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USEPA ANALYTICAL OPERATIONS/DATA QUALITY CENTER (AOC)

NATIONAL FUNCTIONAL GUIDELINES FOR CHLORINATED DIOXIN/FURAN DATA REVIEW

Final

Office of Emergency and Remedial Response
U.S. Environmental Protection Agency
Washington, DC 20460

NOTICE

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

This document can be obtained from the following USEPA Web site at:

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

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ACRONYMS

CDD	Chlorinated Dibenzo-p-Dioxin
CDF	Chlorinated Dibenzofuran (also PCDF)
CDWG	Chlorinated Dioxins Work Group
CLP	Contract Laboratory Program
CPS	Column Performance Solution
CRQL	Contract Required Quantitation Limits
CS	Calibration Standard
CWA	Clean Water Act
DQO	Data Quality Objective
EDL	Estimated Detection Limit
EMPC	Estimated Maximum Possible Concentration
HRGC	High Resolution Gas Chromatograph
HRMS	High Resolution Mass Spectrometer
ISC	Isomer Specificity Check
LCS	Laboratory Control Sample
PCDPE	Polychlorinated diphenyl ether
PE	Performance Evaluation
PES	Performance Evaluation Sample
PFK	Perfluorokerosene
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support
QC	Quality Control
RR	Relative Response
RRF	Relative Response Factor
RSD	Relative Standard Deviation
RT	Retention Time
RRT	Relative Retention Time
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SDWA	Safe Drinking Water Act
SICP	Selected Ion Current Profile
SIM	Single Ion Monitoring
S/N	Signal-to-noise Ratio
SOP	Standard Operating Procedure
SOW	Statement of Work
TCL	Target Compound List
TEF	Toxicity Equivalency Factor
TICP	Total Ion Current Profile
TOPO	Task Order Project Officer
VTSR	Validated Time of Sample Receipt
WDM	Window Defining Mix
USEPA	United States Environmental Protection Agency

INTRODUCTION

This document is designed to offer guidance on USEPA Chlorinated Dibenzo-p-dioxin (CDD) and Chlorinated Dibenzofuran (CDF) data evaluation and review. In some applications it may be used as a Standard Operating Procedure (SOP). In other, more subjective areas, only general guidance is offered due to the complexities and uniqueness of data relative to specific samples. For example, areas where the application of specific SOPs are possible are primarily those in which definitive performance criteria are established. These criteria are concerned with specifications that are not sample dependent; they specify performance requirements that should fully be under a Laboratory's control. These specific areas include blanks, calibration standards, Performance Evaluation (PE) standard materials, and instrument performance checks.

These guidelines include the requirements for the USEPA Statement of Work (SOW) for Analysis of CDDs and CDFs, DLM01.4 dated January 2002. This SOW is based on USEPA Methods 1613B and 8290A which employ High Resolution Gas Chromatography and High Resolution Mass Spectrometry (HRGC/HRMS).

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

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

This document offers guidelines for the review of data generated by the DLM01.4 SOW. Professional judgment should always be used to determine the ultimate usability of the data.

DATA QUALIFIER DEFINITIONS

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

U	The analyte was analyzed for, but was not detected above the Contract Required Quantitation Limit (CRQL) for the sample.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
UJ	The analyte was not detected above the adjusted CRQL. However, the reported adjusted CRQL is approximate and may be inaccurate or imprecise.
R	The sample results are unusable. The analyte may or may not be present in the sample.

PRELIMINARY REVIEW

This document is for the review of analytical data generated through the USEPA Chlorinated Dibenzo-p-dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Statement of Work (SOW) DLM01.4 and any future editorial revisions. In order to use this document effectively, the reviewer should have an understanding of the analytical method and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analysis are essential information. Background information on the site is helpful, but often this information may be difficult to locate. If available, the field notes should be reviewed. The site manager is the best source for answers to questions, or for further direction.

Please note that individual task orders may modify the 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 task order depending on project requirements. Thus, the task order requirements must be taken into consideration, along with the requirements in the National Functional Guidelines (NFG), when reviewing the data.

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

1. The Region where the samples were taken; and

2. Complete list of samples with information on:
   a. Sample matrix;
   b. Field blanks*;

c. Field duplicates*;
d. Field spikes*;
e. Quality Control (QC) audit samples*;
f. Shipping dates;
g. Preservatives; and
h. Laboratories involved.

* If applicable.

The Traffic Report/Chain of Custody (TR/COC) documentation includes sample descriptions and 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 found in the SDG Narrative.

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

DATA REVIEW NARRATIVE

A Data Review Narrative 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 Task Order Project Officer (TOPO) assigned oversight responsibility for the Laboratory producing the data.

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

DIOXIN DATA REVIEW

The data requirements to be checked are listed below:

I. Holding Times, Storage, and Preservation

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I. Holding Times, Storage, and Preservation

A. Review Items:

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

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

2. 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.

3. Analysis of sample extracts must be completed within 30 days of extraction.

4. Sample extracts can be stored up to one year from the date of extraction in the event that reanalysis is required.

5. Holding times for oily matrices have not been established. The aqueous holding times are recommended in this case. Holding times for fish and tissue samples have not been established, however, they should be extracted within one year of collection as recommended in USEPA Method 1613B. As always, the professional judgment of the reviewer remains the final authority in issues such as these.

