DATA VALIDATION PROCEDURES FOR DIOXIN/FURAN ANALYSIS BY HRGC/HRMS

CONTENTS

CONTENTS (cont)

SUPERCEDES: SOP #1019; Revision 0.0; 09/11/92; U.S. EPA Contract 68-03-3482.

DATA VALIDATION PROCEDURES FOR DIOXIN/FURAN ANALYSIS BY HRGC/HRMS

1.0 OBJECTIVE

The objective of this Standard Operating Procedure (SOP) is to outline a procedure to facilitate the validation process of dioxin and furan data reported by subcontracting laboratories and also to ensure that the data is being reviewed in a uniform manner.

2.0 APPLICABILITY

This SOP is applicable to polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/PCDF) data collected from various sample matrices using a high-resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) method. This SOP is applicable to all PCDD/PCDF data submitted by subcontracting laboratories for various SERAS samples. All compounds of interest are listed in Appendix A.

This SOP is based upon the quality assurance and quality control (QA/QC) requirements specified in the draft SW-846 method 8290 (November 1990). Since the specific guidelines on reviewing the HRGC/HRMS PCDD/PCDF data are not available, the SOP for high resolution gas chromatography and low resolution mass spectrometry (HRGC/LRMS) PCDD/PCDF data review published by U.S. EPA, which is based on the Contract Laboratory Program (CLP) Statement of Work (SOW) for HRGC/LRMS PCDD/PCDF analysis (DFLM 01.0) is used as reference. Appendix B explains the meaning of each qualifier.

3.0 DESCRIPTION

3.1 Preliminary Review

A preliminary review is performed to check data completeness and deliverables. Missing, illegible or incorrectly labeled items must be checked off. The subcontracting lab must be immediately contacted, requesting them to submit the missing, illegible or incorrect items.

1. Evaluate deliverable completeness by using the deliverable checklist (Appendix C).

2. Review the case narrative for problems with sample receipt, sample condition, analytical problems, or other comments affecting the data quality. Use professional judgment to evaluate the effect of the noted problems on the data quality.

3. Verify that all the compounds of interest listed in Appendix A had been analyzed and reported.

4. Standard and sample Selected Ion Monitoring (SIM) chromatograms must list date and time of analysis, the file name, sample number, and instrument I.D. number.

5. Percent peak resolution valley must be documented.

6. PCDD/PCDF window defining mix raw data must be present.

7. SIM mass chromatograms must display both quantitation ions and the polychlorinated

diphenylether (PCDPE) ion where applicable.

8. Integrated area and peak height must be listed for all peaks 2.5 times above background, i.e., signal to noise ratio (S/N) >2.5.

9. All peaks must show retention times at the maximum height.

10. SERAS Chain of Custody records must be signed and dated by the subcontracting laboratory.

11. A cross reference of SERAS and the subcontracting laboratory sample IDs must be documented.

ACTION: If deliverables are missing, call the lab for an explanation or for re-submittal of the missing information. If the lab cannot provide the missing deliverables, assess the effect of the missing information on the validity of the data. Note in the reviewer's narrative.

3.2 Holding Times

As per SW-846 method 8290, all samples must be extracted within 30 days and completely analyzed within 45 days of collection.

ACTION: If holding times are exceeded, flag all positive results as estimated (J) and flag all non-detects as unusable (R).

3.3 Instrument Performance

3.3.1 Mass Resolution Check

The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation. However, it is recommended that a visual check of the static resolution be made by using the peak matching unit before and after each analysis. Corrective action must be implemented whenever the resolving power does not meet the requirement. Only raw data printouts of the mass resolving power checks that were analyzed before and after the 12-hour period are required.

ACTION: If the mass resolving power does not meet the requirements, use professional judgment to assess the impact on the data quality.

3.3.2 GC Column Performance Check (Window Defining Mixture)

1. The window defining mixture must be analyzed prior to the initial calibration and at the beginning of each 12-hour period prior to continuing calibration.

2. The window defining mixture must contain the first and the last isomers of each

homologue PCDD/PCDF (Appendix D), as well as the internal and recovery standards.

