

Polychlorinated Dibenzodioxins/
Polychlorinated Dibenzofurans SW-846 Method 8280
DATA Validation



Prepared by: *Russell Arnore*
Russell Arnore, Chemist HWSS

Date: 12/29/10

Peer Reviewed by: *Muhammad Sheikh*
Muhammad Sheikh, Chemist HWSS

Date: 12/29/10

Concurred by: *Michael Mercado*
Michael Mercado, Acting Chief HWSS

Date: 12/29/10

Approved by: *Robert Runyon*
Robert Runyon, Chief, HWSB

Date: 1/6/11

Annual Review

Reviewed by: _____

Date: _____

Reviewed by: _____

Date: _____

1.0 Introduction

1.1 The attached Standard Operating Procedure (SOP) is applicable to polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/PCDF) data. Its scope is to facilitate the data validation process of the data reported by the contracting laboratory and also to ensure that the data is being reviewed in a uniform manner.

1.2 The SOP is based upon the quality control and quality assurance requirements specified in the analytical method PCDD/PCDF Protocol, Statement Of Work 9/91 (DFLM01.1) and its ensuing revision.

2.0 Responsibilities

2.1 The reviewer must be knowledgeable of the analytical method and its QC Criteria.

2.2 The reviewer must complete and/or file the following:

2.2.1 Data Assessment Checklist - The data reviewer must read each item carefully and must check yes if there is compliance, no if there is non compliance and N/A if the question is not applicable to the data.

2.2.2 Data Assessment Narrative - The data reviewer must present professional judgement and must express concerns and comments on the validity of the overall data package. The reviewer must explain the reasons for rejecting and/or qualifying the data.

2.2.3 Rejection Summary Form - The reviewer must submit the completed form using a ratio format. The numerator indicates the number of dioxins/furans data rejected; the denominator indicates the number of dioxins/furans fractions containing rejected compounds.

2.2.4 Organic Regional Data Assessment Summary - The data reviewer is also required to submit the completed Organic Regional Data Assessment Form.

2.2.5 Telephone Record Log - All phone conversations must be initiated by the technical project officer through SMO. If a phone call has been made, the reviewer must transcribe the conversation. After the data review has been completed, the white copy of the telephone log is mailed to the laboratory and the pink copy to SMO. The yellow copy is filed in the appropriate folder. A photocopy of the Telephone Record Log is attached to the Data Assessment Narrative.

2.2.6 Forwarded Paperwork - Upon completion of the review the following are to be forwarded to the Regional Sample Control Center (RSCC):

- a. data package

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2.2.6 Forwarded Paperwork - Upon completion of the review the following are to be forwarded to the Regional Sample Control Center (RSCC):

- a. data package

b. completed data assessment checklist and narrative (original)

The reviewer will forward one copy of the completed Data Assessment and one copy of the Organic Regional Data Assessment to the appropriate Regional TPO.

2.2.7 Filed Paperwork - The following are to be submitted to the Monitoring Management Branch (MMB) files:

- a. a photocopy of the Data Assessment Narrative
- b. a photocopy of the Regional Data Assessment Summary
- c. Telephone record Log (copy)
- d. Rejection Summary Form

2.3 Rejection of Data - All values determined to be unacceptable on the Organic Analysis Data Sheet (Form I) must be flagged with an "R". The qualifier R means that due to significant QA/QC problems the analysis is invalid and it provides no information as to whether the compound is present or not. Once the data are flagged with R any further review or consideration is unnecessary.

- The qualifier "J" is used to indicate that due to QA/QC problems the results are considered to be estimated.
- The qualifier "NJ" indicates that there is presumptive evidence for the presence of the compound at an estimated value.
- The data reviewer must explain in the data assessment narrative why the data was qualified. He or she must also indicate all items of contract non-compliance.
- When 2,3,7,8- substituted TCDD, TCDF, PnCDD and PnCDF data are rejected (flagged "R") or qualified "J" the project officer must be notified promptly. If holding times have not been exceeded reanalysis of the affected samples may be requested.
- All qualifications and corrections to reviewed data must be made in red pencil.