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

D. Evaluation:

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

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

E. Action:

1. If holding times are exceeded, flag all positive results as estimated "J", and sample quantitation limits as estimated "UJ", and document that holding times were exceeded. The reviewer may determine that non-detect data are unusable "R".

2. If shipment and storage conditions are exceeded, either on the first analysis or upon reanalysis, the reviewer may determine that positive results or the associated quantitation limits are estimates and should be qualified with "J" or "UJ", respectively.

3. If sodium thiosulfate preservative has not been added to aqueous samples, qualify all positive results "J" and detection limits "UJ". If a residual chlorine test has been performed and found to be negative, then data should not be flagged due to lack of sodium thiosulphate preservative.

4. Due to limited information concerning holding times for oily samples, it is left to the discretion of the data reviewer to apply water holding time criteria to oily samples. Professional judgment is required to evaluate holding times for oily samples. Professional judgment is also required to evaluate holding times for fish and tissue samples.

5. If extracts are analyzed outside the 30 day holding time, for all sample types, qualify positive results "J" and detection limits "UJ".

6. Whenever possible, the reviewer should comment in the Data Review Narrative on the effect that the exceeded holding times will have on the resulting data.

7. When holding times are exceeded, it should be noted as an action item for the Task Order Project Officer (TOPO).

Table 1. Holding Times, Storage, Preservation

Evaluation	Sample Type	Criteria	Action
Contractual Holding Time	Aqueous	>1 year	Qualify positives as "J" Quality detection limits as "UJ"
	Soil	>1 year	Qualify positives as "J" Qualify detection limits as "UJ"
	Fish, Tissue	>1 year	Use professional judgment
Storage	Aqueous	>6°C shipment and storage	Qualify positives as "J" Qualify detection limits as "UJ"
	Soil	>6°C shipment and storage	Qualify positives as "J" Qualify detection limits as "UJ"
	Fish, Tissue	>4°C shipment >⁻10°C storage	Qualify positives as "J" Qualify detection limits as "UJ"
Preservation	Aqueous	Not added	Qualify positives as "J" Qualify detection limits as "UJ"
Sample Extract Holding Time	All types	>30 days	Qualify positives as "J" Qualify detection limits as "UJ"

II. Performance Evaluation Samples

A. Review Items:

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

B. Objective:

To evaluate the Laboratory's ability to achieve acceptable results through the analysis of PE samples.

C. Criteria:

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

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

D. Evaluation:

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

E. Action:

If a result is outside of the action limits (99% confidence interval) for any congener, the other Quality Control (QC) samples in the SDG should be evaluated [Laboratory Control Sample (LCS), calibration, labeled standard recovery, internal standard recovery, and clean-up standard recovery]. In such situations, the PE sample may not be representative of the field samples. PE samples are only one indicator of technical performance of the Laboratory. In general, for PE sample analytes outside the 95% confidence intervals or action performance windows but within the 99% confidence interval, qualify associated sample data as estimated "J". For data outside the 99% confidence interval, qualify the associated sample data as rejected "R". The Regional Task Order Project Officer (TOPO) should be contacted to determine if reanalysis of samples is required. Under certain circumstances, it may be necessary to utilize data that are not within the 99% confidence interval before reanalysis can take place. As always, the reviewer must use their best professional judgment to determine the usability of the data.

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

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

Table 2. Action Limits

Criteria	Action
Results are outside the 95% confidence interval but inside the 99% interval (<3σ)	Qualify the associated sample data as estimated "J"
Results are outside the 99% confidence interval (>3σ)	Qualify the associated sample data as rejected "R"

III. Mass Calibration and Mass Spectrometer Resolution

A. Review Items:

Hardcopy of mass spectrometer resolution demonstration.

B. Objective:

Mass calibration and mass spectrometer resolution ≥10,000 must be performed by the Laboratory with Perfluorokerosene (PFK) calibrant. This is a fundamental requirement for any Laboratory using DLM01.4 and other High Resolution Mass Spectrometry (HRMS) methods (e.g., 1613B, 8290A). If mass calibration and resolution tuning is not properly performed, interferences may degrade Chlorinated Dibenzo-p-dioxin and Chlorinated Dibenzofuran (CDD/CDF) identification and quantitation. Mass calibration and resolution is the first part of the three fundamental High Resolution Gas Chromatography/HRMS (HRGC/HRMS) system performance checks. The second fundamental performance check is the mass spectrometer Selected Ion Monitoring (SIM) scan descriptor switching times. The third fundamental performance check is Gas Chromatograph (GC) resolution.

C. Criteria:

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

D. Evaluation:

Verify that the mass spectrometer has been tuned to a resolution of ≥10,000. A demonstration of mass spectrometer resolving power is provided within USEPA Method 8290A, Section 8.2.2.3, and in Figure 5.

E. Action:

Mass spectrometer resolution is critical to the success of this method of CDD/CDF analysis. In the event that mass spectrometer resolution is <10,000 or is not demonstrated, all of the associated data should be rejected "R".

