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Guidelines for Reporting Test Results of HDD and HDF Determinations in Commercial Products (40 CFR Parts 707 and 766)

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Final Report

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DISCLAIMER

This document has been reviewed and approved for publication by the Office of Toxic Substances, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency. The use of trade names or commercial products does not constitute Agency endorsement or recommendation for use.

PREFACE

This report provides guidance to the chemical industry for the reporting of results from the testing of chemical products to the Office of Pesticides and Toxic Substances as specified in 40 CFR, Parts 707 and 766, Polyhalogenated Dibenzo-*p*-dioxin/Dibenzofuran Testing and Reporting Requirements, Final Rule (*Fed. Reg.* 52 (108), 21412-21452, June 5, 1987).

This report is the third in a series of guidance documents prepared to assist with compliance to the Rule. The first document, "Guidelines for the Determination of Halogenated Dibenzo-*p*-Dioxins and Dibenzofurans in Chemical Products" (EPA-560/5-87/007), September 1987), was prepared as guidance to the chemical industry in the development of analytical methods and in the preparation of sampling plans, analytical protocols, and quality assurance plans. The second guidance document, "Guidelines for Review of Test Plans Submitted for the Determination of HDDs and HDFs in Commercial Products (40 CFR, Parts 707 and 766)" (Midwest Research Institute, Revised Final Report, February 26, 1988), was prepared specifically for use by EPA's expert panel in the review of protocols. However, this document should also be of use to the chemical industry as guidance to the criteria which will be used to review their protocols.

These reporting guidelines were prepared by Midwest Research Institute (Mr. David Steele, Work Assignment Leader, and Mr. Thomas Dux, Chemical Sciences Department Quality Assurance Coordinator) for the Office of Toxic Substances/Field Studies Branch as part of Work Assignment 33 (Analytical Methodologies for Halogenated Dioxins and Dibenzofurans in Commercial Products) under EPA Contract No. 68-02-4252, Ms. Janet Remmers, Work Assignment Manager, and Dr. Joseph Breen, Project Officer.

Valuable input for this guidance document was provided by the members of the Expert Panel, appointed by EPA to review analytical protocols and data generated under the Rule. The Expert Panel members are Dr. Aubry Dupuy, Jr., Dr. David Firestone, Mr. Robert Harless, Dr. Doug Kuehl, and Dr. Wayne Sovocool.

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TABLE OF CONTENTS

I. INTRODUCTION

The Code of Federal Regulations, Title 40 Parts 707 and 766 (40 CFR 707 and 766), published June 5, 1987, presents a Final Rule for testing and reporting the concentrations of halogenated dibenzo-*p*-dioxins (HDDs) and halogenated dibenzofurans (HDFs) in a group of chemical products selected for testing based on the possibility of contamination by HDDs and HDFs.

This Rule, promulgated under Sections 4 and 8 of the Toxic Substances Control Act (TSCA), 15 U.S.C. 2603, requires manufacturers and importers of 12 commercial organic chemicals to test for the presence of HDDs and HDFs which are either chlorinated or brominated at the 2,3,7,8 and up to three additional positions on the molecules. Testing will be required for 20 additional chemicals not currently manufactured or imported in the United States if their manufacture or importation should resume.

EPA will conduct in-depth reviews of all test data submitted under the Rule. These reviews will require the submission of any and all records and data which support the test results. EPA authority for requesting this information stems from 40 CFR Part 766.10, "All new data, documentation, records, protocols, specimens, and reports generated as a result of testing under Subpart B of this Part must be fully developed and retained in accordance with Part 792 of the chapter. These items must be made available during an inspection or submitted to EPA upon request of EPA or its authorized representative."

EPA reviews of the first data submittals under the Rule have indicated a discrepancy between the level and type of information which has been reported by different members of the regulated community. This demonstrates a need for EPA to provide guidance on the type of information which needs to be submitted to comply with Rule requirements.

This document deals specifically with the reporting of results from the sampling activities and subsequent analytical determination of HDDs and HDFs in the chemical products listed in the Rule. Section II presents a summary of the Rule reporting requirements for test results. Section III contains a detailed listing and description of the type of information needed for EPA to conduct a full review of test results.

This document is provided as guidance only and should not be considered comprehensive. Each submitter is responsible for the submission of the appropriate information based on the approved protocols under which the testing is performed. Different protocols will result in different types of records. This document should also not be used as guidance to the kinds of records which must be developed and maintained for total compliance to the Rule. For example, other documentation and records, in addition to those discussed in this document, must be maintained to be in compliance with TSCA Good Laboratory Practice (GLP) requirements. These may be found in the TSCA GLP Standards (40 CFR 792).

II. SUMMARY OF REQUIREMENTS FOR REPORTING TEST RESULTS

Requirements pertinent to the reporting of HDD/HDF test results are summarized below. The section of the Rule containing the requirement is given in parentheses after the requirement. It should be noted that the Rule contains other reporting requirements which are not directly related to test results. These are not addressed in this document. The Rule should be consulted for these additional requirements.