3. All peaks must be labeled and identified on the Selected Ion Current Profiles (SICPs).

4. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of $\leq$ 25%.

ACTION:

1. If the window defining mixture was not analyzed in the required frequency, use professional judgment to determine the effect on the quality of the data.

2. The percent valley criterion should be evaluated on both the window defining mixture and the continuing calibration solution. If the 25% valley requirement for both solutions is not met, reject (R) all associated data.

3.4 Initial Calibration

The initial calibration standard solutions must be analyzed prior to any sample analysis. All five high-resolution calibration solutions listed in Appendix E must be used for the initial calibration. The calibration standards must be analyzed on the same instrument and using the same GC/MS conditions that were used to analyze the window defining mix.

The following criteria must be met:

1. SIM data were acquired for each of the ions listed in Appendix F including interfering diphenylether ions.

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

3. The two SIM ions for each homologue must maximize simultaneously and within three seconds of the corresponding ions of the labeled isomers.

4. The relative ion abundance criteria for PCDDs/PCDFs listed in Appendix G must be met.

5. The relative ion abundance criteria for the labeled internal and recovery standards listed in Appendix G must be met.

6. For all calibration solutions, the signal to noise ratio (S/N) for all ions of the labeled and unlabeled PCDDs/PCDFs must be greater than 2.5.

7. The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be $\geq$ 10.

8. The percent relative standard deviation (% RSD) of the five Relative Response Factor (RRFs) for the unlabeled PCDDs/PCDFs must not be greater than 20%; the internal standards' %RSD must not exceed 30%.

ACTIONS:
1. If the %RSD for any isomer exceeds 20%, flag the associated sample results for that specific isomer as estimated (J).

2. If any of the other calibration criteria are not met, reject (R) only the data of the analytes, which are directly affected.

9. Sensitivity changes that might occur during the analysis must be monitored. To that effect, a lock-mass ion from the recommended reference compound perfluorokerosene (PFK) should be used to monitor instrument sensitivity. The PFK is metered into the ion chamber throughout the HRGC/HRMS analysis. Should the instrument sensitivity drop, data collected from the specific ion channel will be rejected.

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

To recalculate the response factors use the following equations:

$$RRF_N = \frac{A_N \times Q_{IS}}{A_{IS} \times Q_N}$$

where:

RRF_N = relative response factor of the analyte
A_N = sum of integrated ion abundance of the quantitation ions of the isomer of interest (Appendix F)
Q_{IS} = quantity of the appropriate internal standard injected (pg)
A_{IS} = sum of integrated ion abundance of the quantitation ions of the appropriate internal standard (Appendix F)
Q_N = quantity of the unlabeled PCDD/PCDF analyte injected (pg)

$$RRF_{IS} = \frac{A_{IS} \times Q_{RS}}{A_{RS} \times Q_{IS}}$$

where:

RRF_{IS} = relative response factor of the internal standard
A_{IS} = sum of integrated ion abundance of the quantitation ions of the

appropriate internal standard (Appendix F)

Q_{RS} = quantity of the appropriate recovery standard injected (pg)

A_{RS} = sum of integrated ion abundance of the quantitation ions of the appropriate recovery standard

Q_{IS} = quantity of the appropriate internal standard injected (pg)

3.5 Continuing Calibration Check

Continuing calibration check (CC3) must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance (window defining mix) checks. A continuing calibration is also required at the end of a 12-hour period.

The following GC/MS criteria must be met:

1. SIM data were acquired for each of the ions listed in Appendix F including interfering diphenylether ions.

2. For the continuing calibration solution, the retention times of the isomers must fall within the retention time windows established by the window defining mix.

3. The absolute retention times of the recovery standards $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD shall not change by more than 10 seconds between the initial CC3 and ending CC3 standard analyses.

4. The two SIM ions for each homologue must maximize simultaneously ($\pm$2 sec) and within three seconds of the corresponding ions of the labeled isomers.