IV. Window Defining Mix

A. Review Items:

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

B. Objective:

Prior to the calibration of the High Resolution Gas Chromatrograph/High Resolution Mass Spectrometer (HRGC/HRMS) system, it is necessary to establish the appropriate switching times for the Selected Ion Monitoring (SIM) descriptors (see Table 8 in DLM01.4, Exhibit D, Section 15.0), and to verify the chromatographic resolution. The switching times are determined by the analysis of the Window Defining Mix (WDM) which contains the first and last eluting isomers in each homologue (see Table 5 in DLM01.4, Exhibit D, Section 15.0). Chromatographic resolution is verified by analyzing one of two Isomer Specificity Check (ISC) solutions, depending on the Gas Chromatograph (GC) column used for analysis. The WDM and ISC can be combined in a single Column Performance Solution (CPS) analysis at the discretion of the analyst. Mass spectrometer Selected Ion Monitoring (SIM) scan descriptor switching times is the second of the three fundamental HRGC/HRMS system performance checks.

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

C. Criteria:

1. The WDM shall be analyzed after the Perfluorokerosene (PFK) tune and before any calibration standards on each instrument and GC column used for analysis in order to evaluate the mass spectrometer SIM scan descriptor switching times. This commercially available, 16-component mix contains the first and last eluting isomers in each homologue. Mixes are available for various columns. The mix for the DB-5 (or equivalent) column may not be appropriate for the DB-225 or other columns.

2. The ions in each of the five recommended descriptors are arranged so that there is minimal to no 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, the tetra- and pentachlorinated dioxins and furans are combined in a single descriptor.

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

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

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

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

6. Analysis on a single GC column (as opposed to situations requiring second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for both the DB-5 and DB-225 (or equivalent) columns are met (see Section V, Chromatographic Resolution).

D. Evaluation:

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

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

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

4. Each positive dioxin and furan result (tetra through hepta) must have an RT within the limits established by the WDM for the corresponding homologue. The 2,3,7,8-substituted dioxins and furans must also meet the Relative Retention Time (RRT) limits in Table 2 of Exhibit D, Section 15.0.

E. Action:

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

2. If the chromatography for the calibration standards indicate a significant problem with descriptor switching times, all of the associated data should be rejected "R". The Task Order Project Officer (TOPO) for the Laboratory performing the analysis should be notified to decide if sample reanalysis is necessary.

V. Chromatographic Resolution

A. Review Items:

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

B. Objective:

To evaluate the ability of the Gas Chromatograph (GC) column to resolve the closely eluting dioxin and furan isomers. An evaluation must be made for each column used in the analysis of samples. GC resolution is the third of the three fundamental High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system performance checks listed in Table 3.

C. Criteria:

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

1. For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the commercially available, 4-component DB-5 Isomer Specificity Check (ISC) standard prior to both the initial and continuing calibration procedures for each instrument and GC column used for analysis. The ISC and Window Defining Mix (WDM) can be combined in a single Column Performance Solution (CPS) analysis at the discretion of the analyst.

   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,

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

x = Measurement from baseline to the deepest part of the valley between 2,3,7,8-TCDD and 1,2,3,8-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 and continuing calibration solutions. Evaluate the chromatographic resolution using the Quality Control (QC) criteria stated above.

2. For analyses on a DB-225 (or equivalent) GC column, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of the commercially

available, 3-component DB-225 ISC that contains the TCDF isomers that elute most closely with 2,3,7,8-TCDF on the GC column (1,2,3,9-TCDF and 2,3,4,7-TCDF).

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

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

Where,

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

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

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

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

4. Analysis on a single GC column (as opposed to situations requiring second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for both the DB-5 and DB-225 (or equivalent) columns are met, as stated above.

D. Evaluation:

Verify from the SICPs that the ≤25% valley criteria are met. Examples of GC resolution can be found in USEPA Methods 1613B and 8290.

E. Action:

If the GC resolution does not meet the specifications, all positive sample results and Estimated Detection Limits (EDLs) for 2,3,7,8-TCDD and/or 2,3,7,8-TCDF, whichever failed, should be qualified as "J" and the Task Order Project Officer (TOPO) should be notified to decide on sample reanalysis.

Table 3. System Performance Checks

Criteria	Action
Mass Calibration and Resolution	If mass spectrometer resolution of ≥10,000 is not demonstrated, reject "R" all of the associated sample data.
HRMS SIM Descriptor Switching Times	If the WDM fails or adjustments are not made, or if the WDM is not reported, estimate "J" all affected total homologue results in the associated samples. (If the WDM fails, adjustments are not made and the calibration standards indicate a problem in detecting 2,3,7,8-substituted congeners because of gross errors in the scan descriptor times, "R" all of the associated sample data.)
HRGC Resolution	If the CPS fails or is not reported, estimate "J" all associated sample results for 2,3,7,8-TCDF and/or 2,3,7,8-TCDD, whichever failed.

VI. Instrument Stability

A. Review Items:

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

B. Objective:

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

C. Criteria:

The CS3 solution must meet the following QC criteria:

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

2. Relative Retention Time (RRT) criteria. The RRTs of the native and labeled Chlorinated Dibenzo-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) shall be within the limits defined in Section VII, HRGC/HRMS Initial Calibration (also see Table 2 in DLM01.4, Exhibit D, Section 15.0).

