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National Functional Guidelines

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

Final

NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as EPA) and other governmental employees. They do not constitute rule making by EPA, 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 may be obtained from the EPA'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
%R	Percent Recovery
%RSD	Percent Relative Standard Deviation
%Valley	Percent Valley
ASB	Analytical Services Branch of OSWER/OSRTI
CDD	Chlorinated Dibenzo-p-Dioxin
CDF	Chlorinated Dibenzofuran
CDWG	Chlorinated Dioxins Workgroup
CLP	Contract Laboratory Program
CPS	Column Performance Solution
CRQL	Contract Required Quantitation Limit
CS	Calibration Standard
CWA	Clean Water Act
DCDPE	Decachlorodiphenyl ether
DQO	Data Quality Objective
EDL	Estimated Detection Limit
EMPC	Estimated Maximum Possible Concentration
EPA	United States Environmental Protection Agency
GC	Gas Chromatography/Gas Chromatograph
HRGC	High Resolution Gas Chromatograph
HpCDD	Heptachlorinated Dibenzo-p-Dioxin
HpCDF	Heptachlorinated Dibenzofuran
HpCDPE	Heptachlorodiphenyl Ether
HRMS	High Resolution Mass Spectrometer
HxCDD	Hexachlorinated Dibenzo-p-Dioxin
HxCDF	Hexachlorinated Dibenzofuran
HxCDPE	Hexachlorodiphenyl Ether
ISC	Isomer Specificity Check
LCS	Laboratory Control Sample
MQO	Measurement Quality Objective
NCDPE	Nonachlorodiphenyl Ether
NFG	National Functional Guideline
Ng	Nanograms (10^{-9} grams)
ng/kg	Nanograms per kilogram
ng/L	Nanograms per liter
NRAS	Non-Routine Analytical Services program
OCDD	Octachlorinated Dibenzo-p-Dioxin
OCDF	Octachlorinated Dibenzofuran
OCDPE	Octachlorodiphenyl Ether
OSRTI	Office of Superfund Remediation and Technology Innovation
OSWER	Office of Solid Waste and Emergency Response

PCDF	Polychlorinated Dibenzofuran
PCDPE	Polychlorinated Diphenyl Ether
PE	Performance Evaluation
PES	Performance Evaluation Sample
PeCDD	Pentachlorinated Dibenzo-p-Dioxin
PeCDF	Pentachlorinated Dibenzofuran
PFK	Perfluorokerosene
pg/L	Picograms per liter
PO	EPA Project Officer (under the NRAS program, usually Regional personnel)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support (an EPA contract)
QC	Quality Control
RR	Relative Response
$\overline{RR}$ (Mean RR)	Mean Relative Response
RRF	Relative Response Factor
$\overline{RRF}$ (Mean RRF)	Mean Relative Response Factor
RRT	Relative Retention Time
RSD	Relative Standard Deviation
RT	Retention Time
S/N	Signal-to-Noise
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SDWA	Safe Drinking Water Act
SICP	Selected Ion Current Profile
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SOW	Statement of Work
TCDD	Tetrachlorinated Dibenzo-p-Dioxin
TCDF	Tetrachlorinated Dibenzofuran
TCL	Target Compound List
TEF	Toxicity Equivalency Factor
TEQ	Toxic Equivalent Quantity
TICP	Total Ion Current Profile
TIFSD	Technology Innovation and Field Services Division
TO	Task Order
TOPO	Task Order Project Officer
TOCOR	Task Order Contract Officer Representative
TR/COC	Traffic Report/Chain of Custody
WDM	Window Defining Mixture

INTRODUCTION

These *National Functional Guidelines for Chlorinated Dioxin and Furan Data Review* (hereafter referred to as the NFG) are designed to offer guidance on technical evaluation and review of data for chlorinated dibenzo-p-dioxins (CDD) and chlorinated dibenzofurans (CDF) as generated under the *USEPA Analytical Services Branch Statement of Work for Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Multi-Media, Multi-Concentration (DLM02.2)* (hereafter referred to as DLM02.X or DLM02.2). The DLM02.2 SOW is based on EPA Method 1613 (Revision B) and SW-846 Method 8290A (Revision 1) which use High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS). In some applications, this document 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 Sample (PES) materials, and instrument performance checks.

EPA Method 1613 (Revision B) can be obtained at the following link:

http://www.epa.gov/waterscience/methods/1613.pdf

EPA SW-846 Method 8290A (Revision 1) can be obtained at the following link:

http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8290a.pdf

As stated above, the NFG are intended to assist in the technical review of analytical data generated through the DLM02.2 SOW. Determining contract compliance is not an intended objective of these guidelines. The data review process provides information on the quality of analytical 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 requirements from the data user prior to reviewing the data. When this is not possible, the data 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. 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. 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 that are out of specification may be required to reanalyze samples or resubmit data, even if the previously submitted data have been utilized due to program needs.

Because of the toxicity of the analytes, these guidelines have been designed to be conservative in making decisions that affect the reporting of results as positive or negative. In other words, any error associated with the decision to report a positive result vs. a non-detect should be toward a false positive rather than a false negative. The importance of professional judgment to determine the ultimate presentation and usability of the data cannot be overstated.

Please note that in these guidelines, the isotopically-labeled PCDDs/PCDFs that are added to each sample prior to extraction, and ultimately are used for analyte quantitation, are called, "labeled standards," and the labeled PCDDs/PCDFs that are added just prior to injection are called, "internal standards."

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.

Table 1. Qualifier Definitions

Data Qualifier	Qualifier Definitions
U	The analyte was analyzed for but not detected. The value preceding the "U" may represent the adjusted Contract Required Quantitation Limit (see DLM02.X, Exhibit D, Section 1.2 and Table 2), or the sample specific estimated detection limit (EDL, see Method 8290A, Section 11.9.5).
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample (due either to an issue with the quality of the data generated because certain QC criteria were not met, or the concentration of the analyte was below the adjusted CRQL).
UJ	The analyte was not detected (see definition of "U" flag, above). The reported value should be considered approximate.
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

To use this document effectively, the reviewer must have an understanding of the analytical method and a general familiarity with 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 also helpful, but often this information may be difficult to locate. If available, the field notes should 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 statement of work (SOW) document, when reviewing the data.

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

1. The Region where the samples were taken
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*
    h. Quality Control (QC) audit samples*

    * If applicable.

The 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. As required in DLM02.X, Exhibit B, Section 2.5.1.2, any equations used to process sample data should be provided to enable a recalculation of the data. This should include examples of each type of calculation used to generate the actual results.

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

It is strongly encouraged that a Data Review Narrative should accompany the laboratory data forwarded to the intended data recipient (client) or user to promote communications. A copy of the Data Review Narrative should also be submitted to the TOCOR or SMO. The TOCOR with assigned oversight responsibility for the laboratory producing the data must be kept informed of all contract compliance issues noted during the review process.

The Data Review Narrative should include comments that clearly identify the problems associated with a Case or SDG and state any resulting limitations that should be placed on the data. Documentation must include the sample number, analytical method or modification, extent of the problem, and assigned qualifiers.

Additional information that should be included in the Data Review Narrative includes, but should not be limited to, calculation checks, documentation of any approved laboratory deviations from the contract SOW, and an explanation of any laboratory-assigned data qualifiers that may be found in the data.

I. Holding Times, Storage, and Preservation

A. Review Items:

FORM 1DFA, 1DFB, 1DFC, or 1DFD (FORM I-HR CDD-1, CDD-2, CDD-3, or CDD-4), EPA Sample TR/COC documentation, raw data, and sample extraction sheets. Reference DLM02.X, Exhibit B, Section 3.4.1 – Section 3.4.4 and Exhibit D, various sections.

B. Objective:

To 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:

1. 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 is added. If the aqueous sample pH is >9, it must be adjusted to pH 7-9 with sulfuric acid.
2. Aqueous and soil samples must be extracted and analyzed within 35 days of the last sample receipt date in the SDG per contract requirements. However, technical holding time requirements allow that water and soil samples may be stored at 4°C (± 2°C), and tissue samples and sample extracts can be stored at <-10°C in the dark for up to one year (DLM02.X, Exhibit D, Section 8.3).
3. 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.

   NOTE: **Aqueous samples, subject to compliance with the SDWA and/or CWA (40CFR Part 136.3), may have unique holding time requirements. Check the current 40 CFR Part 136.3 reference. Other analytical protocols may specify different storage conditions.**

4. Holding times for oily matrices have not been established. The aqueous holding times are recommended in this situation. Holding times for fish and tissue samples have not been established; however, they should be extracted within one year of collection as recommended in EPA 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, CDD-3, or CDD-4. To determine whether 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). Special consideration should be given for samples delivered directly from the field to the laboratory. 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.
3. The impact on data quality of holding time exceedances depends on all the factors discussed above. Regional standard operating procedures (SOPs) may have secondary criteria for data qualification when the primary criteria have been exceeded. The reviewer should rely on professional judgment, but should completely document the logic behind data qualification decisions.