5. For the CC3 standard solution the signal to noise ratio for the labeled and unlabeled PCDD/PCDF ions shall be greater than 2.5.

6. The relative ion abundance criteria (Appendix G) for all PCDD/PCDF shall be met.

7. The relative ion abundance criteria for all internal and recovery standards (Appendix G) must be met.

8. The measured RRF of each analyte in the CC3 solution must be $\leq$ 20% difference of the mean RRF established by the initial calibration; the percent difference must be $\leq$ 30 for internal standards.

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

   To calculate the response factor, use the equation mentioned in Section 3.4.

   To calculate percent differences use the following equation:

$$Percent\ Difference\ (\%D) = \frac{RRF_I - RRF_C}{RRF_I} \times 100$$

where:

RRF_I = average relative response factor established during initial calibration
RRF_C = relative response factor established during continuing calibration

9. Was the same internal standard used to calculate the RRF for each PCDD/PCDF homologue as used for the initial calibration?

10. Sensitivity changes that might occur during the analysis must be monitored. To that effect, lock-mass ions from the recommended reference compound perfluorokerosene (PFK) should be used to monitor instrument sensitivity. Should the instrument sensitivity drop significantly, data collected from the specific ion channel will be rejected.

ACTION:

1. If the percent valley criterion ($\leq$ 25) is not met, reject (R) all associated data.

2. If any requirements listed in steps 1, 2, 3, or 9 are not met, use professional judgment to determine the validity of the data.

3. If any requirements listed in steps 4, 5, 6, or 7 are not met, reject (R) all data directly affected by each specific problem.

4. If the %D requirement listed in step 8 is not met, flag the associated sample results for that specific isomer as estimated (J).

5. If CC3 standard was not analyzed at the end of a 12-hour period, use professional judgment to determine the effect on the data quality.

3.6 Sample Data

3.6.1 Identification Criteria

1. For the 2,3,7,8-substituted isomers reported 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 -1 to +3 seconds of the retention time of the corresponding labeled standard.

2. For the 2,3,7,8-substituted isomer reported present and for which a labeled standard does not exist, the relative retention time (RRT) of the analyte must be within $\pm$0.05 RRT units of the RRT established by the continuing calibration standard (CC3).

3. For non-2,3,7,8 substituted compounds (tetra through octa) found present the retention time must be within the window established by the window defining mix for the corresponding homologue.

4. All the specified ions listed in Appendix E for each PCDD/PCDF isomer found present and the labeled standards must be present in the SICP, and must maximize simultaneously (±2 seconds).

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

6. The relative ion abundance criteria (Appendix G) for all PCDDs/PCDFs found present must be met.

7. The relative ion abundance criteria for the internal standards must be met (Appendix G).

ACTION:

1. Reject (R) all positive data for the analytes, which do not meet criteria listed in steps 1, 2, 3 or 4.

2. If the criteria listed in step 5 are not met but all other criteria are met, qualify all positive data of the specific analyte as estimated (J).

3. If the analytes reported positive do not meet ion abundance criteria listed in step 6, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

4. If the internal standards and recovery standards do not meet ion abundance criteria (Appendix G) but they meet all other criteria, flag all corresponding data as estimated (J).

5. If a PCDF is detected but an interfering PCDPE is also detected, reject (R) the PCDF data. The reported value of PCDF is changed to EMPC.

Check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate the concentration or 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:

$$C_N\ (pg/g) = \frac{(A_N)(Q_{IS})(DF)}{(RRF_N)(A_{IS})(W)}$$

$$C_N\ (pg/mL) = \frac{(A_N)(Q_{IS})(DF)}{(RRF_N)(A_{IS})(V)}$$

where:

C_N = concentration of native PCDD/PCDF found in the sample
A_N = sum of the integrated ion abundance of the quantitation ions of the isomer of interest
A_{IS} = sum of the integrated ion abundance of the quantitation ions of the appropriate internal standard
Q_{IS} = quantity (pg) of the appropriate internal standard added to the sample
RRF_N = average relative response factor from initial calibration
W = weight (g) of sample extracted
V = volume (mL) of sample extracted
DF = dilution factor

3.6.2 Estimated Detection Limits (EDL)

An EDL must be calculated for each 2,3,7,8-substituted isomer that was not identified regardless of whether or not other non-2,3,7,8 substituted isomers were present.