3. Ion abundance ratio criteria. All CDDs/CDFs in the CS3 standard (both native and labeled) must be within their respective ion abundance ratios (see Table 9 in DLM01.4, Exhibit D, Section 15.0).

4. Instrument sensitivity criteria. The peaks representing both native and labeled analytes in the CS3 standard must have signal-to-noise (S/N) ratios ≥ 10.0.

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

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

Where,

$Response_{ver}$ = Response established during calibration verification.

$Response_{INT}$ = Mean response established during initial calibration according to DLM01.4 Exhibit D, Equations 4 and 5.

D. Evaluation:

Verify that the CS3 standard meets the criteria for both RT and RRT, ion abundance ratio, S/N ratio, and response (%D associated with RR and RRF). An example of the measurement of S/N can be found in USEPA Method 8290A.

E. Action:

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

2. The ion abundance, sensitivity, and calibration criteria are all critical indicators of instrument stability (see Table 4). Failure to satisfy the ion abundance criteria, S/N 10:1 criteria, or the %D RR and RRF criteria each indicate significant problems with the instrument. The reviewer should qualify all of the associated sample data as estimated "J" if any of these criteria fail. The S/N criteria are especially indicative of severely degraded instrument performance. For all affected analytes, Estimated Detection Limits (EDLs) in associated samples should be rejected "R" if the S/N measurement in the CS3 continuing calibration standard is <10:1.

Table 4. Instrument Stability

Criteria	Action
RT changes >15 seconds or RRT changes outside the values in Table 2 of DLM01.4, Exhibit D, Section 15.0	Use professional judgment
Relative ion abundance criteria is outside windows in CS3 (12-hour) standard	"J" associated sample results
S/N ratio <10:1 in CS3 standard	"J" associated sample results "R" associated EDLs
Percent Difference (%D) greater than criteria in CS3 standard	"J" associated sample results

VII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer Initial Calibration

A. Review Items:

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

B. Objective:

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

The objective of the initial calibration is to establish a linear range and mean Relative Responses ($\overline{RR}$s) and the mean Relative Response Factors ($\overline{RRF}$s) for the instrumentation. The initial calibration is to be used for routine quantitation of samples using the $\overline{RR}$s and $\overline{RRF}$s established from the five Calibration Standards (CS1, CS2, CS3, CS4, and CS5). Subsequent continuing calibrations 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 the initial calibration is used for quantitation of sample data and is not frequently performed. Thus, the initial calibration affects the quality of the data based on it for an extended period of time.

Initial Calibration

Once the Perfluorokerosene (PFK), Window Defining Mix (WDM), Isomer Specificity Check (ISC), and Column Performance Solution (CPS) solutions have all been analyzed, and once the descriptor switching times have all been verified, then the five CSs described in Table 4 of Exhibit D, Section 15.0, shall be analyzed prior to any sample analysis.

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

1. GC resolution criteria. For DB-5, DB-225, or equivalent columns, see the criteria in Section V, Chromatographic Resolution.

2. Ion abundance criteria. The relative ion abundance criteria for Chlorinated Dibenzo-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) listed in Table 9 of DLM01.4, Exhibit D, Section 15.0, 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 8 DLM01.4,

Exhibit D, Section 15.0, for m/z types and exact m/z ratios). The $^{37}Cl_4$-2,3,7,8-TCDD clean-up standard contains no ^{35}Cl, therefore the ion abundance ratio criteria do not apply to this compound.

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

4. Mass Spectrometer sensitivity criteria. For all calibration solutions, including the CS1 solution, the S/N ratio must be $\geq$10.0.

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

6. Concentration criteria. All initial Calibration Standards (CSs) must be analyzed at the concentration levels shown in Table 4 of DLM01.4, Exhibit D, Section 15.0.

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

   - The Contractor takes corrective action which may change or affect the initial calibration criteria discussed directly above.

   - The calibration verification (CS3 continuing calibration) acceptance criteria cannot be met even after corrective action. See Section VI, Instrument Stability, and Section VIII, High Resolution Gas Chromatograph/High Resolution Mass Spectrometer Calibration Verification, for CS3 criteria.

D. Evaluation:

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

2. Verify that all analytes in all calibration solutions are present at the concentrations listed in Table 5.

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

4. Verify that the %RSD of the five RRFs is $\leq$35%.

5. Verify that the %RSD of the five RRs is $\leq$20%.

6. Verify that the ion abundance ratios in each CS are within ±15% of the limits listed in Table 9 of DLM01.4, Exhibit D, Section 15.0.

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

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

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

E. Action:

1. Concentrations and Frequency

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

2. Ion Abundance Ratios

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

   At the reviewer's discretion, a more in-depth review to minimize the qualification of data may be accomplished by considering the following hypothetical examples:

   - If the ion abundance ratio is outside the limits for an analyte in the CS1 solution, then the low-end results for that analyte (below the CS2 concentration from Table 5) are flagged "R".

   - If the ion abundance ratio is outside the limits for an analyte in the CS5 solution, then the high-end results for that analyte (above the CS4 concentration from Table 5) are flagged "R".