E. Action:

1. If holding times are exceeded, qualify all detects as estimated "J" and qualify non-detects as estimated "UJ" or unusable "R" (see Evaluation, Section D, above). Document that holding times were exceeded (see Table 2).
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 affected and qualify with estimated "J" or "UJ", respectively.
3. If sodium thiosulfate preservative has not been added to aqueous samples with a chlorine residual, qualify all detects as estimated "J" and non-detects as rejected "R". 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. It is recommended to apply 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 35-day contractual holding time, but within the 1-year technical holding time, no qualification of the data is necessary.
7. For all sample extracts not correctly stored and analyzed outside the 35-day contractual holding time but within the 1-year technical holding time, qualify detects estimated "J" and non-detects estimated "UJ".
8. Qualify detects in sample extracts analyzed outside the 1-year technical holding time as estimated "J". Qualify non-detects estimated "UJ" or unusable "R", depending on professional judgment.
9. When holding times are exceeded, note in the Data Review Narrative the effect that the exceeded holding times will have on the data and also note as an action item for the TOCOR or SMO.

Table 2. Holding Times, Storage, and Preservation Evaluation Actions

Evaluation	Sample Type	Criteria Exceedance	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Technical 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	Cl_2 present but Thiosulfate not added	J	R
		pH not adjusted when required	J	UJ
Sample Extract Holding Time*	All types	>35 days <1 year	No qualification	
Sample Extract Holding Time**	All types	>35 days <1 year	J	UJ
		>1 year	J	UJ or R

* If correctly stored
** If not correctly stored

II. Performance Evaluation Samples (PES)

A. Review Items:

FORM 1DFA (FORM I-HR CDD-1), Performance Evaluation Sample (PES) scoring information from the QATS laboratory, PES instructions (shipped with samples should be included in the deliverable).

B. Objective:

Data for PESs are generated to provide information on the overall accuracy and bias of the analytical method and on laboratory performance. Results for PESs are evaluated for false negatives, false positives, and accuracy of target compound quantitation.

C. Criteria:

1. The Region may provide the laboratory with PESs to be analyzed with each sample delivery group (SDG). These may include blind spikes and/or blind blanks. The laboratory must analyze a PES when provided by the Region.
2. The Region may score the PES based on data provided by QATS.

D. Evaluation:

1. If PESs are included in the SDG, verify that the results are within the action limits [99% (3σ) confidence interval] and warning limits [95% (2σ) confidence interval]. If a blind blank is included, verify that no target analytes are present. The results of the blind blank analysis should be comparable to the associated method blank (see Section VI of this document, Method Blank Analysis).
2. If a significant number (i.e., half or more) of the analytes in the PES fall outside of the 95% or 99% warning or action criteria, or if a number of false positive results are reported, the reviewer must evaluate the overall impact on data quality.

E. Action:

If a result is not within acceptance criteria 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 cleanup standard recovery]. In such situations, the PES may not be representative of the field samples. Performance evaluation samples are only one indicator of technical performance of the laboratory. In general, for PES analytes not within the 95% confidence intervals or warning 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 95% or 99% confidence intervals and scored as "warning-high" or "action-high", qualify associated sample detects as estimated "J". Non-detect results should not be qualified in this instance. If the results are scored as "action-low", qualify the associated sample detects as estimated "J" and non-detects as unusable "R" (see Table 3). Contact the TOCOR and/or SMO if reanalysis of samples is required.

For Example: If 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. On the other hand, in the situation described in Section D.2 above, it may be necessary to qualify all sample data, and not only those analytes present in the PES.

Table 3. PE Sample Data Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Results are not within the 95% confidence interval (>2σ) but inside the 99% interval (<3σ), and are biased low (Warning – Low)	J	UJ
Results are not within the 95% confidence interval (>2σ) but inside the 99% interval (<3σ), and are biased high (Warning – High)	J	No qualification
Results are outside the 99% confidence interval (>3σ) and biased high (Action – High)	J	No qualification
Results are outside the 99% confidence interval (>3σ) and biased low (Action – Low)	J	R

III. System Performance Checks

Prior to analyzing the calibration solutions, blanks, samples, and QC samples, the analyst must establish the HRGC and HRMS operating conditions necessary to obtain optimum performance. There are three fundamental HRGC/HRMS system performance checks, including Mass Calibration and Resolution, the Mass Spectrometer Selected Ion Monitoring (SIM) scan descriptor switching times, and Gas Chromatographic (GC) resolution. There is a fourth performance check that should be considered in evaluating data quality, instrument stability. These four checks are discussed below.

1. Mass Calibration and Mass Spectrometer Resolution

A. Review Items:

Hardcopy of the Mass Spectrometer resolution demonstration. Reference DLM02.X, Exhibit D, Sections 9.2 and 9.2.1.4.

B. Objective:

Perform mass calibration and set Mass Spectrometer resolution to ≥10,000 using perflurokerosene (PFK) as a calibrant. This is a fundamental requirement for any laboratory using DLM02.X and other HRMS methods. If mass calibration and resolution tuning are not correctly performed, interferences may degrade CDD/CDF identification and quantitation.

C. Criteria:

Laboratories are required to provide evidence of Mass Spectrometer resolving power ≥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 the mass descriptor being checked. The format of the peak profile representation must allow manual determination (i.e., by the data reviewer) of Mass Spectrometer resolution [the horizontal axis should be a calibrated mass scale, with amu or ppm per division. The result of the peak width measurement must appear on the hardcopy. The deviation between the exact mass measured m/z (m/z_{mon}) and the target m/z (m/z_{th}) must be ≤5 ppm (i.e., the value found for m/z 380.9760 must be accurate to ± 0.0019)].

$$Res._{ppm} = \frac{m / z_{th}}{\left| m / z_{th} - m / z_{mon} \right|} \geq 10{,}000$$

D. Evaluation:

Verify that the Mass Spectrometer has been tuned to a resolving power of ≥ 10,000. A demonstration of Mass Spectrometer resolving power is provided in EPA SW-846 Method 8290A (Revision 1), Figure 5. Additional information about interpretation of the chart may be found in 8290A, Figure 2.

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, the risk of false positive results may exist. If a demonstration of the required mass resolution is not provided, the reviewer must carefully evaluate other factors to determine whether or not there is sufficient evidence of adequate resolution to preclude interference from other ions with similar mass-to-charge ratios (m/z). This may include, but should not be limited to: other tunes in the data package for the same instrument, the quality and similarity of peak shapes between the calibrations and the samples, baseline noise in calibrations, blanks and in the lock mass trace, and calibration performance. The appropriate course of action, based on these factors and the professional judgment of the reviewer, may range from no qualification to rejection of all positive results.

2. Window Defining Mixture (WDM)

A. Review Items:

FORM 5DFA (FORM V-HR CDD-1). Reference DLM02.X, Exhibit B, Section 3.4.8 and Section 4 and Exhibit D, Section 9.2.3.

B. Objective:

Prior to the calibration of the HRGC/HRMS system, establish the appropriate switching times for the SIM descriptors (see Table A.1) and verify the chromatographic resolution. The switching times are determined by the analysis of the WDM which contains the first and last eluting isomers in each homologous series (see Table A.2). It is not necessary to analyze the WDM if only 2,3,7,8-TCDD and 2,3,7,8-TCDF are requested. Chromatographic resolution is verified by analyzing one of three Isomer Specificity Check (ISC) solutions, depending on the 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 PFK tune and before any calibration standards on each instrument and GC column used for analysis, once at the beginning and end 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 homologous series. 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. The standard must contain the compounds listed in Table A.2, at a minimum.
2. The ions in each of the five recommended descriptors are arranged for minimal overlap between the descriptors. The ions for the TCDD and TCDF isomers are in the first descriptor, the ions for the PeCDD and PeCDF isomers are in the second descriptor, the ions for the HxCDD and HxCDF isomers are in the third descriptor, the ions for the HpCDD and HpCDF isomers are in the fourth descriptor, and the ions for the OCDD and OCDF isomers are in the fifth descriptor. In some cases, TCDD/DF and PeCDD/DF 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 overlaps 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
   - At the beginning and ending of 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 homologous series 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 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 XI).

D. Evaluation:

1. Verify that the WDM is analyzed at the required frequency.
2. Examine the WDM chromatograms to determine whether the switching times have been optimized properly, demonstrated by complete elution of the first and last isomers in each homologous series.
3. Note the RT of each first and last eluting isomer in each homologous series for identification of switching times.

   Each positive dioxin and furan result (tetra- through hepta-) must have an RT within the limits established by the WDM for the corresponding homologous series. 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 for the individual 2,3,7,8-substituted target analytes, results may be usable without qualification. Qualify total homologue results as estimated "J" or “UJ” since one or more CDDs/CDFs may not have been detected (these are generally all qualified as J/UJ due to the nature of the quantitation method, see X.E.2).
2. If the chromatography for the calibration standards indicates a significant problem with descriptor switching times such that 2,3,7,8-substituted target analytes may have been missed, qualify all associated data as unusable "R". Notify the TOCOR and/or SMO to decide if sample reanalysis is necessary.

3. 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. Reference DLM02.X, Exhibit B, Section 3.4.9 and Section 4, and Exhibit D, Section 9.2.4.

B. Objective:

Evaluate the ability of the GC column to resolve the closely eluting dioxin and furan isomers. An evaluation [isomer specificity check (ISC)] 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 ISC standard prior to both the initial and calibration verification procedures for each instrument and GC column used for analysis. The laboratory may combine the ISC and 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 QC criteria listed above.
2. The chromatographic resolution for analyses on the confirmational (DB-225 or equivalent) GC column is evaluated using a commercially available, 3-component DB-225 ISC standard containing the tetrachlorinated dibenzofuran (TCDF) isomers that elute most closely with 2,3,7,8-TCDF (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

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 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.

