Validation of Dioxin Furan Analytical Data

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Hazard Class: ☒ Low ☐ Moderate ☐ High/Complex

Usage Mode: ☒ Reference ☐ UET ☐ Both UET & Reference

The Responsible Manager has determined that the following organizations' review is required for initial procedure release as well as subsequent major revisions. Review documentation is contained in the Document History File.

Technical Leads Quality Assurance

Classification Review: ☒ Unclassified ☐ UCNI ☐ Classified

Diana Hollis	/ 111125	/ /s/ Diana Hollis	/ 4/18/2017
Name (print)	Z#	Signature	Date

Responsible Manager, Division and Title

Nita Patel	/ 153003	/ /s/ Nita Patel	/ 4/20/2017
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REVISION HISTORY

Document No./Revision No.	Issue Date	Action	Description
OIO-TP-5169, Rev. 0.1	4/20/2016	Minor Revision	Periodic Review, changed Document type and Organization. Replacing SOP-5169.
ER-AP-20317, R0	4/24/2017	Major Revision	Revised to reflect the guidance from the National Functional Guidelines for High Resolution Superfund Methods Data Review, April 2016 (EPA-542-B-16-001) holding time requirements and remove NNSA Model Validation

TABLE OF CONTENTS

Section — Page

TITLE PAGE 1
REVISION HISTORY 2
TABLE OF CONTENTS 3

1. PURPOSE 4

2. SCOPE 4

3. BACKGROUND 4

4. PRECAUTIONS AND LIMITATIONS 4

5. PREREQUISITE ACTIONS 4

6. PERFORMANCE 5
6.1 Validation Process 5
6.2 Analyte Quantitation 6
6.3 Analyte Identification 7
6.4 Holding Times and Sample Preservation 8
6.5 Initial and Continuing Calibration 8
6.6 Internal Standards 8
6.7 Blanks 9
6.8 Matrix Spike and Laboratory Control Samples 9

7. RECORDS 10

8. REFERENCES 10

9. ATTACHMENTS 10

Attachments

Attachment 1, Data Validation Cover Sheet 11
Attachment 2, Dioxin/Furan Analytical Data Validation Checklist 12
Attachment 3, Theoretical Ion Abundance Ratios and Acceptance Limits for PCDDs and PCDFs for Method 8290 17

1. PURPOSE

This procedure establishes guidance for the qualification of dioxin furan analytical data.

2. SCOPE

This document is intended to assist in the technical review of analytical data generated by environmental laboratories. Qualification of data is the product of data validation, analytical laboratory analysis, and focused validation that describe validation anomalies and their consequences.

3. BACKGROUND

Data qualifiers and reason codes are assigned to analytical results from dioxins and furans analyses according to the specifications in this method-specific procedure. These guidelines are developed using the EPA method-specific data quality criteria and/or National Functional Guidelines for High Resolution Superfund Methods Data Review.

4. PRECAUTIONS AND LIMITATIONS

Nothing in this procedure precludes the data validator from going beyond the minimum requirements specified within this procedure. If additional directions are required, the data validator shall reference EPA method-specific guidelines and/or EPA National Functional Guidelines for High Resolution Superfund Methods Data Review. Implementation of this procedure may be followed by a more focused and data use-specific evaluation of the data by the project chemist, especially if the implementation of this procedure indicates the data may contain technical deficiencies.

5. PREREQUISITE ACTIONS

Data Validators must:

- Possess a minimum of a bachelor's degree in chemistry or one of the physical sciences and either two (2) years of experience in generating analytical data in an environmental analytical laboratory OR two (2) years of data validation experience.
- Complete Attachment 1, Data Validation Cover Sheet, and Attachment 2, Dioxin/Furan Analytical Data Validation Checklist, during data validation.

6. PERFORMANCE

6.1 Validation Process

EIM applies a subset of qualifiers described in this procedure to analytical data using auto-validation subroutines. EIM auto-validation applies qualification to analytical records using tests listed in Attachment 2 that have a Valid Reason Description containing "(AV)". When the project leader requests a focused validation the assigned data validator completes the following steps to assess all potential analytical data qualification:

[1] **REVIEW** the qualifiers assigned during EIM auto-validation to verify that qualifiers were assigned consistently with this procedure. If auto-validation qualification is found to be inconsistent with this procedure then the validator initiates a change request using ER-AP-20304, Change Control for Data in the Environmental Information Management (EIM) Database.