Use the equation provided by the subcontracted laboratory or the equation below to check EDL calculations:

For Soil:

$$EDL = \frac{(2.5)(H_X)(Q_{IS})(DF)}{(H_{IS})(RRF_N)(W)}$$

For Water:

$$EDL = \frac{(2.5)(H_X)(Q_{IS})(DF)}{(H_{IS})(RRF_N)(V)}$$

where:

H_X = the peak height of the noise of the quantitation ion of the 2,3,7,8-substituted isomer of interest
H_{IS} = the peak height of the quantitation ion of the appropriate internal standard.
Q_{IS} = quantity of the appropriate internal standard injected (pg)

RRF_N = relative response factor of the analyte
DF = dilution factor
W = weight (g) of sample extracted
V = volume (mL) of sample extracted

3.6.3 Estimated Maximum Possible Concentration (EMPC)

EMPC must be calculated for 2,3,7,8-substituted isomers that had S/N ratio for the quantitation ions greater than 2.5 but did not meet all the identification criteria.

Use the equation below to check EMPC calculations:

For Soil:

$$EMPC = \frac{(A_X)(Q_{IS})(DF)}{(A_{IS})(RRF_N)(W)}$$

For Water:

$$EMPC = \frac{(A_X)(Q_{IS})(DF)}{(A_{IS})(RRF_N)(V)}$$

where:

A_X = area of the quantitation ion 2,3,7,8-substituted isomer of interest
A_{IS} = sum of the integrated ion abundance of the quantitation ions of the appropriate internal standard
Q_{IS} = quantity (pg) of the appropriate internal standard added to the sample
RRF_N = average relative response factor from initial calibration
DF = dilution factor
W = weight (g) of sample extracted
V = volume (mL) of sample extracted

3.7 Method Blank

1. A method blank (per matrix) must be extracted and analyzed with each batch of $\leq$24 samples.

2. Reporting a method blank contamination level for any of the 2,3,7,8-substituted congeners, except OCDD and OCDF, that exceeds 10% of the desired detection limit would invalidate the results and require automatic sample reruns for all positive samples found in that batch of samples. A positive sample is defined as a sample found to contain at least one 2,3,7,8-substituted PCDD/PCDF congener (except OCDD and OCDF). A valid method blank run is an analysis during which all internal standard signals are characterized by S/N of at least 10:1.

ACTION: 1. If the proper number of method blanks were not submitted, notify the

subcontracting laboratory. If they are unavailable, reject (R) all positive sample data.

2. If the blank is contaminated with 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDD, or 2,3,4,7,8-PeCDF at a concentration of < 0.1 ppb, no action is required. If the concentration of any of the above compounds is > 0.1 ppb, reject (R) all positive data for the associated samples and request reanalysis.

3. If the method blank is contaminated with other 2,3,7,8 substituted isomers and the concentration in the sample is less than five times the concentration in the blank, change the sample results to the EMPC. If the concentration in the sample is higher than five times the concentration in the blank, no action is taken.

4. If the method blank is grossly contaminated, reject (R) all the data.

3.8 Internal Standard Recoveries

1. The recommended QC limits for internal standard recovery is between 40-120%.

2. If the internal standard recovery is below 40%, use professional judgment to qualify the non-detect data (EMPC and EDL) and qualify the positive data as estimated (J).

3. If the internal standard recovery is above 120%, flag all associated data (positive and non-detect data) as estimated (J).