D. Evaluation:

Verify that the ISC or CPS has been analyzed at the appropriate frequency, and examine the SICPs to verify that the ≤ 25% valley criteria have been met. Examples of GC resolution can be found in EPA Method 1613, (Revision B), Figures 6 and 7, and SW-846 Method 8290A (Revision 1), Figure 4.

Technical acceptance criteria must be met before any standards, samples, QC samples, and required blanks are analyzed. However, if the ISC or CPS is not present, but a successful calibration check standard has been analyzed, and chromatographic performance in the samples does not indicate interference with and target analyte peaks, especially 2,3,7,8-TCDD (or 2,3,7,8-TCDF on the confirmation column), the data may still be usable. In this case, all SICPs must be carefully evaluated to verify that analyte and/or labeled analog peaks are clearly within the expected RT window, and that no persistent interference is evident.

E. Action:

If the GC resolution on the DB-5 (or equivalent) column does not meet the specifications for TCDD, professional judgment should be used to evaluate the severity of the non-compliant chromatographic resolution and qualify results as necessary. These failed resolution criteria can be indicative of the potential for poor resolution between other closely eluting homologues, as well as between CDD/CDFs and interfering compounds. Qualify all detects as estimated "J" (see Table 4) and notify SMO to schedule sample reanalysis. Please note that resolution criteria should not affect HpCDD, OCDD, or OCDF since there is only one isomer in each group, and these results should not be qualified. Non-detect results should not be affected by resolution non-compliance.

4. Instrument Stability

A. Review Items:

Raw data for the midpoint (CS3) standard and WDM at the beginning of the 12-hour sample analysis period and lock-mass trace (should be present in each injection).

B. Objective:

Demonstrate that the HRGC/HRMS system has retained adequate stability.

1. The WDM or CPS is analyzed at the beginning and end of each 12-hour period or analytical sequence during which samples and standards are analyzed. The use of the WDM as a measure of instrument stability includes the evaluation of the presence of the WDM isomers in each descriptor over time.
2. The CS3 standard is analyzed at the beginning and end of each 12-hour period or analytical sequence, after the WDM. 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 GC retention times, relative ion abundance criteria, sensitivity, and calibration criteria.
3. A channel monitoring one of the ions of the PFK that is continuously bled into the system should be present in each set of SICPs. The use of the lock-mass trace as a measure of instrument stability includes evaluating the shape of the response peaks in the peak matching experiment, and the ability, over time, of the system to show adequate peak shape.

C. Criteria:

The CS3 solution must meet the following QC criteria:

1. Absolute RT criteria: The absolute RT of the first internal standard must exceed 25.0 minutes on the DB-5 column (or equivalent column), and 15.0 minutes on the DB-225 column (or equivalent column).
2. Relative Retention Time (RRT) criteria: The RRTs of the native and labeled CDDs/CDFs shall be within the limits described in Section V 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 Percent Difference (%D) of the Relative Response (RR) must be within ±25% of the mean RR of the initial calibration. The %D of the mean Relative Response Factor (RRF) must be within ±35% of the initial calibration. Use the following equation to calculate the %D:

$$\%D = \frac{\text{Response}_{ver} - \text{Response}_{int}}{\text{Response}_{int}} \times 100$$

Where,

Response_{ver} = Response (RR or RRF) observed during calibration verification

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

D. Evaluation:

1. 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). 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 RTs of the internal standards are consistent throughout the 12-hour period. If the CS3 internal standard RTs have changed by more than ± 15 seconds but subsequent sample internal standards are consistent and in compliance with the initial calibration, the cause may have been a delayed injection. Similarly, if ion abundance ratios are outside the ± 15% window, examine other peaks in the standard, and sample analyses to determine whether there is a consistent pattern. This may be caused by a co-eluting interferent with a response on one channel, or there may be an issue with mass spectrometer tuning.
2. An example of the measurement of S/N can be found in EPA SW-846 Method 8290A (Revision 1) and can be obtained at: http://www.epa.gov/sw_846/pdfs/8290a.pdf. Also, as a qualitative check, examine the lock-mass trace for each descriptor. In a calibration standard, it should be quiet, with no excursions over 10% of scale. Excessive spikes or drift may indicate sample carryover or a poorly performing system.

E. Action:

1. The RTs and RRTs of the CS3 internal standards are indicative of the stability of the chromatographic system. Notify SMO to schedule sample reanalysis under a compliant calibration. If this is not possible, use caution in interpreting the data (see Table 4). If the evidence indicates system RTs have changed, descriptor switching times may no longer be valid. However, for the recommended DB-5 and DB-225 (or equivalent) columns, this should have no impact on the 2,3,7,8 target analytes, only on the combined homologue totals. The direction of bias in homologue totals in this situation is unknown (and these are generally all qualified as J/UJ anyway due to the nature of the quantitation method, see X.E.2).
2. The relative ion abundance, sensitivity (S/N, RRF), and stability (%D) determined from the CS3 calibration check are all indicators of instrument stability. Qualify detects as estimated "J" if any of these criteria fail. Failure of the S/N criteria (S/N ratio <10:1 in the CS3 calibration verification standard) is especially indicative of degraded instrument performance. Qualify all positive results in associated samples as estimated "J" and reject non-detects ("R") because of the possibility of false negatives. When relative ion abundances are non-compliant in the calibration check standard, and a trend is evident, the laboratory should be contacted to repeat the analytical sequence. If no trend is observed, the impact should be on quantitation of detects and non-detects. All results should be “J” qualified. If only the %D criterion is not met, follow the data qualification action described in Section V and Table 6 (“J” all).

Table 4. System Performance Checks

Criteria	Action[1]	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
Mass Spectrometer resolution of□ □10,000 is not demonstrated	R or professional judgment	No qualification
WDM fails, or WDM adjustments are not made, or WDM is not reported, and Calibration standard performance is acceptable	J-Homologue Totals Only	UJ-Homologue Totals Only
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	R
ISC fails (GC Resolution (% Valley) of >25%), or ISC adjustments are not made	J all tetra – hexa-congeners	Not qualified
ISC fails, or ISC adjustments are not made, and Calibration standards or samples indicate a problem in resolving 2,3,7,8-substituted congeners	R	R
RT changes >15 seconds or RRT changes not within the values in Table A.3	Use professional judgment for qualification of target analytes; qualify homologue totals as estimated (J, UJ).	
Relative ion abundance criteria is not within windows in CS3 (12-hour) standard	J	UJ
S/N ratio <10:1 in CS3 standard	J	R
%D greater than criteria in CS3 standard	J	UJ

1. In any case where data would by rejected by these rules, the reviewer should contact the TOPO to discuss requesting the laboratory to reanalyze or to re-extract and reanalyze.

IV. 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. Reference DLM02.X, Exhibit B, Section 3.4.11, Section 3.4.12, and Section 4, and Exhibit D, Section 9.3.

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 CDDs/CDFs.

The objective of the initial calibration is to establish a linear range, Mean Relative Responses ($\overline{RR}$ s) of the unlabeled native analytes and the Mean Relative Response Factors ($\overline{RRF}$) for the labeled internal standards and cleanup standard. The initial calibration is to be used for routine quantitation of samples using the $\overline{RR}$ s and $\overline{RRF}$ 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.

Once the perfluorokerosene (PFK), window defining mixture (WDM), isomer specificity check (ISC), and column performance solution (CPS) solutions have all been analyzed, and after the descriptor switching times have all been verified, the five calibration standards 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: 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 III.3).
2. Ion abundance criteria: The relative ion abundance criteria for 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 Table A.4 for m/z ratios). The $^{37}Cl_4$-2,3,7,8- TCDD cleanup standard contains no ^{35}Cl, therefore the ion abundance ratio criteria do not apply to this compound.
3. Retention Time 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 to ensure adequate resolution between targets and to separate known interfering substances.
4. Mass Spectrometer sensitivity criteria: For all calibration solutions, including the CS1 solution, the S/N ratio must be ≥10.
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 percent relative standard deviation (%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 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 III.4 and V).

D. Evaluation:

1. Verify that the PFK resolution check was performed, and 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 ≤35%.
5. Verify that the five RR %RSDs are ≤20%.
6. Verify that the ion abundance ratios in each calibration standard are within ±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 for each target analyte and internal standard have been met. If this cannot be verified in the documentation, examine the SICPs for each descriptor. All analytes must be present in the proper descriptor, and RRT and minimum RT criteria must be met. Verify that RTs are consistent between the calibration standards, and between the calibration and any subsequent samples.

E. Action:

1. Concentrations and Frequency

   All initial calibration standards, except CS1, must be analyzed at the concentrations described in the DLM02.X Statement of Work (SOW). Calibration standard CS1 may be analyzed at either the specified 0.5 ng/mL concentration, or at a lower level such as 0.1 ng/mL. As long as the criteria specified in the method (and in Item D above) are met, this is a measure that adds value and is generally allowed. 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. If no initial calibration has been performed, the data should not be considered definitive (reject or flag as screening-level only). If the prescribed calibration levels have not been used, it may be necessary to modify the linear range for reporting (with approval of the data user). If an otherwise compliant initial calibration has been performed, but not at the prescribed frequency, the data may be usable with qualification as estimated.