3. GC Resolution

   If failed resolution criteria involved TCDD isomers, then only those isomers would be flagged as "J". Reanalysis should be requested for all samples following a failed resolution to ensure the quantity of isomers present. When GC resolution capability is lacking, the only alternative is to assume that 2,3,7,8-TCDD is the only isomer present. This worst-case scenario may not be warranted.

4. Analyte Response

   If the %RSD is >20% and >35% for the RR and RRF, respectively, the positive hits shall be qualified as estimated "J". The reviewer may choose to look at the RR and RRF values for the initial calibration, discard either the CS1 or CS5 values, and recalculate the %RSD. If discarding either of these points brings the %RSD within the specified limits, then the reviewer should qualify either the low- or high-end hits, depending on which point was discarded. If either of these scenarios affected a majority of the data, then reanalysis should be performed.

5. Sensitivity

   If the S/N 10:1 sensitivity requirements are not met, qualify any Estimated Detection Limits (EDLs) for those analytes as unusable "R" for all associated samples.

6. Retention Time

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

Table 5. Initial Calibration

Criteria	Action
Concentrations in Table 4 of DLM01.4, Exhibit D, Section 15.0 Frequency as described above	Reject "R" all associated sample results if initial calibrations are not performed at the prescribed concentration and frequency
Ion Abundance Ratios, ±15% of theoretical values, as described in Table 9 of DLM01.4, Exhibit D, Section 15.0	Reject all associated sample data for compounds with failed ion ratios in the initial calibration
GC Resolution (% Valley) of ≤25%	Qualify all associated sample data as estimated "J"
Linearity: RRF %RSDs ≤35%; RR %RSDs ≤20%	Qualify all associated sample data as estimated "J" for those analytes failing the initial calibration RSD criteria If there are points from the low- or high- end of the calibration curve, qualify either the low- or the high-end detect as estimated "J"
Sensitivity: 10:1 S/N for all SICPs	Reject "R" all associated EDLs

Table 5. Initial Calibration Cont.

Criteria	Action
RTs: 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	Reject "R" all associated sample data

VIII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer Calibration Verification

A. Review Items:

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

B. Objective:

Compliance requirements for satisfactory calibration are established 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 check for satisfactory performance of the instrument on a day-to-day basis.

C. Criteria:

Calibration verification criteria. The Laboratory shall 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 9 of DLM01.4, Exhibit D, Section 15.0, shall be met for all Chlorinated Dibenzo-p-Dioxin/Chlorinated Dibenzofuran (CDD/CDF) peaks, including the labeled versions of native compounds and the internal standards.

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

3. RRT criteria. The RRTs of the native and labeled CDDs/CDFs shall be within the limits defined in Section VII, HRGC/HRMS Initial Calibration.

4. Instrument sensitivity criteria. For the CS3 solution, the signal-to-noise (S/N) ratio shall be $\geq$10.0 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 ±35% (RRF) and within ±20% (RR) of the mean values established during initial calibration:

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

Where,

RRF_i = RRF established during initial calibration

RRF_c = RRF established during continuing calibration

And:

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

Where,

RR_i = RR established during initial calibration

RR_c = RR established during continuing calibration

D. Evaluation:

1. Verify that the calibration verification was run at the required frequency [following the Window Defining Mix (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 9 of DLM01.4, Exhibit D, Section 15.0, were all met.

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

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

5. Verify from the raw Selected Ion Current Profile (SICP) data that the S/N ratio is $\geq$10.0 for the unlabeled CDD/CDF ions, and $\geq$10.0 for the labeled compounds and internal standards.

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

E. Action:

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

1. Any analyte in samples associated with a continuing calibration not meeting the RT and/or RRT criteria should be qualified using professional judgment.

2. Any analyte in samples associated with a continuing calibration not meeting the ion abundance criteria listed in Table 9 of DLM01.4, Exhibit D, Section 15.0, is to be estimated "J". The High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGS/HRMS) must be recalibrated and the affected samples must be reanalyzed.

3. If the ≥10.0 S/N ratio limit is not met in a continuing calibration, all associated data should be estimated "J" and all associated EDLs should be rejected "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 ($\overline{RR}$s) or RRF ($\overline{RRF}$s) is a crucial criterion for review. Data associated with an analyte with a %D >20% (RR) and > 35% (RRF) should be estimated "J". The HRGS/HRMS must be recalibrated and the affected samples should be reanalyzed.

Table 6. Calibration Verification

Criteria	Action
Ion abundance ratios inside 15% window	Estimate "J" all associated sample results
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 Internal standards must be within 15 seconds of the RTs in the initial calibration RRTs must be within the limits defined in Table 2 of DLM01.4, Exhibit D, Section 15.0	Use professional judgment
Sensitivity: S/N 10:1 for all compounds	Estimate "J" all of the associated sample results Reject "R" associated EDLs
%D for RRs must be within ±20% %D for RRFs must be within ±35%	Estimate "J" all associated sample results

IX. Identification Criteria

A. Review Items:

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

B. Objective:

To unambiguously identify a Gas Chromatographic (GC) peak as a Chlorinated Dibenzo-p-Dioxin (CDD) or a Chlorinated Dibenzofuran (CDF).