[2] **PRINT** Attachment 1 and **REVIEW** the data package for potential qualification using Attachment 2.

[3] **NOTE** conditions causing recommendation for qualification and options for qualification.

[4] **FILL** out Attachment 1 and **FORWARD** to the project leader with conditions and options.

The project leader is the responsible party for making the decision of record if validation qualifiers should be assigned and EIM validation records updated. This record of decision is added to comments section of Attachment 1.

Once the decision of record has been made, Attachment 1 is sent to the Sample Management Office (SMO) staff. The SMO staff re-print the data validation record from EIM and add Attachment 1 that includes the record of decision to the final records package.

6.2 Analyte Quantitation

The assignment of the detection status to analytical measurements is the first step of analytical data validation. Most validation qualifiers and validation reason codes are applied based on the measurement's initial detection status. Results that are less than the report method detection limit (RMDL) are qualified as nondetect with the U validation qualifier and U_LAB validation reason code. Results greater than or equal to the RMDL and less than the report detection limit (RDL) are qualified as detected and estimated with the J validation qualifier and J_LAB validation reason code. Results greater than or equal to the RDL are qualified as detected with the NQ validation qualifier.

Criteria	Validation Qualifier	Validation Reason Code
Target analyte result is < RMDL; a nondetect	U	U_LAB
Target analyte result is ≥ RMDL and < RDL; a detect	J	J_LAB
Target analyte result is ≥ RDL; a detect	NQ	NQ

Since a result can have only one validation qualifier and one validation reason code the sequencing of validation steps is important. Analyte quantitation occurs first, then analyte identification, because most other validation functions depend on the correct identification and quantitation of the analytical parameter. When two or more qualifiers can be applied to a record, the qualifier representing the more severe consequence to data usability supersedes the qualifier with less severe consequence. The R validation qualifier has the greatest impact on data usability and supersedes other validation qualifiers.

6.2 Analyte Quantitation (continued)

Order Of Severity	Validation Qualifier	Description
1	R	The reported sample result is classified as rejected due to serious non-compliances regarding quality control acceptance criteria. The presence or absence of the analyte cannot be verified.
2	UJ	The analyte is classified as not detected, with an expectation that the reported result is more uncertain than usual.
3	U	The analyte is classified as not detected.
4	J	The analyte is classified as detected but the reported concentration value is expected to be more uncertain than usual.
5	NQ	No validation qualifier flag is associated with this result, and the analyte is classified as detected.

LANL project chemists may identify quality deficiencies in analytical results affecting analyte quanitation. These deficiencies can include analytical results with detection limits elevated above project data-quality objectives, concentrations above the calibration range of the instrument or method, results exhibiting carryover or detector contamination, large relative percent difference between dual-column detects, chromatographic interference from another analyte, and other quality deficiencies. The reason code of DF19 is applied to affected records by the project chemist to identify these quality deficiencies when they are identified.

6.3 Analyte Identification

The identification of an analytical parameter is the second step of analytical data validation. Identification of dioxin and furan compounds depends upon the relative retention time of the compound of interest to the known retention time of the compound in the calibration standard, and the relative intensity of the mass spectrum of the compound of interest in a sample to the known intensity of the compound in a calibration standard. When mass spectral analyte identification criteria are not met the DF8 series of reason codes are applied to affected parameters. When relative retention time criteria are not met the DF0 series of reason codes are applied to affected parameters.

6.4 Holding Times and Sample Preservation

Sample handling requirements are specified to ensure integrity and defensibility of analytical measurements. Samples are to be prepared and analyzed within specified time limits. Samples are also preserved chemically and physically by controlling temperature and light. When sample handling requirements are not met the DF9 series of reason codes are applied to affected samples.

6.5 Initial and Continuing Calibration

Calibration is performed to set the operating range of the instrument and to ensure that the instrument is performing within specifications. The initial calibration and verification is performed prior to the start of analyses. Continuing calibration checks and instrument performance samples are performed periodically during analysis to ensure the instrument is providing accurate results. When initial calibration criteria are not met the DF7 series of reason codes are applied to affected analytes in all samples analyzed after the unacceptable initial calibration to the next acceptable initial calibration for that instrument. When continuing calibration criteria or are not met the DF7 series of reason codes are applied to affected analytes in all samples analyzed after the unacceptable continuing calibration to the next acceptable continuing calibration for that instrument. When instrument performance checks do not meet criteria the DF16 series of qualifiers are applied to affected analytes in all samples analyzed after the unacceptable instrument performance check to the next acceptable instrument performance check for that instrument.