2. Ion Abundance Ratios

   Failed ion abundance ratio criteria for any analyte is a cause for concern, and may indicate that the Mass Spectrometer is not tuned correctly, that the ion source is dirty, or that other electronic problems exist. If there is a systemic problem resulting in failed ion ratios in the calibration, qualify sample results analyzed immediately after that initial calibration using the $\overline{RRF}$ or $\overline{RR}$ 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.

Using professional judgment, a more in-depth review may be performed to minimize the qualification of data. To illustrate this approach, consider the following hypothetical example:

- 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", or qualify as a non-detect at the level of the next lowest standard (in this example, the CS2 standard).
- The logic for allowing this flexibility is that system baseline noise near the lower limit of detection may cause calibration peaks to fail even in an otherwise adequately performing system. However, if the ion abundance ratio is not within the limits for an analyte in the CS3 - CS5 solutions (see Table A.4), qualify all results for that analyte as unusable "R".

3. GC Resolution

   Failed resolution criteria can have an impact on closely eluting pairs other than the TCDD isomers subject to these criteria. Qualify all results as estimated "J". Request a reanalysis for all samples following a failed resolution to ensure the qualitative and quantitative results. The factors at play here affect calculated detection limits as well as positive results. Qualify all results as estimated ("J/UJ").

4. Analyte Response

   If the %RSD is not within ± 20% and ± 35% for the RR and RRF, respectively, qualify detects and non-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, based on the newly defined linear range. It may be necessary to request reanalysis if either of these scenarios affects a majority of the data, or project data quality objectives (DQOs) are negatively impacted.

5. Sensitivity

   Problems with the S/N ratio not being met usually occur in the CS1 standard. If this is the case, professional judgment could be used to increase the reporting limit to the lowest calibration standard which meets criteria (CS2 standard concentration), depending on data requirements. Qualify any positive results below the CS2 standard as estimated. As stated in the paragraph above on ion ratios, the logic for allowing this flexibility is that system baseline noise near the lower limit of detection may cause calibration peaks to fail even in an otherwise adequately performing system. Therefore, this approach should not be applied to standards higher than CS1. If the 10:1 S/N ratio requirements are not met due to a more systematic lack of sensitivity, qualify any detects as estimated "J" and non-detects as unusable "R" for all associated samples.

6. Retention Time

   If the RT criteria described above have not been met, contact the TOCOR or SMO to discuss reanalysis of the initial calibration and all samples, or reject the data. In sample-specific, potentially matrix-caused cases of RTs not meeting the absolute RT criteria, the RRTs of the analytes and their respective labeled compound should still be valid. In this case, identification can still be made, although quantitative interferences may be present.

Table 5. Initial Calibration

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Initial calibrations are not performed	R	R
Initial calibration not performed at proper frequency (but other factors are acceptable)	J	UJ
Ion Abundance Ratio is not within ± 15% of theoretical values, as described in Table A.4	R or professional judgment	R or professional judgment
GC Resolution (% Valley) of >25%	J	UJ
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 or professional judgment
RTs: Not within appropriate windows and 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	R	R

V. 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. Reference DLM02.X, Exhibit B, Section 3.4.13 and Section 4, and Exhibit D, Section 9.4.

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:

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 CDD/CDF peaks, including the labeled versions of native compounds and the internal standards.
2. Absolute 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. In addition, if the absolute RTs of the internal standards are not within ± 15 seconds of the RTs obtained during the initial calibration, the descriptor switching times may not be optimum for detecting all homologues.
3. RRT criteria: The RRTs of the native and labeled CDDs/CDFs must be within the defined limits (see Table A.3).
4. Instrument sensitivity criteria: For the CS3 solution, the 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 ±25% (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. Although the statement of work (SOW) no longer includes the requirement for the laboratory to verify that absolute retention times are within ± 15 seconds of the initial calibration, an excursion outside this range may mean that some homologues will be missed.
4. Verify from the raw data that the RRT criteria for the native and labeled CDDs/CDFs were met.
5. Verify from the raw 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 TOCOR and/or SMO 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. The failure to meet the ion abundance criteria listed in Table A.4 is indicative of poor tuning, gross contamination, or system instability. Qualify positive results as estimated “J” and non-detects as rejected ("R") because of the possibility of false negatives. Notify SMO to schedule sample reanalysis under a compliant calibration.
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 ±25% (RR) and not within ±35% (RRF) as estimated "J". Recalibrate the HRGS/HRMS and reanalyze 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	R
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 RT in the initial calibration	Use professional judgment for qualification of target analytes; qualify homologues as estimated (J, UJ).	
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 ± 25%, %D for RRFs not within ± 35%	J	UJ

VI. Method Blank Analysis

A. Review Items:

FORM 4DF (FORM IV-HR CDD) and raw data. Reference DLM02.X, Exhibit B, Section 3.4.7, and Exhibit D, Section 12.1.

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. It is recommended to handle the Total Homologues contamination in the same way as the evaluation for OCDD/OCDF.

It should be noted that other QC samples, i.e., field equipment rinsates, or laboratory solvent blanks, should also be considered in making decisions regarding system contamination.

C. Criteria:

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 CDD/CDF ions (the concentration of OCDD/OCDF in the method blank must be less than three times the CRQL). The levels of non-2,3,7,8 homologues should also not exceed the CRQLs for the target congeners in the series.

1. There must be at least one laboratory method blank for each batch of samples extracted. The laboratory is required to analyze the method blank on each analytical system used to analyze samples. This includes both the DB-5 primary column (or equivalent) and the DB-225 confirmatory column (or equivalent) whenever any associated samples require 2,3,7,8-TCDF confirmation (either a positive result or an estimated maximum possible concentration (EMPC) value exceeds the CRQL).
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 OCDD/OCDF and Total Homologues, where the maximum allowable amount is less than three times (<3x) the CRQL.
3. If a group of samples and the associated method blank are contaminated, rerun the associated detects and any samples containing peaks that meet the qualitative identification criteria.

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

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

D. Evaluation:

1. Verify that each sample extract has an associated method blank that meets the acceptance criteria in DLM02.X, Exhibit D, Section 12.1.4. This section requires that a blank reference matrix of an equivalent initial weight or volume be prepared by the same procedures, including extract cleanup, and analyzed on each instrument used to analyze the samples. Care should be exercised when evaluating the method blank(s) that were prepared with a given sample extract. In addition, the reviewer may consider blanks analyzed in the same analytical sequence and any performance evaluation sample (PES) blind blanks submitted with the samples. Evaluation of field and equipment blanks should be done according to Regional policy and the criteria established in the project Quality Assurance Project Plan (QAPP). The reviewer should use the highest result from the same column to make decisions about data qualification.
2. Verify that, with the exception of OCDD and OCDF (and Total Homologues), 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. The levels of non-2,3,7,8 homologues should also not exceed the CRQLs for the target congeners in the series. Even though the statement of work (SOW) cites the CRQL as the limit for method blank contamination, users who report data down to the estimated detection limit (EDL) or EMPC should consider for data qualification any target analytes that are present, in addition to any chemical or electronic interference. This may require examination of the raw data in addition to reported results.

3. For those users who use the EDL or EMPC as a surrogate for calculating the toxic equivalent quantity (TEQ) for non-detects, the issue of blank contamination is of particular significance. Special caution is advised to evaluate as many factors as possible that indicate system stability and the possible sources of interference for their contribution to positive interference in those analytes with the highest Toxicity Equivalence Factors (TEF), (i.e., TCDD and PeCDD in the 2005 WHO mammalian TEFs).

E. Action:

1. If the highest associated method blank is contaminated with a CDD/CDF greater than or equal to the CRQL, qualify all detects as estimated "J". Non-detects for those analytes should not be affected.
2. Most data users want to use results reported down to the EDL or EMPC. Therefore, whereas the SOW describes in terms of laboratory requirements, the following actions are presented in terms of the EDL/EMPC. The EDLs for individual CDD/CDFs are not listed in the SOW, but are determined for each sample (see Section XIII).
   a. If method blanks are contaminated with CDD/CDFs above the EDL, then there is a potential impact on all sample results. Using this approach, all associated positive results should be qualified as estimated "J". Non-detects should not be affected.
   b. In the case where minimal contamination may exist, but it is significantly exceeded by the response in the samples, the reviewer may apply no qualification to the data. Alternatively, the reviewer may apply expanded criteria to qualify associated sample results. For example, sample results may be qualified as non-detects up to a value of 2 to 5 times the amount present in the highest associated blank (10x for OCDD/F & homologues) to discount possible contamination, but not qualified above that. Use of either approach requires careful professional judgment in the evaluation of the effects of contamination to avoid reporting false negatives.
   c. The validator should note that blank analyses may not include the same weights, volumes, or dilution factors as the associated samples. In particular, aqueous blank results may be associated with soil/sediment sample results. The total amount of contamination must be considered, compared, and qualifiers applied accordingly. It may be advantageous to use the raw data (i.e., instrument quantitation reports) to compare soil sample data to aqueous blank data. Another approach would be to calculate sample specific blank action results by adjusting the blank concentration with sample specific factors.
3. There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed appropriate. Professional judgment should be used in these situations. One example would be where the method blank did not satisfy one of the identification criteria, either the 2.5 * S/N requirement, or the ion ratio requirement to report an analyte present, but the actual sample contained the analyte with an acceptable ion ratio, and/or with slightly greater than 2.5 * S/N and less than five times the possible blank concentration. An explanation of the rationale used for this determination should be provided in the Data Review Narrative.
4. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentrations, the sample analysis results must be evaluated for carryover. Professional judgment should be used to determine if instrument cross-contamination has affected any positive compound identification(s).