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER: _____

LAB: _____

SITE: _____

I.0 Data Completeness and Deliverables

YES NO N/A

1.1 Are the Traffic Report Forms present for all samples? ___ ___

1.2 Is the Narrative or Cover letter present? ___ ___

1.3 Are the Case Number and/or SAS numbers
 contained in the case narrative? ___ ___

1.4 Do the Traffic Reports or Lab Case Narrative indicate
 problems with sample receipt, sample condition,
 analytical problems, or other comments affecting the
 quality of the data? ___ ___

 ACTION: Use professional judgement to evaluate the
 effect of the noted problems on the quality
 of the data.

2.0 Reporting Requirements and Deliverables

2.1 All deliverables must be clearly labeled with the SMO
 number and the associated sample/traffic number.
 Missing or illegible or incorrectly labeled items must
 be identified. The contractor must immediately be
 contacted and requested to submit the missing or
 incorrect items.

2.2 Are the following forms present?

a. Sample Data Summary (Form I PCDD-1) ___ ___

b. PCDD/PCDF Toxicity Equivalency Factor (Form I, PCDD-2) ___ ___

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

	<u>YES</u>	<u>NO</u>	<u>N/A</u>
d. Total Homologue Concentration Summary (Form II PCDD)	[]	___	___
e. PCDD/PCDF Spiked Sample Summary (Form III PCDD-1)	[]	___	___
f. PCDD/PCDF Duplicate Sample Summary (Form III PCDD-2)	[]	___	___
g. PCDD/PCDF Method Blank Summary (Form IV-PCDD)	[]	___	___
h. PCDD/PCDF Window Defining Mix Summary (Form V-PCDD-1)	[]	___	___
i. Chromatographic Resolution Summary (Form V PCDD-2)	[]	___	___
j. PCDD/PCDF Analytical Sequence Summary (Form V PCDD-3)	[]	___	___
k. Initial Calibration (Form VI, PCDD-1, PCDD-2)	[]	___	___
l. Continuing Calibration (Form VII,PCDD-1, Form VII,PDD-2)	[]	___	___
2.3 GC/MS Displays			
a. Standard and sample SIM chromatograms. SIM and TIC chromatograms must list date and time of analysis; the file name; sample number; and instrument I.D. number.	[]	___	___
b. Percent peak resolution valley	[]	___	___
c. PCDD/PCDF window defining mix raw data	[]	___	___
d. SIM mass chromatograms must display quantitation ion, confirmation ion, daughter ion (M-COC1) and polychlorinated diphenylether ion where applicable.	[]	___	___
e. Integrated area and peak height must be listed for all peaks 2.5 times above background.	[]	___	___
f. All peaks must show retention time at the maximum height.[]	[]	___	___
2.4 Chain of Custody Records and in-house Laboratory Control Documents			
a. EPA Chain of Custody Records	[]	___	___
b. SMO Sample Shipment Records	[]	___	___

- | | <u>YES</u> | <u>NO</u> | <u>N/A</u> |
|---|--------------------------|-----------|------------|
| c. Sample log-in sheets | <input type="checkbox"/> | ___ | ___ |
| d. GC/MS Standard and Sample Run Log in chronological order | <input type="checkbox"/> | ___ | ___ |
| e. Sample Extraction Log | <input type="checkbox"/> | ___ | ___ |

2.5 The Sample Package Data must be paginated.

ACTION: If deliverables are missing call the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the reviewers narrative.

3.0 Holding Times

3.1 Have any holding times been exceeded?

- | | | | |
|--|--------------------------|-----|-----|
| a. For aqueous samples 30 days from sample collection to extraction. | <input type="checkbox"/> | ___ | ___ |
| b. For soil/sediment samples 30 days from sample collection to extraction. | <input type="checkbox"/> | ___ | ___ |
| c. For all samples 40 days from time of extraction to time of analysis. | <input type="checkbox"/> | ___ | ___ |

ACTION: If holding times are exceeded, flag all data as estimated ("J"). Holding time criteria do not apply to PE samples.

4.0 Instrument Performance

4.1 Mass Calibration - Mass calibration of the MS is recommended prior to analyzing calibration solutions, blanks, samples, and QC samples. The lab is not required to submit mass calibration data.