C. Criteria:

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

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

    - To make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled counterpart or internal standard is present in the sample extract, the Relative Retention Time (RRT) at the maximum peak height of the analyte must be within the RRT window in Table 2 of DLM01.4, Exhibit D, Section 15.0. The RRT is calculated as follows:

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

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

2. Peak Identification

    Both of the specified ions listed in Table 8 of DLM01.4, Exhibit D, Section 15.0, and on Form I for each CDD/CDF homologue, must be present in the Selected Ion Current Profile (SICP). The ion current response for the two quantitation ions for the analyte in question must maximize simultaneously within the same 2 seconds. This requirement also applies to the labeled versions of the native standards and to the internal standards. For the clean-up standard, only one ion is monitored.

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

   The integrated ion current for each native analyte ion listed in Table 8 of DLM01.4, Exhibit D, Section 15.0, must be at least 2.5 times (2.5x) the background noise and must not have saturated the detector (applies to sample extracts only). The labeled and internal standard ions, however, must be at least 10.0x the background noise and must also not have saturated the detector (applies to sample extracts only). In the case of the various calibration standard solutions, the S/N ratio must be $\geq$ 10.0 for all of the CDD/CDF compounds, whether or not they are labeled.

4. Ion Abundance Ratios

   The ion abundance ratio criteria listed in Table 9 of DLM01.4, Exhibit D, Section 15.0, for native and labeled analytes and for internal standards must be met using peak areas to calculate ratios.

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

   If the Laboratory High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Interpretation Specialist has judged the peak to be a CDD/CDF, then the ion abundance ratios may be determined using peak heights instead of areas. Quantitate the peaks using peak heights rather than areas for both the target analyte and the labeled compound or internal standard. The Laboratory should have flagged this data "H".

5. Polychlorinated Diphenyl Ether (PCDPE) Interferences

   If PCDPE interferences are detected above the 2.5 S/N ratio limit, as indicated by the presence of peaks at the exact m/z(s) monitored for these interferents (see Table 8 of DLM01.4, Exhibit D, Section 15.0), all CDF sample results with a coeluting PCDPE interference should be qualified as estimated "J".

D. Evaluation:

1. Verify that the RRTs for the 2,3,7,8-substituted compounds are within the RRT windows listed in Table 2 of DLM01.4, Exhibit D, Section 15.0.

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

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

4. Verify from the SICPs that for each analyte ion listed in Table 8 of DLM01.4, Exhibit D, Section 15.0, the S/N ratio is $\geq$ 2.5 and that the detector has not been saturated. If an analyte is flagged with an asterisk (*), then verify the presence of the CDD/CDF using professional judgment.

5. Verify from the Forms I that the ion abundance ratios are within the criteria listed in Table 9 of DLM01.4, Exhibit D, Section 15.0.

6. Verify that no PCDPE interferences exist.

E. Action:

1. If a peak falls outside of the Table 3 and/or the WDM windows, then the results are rejected "R".

2. If ion current responses for the two quantitation ions for an analyte fail to maximize simultaneously (within 2 seconds), the result should be rejected "R".

3. If ion abundance criteria are not satisfied, then the data should be rejected "R".

4. If S/N criteria are not satisfied, then the data should receive a "J" flag.

5. If PCDPE interferences exist above the 2.5 S/N ratio limit, qualify associated CDFs as estimated "J".

Table 7. Identification Criteria

Criteria	Action
Signals must maximize within 2 seconds	If signals do not maximize simultaneously (within 2 seconds) the result is rejected "R"
S/N ratio must be >2.5	If the signals do not satisfy the S/N ratio, the result is estimated "J"
Ion abundance ratios must be within the limits in Table 9 of DLM01.4, Exhibit D, Section 15.0, or within 10% of the ratio in the most recent CS3 standard	If the ion abundance criteria are not satisfied, the result is rejected "R"
RRTs for 2,3,7,8-substituted CDD and CDF must be within the limits in Table 2 of DLM01.4, Exhibit D, Section 15.0 The RT of non-substituted CDDs/CDFs must be within the RTs established by the WDM	Reject "R" sample results failing the RT criteria
PCDPE ion S/N >2.5	Qualify associated CDF sample result as estimated "J"

NOTE: Professional judgment should always be used in determining the proper identification of analytes.

X. Method Blank Analysis

A. Review Items:

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

B. Objective:

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

C. Criteria:

Method Blank Criteria

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

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

3. If the method blank extracted along with a group of samples is contaminated, then the associated positive samples, and any samples containing peaks that do not meet all of the qualitative identification criteria for a contaminated method blank, should have been rerun.

   NOTE: Report results for all peaks with signal-to-noise (S/N) ratio >2.5, even if they are <CRQL (see DLM01.4, Exhibit C for CDD/CDF CRQLs).

4. The method blank, like any other sample in the Sample Delivery Group (SDG), must meet the technical acceptance criteria for sample analysis (see DLM01.4, Exhibit D, Section 11.3).

D. Evaluation:

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

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

E. Action:

1. If the method blank is contaminated with a CDD/CDF > the CRQLs listed in the Statement of Work (SOW), or 3x the CRQLs for OCDD/OCDF, qualify all associated positive sample results and EDLs for those analytes as estimated "J".

2. In some cases, the reviewer might also consider rejecting positive sample results which are below method blank contaminant concentrations. Also, a sample or sample set with results at levels similar to the levels reported in the method blank might also be rejected.