5. Blanks or samples run after a Performance Evaluation Sample (PES), Laboratory Control Sample (LCS), or Calibration Verification should be carefully examined to determine the occurrence of instrument or syringe carry-over. Since the efficiency of sample transfer can vary dramatically according to apparatus and operator techniques, professional judgment should be used in each case to determine whether sample or blank results are attributable to carry-over.
6. When there is convincing evidence that contamination is isolated to a particular instrument, matrix, or concentration level, professional judgment should be used to determine if qualification should only be applied to certain associated samples (as opposed to all of the associated samples).
7. If gross contamination exists (i.e., saturated peaks), all samples in the sequence, including the calibration checks, may be affected. All affected compounds in the associated samples may be considered to be unusable ("R" qualifier) in this case. This is a contract issue, as the laboratory should take corrective action prior to reporting the data, and should be regarded as an action item to be reported to the TOCOR and/or SMO for resolution with the contract laboratory.

Table 7. Method Blank Evaluation Actions

Method Blank Result	Sample Result	Action
< < CRQL or EDL	Not detected	No qualification
	≥CRQL or EDL and >> Blank Result	No qualification or use professional judgment to avoid false pos. or neg. (see E.2.b above)
≥ CRQL or EDL	Not detected	No qualification
	≥CRQL or EDL and < Blank Result	U*
	> CRQL or EDL and ≥ Blank Result	J or use professional judgment
Gross contamination	Positive	R

* The calculated sample result should be reported with a “U” flag in these cases.

VII. Laboratory Control Sample (LCS) Analysis

A. Review Items:

FORM 3DFA (FORM III-HR CDD-1) and raw data. Reference DLM02.X, Exhibit B, Section 3.4.6, and Exhibit D, Section 12.2.

B. Objective:

Provide data on the accuracy of the analytical method by preparing and analyzing a sample of spiked reference matrix 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. EPA 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, Section 7.6). When a reference matrix that simulates the sample matrix under test is not readily available, EPA retains the option to supply the laboratory with a reference matrix containing the expected interferences for a particular project.

C. Criteria:

1. For each 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, Section 11.3).

D. Evaluation:

Confirm that the spiking solution was added to the LCS, and that the 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 detected associated sample data for those analytes which fail in the LCS as estimated "J" (see Table 8). Notify the TOCOR and/or SMO concerning samples associated with a non-compliant LCS to decide on re-extraction and reanalysis.
2. Recovery of the LCS below the lower primary recovery range, but above 10%, may be indicative of a low bias in laboratory performance, and as such should only warrant a "J" or a "UJ" qualifier. It also may, in conjunction with other performance factors, lead to the conclusion that laboratory performance is unacceptable. In this case, qualification of non-detected results should be based on professional judgment.
3. If LCS results are <10%, qualify positive results for those analytes as estimated ("J") and non-detects as unusable ("R") in all of the associated samples. Notify SMO concerning samples associated with a non-compliant LCS to decide on re-extraction and reanalysis.
4. If the laboratory failed to prepare and analyze the LCS at the required frequency, note this in the Data Review Narrative and notify the TOCOR and/or SMO. If no LCS was done and performance of other QC is poor (i.e., poor recovery in samples, compromised method blanks), the reviewer may not be able to determine whether the fault lies with the laboratory or the matrix. The only option may be to reject the data ("R").

Table 8. Laboratory Control Sample (LCS) Recovery Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
% R >10% but < Lower Acceptance Limit	J	UJ
% R <10%	J	R
LCS performed but not at required frequency	J	Use professional judgment
LCS not performed	J	Use professional judgment

VIII. Sample Dilution

A. Review Items:

Raw data (quantitation reports and chromatograms, prep and/or injection logs). Reference DLM02.X, Exhibit D, Section 10.6.6.

B. Objective:

A calibrated range is defined by the initial calibration. All sample results must be within the calibrated range to be reported without qualification.

C. Criteria:

If the selected ion current profile (SICP) area at either quantitation m/z for any compound (except OCDD and OCDF) exceeds the calibration range of the system, the laboratory must take steps to bring those analytes within the calibration range. According to the DLM02.X SOW, the laboratory must first perform a solvent dilution of the extract after adding additional labeled compounds, followed by (if the maximum allowable dilution was unsuccessful) re-extraction of the sample with a smaller or diluted sample aliquot. The sample extract may be diluted by a factor of up to 100 times (100x) with n-nonane. The instrument internal standard in the extract is adjusted to 100 pg/µL, and an aliquot of this diluted extract is analyzed by the internal standard method. If more than a dilution of 100x is required, the laboratory must prepare a smaller aliquot of the original sample and take the smaller aliquot through the processing and cleanup steps.

D. Evaluation:

1. Extract Dilution:
    a. Verify that all reported sample values (except OCDD or OCDF) are within the calibration range. Even though the laboratory is not required to take action if the response of OCDD or OCDF exceeds the calibration range, extremely high levels of these analytes may carry over between injections and affect overall chromatographic and detector performance. Most laboratories will perform dilutions in the event that any analyte, including OCDD/OCDF, exceeds the system linear range (i.e., produces a flat-topped peak).
    b. Examine the preparation and/or run logs to verify a proper dilution scheme. Also, examine the SICPs to determine whether any peaks saturated the detector. If the laboratory calculated or reported the results incorrectly, it may be necessary to request a re-submission of the data.
    c. Verify that the internal standard calculations used to determine analyte concentrations in the diluted sample were performed correctly.

        NOTE: Under this dilution scheme, the recovery correction aspect of the isotope dilution technique is lost. However, the laboratory should not correct for the recovery determined from the initial run. Initial labeled compound recovery is a factor that should be considered qualitatively by the reviewer.

    d. Verify that a dilution factor of ≤100x was used and correctly documented, or that prior communication with the Regional customer was documented.
2. Dilution by Re-extraction and Reanalysis:
    a. Verify that all reported sample values (except OCDD or OCDF) are within the calibration range. If substantial differences are noted between the initial analysis and the dilution/reanalysis of a sample, examine the preparation and/or run logs to verify a proper dilution scheme. Also examine the SICPs to determine whether any peaks saturated the detector. If the laboratory calculated or reported the results incorrectly, it may be necessary to request a re-submission of the data.

b. Examine the prep and/or run logs to verify a proper approach to analyzing a smaller aliquot. Also examine the SICPs to determine whether any peaks saturated the detector. If the laboratory calculated or reported the results incorrectly, it may be necessary to request a re-submission of the data.

E. Action:

1. Qualify all of the sample detects as estimated "J" which are not within the calibration range, taking into account the initial run and all successfully analyzed dilutions.
2. If unexplained differences are identified between undiluted and diluted results, the reviewer may choose to request further analytical work, qualify the results, use the original results, or reject the results. Be sure to attach adequate justification in the Data Review Narrative for your decision.

IX. Identification Criteria

A. Review Items:

FORM 1DFA (FORM I-HR CDD-1), FORM 2DF (FORM II-HR CDD), and raw data. Reference DLM02.X, Exhibit B, Section 3.4.1 – 3.4.5, and Exhibit D, Section 11.1.

B. Objective:

Unambiguously identify a gas chromatograph (GC) peak as a CDD or a 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 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.

   a. 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 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:

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

   b. 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 homologous series.

2. Peak Identification

   Both of the specified ions listed in Table A.1, and on the FORMs Is for each CDD/CDF homologue, must be present in the 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, as well as to the non-2,3,7,8 CDD/CDF congeners. For the cleanup 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 10x 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 $\geq$10:1 for all of the CDD/CDF compounds, whether or not they are labeled. Each peak representing a non-2,3,7,8 CDD or CDF should also meet the minimum S/N requirement.

4. Ion Abundance Ratios

   The ratio of the integrated areas of the two exact m/z's must be within the limit specified in Table A.4, or within ±10% of the ratio in the most recent Midpoint Calibration Standard (CS3). The ion ratio criterion applies to all 2,3,7,8-native and labeled CDDs/CDFs as well as to peaks representing non-2,3,7,8-substituted CDDs/CDFs.

   The ion abundance ratio criteria for native and labeled analytes and for internal standards must be met using peak areas to calculate ratios, if possible. 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. In this event, the laboratory must 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), their presence may interfere with quantitative determination of any of the furans. Additional extract cleanup with clean glassware and reagents can eliminate these interferents.

6. Homologous Series Totals

   Peaks are commonly found in each descriptor which pass all identification criteria for target 2,3,7,8-substituted CDD/CDF analytes except retention time. These peaks represent the many less toxic non-2,3,7,8-substituted CDDs/CDFs. These compounds do not have associated toxic equivalent quantities (TEQs), but the total quantity of CDDs or CDFs in each homologous series is required by certain data users. All peaks identified as non-2,3,7,8 CDDs/CDFs must meet the same qualitative criteria as the 2,3,7,8-substituted target analytes, except RT.