6.6 Internal Standards

Internal standards are compounds not normally found in the environment, but which are easily measurable. They are added to samples, standards, and QC samples to compensate for fluctuations in the analytical system. Sample results are quantitated or adjusted by the relative response of associated internal standards. When internal standard criteria are not met the DF1 series of reason codes are applied to the affected sample.

6.7 Blanks

The Method Blank is an analyte-free matrix that is prepared and analyzed in the laboratory with the samples. The method blank determines contamination from the analytical processes. Method blanks are prepared with every preparation batch. If more than one method blank is associated with a given sample, qualification is based upon a comparison with the associated blank having the highest concentration of the parameter. When method blank criteria are not met the DF4 series of reason codes are applied affected samples.

The Field Blank is an analyte-free matrix opened to the atmosphere at the time of sample collection. Field blanks are used to determine if atmospheric conditions resulted in contamination of samples during sample collection. Samples collected the same day as a field blank with detected concentrations of an analyte of interest are qualified with the DF4 series of reason codes.

The Equipment Blank is an analyte-free matrix poured over or through sample collection equipment. Equipment blanks are used to determine if the cleaning effectiveness of sampling equipment between samples. Samples collected using the same tools as the equipment blank with detected concentrations of an analyte of interest are qualified with the DF4 series of reason codes.

6.8 Matrix Spike and Laboratory Control Samples

The laboratory control sample is created by adding known amounts of parameters of interest to an aliquot of a blank matrix. The laboratory control sample is used to evaluate the effect of the analytical process of the recovery of analytes. When laboratory control sample criteria are not met the DF12 series of reason codes are applied to all associated samples.

7. RECORDS

Records generated by this procedure will be submitted to the Environmental Protection Records Management Office for document management in accordance with Institutional Records Management Procedure, P1020-1 and EP-AP-10003, Records Management.

- Completed Data Validation Cover Sheets
- Completed Dioxin/Furan Analytical Data Validation Checklists.

8. REFERENCES

EP-AP-10003, Records Management

ER-AP-20304, Change Control for Data in the Environmental Information Management (EIM) Database

P1020-1, Laboratory Records Management

9. ATTACHMENTS

Attachment 1: Data Validation Cover Sheet
Attachment 2: Dioxin/Furan Analytical Data Validation Checklist
Attachment 3: Theoretical Ion Abundance Ratios and Acceptance Limits for PCDDs and PCDFs for Method 8290

ATTACHMENT 1

Page 1 of 1

Data Validation Cover Sheet

Section I.

Request Number: _____ Validation Date: _____ Lab Code: _____

Contract Laboratory Name: _____

Validator: _____ Organization: _____

Analytical Suite (Check All That Apply):

☐ **TPH-GRO**	☐ **High Explosives**	☐ **Dioxin Furans**	☐ **LCMSMS Perchlorates**
☐ **TPH-DRO**	☐ **Metals & Cyanide**	☐ **PCB Congeners**	☐ **Organochlorine Pesticides/Polychlorinated Biphenyls**
☐ **General Chemistry**	☐ **Radiochemistry**	☐ **LCMSMS High Explosives**	

☐ **Other (Describe):** _____

_____

Section II. Completeness Check

YES	NO	N/A	(check one)	YES	NO	N/A	(check one)
☐	☐	☐	1. Chain-Of-Custody Form(S)	☐	☐	☐	6. Raw/BSS Data
☐	☐	☐	2. Case Narrative	☐	☐	☐	7. Quality Control Forms
☐	☐	☐	3. Sample Result Forms	☐	☐	☐	8. Quantitation Reports
☐	☐	☐	4. Sample Chromatograms	☐	☐	☐	9. TICS Forms
☐	☐	☐	5. Standard Chromatograms	☐	☐	☐	10. TICS Mass Spectra

Comments/problems noted (include information about requests for further information submitted to the contract laboratory and agreed-upon date of resolution and contract laboratory point of contact):

Validator's Signature: _____ Date: _____

ER-AP-20317, R0	Los Alamos Environmental Safety & Health
	(Attach additional comment sheets as necessary)