Calculate the percent recovery of internal standard (R_{IS}) in the sample extract using the following equation:

$$\%R_{IS} = \frac{(A_{IS})(Q_{RS})}{(A_{RS})(RRF_{IS})(Q_{IS})} \times 100$$

where:

A_{IS} = sum of the integrated ion abundance of the quantitation ions of the appropriate internal standard
Q_{RS} = quantity (pg) of the recovery standard added to the sample extract
A_{RS} = sum of integrated ion abundance of the quantitation ions of the recovery standard
RRF_{IS} = average relative response factor of the internal standard from initial calibration
Q_{IS} = quantity (pg) of the appropriate internal standard added to the sample

3.9 Recovery Standards

1. The retention time of each recovery standard in the samples must be within 10 seconds of the associated continuing calibration standard.

2. If the retention time of the recovery standard differs by more than 10 seconds, use professional judgment to determine the effect on the results. A greater than 10 second shift may cause certain analytes to elute outside the retention time window established by the window defining mix.

3.10 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

The QC limits for recovery are not specified by method 8290; the QC limits will be adopted from CLP SOW (DFLM 01.0). The percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted compounds must be within 60 to 140%. The relative percent difference (RPD) must be less than 20%.

$$RPD = \frac{|R_{MS} - R_{MSD}|}{(R_{MS} + R_{MSD})/2} \times 100$$

R_{MS} and R_{MSD} represent MS/MSD recoveries.

ACTION: No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS/MSD results in conjunction with other QC criteria and determine the need for some qualification of the data. Should any qualification be applied, it should only be on the sample chosen for the spike.

4.0 RESPONSIBILITIES

4.1 Data Reviewer

The Data Reviewer is responsible for a working knowledge of the method used to obtain the data and to ensure that all documents are included and complete (see Appendix C), the laboratory is in compliance with the method, and all requested analyses were performed.

The Data Reviewer must present professional judgment and must express concerns and comments on the validity of the overall data package. The Data Reviewer must also explain, in writing, the reason for rejecting and/or qualifying the data. He or she must also note all the items of method non-compliance.

The Data Reviewer is responsible for informing the Data Validation and Report Writing Group Leader of any major non-compliance of the method that may affect the usability of the data.
The Data Reviewer will prepare any written communication to the laboratories detailing anomalies of the method.

4.2 Data Validation and Report Writing Group Leader

The Data Validation and Report Writing Group Leader is responsible for the accurate updating of this

SOP as requirements change.

The Data Validation and Report Writing Group Leader is also responsible for communication of any major non-compliance of the method that may affect the usability of the data to the Task Leader and to the Analytical Section Leader.

4.3 Analytical QA/QC Officer

The Analytical QA/QC Officer audits the review process to ensure compliance with this SOP.

The Analytical QA/QC Officer identifies the need to update this SOP on a timely basis.

4.4 Analytical Section Leader

The Analytical Section Leader ensures adherence to the guidelines prior to authorizing the release of analytical deliverables.

APPENDIX A
Target Compound List for Dioxin/Furan
SOP #1019
September 1994

TARGET COMPOUND LIST (TCL)

PCDD/ PCDF	CAS NUMBER
2,3,7,8-TCDD	1746-01-6
2,3,7,8-TCDF	51207-31-9
1,2,3,7,8-PeCDF	57117-41-6
1,2,3,7,8-PeCDD	40321-76-4
2,3,4,7,8-PeCDF	57117-31-4
1,2,3,4,7,8-HxCDF	70648-26-9
1,2,3,6,7,8-HxCDF	57117-44-9
1,2,3,4,7,8-HxCDD	39227-28-6
1,2,3,6,7,8-HxCDD	57653-85-7
1,2,3,7,8,9-HxCDD	19408-74-3
2,3,4,6,7,8-HxCDF	60851-34-5
1,2,3,7,8,9-HxCDF	72918-21-9
1,2,3,4,6,7,8-HpCDF	67562-39-4
1,2,3,4,6,7,8-HpCDD	35822-46-9
1,2,3,4,7,8,9-HpCDF	55673-89-7
OCDD	3268-87-9
OCDF	39001-02-0

APPENDIX B
Data Qualifiers and Definitions
SOP #1019
September 1994

Data Qualifiers and Definitions

R Sample result is unusable due to significant QA/QC problems. The analysis is invalid and it provides no information as to whether the compound is present or not.