D. Evaluation:

1. Evaluate chromatograms for each selected ion current profile (SICP) to verify adequate system performance, proper scaling, and adequate presentation to allow a visual comparison of lock-mass trace and PCDPE interference channel to the associated target ion channels for the purpose of verifying positive identifications.
2. Verify that the RRTs for the 2,3,7,8-substituted compounds are within the RRT windows listed in Table A.3.
3. 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).
4. Verify from the SICPs that the ion current responses for the two quantitation ions for each analyte maximize simultaneously (within the same 2 seconds).
5. Verify from the SICPs that for each analyte ion listed in Table A.1, the S/N ratio is $\geq$ 2.5:1 and that the detector has not been saturated. If an analyte is flagged with an asterisk (*), it means the laboratory determined that the analyte failed one or more qualitative identification criteria and an estimated maximum possible concentration (EMPC) has been reported. Examine the SICPs to determine whether there is some interference (i.e., PCDPEs) that could potentially cause the ion ratio to fail, and if so, note the magnitude of that interference (see Items 3 and 5, below).
6. Verify from the Forms I that the ion abundance ratios are within the criteria listed in Table A.4, or within ±10% of the ratio in the most recent Midpoint Calibration Standard (CS3).
7. Verify that no PCDPE interferences exist at the retention time of each target analyte.
8. If homologue totals are to be reported, check to see that both ions are present and maximize within two seconds, and that they meet the S/N and ion ratio requirements. It is not common practice to calculate EMPC values for non-2,3,7,8-substituted CDDs/CDFs that fail the ion ratio test. If detector saturation occurs in a region of the SICP that is clearly due to either a non-2,3,7,8 CDD/CDF or to an interferent, it is normally not interpreted as a positive result and no further action is required by the laboratory.

E. Action:

1. If a peak falls outside of the Table A.3 and/or the WDM windows, examine the SICP to evaluate whether there is a peak within the Table A.3 and/or WDM criteria. If there is no peak, consider the analyte as a non-detect. Refer to Section XIII for determination of an EDL or EMPC.
2. If ion current responses for the two quantitation ions for an analyte fail to maximize simultaneously (within 2 seconds), examine the SICP to evaluate whether there are peaks or shoulders that do meet the 2-second criterion. If there are no peaks or shoulders that meet the 2-second criterion, consider the analyte as a non-detect. Refer to Section XIII for determination of an EDL or EMPC.
3. If PCDPE interferences are identified above the 2.5:1 S/N ratio limit, consider the magnitude of the PCDPE vs. that of the target analytes. If the raw abundance of the PCDPE interference is significant (i.e., greater than 10% of that for the associated target furans), qualify associated CDFs as non-detects at an estimated quantity ("UJ"), or rejected ("R"), depending on professional judgment. If the interference is minor (i.e., ≤10% of the associated target furans), qualify detects and non-detects as estimated (J or UJ respectively).
4. If S/N criteria are not satisfied, consider the analyte to be not detected. Refer to Section XIII for determination of an EDL or EMPC.
5. If ion abundance criteria are not satisfied, examine the other information provided to be sure the other criteria have been met. Check the calculation of EMPC results and/or ask the laboratory to recalculate and re-report these results. The isotope dilution method provides the ability to calculate ion ratios for the two ions monitored. This is an added benefit to unequivocally confirm that the peak present is dioxin/furan. But ion abundance outside the criteria does not unequivocally prove that dioxins/furans are not present. It only indicates that either an interference is present for one of the ions, or that another compound may be present. The standard qualifiers ("U" or "J") may not be appropriate in this case. The reviewer should rely on professional judgment and organizational policy to decide how to qualify EMPCs. Refer to Section XIII for determination of an EDL or EMPC.
6. In the event that non-2,3,7,8-substituted CDDs/CDFs are improperly identified, the reviewer may need to re-evaluate the raw data or forward a request, through the Task Order Contract Officer Representative (TOCOR), for a data re-submission from the laboratory.

X. Compound Quantitation

A. Review Items:

FORM 1DFA (FORM I-HR CDD-1), FORM 2DF (FORM II-HR CDD), and raw data. Reference DLM02.X, Exhibit D, Section 11.2.

B. Objective:

The objective is to verify that sample results for 2,3,7,8-substituted congeners, and that homologue totals were reported correctly.

C. Criteria:

1. In an isotope dilution method, a known amount of labeled compounds is added to every sample prior to extraction. This provides a correction for recovery of each corresponding native compound because the native compound and its labeled compound exhibit similar effects upon extraction, concentration, and Gas Chromatography (GC). Method 1613B uses labeled standards for determining quantitative results for all target analytes except 1,2,3,7,8,9-HxCDD and OCDF. The labeled 1,2,3,7,8,9-HxCDD is used as an internal standard (along with the labeled 1,2,3,4-TCDD) to measure the recovery of the other labeled congeners. It is added to the extract just prior to analysis. The labeled OCDF is not used because of a potential interference problem.
2. Native 1,2,3,7,8,9-HxCDD is quantitated using the average of the responses of the labeled compound of the other two 2,3,7,8-substituted HxCDDs: 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. As a result, the concentration of native 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other two HxCDDs. Also, because there is no labeled OCDF added prior to extraction, in instances where OCDD and OCDF behave differently during sample extraction, concentration, and cleanup procedures, this may decrease the accuracy of the OCDF results. However, given the low toxicity of this compound relative to the other dioxins and furans, the potential decrease in accuracy is not considered significant.
3. An estimate of quantitative results is determined for any peaks representing non-2,3,7,8-substituted CDDs/CDFs using an average of the response factors from all of the labeled standard 2,3,7,8-isomers at the same level of chlorination. The homologue totals are then determined by summing the results of target and non-target CDDs/CDFs for each level of chlorination.
4. The mean Relative Response ($\overline{RR}$)values from the initial calibration data are used to determine concentrations directly using the following equations:

   All Matrices Other than Aqueous:

$$\text{Solids (ng/kg)} = \frac{C_L \times (A_{x1} + A_{x2})\, V_{ex}}{W \times (A_{L1} + A_{L2}) \times \overline{RR}}$$

Where,

C_L	=	Concentration of the labeled standard added to the extract (includes any amount added during dilution procedures, see Section VIII)
A_{x1},A_{x2}	=	Areas of the signals for both quantitation ions of the CDD/CDF
A_{L1},A_{L2}	=	Areas of the labeled standard ions
V_{ex}	=	Effective final volume of the extract
W	=	The Sample Weight
$\overline{RR}$	=	The Mean Relative Response for the isomer of interest from the initial calibration (see DLM02.X, Exhibit D)

Aqueous:

$$\text{Aqueous (pg/L)} = \frac{C_L \times (A1_s + A2_s)\, V_{ex}}{V_s \times (A1_l + A2_l \times \overline{RR}}$$

Where,

C_L = Quantity (pg) of appropriate labeled standard added to the extract (includes any amount added during dilution procedures, see Section VIII)

$A1_s$, $A2_s$ = Areas of the signals for both quantitation ions of the CDD/CDF

$A1_l$, $A2_l$ = Areas of the labeled standard ions

V_{ex} = Effective final volume of the extract

V_i = Sample volume extracted in liters

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

5. The internal standard method is used to compute the concentrations of the 1,2,3,7,8,9-HxCDD, OCDF, ^{13}C-labeled analogs, and the ^{37}Cl-labeled cleanup standard in the extract using the mean Relative Response Factors (RRFs) determined from the initial calibration data (see DLM02.X, Exhibit D, Section 11.2.2) and the following equation:

$$C_{EX}\,(\text{ng/mL}) = \frac{(A1_S + A2_S)C_{IS}}{(A1_{IS} + A2_{IS})\,\overline{RRF}}$$

Where,

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

C_{IS} = The concentration of the internal standard

$\overline{RRF}$ is defined in DLM02.X, Exhibit D, Section 9.3.4.4. The other terms are as defined in DLM02.X, Exhibit D, Section 9.3.4.2.

6. The amount of moisture in solid samples should not have an impact on the calculation of quantitative results, since the SOW (Exhibit D, 10.1.3) requires the laboratory to prepare a equivalent of 10 grams dry-weight of aqueous samples containing greater than one percent solids, the fact that most laboratories report sample weight on a dry-weight basis, because of the extremely low water solubility of CDD/CDF analytes, and due to the prescribed use of the Soxhlet-Dean/Stark procedure. Values utilized as CRQLs should be equal to those given in DLM02.X, Exhibit C, provided that sample volume or dry weight, extract final volume, and injection volume are the same as those in DLM02.X, Exhibit D. However, if any one of these factors is different, the CRQL used for data qualification should be adjusted, as shown below:

Aqueous Adjusted CRQL:

$$\text{Adjusted CRQL} = \text{Contract CRQL x } \frac{(V_X)(V_T)}{(V_0)(V_C)}$$

Where,

V_t = Volume of the concentrated extract (µL)

V_o = Actual sample volume used (ml)

V_x = Contract sample volume (1000 mL)

V_c = Contract concentrated extract volume (µL)

Soil/Sediment Adjusted CRQL:

$$\text{Adjusted CRQL} = \text{Contract CRQL x } \frac{(W_X)(V_T)}{(W_S)(V_C)}$$

Where,

Vt = Volume of the concentrated extract (µL)
W_s = Actual mass extracted (g)
W_x = Contract sample weight (10 g)
V_c = Contract concentrated extract volume (µL)

Extract Concentrations by Relative Response:

$$C_{EX}\ (\text{ng/ml}) = \frac{(A1_N + A2_N)C_L}{(A1_L + A2_L)RR}$$

Where,

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

RRF is defined in DLM02.X, Exhibit D, Section 9.3.4.4. The other terms are as defined in DLM02.X, Exhibit D, Section 9.3.4.2

There is only one m/z for the ^{37}Cl-labeled cleanup standard.