ATTACHMENT 2

Page 1 of 5

Yes	No	N/A	Dioxin/Furan Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Holding Times and Sample Preservation					
☐	☐	☐	1. The preserved sample was extracted > 365-day holding time. (AV)	UJ, DF9b	J, DF9b
☐	☐	☐	2. The sample extract was analyzed > 365-day holding time. (AV)	UJ, DF9b	J, DF9b
Blanks					
☐	☐	☐	3. The sample result is ≤5 times the concentration of the related analyte in the method blank. (AV)	N/A	U, DF4
☐	☐	☐	4. The affected analytes are considered estimated and biased high because this analyte was identified in the method blank but was >5 times the concentration in the method blank. (AV)	N/A	J+, DF4a
☐	☐	☐	5. The sample result is ≤5 times the concentration of the related analyte in the trip blank, rinsate blank, or equipment blank. (AV)	N/A	U, DF4d
☐	☐	☐	6. Required method blank information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, DF4e	R, DF4e
Analyte Identification					
☐	☐	☐	7. The affected analyte is considered rejected because the ion abundances did not meet specifications.	N/A	R, DF8
☐	☐	☐	8. The ion abundance documentation is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, DF8a	R, DF8a
☐	☐	☐	9. If gas chromatograph (GC) column performance was not evaluated at the required frequency or if method criteria were not met, qualify all associated detects as J and all associated non-detects as UJ.	UJ, DF8b	J, DF8b
☐	☐	☐	10. If 2,3,7,8-tetrachlorodibenzofuran (TCDF) was detected in a sample and the result was not confirmed on a second column with successful analysis of the GC column performance mix, qualify all associated detects as U.	N/A	U, DF8c

ATTACHMENT 2

Page 2 of 5

Yes	No	N/A	Dioxin/Furan Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Initial and Continuing Calibration					
☐	☐	☐	11. The affected results were not analyzed with a valid 5-point calibration curve and/or a standard at the reporting limit.	UJ, R, DF7	J, DF7
☐	☐	☐	12. The affected analytes were analyzed with an initial calibration curve that exceeded the percent relative standard deviation (%RSD) criteria.	UJ, R, DF7a	J, DF7a
☐	☐	☐	13. The affected analytes were analyzed with an out-of-range ion abundance given in Attachment 3 in the initial calibration and/or continuing calibration verification (CCV).	R, DF7b	R, DF7b
☐	☐	☐	14. The initial calibration verification (ICV) and/or CCV ion abundance ratio for any compound is outside of the method limits.	UJ, DF7c	J, CF7c
☐	☐	☐	15. The initial calibration verification (ICV) and/or CCV %D criteria were not met for any CCV compound at the beginning of a 12-hour period and the %D is positive.	N/A	J+, CF7c
☐	☐	☐	16. The %D criteria were not met for any CCV compound at the beginning of a 12-hour period and the %D is negative, qualify all associated detects as J-, and if any other calibration criteria have been exceeded for that compound, qualify all associated non-detects as UJ.	UJ, CF7c	J-, CF7c
☐	☐	☐	17. The %D criteria were not met for any compound at the end of a 12-hour period, a new initial calibration was analyzed within 2 hours of sample analysis, and the %D is positive, qualify all associated detects as J+.	N/A	J+, CF7c
☐	☐	☐	18. The %D criteria were not met for any compound at the end of a 12-hour period, a new initial calibration was analyzed within 2 hours of sample analysis, and the %D is negative, and any other calibration criteria have been exceeded for that compound.	UJ, CF7c	J-, CF7c
☐	☐	☐	19. The %D criteria were not met for any compound at the end of a 12-hour period and a new initial calibration was not analyzed within 2 hours of sample analysis.	R, DF7c	R, DF7c
☐	☐	☐	20. The ICV and/or CCV were not analyzed at the appropriate method frequency.	UJ, DF7d	J, DF7d
☐	☐	☐	21. Required calibration information is missing, or samples were analyzed on an expired calibration. Contact the SMO or external laboratory for information.	R, DF7f	R, DF7f