J Sample result is considered estimated due to QA/QC problem.

APPENDIX C
Deliverable Checklist for Dioxin/Furan Analysis by HRGC/HRMS
SOP #1019
September 1994

DATA VALIDATION PROCEDURES FOR DIOXIN/FURAN ANALYSIS BY HRGC/HRMS

Rev.10/26/93

FOR LOCKHEED/SERAS USE ONLY			
Work Assignment Name:	WA#:	Data Pkg.#	Date:

8290 Dioxin HRGC/HRMS Checklist

All of the following information must be included in the data package. Please check all blanks and submit this list along with your report.

_____Case narrative, if any

_____Chain of Custody (signed with date of receipt)

_____All extraction logs (include initial and re-extractions, spike amounts, volumes and concentrations for Internal Standard, Clean-up Standard, Recovery Standard and Matrix Spike/Matix Spike Duplicate)

_____Worksheet for % solid (if applicable)

_____Analysis logs (include all columns used for analysis)

Initial Calibration Data (for all columns)

_____Window defining mixture (with first/last eluters labeled)

_____ICAL Curve Summary Table

_____Quant. Report for individual calibration standards

_____Ion chromatograms for all calibration standards, lock-masses, and Column performance check solution (CPSM) with 25% valley check

_____Mass Resolution check

_____Blank

Continuing Calibration Data (for all columns)

_____Mass Resolution check

_____Column performance check (25% valley and first/last eluters labeled)

_____RRF % Difference with ICAL

_____Blank

_____Each 12-hour period standard run

_____Quant report

_____Ion chromatograms

Monitoring for PCP Ethers - indicate which ions monitored and provide associated chromatograms

M/Z

_____HxCDPE

_____HpCDPE

_____OCDPE

_____NCDPE

_____DCDPE

Lock Mass Monitoring (PFK Masses) - indicate masses monitored and provide associated chromatograms

Ex.	lock-mass	330.9792	Group 1
	lock-mass	442.9728	Group 2
	lock-mass	442.9728	Group 3

Sample Analysis (including method blanks and MS/MSD)

DATA VALIDATION PROCEDURES FOR DIOXIN/FURAN ANALYSIS BY HRGC/HRMS

_____Result Summary table(s) with the unit of ppt

_____Internal Standard Recoveries

_____Quant report

_____Ion chromatograms

- indicate noise levels wherever calculated
- include an example calculation of detection limits (DL)
- show noise level (height or area) on ion chromatogram and indicate any factors used

_____ _____
Signature Date

Revised 10/26/93

APPENDIX D
Composition of the GC Performance Evaluation Solution (Window Defining Mixture)
SOP #1019
September 1994

Composition of the GC Performance Evaluation Solution
(Window Defining Mix)[1]

No. of Chlorine Atoms	PCDD-Positional Isomer		PCDF-Positional Isomer	
	Early Eluter	Late Eluter	Early Eluter	Late Eluter
4[2]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/ 1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,3,4,7,9/ 1,2,3,4,6,8	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8		1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9

(1) On a 60m DB-5 column

(2) In addition to these two PCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present.

APPENDIX E
Concentration of High-Resolution Calibration Solutions
SOP #1019
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Concentration of High-Resolution Calibration Solutions

Compound	Concentration (pg/uL) CC1	CC2	CC3	CC4	CC5
Unlabeled Analytes					
2,3,7,8-TCDD	1	2.5	10	50	200
2,3,7,8-TCDF	1	2.5	10	50	200
1,2,3,7,8-PeCDD	2.5	6.25	25	125	500
1,2,3,7,8-PeCDF	2.5	6.25	25	125	500
2,3,4,7,8-PeCDF	2.5	6.25	25	125	500
1,2,3,4,7,8-HxCDD	2.5	6.25	25	125	500
1,2,3,6,7,8-HxCDD	2.5	6.25	25	125	500
1,2,3,7,8,9-HxCDD	2.5	6.25	25	125	500
1,2,3,4,7,8-HxCDF	2.5	6.25	25	125	500
1,2,3,6,7,8-HxCDF	2.5	6.25	25	125	500
1,2,3,7,8,9-HxCDF	2.5	6.25	25	125	500
2,3,4,6,7,8-HxCDF	2.5	6.25	25	125	500
1,2,3,4,6,7,8-HpCDD	2.5	6.25	25	125	500
1,2,3,4,6,7,8-HpCDF	2.5	6.25	25	125	500
1,2,3,4,7,8,9-HpCDF	2.5	6.25	25	125	500
OCDD	5	12.5	50	250	1,000
OCDF	5	12.5	50	250	1,000
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	125	125	125	125	125
$^{13}C_{12}$-OCDD	250	250	250	250	250
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD[1]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[2]	125	125	125	125	125