D. Evaluation:

1. Use raw data to verify the correct calculation of all sample results reported by the laboratory. Before verifying calculations for solid samples, the reviewer should check whether the reported weight is a dry weight or a total weight (including any moisture). Only the dry weight should be used in these calculations. Each type of calculation should be verified, including those from the confirmational column.
2. Compare retention times, internal standard recoveries, ion ratios, S/N determination, positive results, dilution results, estimated detection limits (EDLs), estimated maximum possible concentrations (EMPCs), and quantitation limits between the processed raw data reports and the reported detects and non-detects in the sample results.
   a. Check the reported CRQLs for accuracy and compliance with DLM02.X, Exhibit C. Check reported results to verify that those less than the quantitation limit are qualified as estimated. If, due to a difference in weights or volumes used, the CRQL should be adjusted, verify that this has been done properly using the example equations above.
   b. SOW requirements for the laboratory to complete the results reporting form (FORM I-HR CDD-1) are given in DLM02.X, Exhibit B, Section 3.4.1.
3. Check qualifiers applied by the laboratory before finalizing data qualification. Data qualifiers applied by the laboratory must conform to the instructions in DLM02.X, Exhibit D, Section 3.4.1.5.
4. The amount of moisture in a solid sample may have an impact on data representativeness (i.e., if there is >70% moisture in a solid sample), depending on the nature of the equilibria between the two phases, and analyte solubility characteristics. However, due to the extremely low solubility of dioxins/furans in water, they should be expected to be contained in the solid phase. This fact notwithstanding, the reviewer should be aware of any local standard operating procedures (SOPs) and/or concerns of the data user and evaluate the data on this basis.

E. Action:

1. If any discrepancies are found, the Region's designated representative may contact the laboratory to obtain additional information that could provide a resolution. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate. Under these circumstances, the reviewer may determine that qualification of data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.
2. Because of the quantitation technique used for non-2,3,7,8-substituted CDDs/CDFs (see Section III under Criteria), it is common practice to qualify all homologue totals as estimated ("J" qualifier) or “UJ” if all are non-detect.
3. Note, for Task Order Contract Officer Representative (TOCOR) action, numerous or significant failures to accurately quantify the target compounds, homologue totals, or toxic equivalent quantities (TEQs), or to properly evaluate and adjust quantitation limits.
4. Apply appropriate qualification to the data, including all QC criteria discussed in these guidelines, in addition to those appropriate to any Regional data reporting policies. It is recommended that a Data Review Narrative be developed to document the review process, including the impact on data quality of any anomalies found.
5. It is highly recommended that the data review process applied to each analyte, sample, sample delivery group (SDG), and/or project be characterized for the benefit of those who may subsequently review or use the data. The terminology and labels for communicating the stages and processes used for laboratory analytical data verification and validation have been developed by an EPA workgroup and are published in *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use*, EPA-540-R-08-005, 13 January, 2009.

XI. Second Column Confirmation and Isomer Specificity

A. Review Items:

FORM 1DFC (FORM I-HR CDD-3) and raw data. Reference DLM02.X, Exhibit B, Section 3.4.3 and Exhibit D, Section 11.1.2.

B. Objective:

Isomer specificity for all 2,3,7,8-substituted 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 closely eluting isomers, 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. The confirmatory analysis is not required when the GC column that was used meets isomer specificity requirements for both 2,3,7,8-TCDD and 2,3,7,8-TCDF. The column must meet all criteria established in DLM02.X, Exhibit D, Section 9.

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 (or equivalent) alone.
2. The sample extract may be reanalyzed on a DB-225 (or equivalent) GC column to achieve better GC resolution and, therefore, better identification and quantitation of the individual 2,3,7,8-substituted isomers.
3. 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.
4. 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, S/N ratio, RT, etc.). If using any GC column other than those specified (DB-5, DB-225), the laboratory shall clearly document in the SDG Narrative the elution order of all analytes of interest on any such column (DLM02.X, Exhibit B, Section 2.5.1.1).
5. 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 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 or is reported as an EMPC in any sample at or above the CRQL. The confirmatory analysis is not required when the GC column that was used meets isomer specificity requirements for both 2,3,7,8-TCDD and 2,3,7,8-TCDF. The column must meet all criteria established in DLM02.X, Exhibit D, Section 9. 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. Verify that the final sample result for 2,3,7,8-TCDF is reported from the confirmation column (the column having greater specificity for 2,3,7,8-TCDF).
2. 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. The confirmatory analysis is not required when the GC column that was used meets isomer specificity requirements for both 2,3,7,8-

TCDD and 2,3,7,8-TCDF. The column must meet all criteria established in DLM02.X, Exhibit D Section 9.

E. Action:

1. If second-column confirmation was required but was not performed, contact the TOCOR and/or SMO to direct the laboratory to perform the analysis.
2. If second-column confirmational analysis was performed, but the result is a non-detect, report the lowest value obtained (from either column), qualified as "U".

XII. Toxicity Equivalent Quantity Determination

A. Review Items:

FORM 1DFB (FORM I-HR CDD-2) and raw data. Reference DLM02.X, Exhibit B, Section 3.4.2 and Exhibit D, Section 11.2.8.

B. Objective:

The exclusion of homologues such as mono-, di-, tri-, and the non-2,3,7,8-substituted isomers in the higher homologous series does not mean that they are not toxic. Their toxicity, as estimated at this time, is relatively 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 Toxic Equivalent Quantity (TEQ) or Toxicity Equivalence Factors (TEF)-adjusted concentration calculations. The TEFs used in these calculations are derived and published by the World Health Organization (WHO). Updates of TEFs are published by WHO approximately every five years for mammalian toxicity. The timetable has been longer for other types of organisms (i.e., birds and fish).

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

C. Criteria:

1. The criteria for calculating TEQ will depend upon Regional policies. Two common approaches are outlined below:
   a. The first approach is to include only those 2,3,7,8-substituted congeners that were detected in the sample (per DLM02.X, Exhibit B, Section 3.4.2.2) and that meet all of the qualitative identification criteria. Under this approach, a zero is used for any estimated maximum possible concentration (EMPC) or estimated detection limit (EDL) values in the TEF calculations. The results of this calculation (usually for mammalian toxicity only) are reported on FORM I-HR CDD-1 and FORM I-HR CDD-2, and if confirmations were performed, also on FORM I-HR CDD-3.
   b. In the second approach, in addition to the results of any positively identified 2,3,7,8-substituted congeners, the reported values of any EMPCs or EDLs are also included in the calculation as surrogates for the non-detect results.
2. If directed by the Regional customer, the laboratory will use the TEFs for birds and fish to determine TEQs for these other organisms as well. The results of this calculation are reported on optional FORM I-HR CDD-4.

D. Evaluation:

1. Verify that the TEF calculations were correctly performed, in accordance with Regional policy.
2. In the determination of total TEQ for a sample, consider the impact of using estimated quantities in the TEQ calculation. If any, or a portion, of the total TEQ number has been derived from qualified results, the reviewer may decide to qualify the TEQ. For example if more than 10% of the total represents "J"-qualified values, then the total may also be "J" qualified.

E. Action:

If calculations were not correctly performed by the laboratory, notify the TOCOR and/or SMO of the deficiency.

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

A. Review Items:

FORM 1DFA (FORM I-HR CDD-1) and raw data. Reference DLM02.X, Exhibit D, Section 11.2.5 and Section 11.2.6.

B. Objective:

For each analyte that is not detected, calculate an 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 CDDs/CDFs; therefore, the EDL value is reported for non-detected analytes rather than simply reporting the respective CRQL.

The EMPC value is applied to a sample when the 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 homologous series 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 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 HRGC/HRMS system that was used for the analysis of the samples that are associated with the EDL calculations. In addition, if there is a matching labeled analog present, the RT of the expected analyte should be within ± 2 sec. of that of the labeled analog.

   All Matrices Other than Aqueous:

$$\text{Solids EDL (ng/kg)} = \frac{2.5 \times Q_L \times (H_{x1} + H_{x2}) \times D}{W \times (H_{L1} + H_{L2}) \times \overline{RR}}$$

   Where,

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

   Q_L = Quantity (pg) of appropriate labeled standard added prior to sample extraction

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

   H_{L1},H_{L2} = Peak heights of the labeled 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:

$$\text{Aqueous EDL (pg/L)} = \frac{2.5 \times Q_L \times (H_{x1} + H_{x2}) \times D}{V \times (H_{L1} + H_{L2}) \times \overline{RR}}$$

Where,

EDL = Estimated Detection Limit for 2,3,7,8-substituted CDDs/CDFs
Q_L = Quantity (pg) of appropriate labeled standard added prior to sample extraction
H_{x1},H_{x2} = Peak heights of the noise for both quantitation ions of the CDD/CDF
H_{L1},H_{L2} = Peak heights of the labeled 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. EMPC

An EMPC is calculated for 2,3,7,8-substituted isomers that are characterized by a response with an 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 quantity of the native compound in the extract in nanograms (ng/ µL * extract volume in µL)

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 quantity of the native compound in the extract in picograms (pg/ µL * extract volume in µL)

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:

If calculations were not correctly performed by the laboratory, notify the TOCOR and/or SMO of the deficiency.