ATTACHMENT 2

Page 3 of 5

Yes	No	N/A	Dioxin/Furan Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes: Non-detected Analyte	Assign Qualifier Listed Below If Criterion = Yes: Detected Analyte
Analyte Identification					
☐	☐	☐	22. The internal standard (IS) retention time and qualitative criteria for target compound identification were not met. For 2,3,7,8-substituted compounds that have an isotopically labeled IS or recovery standard present in the sample extract, the retention time (RT) must be −1 to +3 seconds of the isotopically labeled standard. For 2,3,7,8-substituted compounds that do not have an isotopically labeled IS or recovery standard present in the sample extract, the RT must fall within 0.005 required retention time (RRT) units of the RRT measured in the continuing calibration. For non-2,3,7,8-substituted compounds, the RT must be within the corresponding homologous RT windows established by analyzing the column performance check solution.	R, DF0	R, DF0
☐	☐	☐	23. Required retention time documentation is missing. Data may not be acceptable for use. Contact the Sample Management Office (SMO) or external laboratory for information.	R, DF0b	R, DF0b
Internal Standards					
☐	☐	☐	24. Required IS information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, DF1d	R, DF1d

ATTACHMENT 2

Page 4 of 5

Yes	No	N/A	Dioxin/Furan Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Laboratory Control Samples					
☐	☐	☐	25. The laboratory control sample (LCS) percent recovery was <10%. (AV)	R, DF12	J-, DF12
☐	☐	☐	26. The LCS percent recovery was less than the lower acceptance limit but >10%. Follow the external laboratory limits. (AV)	UJ, DF12a	J-, DF12a
☐	☐	☐	27. The LCS percent recovery was greater than the upper acceptance limit. Follow the external laboratory limits. (AV)	N/A	J+, DF12b
☐	☐	☐	28. The LCS documentation is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, DF12c	R, DF12c
☐	☐	☐	29. The matrix spike / matrix spike duplicate (MS/MSD) percent recovery was <10%. (AV)	R, DF12d	R, DF12d
☐	☐	☐	30. The MS/MSD percent recovery was >10% but <70%. (AV)	UJ, DF12e	J, DF12e
☐	☐	☐	31. The MS/MSD percent recovery was >130%. (AV)	N/A	J+, DF12f
☐	☐	☐	32. The MS/MSD relative percent difference was >30%. (AV)	UJ, DF12g	J, DF12g
☐	☐	☐	33. The fortification sample percent recovery was <10%.	R, DF12h	J-, DF12h
☐	☐	☐	34. The fortification sample percent recovery was <40% but >10%	UJ, DF12i	J-, DF12i
☐	☐	☐	35. The fortification sample percent recovery was >135%.	N/A	J+, DF12j
☐	☐	☐	36. The fortification sample documentation is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, DF12k	R, DF12k

ATTACHMENT 2

Page 5 of 5

Yes	No	N/A	Dioxin/Furan Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Instrument Performance Sample					
☐	☐	☐	37. The instrument performance sample did not pass method acceptance criteria.	R, DF16	R, DF16
☐	☐	☐	38. The required instrument performance sample information is missing. Contact the SMO or external laboratory for information.	R, DF16c	R, DF16c
Analyte Quantitation					
☐	☐	☐	39. The non-detected analytes have elevated detection limits and may not meet project data-quality objectives because the sample was diluted without any target analytes identified as a result of matrix interference. Reject non-detected results if the analytical laboratory cannot provide proof for matrix interference.	UJ, R, DF15	NA
☐	☐	☐	40. Sample cleanup was not performed. If run-log notations, spectral data, and/or IS or labeled compound recoveries indicate interferences and extract cleanup was not performed, qualify all associated detects as J and all non-detects as UJ.	UJ, DF15a	J, DF15a
☐	☐	☐	41. The Los Alamos National Laboratory (LANL) project chemist identified quality deficiencies in the reported data that require further qualification. This code can be used only by and/or under advisement of the LANL project chemist.	UJ, R, DF19	J, R, DF19
☐	☐	☐	42. Qualification of data via data validation did occur, however no data quality control requirements in this procedure were applicable. Adhere to the external laboratory qualifiers found within the Form 1 analytical data summary sheets generated by the external laboratory. (AV)	U, U_LAB	J, J_LAB NQ, NQ (No qualification)

ATTACHMENT 3

Page 1 of 1

Theoretical Ion Abundance Ratios and Acceptance Limits for PCDDs and PCDFs for Method 8290

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Acceptance Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

a Used only for ^{13}C-HxCDF (internal standard).
b Used only for ^{13}C-HpCDF (internal standard).