4.2 Window Defining Mixture/Column Performance Mixtures

4.2.1 The Window Defining Mixture and the Column Performance Mixture must be analyzed prior to the initial calibration. It must also be analyzed whenever the retention time of either recovery

standard in any analysis varies by more than 10 seconds from the most recent continuing calibration standard.

4.2.2 The window defining mix must contain the first and the last isomers of each homologue PCDD/PCDF, (the internal and recovery standards are optional).

4.2.3 All peaks must be labeled and identified on the SICPs.

ACTION: If the window defining mix was not analyzed at the required frequency use professional judgement to determine the effect on the quality of the data.

4.3 Chromatographic Resolution

4.3.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the CC3 Standard Solution during the initial and continuing calibration.

4.3.2 For analyses on a SP-2331 (or equivalent) GC column the chromatographic resolution is evaluated before the analysis of initial calibration by the analysis of the column performance mixture. This commercially available solution contains the 2378-TCDD and the isomers eluting immediately prior and after the 2378-TCDD on SP-2331 or equivalent.

4.3.3 For SP-2331 or equivalent, the peak separation between the unlabeled 2378-TCDD and the peaks of 1468-TCDD and the 1237/1238-TCDD isomer pair shall be resolved with a valley of < 25 percent.

$$\text{Valley} = (x/y) \times (100)$$

Y = The peak height of 2,3,7,8-TCDD isomer or any TCDD isomer

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

ACTION: If the percent valley criteria are not met, qualify all positive data J. Do not qualify non-detects.

5.0 Initial 5-Point Calibration - The initial calibration standard solutions (CC1-CC5) must be analyzed prior to any sample analysis. They do not have to be analyzed daily provided the continuing calibration standard met all criteria. However,

YES NO N/A

initial calibration should be analyzed at least once every week and/or whenever the continuing calibration standard does not meet all criteria.

The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the window defining mix. The CC3 solution must contain the supplemental calibration solution (see analytical method - Table 3).

5.1 The following MS/DS conditions must be used:

5.1.1 Scanning time was < 1 second.

5.1.2 SIM data were acquired for each of the ions listed in Table 5 including interfering ions (see analytical method)

5.2 The following GC criteria must be met:

5.2.1 The chromatographic resolution between the $^{13}\text{C}_{12}2378\text{-TCDD}$ and $^{13}\text{C}_{12}1234\text{-TCDD}$ isomers must be resolved with a valley of < 25 percent method.

5.2.2 In the CC3 solution, the chromatographic peak separation between 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD shall be resolved with a valley of ≤ 50 percent.

5.2.3 For all calibration solutions the retention times of the isomers must fall within the retention time windows established by the window defining mix. In addition the absolute retention time of recovery standards, $^{13}\text{C}_{12}1234\text{-TCDD}$ and $^{13}\text{C}_{12}\text{-123789HxCDD}$ shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard.

5.2.4 The three SIM ions for each homolog must maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions.

5.2.5 The relative ion abundance criteria for PCDDs/PCDFs listed in table 6 (see analytical method) must be met.

5.2.6 The relative ion abundance criteria for the labeled internal and recovery standards listed in table 6 must be met.

5.2.7 For all calibration solutions, including CC3, the signal to noise ratio (S/N) for all ions of the unlabeled PCDDs/PCDFs must

be greater than 2.5.

5.2.8 For the internal and recovery standards, the signal to noise ratio for all ions must be greater than 10.

5.2.9 The percent relative standard deviation (% RSD) of the five RRFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards must not be greater than 15 percent.

- ACTION:
1. If the 25% percent valley for TCDD and 50% valley for HxCDD requirement is not met, quality positive data J. Do not qualify non-detects. The tetra, pentas and hexas (dioxins and furans) are affected. Heptas and Octas are not affected.
 2. If the %RSD for each isomer exceeds 20% percent, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.
 3. If the ion abundance ratio for an analyte is outside the limits flag the results for that analyte R (reject).
 4. If the ion abundance ratio for an internal or recovery standard falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.
 5. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.
 6. If the selected monitoring ions specified in Table 5 were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.

5.2.10 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and internal standards were used. In addition verify that the appropriate internal standard was used for each isomer.

