,3,7 and 1,2,3,8-TCDD
2,3,7,8-TCDD
1,2,3,9-TCDD

DB-225 Column TCDF Isomer Specificity Check Standard

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

Sp-2331 Column TCDD Isomer Specificity Check Standard
2,3,7,8-TCDD
1,4,7,8-TCDD
1,2,3,7-TCDD
1,2,3,8-TCDD

Table A.3. Relative Retention Times and Quantitation Reference of the Native and Labeled Chlorinated Dibenzo-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs)

CDD/CDF	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the injection internal standard		
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999–1.003
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999–1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999–1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999–1.002
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999–1.002
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923–1.103
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976–1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989–1.052
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011–1.526
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.567
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the injection internal standard		
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999–1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997–1.005
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999–1.001
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999–1.001
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999–1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998–1.004
1,2,3,7,8,9-HxCDD[1]		1.000–1.019
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999–1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999–1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999–1.001
OCDF	$^{13}C_{12}$-OCDD	0.999–1.008
OCDD	$^{13}C_{12}$-OCDD	0.999–1.001
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944–0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949–0.975
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.047
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959–1.021
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.000

Table A.3. Relative Retention Times and Quantitation Reference of the Native and Labeled Chlorinated Dibenzo-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) (con't)

CDD/CDF	Retention Time and Quantitation Reference	Relative Retention Time
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981–1.003
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043–1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057–1.151
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086–1.110
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032–1.311

[1]The retention time reference for 1,2,3,7,8,9-HxCDD is ^{13}C12-1,2,3,6,7,8-HxCDD.

1,2,3,7,8,9-HxCDD is quantified using the averaged responses of ^{13}C12-1,2,3,4,7,8-HxCDD and ^{13}C12-1,2,3,6,7,8-HxCDD.

Table A.4. Theoretical Ion Abundance Ratios and Quality Control (QC) Limits

Number of Chlorine Atoms	m/z's Forming Ratio	Theoretical Ratio	QC Limit[1]	
			Lower	Upper
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6[3]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7[4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1]QC limits represent ±15% windows around the theoretical ion abundance ratios.

[2]Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).

[3]Used for $^{13}C_{12}$-HxCDF only.

[4]Used for $^{13}C_{12}$-HpCDF only.

Table A.5. Concentration of CDDs/CDFs in Calibration and Calibration Verification Solutions

CDD/CDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100

Table A.5. Concentration of CDDs/CDFs in Calibration and Calibration Verification Solutions (con't)

CDD/CDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
$^{13}C_{12}$-OCDD	200	200	200	200	200
Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table A.6. Acceptance Criteria for Laboratory Control Sample (LCS)

CDD/CDF	Test conc (ng/mL)	LCS (% Recovery)
2,3,7,8-TCDD	10	67-158
2,3,7,8-TCDF	10	75-158
1,2,3,7,8-PeCDD	50	70–142
1,2,3,7,8-PeCDF	50	80-134
2,3,4,7,8-PeCDF	50	68-160
1,2,3,4,7,8-HxCDD	50	70-164
1,2,3,6,7,8-HxCDD	50	76-134
1,2,3,7,8,9-HxCDD	50	64-162
1,2,3,4,7,8-HxCDF	50	72-134
1,2,3,6,7,8-HxCDF	50	84-130
1,2,3,7,8,9-HxCDF	50	78-130
2,3,4,6,7,8-HxCDF	50	70–156
1,2,3,4,6,7,8-HpCDD	50	70–140
1,2,3,4,6,7,8-HpCDF	50	82-132
1,2,3,4,7,8,9-HpCDF	50	78-138
OCDD	100	78-144
OCDF	100	63-170

Table A.7. Labeled Compound Recovery in Samples When All CDDs/CDFs are Tested

Compound	Test conc (ng/mL)	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138
$^{13}C_{12}$-OCDD	200	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	35-197