XIV. Labeled Compound Recoveries

A. Review Items:

FORM 1DFA (FORM I-HR CDD-1) and raw data. Reference DLM02.X, Exhibit B, Section 3.4 and Exhibit D, Section 11.2.7, and Exhibit D, Tables 2 and 7.

B. Objective:

The 15 labeled CDDs/CDFs serve as the isotopic dilution quantitative mechanism in this method. The recovery of these compounds, along with the recovery of the cleanup standard, is a critical measure of the effectiveness of the laboratory and method to extract the compounds of interest.

C. Criteria:

1. Recovery of the labeled cleanup standard should be monitored as an indicator of method efficiency through the extract cleanup. If the original sample, prior to any dilutions, has more than one labeled compound or cleanup standard with a Percent Recovery (%R) not within the limits specified in Table A.7, re-extract and reanalyze 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 cleanup of 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 reanalyze if the labeled compounds are not present with at least a 10:1 S/N ratio 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, reanalyze the sample extract on an analytical system meeting system performance, and initial and calibration verification criteria. 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. If the failed ion abundance ratios persist through the second analysis, process the extract through additional cleanup steps, or re-extract and reprocess the sample through sufficient cleanup steps to remove possible interferences.
4. 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 HRGC/HRMS operating conditions, recalibrate the instrument, and reanalyze 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, reanalyze associated samples after instrument recalibration. Re-extraction is not ordinarily required unless the resolution difficulties reappear after recalibration.

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 labeled compound, internal standard, and clean-up standard recoveries fall within the required limits, prior to any dilutions being performed.

E. Action:

1. If the recoveries of the labeled compounds are not within the limits in Table A.7, but other identification criteria and the S/N requirement have not been met, the laboratory should have performed a reanalysis. If no reanalysis is found, contact the TOCOR or SMO to initiate reanalysis.
2. The ^{37}Cl-labeled cleanup standard is used to monitor the efficiency of the cleanup; it is added to the sample extracts after extraction and before any cleanup steps. Low recovery of the labeled compounds and the cleanup standard suggests that losses may be due to the performance of the cleanup steps. Thus, re-extraction and reanalysis of the sample may yield better results. If the labeled compound recoveries are low (<40%), and the cleanup 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". If recovery of only the cleanup standard is low, the presence of interference should be investigated. Otherwise, the possibility of improper calibration of the cleanup standard or a spiking error should be considered. Qualify all results associated with non-compliant clean-up standard performance as estimated (“J” or “UJ”).
3. In the event that labeled compound recoveries are <10%, the reviewer should note whether this is accompanied by a loss of signal (i.e., S/N <10). If this is the case, the impact may make both positive and non-detect results unusable ("R"-qualify all results). Otherwise, positive results should be considered estimated ("J").
4. If any of the labeled compounds (exclusive of the recovery standard) fail the ion ratio criteria but the associated calibration standard was acceptable, quantitative results may have been influenced by interference. Qualify all associated results as estimates ("J" or "UJ"). If ion ratio criteria were not met in the calibration standard, follow the actions prescribed in Table 6.
5. Professional judgment is advised before taking action based on recovery standard performance. If a wide range is noted in cleanup standard recoveries between samples and laboratory quality control (QC) that correspond to other QC indicators, this parameter may be used as a data quality issue.

Table 9. Labeled Compound Recovery Actions

Criteria		Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
%R >Upper Acceptance Limit		J	UJ
% R >10% but less than Lower Acceptance Limit		J	UJ
% R <10%		(see below)	
<10% and S/N >10:1		J	R
<10% and S/N <10:1		R	R
Ion abundance ratio criteria not met	Calibration compliant	J	UJ
	Calibration non-compliant	J	R
Clean-up Standard Recovery < Lower Acceptance Limit		J	UJ

XV. Regional Quality Assurance/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. Performance evaluation sample (PES) scoring information from the Quality Assurance Technical Support (QATS) laboratory is evaluated as per Section II, above. Reference DLM02.X, Exhibit B, Section 3.4, and Exhibit D, Section 11.2.

B. Objective:

In addition to evaluating the results of performance evaluation spikes and/or blind blanks, assess the impact on data quality of any other QA/QC samples initiated by the Region, including field duplicates, equipment rinsates, or reagent blanks.

C. Criteria:

1. The frequency of Regional QA/QC samples should be defined in the quality assurance project plan (QAPP).
2. Performance criteria for Regional QA/QC samples should also be defined in the Quality Assurance Project Plan (QAPP).

D. Evaluation:

The reviewer must decide whether the results of Regional QA/QC samples impact all samples in the project, or only those directly associated (i.e., in the same sample delivery group (SDG), collected the same day, prepared together, or contained in the same analytical sequence). Results for PESs are evaluated for false negatives, false positives, and accuracy of target compound quantitation (see Section II). Equipment rinsate samples should not contain any CDD/CDF contamination. Moreover, they should be comparable to the associated method blank(s). Field duplicates should be evaluated for comparability (i.e., precision). The reviewer must decide whether poor precision is the fault of the laboratory, or a result of sample nonhomogeneity in the field. Laboratory observations of sample appearance may become important in these situations.

E. Action:

Any action must be in accordance with Regional specifications and criteria for acceptable QA/QC sample results. Note in the Data Review Narrative any observations and the impact on data quality of any QA/QC issues.

Like PES, Regional QA/QC samples are only indicators of technical performance of laboratory and/or field operations. If a result is not within acceptance criteria 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 cleanup standard recovery]. Consider the possibility that the Regional QA/QC samples may not be representative of the field samples. In general, for Regional QA/QC performance not within QAPP specifications, qualify associated sample detects as estimated "J" and non-detects as estimated "UJ"; however, QAPP-specific rules should be controlling. The impact on overall data quality should be assessed after consultation with the data user and/or field personnel. Contact the TOCOR if reanalysis of samples is required.

XVI. 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 collection of observations and findings as a result of the review process, and discussion the impact of qualifications on the overall use of the data. In addition, contract compliance issues should be brought to the attention of the TOCOR and/or SMO.

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 Measurement Quality Objectives (MQOs)], 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. Include a summary of these observations in the Data Review Narrative to give the data user an indication of any limitations on the use of the data. 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.
2. Also, usually under separate cover, document any contract-related deficiencies, including completeness and usability of the Case Narrative for TOCOR and/or Contract Officer records and possible action.

APPENDIX A: DATA TABLES

Extracted from:
USEPA Statement of Work (SOW) for Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs), Multi-Media, Multi-Concentration, DLM02.2, Dated December 2009

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

Descriptor	Exact m/z[1]	m/z Type	Elemental Composition	Substance[2]
1	292.9825	Lock	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF[3]
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF[3]
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD[4]
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD[3]
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD[3]
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF[3]
	354.9792	Lock	C_9F_{13}	PFK
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD[3]
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD[3]
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF[3]
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF[3]
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	Lock	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD[3]
	403.8529	M+4	$^{13}C_{12}H^2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD[3]
	430.9729	QC	C_9F_{17}	PFK
	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]

Descriptor	Exact m/z[1]	m/z Type	Elemental Composition	Substance[2]
	437.8140	M+4	$^{13}C_{12}$ H $^{35}Cl_5$ $^{37}Cl_2$ O_2	HpCDD[3]
	479.7165	M+4	C_{12} H $^{35}Cl_7$ $^{37}Cl_2$ O	NCDPE
5	441.7428	M+2	C_{12} $^{35}Cl_7$ ^{37}Cl O	OCDF
	442.9728	Lock	C_{10} F_{17}	PFK
	443.7399	M+4	C_{12} $^{35}Cl_6$ $^{37}Cl_2$ O	OCDF
	457.7377	M+2	C_{12} $^{35}Cl_7$ ^{37}Cl O_2	OCDD
	459.7348	M+4	C_{12} $^{35}Cl_6$ $^{37}Cl_2$ O_2	OCDD
	469.7779	M+2	$^{13}C_{12}$ $^{35}Cl_7$ ^{37}Cl O_2	OCDD[3]
	471.7750	M+4	$^{13}C_{12}$ $^{35}Cl_6$ $^{37}Cl_2$ O_2	OCDD[3]
	513.6775	M+4	C_{12} $^{35}Cl_8$ $^{37}Cl_2$ O	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]homologous series Definition:

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) Retention Time (RT) Window Defining Mixture (WDM) and Isomer Specificity Check (ISC) 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 (RRT) and Quantitation Reference of the Native and Labeled 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
$^{13}C_{12}$-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
$^{13}C_{12}$-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 $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

1,2,3,7,8,9-HxCDD is quantified using the averaged responses of $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-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
$^{13}C_{12}$-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

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