To recalculate the response factor use the equation:

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

YES NO N/A

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

Where:

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

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

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

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

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

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

6.0 Continuing Calibration - The continuing calibration consists of two parts: evaluation of the chromatographic resolution and verification of the RRF values to be used for quantitation.

6.1 Chromatographic Resolution - At the beginning of each 12 hour period the chromatographic resolution is verified in a similar fashion as in the initial calibration: through the analysis of CC3 Standard Solution on the DB-5 (or equivalent) column or through the analysis of the column performance solution on the SP2331 (or equivalent) column.

6.1.2 Was the continuing calibration and the column performance solution (when applicable) run at the required frequency?

6.1.3 Was the chromatographic peak separation on DB-5 (or equivalent) column between $^{13}C_{12}$ -2378TCDD and $^{13}C_{12}$ 1234-TCDD isomers resolved with a valley of <25 percent?

6.1.4 Was the chromatographic peak separation on the SP-2331

(or equivalent) column between the unlabeled 2378-TCDD and the adjacent TCDD isomers resolved with a valley of <25 percent?

YES NO N/A

In addition, was the chromatographic peak separation between the 123478-HxCDD and the 123678-HxCDD in the CC3 solution resolved with a valley of <50 percent?

- ACTION**
1. If the continuing calibration standard was not analyzed at the required frequency, reject all the data. Contact TPO to initiate reanalysis.
 2. If the 25 percent valley and 50 percent valley criteria are not met qualify all positive data with J. Do not qualify non-detects.

Note: The tetras, pentas and hexas (dioxins and furans) are affected. Heptas and octas are not affected. If the percent valley is >75 percent and 2378-TCDD is non-detect but 1234-TCDD or an adjacent TCDD isomer is present, the data is questionable. The sample must be reanalyzed. Contact TPO. If the valley criteria for HxCDD are not met but the valley criteria for TCDD are met or vice-versa, use professional judgement to determine which data must be qualified.

6.2 Continuing Calibration (CC3): The CC3 shall be analyzed at the beginning of a 12 hour period.

6.2.1 The following MS/DS conditions were used:

6.2.2 Scanning time was < 1 second.

6.2.2.1 SIM data were acquired for each of the ions listed in Table 5 including diphenylether interfering ions (see analytical method).

6.2.3 The following GC criteria must be met:

6.2.3.1 For all calibration solutions the retention time of the isomers must fall within the retention time windows established by the window defining mix.

6.2.3.2 The absolute retention time of the recovery standards ¹³C₁₂1234-TCDD and ¹³C₁₂123679-HxCDD shall not change by more than 10 seconds between the initial CC3 and ending CC1 standard analyses.

YES NO N/A

6.2.3.3 The three SIM ions for each homolog must maximize simultaneously (± 2 sec) and within 3 seconds of the corresponding ions of the labeled isomers.

6.2.3.4 For the CC3 standard solution, the signal to noise ratio (S/N) for the unlabeled PCDD/PCDF ion shall be greater than 2.5.

6.2.3.5 For the internal standards and the recovery standards, the signal to noise ratio (S/N) shall be greater than 10.

6.2.3.6 The relative ion abundance criteria (Table 6 – analytical method) for all PCDD/PCDF shall be met.

6.2.3.7 The relative ion abundance criteria for all internal and recovery standards (Table 6 - analytical method) must be met.

6.2.3.8 The measured RRF of each analyte and internal standard in the CC3 solution must be within ± 30 percent of the mean RRF established during the initial calibration and within ± 30 percent of the single point RRFs obtained during initial calibration for the supplemental calibration standards.

Spot check response factor calculations and ion ratios. Verify that the appropriate quantitation ions for the unlabeled PCDD/PCDFs and internal standards were used.

6.2.3.9 Was the same internal standard used to calculate RRF for each PCDD/PCDF homolog in the initial calibration?

ACTION: 1. If any of the requirements listed in sections 6.2.2, 6.2.2.1, 6.2.3.1, 6.2.3.2, and 6.2.3.9 are not met, use professional judgement to determine the validity of the data.