Table 8. Blank Actions for Laboratory Analyses

Method Blank Result	Sample Result	Action for Samples
<CRQL	Not detected	No action
	<CRQL	Report CRQL value with a "U"
	≥CRQL	Use professional judgment
>CRQL	<CRQL	Report CRQL value with a "U"
	≥CRQL but <Blank Result	Report the blank concentration for the sample with a "U" or qualify the data as estimated (J)
	>CRQL and ≥Blank Result	Use professional judgment
=CRQL	<CRQL	Report CRQL with a "U"
	≥CRQL	Use professional judgment
Gross contamination	Positive	Qualify results as unusable (R)

XI. Laboratory Control Sample Analysis

A. Review Items:

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

B. Objective:

To provide data on the accuracy of the analytical method, the Laboratory is required to prepare and analyze a sample of spiked reference matrix [the Laboratory Control Sample (LCS)] for each matrix analyzed. If a matrix is not represented in a Sample Delivery Group (SDG), then no spiked sample (LCS) is required for that matrix. USEPA has identified a number of reference matrices to be used for the spiked LCS, and the Laboratory must use an aliquot of that matrix for its own LCS work (see DLM01.4, Exhibit D, Section 7.6). When a reference matrix that simulates the sample matrix under test is not readily available, USEPA retains the option to supply the Laboratory with a reference matrix containing the expected interferences for a particular project.

C. Criteria:

1. For each SDG, the Laboratory must prepare a spiked sample (LCS) for all of the matrix types that occur in that SDG (see DLM01.4, Exhibit D, Section 1.1).

2. The recovery of each spiked analyte must be in the range in Table 6 (see DLM01.4, Exhibit D, Section 15.0).

3. The LCS must meet the technical acceptance criteria for sample analysis (see DLM01.4, Exhibit D, Section 11.3).

D. Evaluation:

Confirm that the spiking solution was added to the reference matrix sample (LCS), and that the Chlorinated-p-Dioxin/Chlorinated Dibenzofuran (CDD/CDF) analytes were at their correct concentrations. Verify that calculations, and transcriptions from raw data, were performed correctly.

E. Action:

1. If LCS recovery results are outside of the recovery limits, then the reviewer should qualify all associated sample data for those analytes which fail in the LCS as estimated "J". If the Laboratory failed to prepare and analyze the LCS at the required frequency, note this in the Data Review Narrative and notify the Task Order Project Officer (TOPO).

2. If LCS results are <10%, those analytes and Estimated Detection Limits (EDLs) should be rejected "R" in all of the associated samples. The TOPO should be contacted concerning samples associated with a non-compliant LCS to decide on reextraction and reanalysis.

XII. Toxicity Equivalency Factor and Isomer Specificity

A. Review Items:

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

B. Objective:

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

The exclusion of homologues such as mono-, di-, tri-, and the non-2,3,7,8-substituted isomers in the higher homologues, does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less than the toxicity of the native 2,3,7,8-substituted isomers listed in Table 6 (DLM01.4, Exhibit D, Section 15.0). Hence, only the 2,3,7,8-substituted tetra through octa isomers are included in the Toxicity Equivalency Factor (TEF) calculations. The procedure for calculating the 2,3,7,8-TCDD TEFs for the Target Compound List (TCL) analytes is not claimed by the Chlorinated Dioxins Work Group (CDWG) to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

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

C. Criteria:

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

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

D. Evaluation:

Verify that the TEF calculations were properly performed.

NOTE: A Region may require that the reviewer recalculate the TEFs using EMPCs and EDLs. The Laboratory, however, is not required to perform such calculations.

E. Action:

The reviewer has all of the data needed to calculate TEFs. If calculations were not properly performed by the Laboratory, then notify the Task Order Project Officer (TOPO) of the deficiency.

XIII. Dilution by Addition of Solvent

A. Review Items:

Raw data (quantitation reports and chromatograms).

B. Objective:

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

C. Criteria:

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

D. Evaluation:

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

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

3. Verify that a dilution factor of ≤20 was employed and properly documented.

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

E. Action:

1. Compare the original and diluted analyses of the sample. If substantial differences are noted, use professional judgment to qualify results.

2. If a sample value is outside of the calibration range, and appropriate dilution was not performed, qualify all of the sample data which are out of range as estimated "J".

XIV. Dilution by Reextraction and Reanalysis

A. Review Items:

Raw data (quantitation reports and chromatograms).

B. Objective:

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

C. Criteria:

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

D. Evaluation:

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

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

3. Verify that a smaller sample size was employed and properly documented.

4. Verify that the Percent Solids (% Solids) procedure in DLM01.4, Exhibit D, Section 10.1.4.1, was carried out for soil/sediment samples, even if no dilutions were subsequently required.

E. Action:

If a sample value is outside of the calibration range, and reextraction was not performed, all of the sample data that is out-of-range should be estimated "J".

XV. Second Column Confirmation

A. Review Items:

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

B. Objective:

Isomer specificity for all 2,3,7,8-substituted Chlorinate-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) cannot be achieved on the 60 meter DB-5 column alone. Historically, problems have been associated with the separation of 2,3,7,8-TCDF from 1,2,3,9-TCDF and 2,3,4,7-TCDF. Because of the toxicological concern associated with 2,3,7,8-TCDF, a second column confirmation is employed.