(1) Used for recovery determinations of TCDD, TCDF, PeCDD, and PeCDF internal standards.

(2) Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF, and OCDD internal standards.

APPENDIX F
Ions Monitored for HRGC/HRMS Analysis of PCDD/PCDF
SOP #1019
September 1994

DATA VALIDATION PROCEDURES FOR DIOXIN/FURAN ANALYSIS BY HRGC/HRMS

Ions Monitored for HRGC/HRMS Analysis of PCDD/PCDF
(S = Internal/ Recovery Standard)

Descriptor	Accurate[1] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}C1_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}C1_3{}^{37}C1O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}C1_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}C1_3{}^{37}C1O$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}C1_4O_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}C1_3{}^{37}C1O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}C1_4O_2$	TCDD (S)
	333.9339	M + 2	$^{13}C_{12}H_4{}^{35}C1_3{}^{37}C1O_2$	TCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}C1_6O$	HxCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
2	339.8597	M + 2	$C_{12}H_3{}^{35}C1_4{}^{37}C1O$	PeCDF
	341.8567	M + 4	$C_{12}H_3{}^{35}C1_3{}^{37}C1_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_3{}^{35}C1_4{}^{37}C1O$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_3{}^{35}C1_3{}^{37}C1_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}C1_4{}^{37}C1O_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}C1_3{}^{37}C1_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_3{}^{35}C1_4{}^{37}C1O_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_3{}^{35}C1_3{}^{37}C1_2O_2$	PeCDD (S)
	409.7974	M + 2	$C_{12}H_3{}^{35}C1_7O$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK

Ions Monitored for HRGC/HRMS Analysis of PCDD/PCDFs (cont'd)
(S = Internal/ Recovery Standard)

Descriptor	Accurate[1] Mass	Ion ID	Elemental Composition	Analyte
3	373.8208	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8642	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M + 2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK

Ions Monitored for HRGC/HRMS Analysis of PCDD/PCDFs (cont'd)
(S = Internal/ Recovery Standard)

Descriptor	Accurate[1] Mass	Ion ID	Elemental Composition	Analyte
5	441.7428	M + 2	$C_{12}{}^{35}C1_7{}^{37}C1O$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}C1_6{}^{37}C1_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}C1_7{}^{37}C1O_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}C1_6{}^{37}C1_2O_2$	OCDD
	469.7779	M + 2	$^{13}C_{12}{}^{35}C1_7{}^{37}C1O_2$	OCDD (S)
	471.7750	M + 4	$^{13}C_{12}{}^{35}C1_6{}^{37}C1_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}C1_8{}^{37}C1_2O$	DCDPE
	[442.9278]	LOCK	$C_{10}F_{17}$	PFK

(1) The following nuclidic masses were used:

H	= 1.007825	O	= 15.994915
C	= 12.000000	^{35}C1	= 34.968853
^{13}C	= 13.003355	^{37}C1	= 36.965903
S	= Internal/recovery standard		

APPENDIX G
Theoretical Ion Abundance Ratios and Their Control Limits
for PCDD/PCDF
SOP #1019
September 1994

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits Lower	Control Limits 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[(1)]	M / M+2	0.51	0.43	0.59
7[(2)]	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

(1) Used only for ^{13}C-HxCDF (IS)
(2) Used only for ^{13}C-HpCDF (IS)