2. If any requirements listed in sections 6.2.3.3, 6.2.3.4, 6.2.3.5, 6.2.3.6, and 6.2.3.7 are not met reject all data (flag R) directly affected by each specific problem.

3. When the %D of the RRF is in between 30% and 50% all the data for the outlier congeners are flagged J. Data with %D above 50% are rejected (R).

YES NO N/A

6.2.3.10 To recalculate RRFs for the unlabeled target analytes, and the RRFs for the five labeled internal standards, use the following equations:

$$RRFn = \frac{(An^1 + An^2) \times Qis}{(Ais^1 + Ais^2) \times Qn}$$

$$RRFis = \frac{(Ais^1 + Ais^2) \times Qrs}{(Ars^1 + Ars^2) \times Qis}$$

An¹, An², Ais¹, Ais², Ars¹, Ars², Qn, Qis and Qrs are defined in Section 5.2.10.

To calculate percent difference, use the following equation:

$$\% \text{ Difference} = \frac{(RRFi - RRFc) \times 100}{RRFi}$$

Where

RRFi = Relative response factor established during initial calibration

RRFc = Relative response factor established during continuing calibration

6.3 Instrument Sensitivity - In order to demonstrate that the GC/MS system has retained adequate sensitivity, during the course of sample analysis, the lowest of the initial calibration standards (CC1) is analyzed at the end of each 12-hour period.

6.3.1 Did all analytes in the CC1 solution meet ion abundance criteria?

6.3.2 Did the retention time of the two recovery standards ¹³C₁₂1234-TCDD and ¹³C₁₂123678HxCDD change by more than +/- 10 seconds?

6.3.3 For CC1 was the S/N ratio for all unlabeled PCDD/PCDF ions greater than 2.5 and greater than 10 for the labeled internal and recovery standards?

ACTION: If the CC1 standard did not meet criteria examine the samples which were analyzed prior to this standard and use professional judgement to determine if data qualification is necessary. (See Recovery Standard areas - Section 9.0)

YES NO N/A

7.0 Sample Data

7.1 The following MS/DS conditions were used:

7.1.1 Scanning time was < 1 second.

7.1.2 SIM data were acquired for each of the ions listed in Table 5 (see analytical method) including diphenylether interfering ions.

7.2 Identification Criteria

7.2.1 For the 2378 substituted isomers found present and for which an isotopically labeled internal standard is present in the sample extract, the absolute retention time at the maximum peak height of the analyte must be within 3 seconds of the retention time of the corresponding labeled standard.

7.2.2 For the 2378 substituted isomer reported present, and for which a labeled standard does not exist, the relative retention time (RRT) of the analyte must be within ± 0.05 RRT units of the RRT established by the continuing calibration standard (CC3).

7.2.3 For non-2378 substituted compounds (tetra through hepta) found present, the retention time must be within the window established by the window defining mix for the corresponding homologue.

7.2.4 All specified ions listed in Table 5 (analytical method) for each PCDD/PCDF isomer found present and the labeled standards must be present in the SICP. The three SIM ions for the analyte, the internal standards and recovery standards must maximize simultaneously (± 2 seconds).

7.2.5 The integrated ion current for each characteristic ion of the analyte identified as positive must be at least 2.5 times background noise and must have not saturated the detector.

If the M-[COC1]+ ion does not meet the 2.5 times S/N requirement but meets all other criteria, the reviewer must use professional judgement to determine whether the compound is present.

7.2.6 The integrated ion current for the internal standard characteristic ions must be at least 10 times background noise.

7.2.7 The relative ion abundance criteria (Table 6 - analytical method) for all PCDDs/PCDFs found present must be met.

YES NO N/A

7.2.8 The relative ion abundance criteria for the internal standards must be met (Table 6 - analytical method).

- ACTION:
1. Reject (flag R) all positive data for the analytes which do not meet criteria listed in Sections 7.2.1, 7.2.2, 7.2.3, and 7.2.4.
 2. If the criteria listed in section 7.2.5 are not met but all other criteria are met, qualify all positive data of the specific analyte with J.
 3. If the requirements listed in section 7.2.6 are not met but all other requirements are met qualify the positive data of the corresponding analytes with "J".
 4. If the analytes reported positive do not meet ion abundance criteria, section 7.2.7, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).
 5. If the internal standards and recovery standards do not meet ion abundance criteria (Table 6 – analytical method) but they meet all other criteria flag all corresponding data with "J".
 6. If PCDF is detected but an interfering PCDFE is also detected reject the PCDF data (R). The reported value of PCDF is changed to EMPC.
 7. If the lab did not monitor for PCDFE's qualify all positive furan data N.