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 either of the two options listed below to achieve better isomer specificity than can be obtained on the DB-5 column alone.

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

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

2. Regardless of the GC column used, for a GC peak to be identified as a 2,3,7,8-substituted CDD/CDF isomer, it must meet all of the criteria listed in DLM01.4, Exhibit D, Section 11, such as ion abundance ratio, signal-to-noise (S/N) ratio, Retention Time (RT), etc. In addition, when using any GC column other than those specified here (DB-5, DB-225), the Laboratory shall clearly document, in the Sample Delivery Group (SDG) Narrative, the elution order of all of the analytes of interest on any such column.

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

D. Evaluation:

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

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

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

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

E. Action:

If second column confirmation is required but was not performed, the reviewer should reject "R" the 2,3,7,8-TCDF results.

XVI. Estimated Detection Limit and Estimated Maximum Possible Concentration

A. Review Items:

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

B. Objective:

For each analyte that is not detected, an Estimated Detection Limit (EDL) is calculated. The sample-specific EDL is an estimate made by the Laboratory of the concentration of a given analyte that would have to 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. Because of the toxicological significance of Chlorinated-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs), the EDL value is reported for non-detected analytes rather than simply reporting the respective Contract Required Quantitation Limit (CRQL).

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

C. Criteria:

1. Estimated Detection Limit

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

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

   All Matrices Other than Water:

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

Water:

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

Where,

EDL	=	Estimated Detection Limit for 2,3,7,8-substituted CDDs/CDFs
Q_{IS}	=	Quantity (pg) of appropriate internal standard added prior to sample extraction
H_{x1},H_{x2}	=	Peak heights of the noise for both quantitation ions of the CDD/CDF
H_{IS1},H_{IS2}	=	Peak heights of the internal standard ions
D	=	Dilution Factor
V	=	Volume extracted in liters
W	=	Weight extracted in grams
$\overline{RR}$	=	The mean Relative Response for the isomer of interest from the initial calibration (See DLM01.4, Exhibit D, Section 9.3.4.3)

2. Estimated Maximum Possible Concentration

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

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

   All Matrices Other than Water:

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

Where,

D	=	Dilution Factor
W_S	=	Sample weight (dry weight) in Kg
C_{EX}	=	The concentration of the native compound in the extract

Water:

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

Where,

D = Dilution Factor

V_S = Sample volume in liters

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

D. Evaluation:

1. Verify that EDLs and EMPCs are properly calculated.

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

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

E. Action:

Reject "R" all EDLs and EMPCs that were not properly calculated.

XVII. Labeled Compound Recoveries

A. Review Items:

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

B. Objective:

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

C. Criteria:

1. If the original sample, prior to any dilutions, has any labeled compound or internal standard with a Percent Recovery (% Recovery) outside the limits specified in Table 9 (DLM01.4, Exhibit D, Section 15.0), then reextraction and reanalysis of that sample is required.

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

2. If the labeled compounds are not present with at least a 10:1 signal-to-noise (S/N) ratio at their respective m/z(s), then reextraction and reanalysis are required.

3. If any of the labeled compound ion abundance ratios specified in Table 9 (DLM01.4, Exhibit D, Section 15.0) are outside of the contract-specified control limits, then the sample extract must be reanalyzed on the same Gas Chromatograph (GC) column and Mass Spectrometer used for the original analysis. If the problem corrected itself, then the Laboratory should have used the data from the second analysis and disregarded the data from the first analysis. No additional reextraction and reanalysis are required. If, however, the failed ion abundance ratios persist through the second analysis, then reextraction and reanalysis are required.

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

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

applies to sample analysis, and no reextraction and reanalysis are required if the second analysis resolves the problem. If this criterion is not met for a calibration standard, however, then all associated samples must be reanalyzed after instrument recalibration. Reextraction should not ordinarily be required in this case, but is required if 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.

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

E. Action:

1. If the recovery of the labeled compounds are outside of the limits in Table 9 (DLM01.4, Exhibit D, Section 15.0), the reviewer should qualify all associated sample results as estimated "J". If no reanalysis is found, then contact the Task Order Project Officer (TOPO) to initiate reanalysis.

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

XVIII. Regional Quality Assurance and Quality Control

A. Review Items:

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

B. Objective:

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

C. Criteria:

Criteria are determined by each Region.

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

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

D. Evaluation:

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

E. Action:

Any action must be in accordance with Regional specifications and criteria for acceptable PE sample results. Unacceptable results for PE samples should be noted for Task Order Project Officer (TOPO) action.

XIX. Overall Assessment of Data

A. Review Items:

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

B. Objective:

Assess the overall quality of the data.

C. Criteria:

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

D. Evaluation:

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

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

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

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

E. Action:

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

2. Write a brief narrative to give the data user an indication of the analytical limitations of the data. Any inconsistencies between data and the Sample Delivery Group (SDG) Narrative should be noted for Task Order Project Officer (TOPO) action. If sufficient information on the intended use and required quality of the data is available, then the reviewer should include their assessment of the usability of the data within the given context.