7.2.9 Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration and EMPC. Ensure that the proper PCDDs/PCDFs and internal standards were used.

To recalculate the concentration of individual PCDD/PCDF isomers in the sample use the following equation:

ALL MATRICES OTHER THAN WATER

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

YES NO N/A

WATER

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

Where:

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

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

W= Weight (g) of sample extracted

V= Volume (ml) of sample extracted

Q_{is}= Quantity (ng) of the appropriate internal standard
added to the sample prior to extraction

RRF_n= Calculated relative response factor from continuing
calibration (see Section 7.3).

Note: See SOW, Section 15.3 for calculations when any internal
standard in a diluted sample is less than 10% of the internal
standard area in the continuing calibration standard.

7.3 Estimated Detection Limits (EDL)

7.3.1 Was an EDL calculated for each 2,3,7,8-substituted isomer that
was not identified regardless of whether other non-2378
substituted isomers were present?

7.3.2 Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

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

WATER

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

YES NO N/A

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor (see Paragraph 10.4.3).

Qis, RRFn, W and V are defined in Section 5.2.10

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the laboratory for recalculation. The TPO must be notified.

7.4 Estimated Maximum Possible Concentration (EMPC)

7.4.1 Was an EMPC calculated for 2378-substituted isomers that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria?

7.4.2 Use the equation below to check EMPC calculations:

ALL MATRICES OTHER THAN WATER

$$\text{EMPC (ug/L)} = \frac{(Ax^1 + Ax^2) \times Qis \times D}{(Ais^1 + Ais^2) \times RRFn \times W}$$

WATER

$$\text{EMPC (ng/L)} = \frac{(Ax^1 + Ax^2) \times Qis \times D}{(Ais^1 + Ais^2) \times RRFn \times V}$$

Where:

Ax^1 and Ax^2 = areas of both quantitation ions.

Ais^1 , Ais^2 , Qis, RRF, D, W, and V are defined in Paragraph 7.3.3 and 10.4.3 and Section 15.1.

Action: 1. If EDL or EMPC of an analyte which was not reported as present is missing, contact the laboratory for correction.

YES NO N/A

2. If the spot check calculations yielded EDLs or EMPCs different from those reported in Form I, contact the laboratory for an explanation.

3. If EDLs or EMPCs for the most toxic analytes (TEF_≥ 0.05) are above CRQLs contact TPO for sample reanalysis.

7.5 Method Blanks

- | | |
|---|--|
| 7.5.1 Has a method blank per matrix been extracted and analyzed with each batch of 20 samples? | [<input type="checkbox"/>] <u> </u> <u> </u> |
| 7.5.2 If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event? | [<input type="checkbox"/>] <u> </u> <u> </u> |
| 7.5.3 Acceptable method blanks must not contain any signal of 2378-TCDD, or 2378-TCDF, equivalent to a concentration of > 0.1 ppb for soils or 1 ppt for water samples. | [<input type="checkbox"/>] <u> </u> <u> </u> |
| 7.5.4 For other 2378- substituted PCDD/PCDF isomers of each homologue, the allowable concentration in the method blank is less than 1/10 of the CRQL listed in the SOW or the area must be less than 2% of the area of the nearest internal standard. | [<input type="checkbox"/>] <u> </u> <u> </u> |
| 7.5.5 For the peak which does not meet identification criteria as PCDD/PCDF in the method blank, the area must be less than 5% of the area of the nearest Internal Standard. | [<input type="checkbox"/>] <u> </u> <u> </u> |

ACTION: 1. If the proper number of method blanks were not analyzed, notify the contractor. If they are unavailable, reject all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the CRQL listed in the SOW, reject all contaminant compound positive data for the associated samples (flag R) and contact the technical project officer to initiate reanalysis if it is deemed necessary.

YES NO N/A

3. If the method blank is contaminated with any of the above isomers at a concentration of less than the CRQL or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

7.6 Rinsate Blank

- 7.6.1 One rinsate blank must be collected for each batch of 24 soil samples or one per day whichever is more frequent.

- 7.6.2 Do any rinsate blanks show the presence of 2378-TCDD, 2378-TCDF, and 12378PeCDD at amounts > .5 ug/L or any other analyte at levels > 1µg/L?

ACTION: If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the technical project officer to discuss what proper action must be taken.

7.7 Field Blanks

- 7.7.1 The field blanks are PEM samples (blind blanks) supplied by EPA from EMSL-LV at the frequency of one field blank per 24 samples or less collected over a period of one week whichever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

- 7.7.2 Acceptable field blanks must not contain any signal of 2378-TCDD and 2378-TCDF equivalent to a concentration of > 0.1 ppb.

- 7.7.3 For other 2378-substituted PCDD/PCDF isomers of each homologue the allowable concentration in the field blank is less than 1/10 the CRQL listed in the SOW.

ACTION: When the field blank is found to be contaminated with target compounds apply the same action as described for the method blank (section 7.5).

NOTE: Contact EPA EMSL/LV to verify that the PEM blank (field blank)

YES NO N/A

did not contain any PCDD/PCDF isomers and ask their assistance in the evaluation of the PE field blank.

8.0 Internal Standard Recoveries (Form I)

8.1 Were the samples spiked with all the internal standards as specified in the method?

8.2 Were internal standard recoveries within the required limits?

8.3 If not, were samples reanalyzed?

ACTION: 1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.

2. If the internal standard recovery is above the upper limit (150 percent) flag all associated data (positive and non-detect data) with "J".

3. If the internal standard recovery is less than 10% qualify all associated data R (Reject). When highly toxic isomers ($TEF \geq 0.05$) are affected, notify TPO to initiate reanalysis.

Calculate the percent recovery of internal standard (Ris) in the sample extract using the following equation.

Recalculate the percent recovery for each internal standard in the sample extract, Ris, using the formula:

$$Ris = \frac{(Ais^1 + Ais^2 \times Qrs \times 100\%)}{(Ars^1 + Ars^2 \times RRFis \times Qis)}$$

Ais¹, Ais², Ars¹, Ars², Qis, Qrs and RRFis are defined, previously.

9.0 Recovery Standards

There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

9.1 Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?

Area upper limit= +100% of recovery standard area.

Area lower limit= -50% of recovery standard area.

9.2 Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

- ACTION:
1. If the recovery standard area is outside the upper or lower limits flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.
 2. If extremely low area counts (<25%) are reported flag all associated non-detect data as unusable (R) and the positive data J.
 3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the window defining mix.

10.0 Matrix Spikes (PEM Blanks)

- 10.1 One known blank usually an interference fortified soil/sediment sample, supplied by EPA, EMSL-LV, is designated by the sampling team for the laboratory for spiking. The frequency of this QC sample is one per group of 24 environmental samples or less collected over a period of one week whichever is first. The sample is spiked by the laboratory with the appropriate volume of the matrix spiking solution specified in the analytical protocol (SOW) and then extracted and analyzed with the other samples.
- 10.2 Was a fortified PEM blank analyzed at the frequency described above?
- 10.3 Was the percent recovery of 2378-TCDD and other 2378-substituted compounds within the 50 to 150 percent control limit?

- ACTION:
1. If the recovery of a 2,3,7,8-substituted isomer falls outside the 50-150 percent control limit, flag all positive and non-detect data of

the same and related isomers in the same homolog series with J. However, if the recovery is below 20 percent qualify all associated non-detects R. Notify the Technical Project Officer. Reanalysis may be initiated.

2. If no fortified PEM blank was analyzed use professional judgement to assess data validity.

11.0 Matrix Spike (Field Sample)

- 11.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?
- 11.2 Was the percent recovery of 2378-TCDD and other 2378-substituted PCDDs/PCDFs within the same 50 to 150 percent?

ACTION: If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 50-150% limits of the matrix spike data may be used to flag data of the spiked sample only. The matrix spike data of the PE blank sample are more important and must be used primarily in data validation.

12.0 Environmental Duplicate Samples

- 12.1 For every batch of 24 samples or less collected over a period of one week whichever comes first there must be a sample designated as duplicate. Results of the duplicate samples must agree within 50% relative difference.

ACTION: The duplicate results must be used in conjunction of other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.

13.0 Performance Evaluation Samples

- 13.1 Included among the samples are sets of performance evaluation samples containing known amounts of unlabeled 2378-TCDD or a mixture of 2378-TCDD and other PCDD/PCDF isomers. The PE samples are provided by the Region, and must be analyzed at the frequency of one set per batch of 24 samples or less collected over a period of one week whichever

occurs first.

13.2 The analytical results must be within the EPA 99% acceptance criteria.

ACTION: 1. The PE samples must be validated as if they were environmental samples.
There is no holding time for PE samples.

2. PE samples containing only 2378-TCDD

When 2378-TCDD was not qualitatively identified, or if the reported concentration is outside the 99% acceptance window all positive and negative (EMPC/EDL) data for all associated samples are rejected.

3. PE samples containing a mixture of PCDD/PCDF isomers

When the reported concentration of any analyte is outside the EPA 99% confidence interval, all positive and negative (EMPC/EDL) data of the 2378 substituted isomers within the same homologue for all associated samples are rejected.

4. When PCDD/PCDF data are rejected because of PE results, the EPA technical project officer must be notified. Reanalysis may be initiated.

5. For PE blind blanks see 7.7 (Field Blanks)

14.0 Second Column Confirmation

14.1 Was a second column confirmation performed?

14.2 Was the sample extract reanalyzed on a 60m SP-2330 or SP-2331 GC column for better GC resolution and better identification of the individual 2378-substituted isomers?

14.3 Did the second column meet the calibration and linearity specification in the SOW (See sections 5.0 and 6.0).

14.4 Was the % D of the quantitation results of the two columns less than 50?

ACTION: Use professional judgement to decide which quantitation data to use. The two quantitation

data should not be combined.

NOTE: If the sample extract was analyzed on a single GC column capable of resolving all 2378-substituted isomers, confirmation is not necessary.

15.0 Sample Reanalysis

15.1 The Region II TPO will evaluate the need for reanalyzing the samples with qualified data based on site-specific Regional Data Quality Objectives. The rerun may be billable or non billable as specified in the SOW. SMO should be notified of all reruns.

15.2 Due to a variety of situations that may occur during sample analysis the laboratory is required to reanalyze or reextract and reanalyze certain samples. If a reanalysis was required but as not performed, contact TPO to initiate reanalysis. List below all reextractions and reanalyses and identify the PCDD/PCDF sample data summaries (Form I) which must be used by the data user (when more than one is submitted).

16.0 Isomer Specificity and Toxicity Equivalency Factor (TEF) -

When calculating the 2378-TCDD Toxicity Equivalency of a sample only those 2378 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve isomer specificity.

16.1 The lab did not include EMPC or EDL values in the toxicity equivalency calculations.

16.2 All samples whose toxicity equivalency exceeded the required values were reanalyzed on a confirmation column to establish isomer specificity.

ACTION: 1. If the toxicity equivalency calculations were not performed properly notify TPO.

2. If the toxicity equivalency exceeded the required limits (0.7 ppb for soil/sediment, 7ppt for aqueous and 7ppb for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify TPO.

PCDFs/PCDDs Data Assessment

CASE NO. _____ LABORATORY _____
Site _____

SAMPLE
NO. _____

DATA ASSESSMENT:

All data are valid and acceptable except those values which have been qualified R (rejected) or qualified "J" (estimated). Rejected data does not imply the analyte is not present. It means that due to significant QC problems the analysis is invalid and it provides no information as to whether the compound is present or not.

All action is detailed below and on the attached sheets.

Reviewer's Signature: _____
Date: ____ / ____ /20 ____

Verified By: _____
Date: ____ / ____ /20 ____

Case# _____

Site: _____

Lab: _____

Overall Assessment

Case# _____

Site: _____

Lab: _____

Contract Problems/Non-Compliance