A. All information submitted to EPA must bear the applicable CFR section number and must be addressed to: Document Control Office (TS-790), Office of Pesticides and Toxic Substances, Environmental Protection Agency, 401 M Street, S.W., Washington, D.C. 20460. (766.7)

B. All new data, documentation, records, protocols, specimens, and reports generated as a result of testing must be made available during an inspection or submitted to EPA upon request of EPA or its authorized representative. (766.10)

C. Sponsors are responsible for ensuring that laboratories conducting the testing abide by the TSCA GLP standards. At the time test data are submitted, manufacturers must submit a certification to EPA that the laboratory performing the testing adhered to the TSCA GLPs. (766.10)

D. The results of the Limit of Quantitation (LOQ) demonstration for each of the analytes specified in the Rule must be presented. This requires fortification of two samples with isotopically labeled internal standards of each of the analytes at the LOQ specified in 766.27. This fortification is done at the beginning of sample preparation. The LOQ is demonstrated by a recovery of the internal standard between 50% and 150% of the amount spiked and a relative percent difference between the two samples of less than 20%. (766.18)

E. Analysis results for all the HDDs and HDFs specified in the test protocol must be submitted. Only the chlorinated and brominated congeners specified in 766.27 need to be quantified. (766.27)

F. Test results must be reported to EPA no later than 270 days after EPA's transmission of comments or 180 days after a final protocol is submitted to EPA, whichever is shorter. (766.35)

III. GUIDELINES FOR REPORTING TEST RESULTS

EPA will conduct an in-depth review of all data submitted under the Rule. The information required for EPA review consists of all raw data needed to completely trace the sample from field activities to final data and allow the reviewer to independently calculate the sample results. Sufficient information should be given so that a reviewer can determine whether the test protocol was followed in the field, sample preparation laboratory, and analysis laboratory. The reviewer should be able to calculate final test results from sample size, internal standard fortification amounts, sample dilution or concentration factors, instrument calibration factors, and raw instrument output (e.g., areas of chromatographic peaks).

The information which is needed for review is presented in the remainder of this section. This listing should not be considered to be comprehensive since each test protocol will be different and will have different types of records.

The submittal should be made in report form and should contain all of the elements described below:

A. A cover letter, properly addressed to the Office of Pesticides and Toxic Substances Document Control Officer, with the appropriate CFR reference should be submitted. This letter should specifically cite the approved test protocol used for the study, and detail any pertinent time extensions in regard to the reporting requirements.

B. A title page and complete table of contents outlining the submittal including all appendices and attachments.

C. A certification from the submitter that the laboratory performing the testing adhered to TSCA GLPs, given in 40 CFR Part 792, August 17, 1989.

D. A summary section. This section should summarize the overall test results in terms of the objectives of the study. It should detail any additional work which is warranted by results which do not meet the data quality objectives defined by the Rule. It should also describe any additional reporting required as a result of the testing and the time frame for subsequent reports.

E. A section discussing the sampling of the chemical product. This section should contain all of the following elements.

   1. A statement as to whether the sampling protocol was followed.

   2. A discussion of any deviations from the sampling protocol and the reasons for the deviations.

3. A discussion of any problems encountered in sampling, the resolution of the problems, and any possible impact the problems may have on the quality of the data.

4. A statement describing the transfer of samples from the sampling location to the analytical laboratory.

5. An inventory of all samples which were taken, the amount of sample, and the disposition of the sample (shipped for analysis, archived on site, etc.).

F. A section discussing the preparation of the samples for chemical analysis. This section should contain all of the following elements.

1. A statement as to whether the analytical protocol was followed.

2. A discussion of any deviations from the analytical protocol, the reasons for the deviations, and any possible impact which the deviations may have on the quality of the data.

3. A discussion of any options in the analytical protocol which were taken. Examples of options might include cleanup procedures or fortification levels.

4. A discussion of any problems encountered in sample preparation, the resolution of the problems, and any possible impact the problems may have on the quality of the data.

G. A section discussing the instrumental analysis of the prepared chemical product. This section should include the following elements.

1. A statement as to whether the protocol was followed.

2. A discussion of any deviations from the protocol and the reasons for the deviations.

3. A discussion of any options in the protocol which were taken. Examples of options might include instrumentation, injection volumes, etc.

4. A discussion of any problems encountered during sample analysis, the resolution of the problems, and any possible impact on data quality.

H. A summary of all initial calibration and continuing calibration results. These should be presented in tables. Quality control information should be calculated and included in this section.

This include average response factors, percent relative standard deviation, and relative percent difference. Data for any analyte which does not meet the required criteria should be clearly identified in the table. The use of instrument calibration which does not meet criteria must be justified in terms of overall data quality and impact on the sample results.

I. A section presenting the results for the chemical product samples. These results should be presented in a table. Results which do not meet data quality objectives should be flagged and discussed in the text. Internal standard recovery statistics such as average recovery for a specific analyte, standard deviation, and relative standard deviation should be calculated and presented. An example table of sample results is shown in Table 1.

J. A section detailing the quality control results from the sample analysis. This section should contain all of the following elements.

1. The results of the limit of quantitation determination as specified in 40 CFR Part 766.27. The results from these spiked duplicate samples should be presented in a table which contains the internal standard spiking levels, the internal standard recoveries (% of amount spiked) for each analyte in each sample, and the calculated relative percent difference of the recoveries from the two samples for each analyte. Any value which does not meet the spiking level (LOQ), recovery (50% to 150%), or precision (±20%) requirements of the Rule must be clearly identified in the table and discussed in the accompanying text. If the sensitivity requirements defined in 40 CFR Part 766.27 are not met, a discussion should be included which details the reasons the associated sample results should be accepted by EPA. An example table for a limit of quantitation determination has been provided (Table 2).

2. The results of any matrix spikes of the chemical product. These results should also be presented in a table. Any value which does not meet the data quality objectives specified in the test protocol should be clearly identified and the impact on data quality discussed in the text.

3. The recoveries of all isotopically labeled internal standards should be presented in a table. This table should include the data from all blanks, samples, and spikes. Results which do not meet data quality objectives should be flagged and discussed in the text. Statistics such as average recovery for a specific analyte, standard deviation, and relative standard deviation should be calculated and presented.

K. All raw data and documentation should be included in the form of one or more appendices to the report. Information which should be included is listed below. This list should not be considered to be comprehensive since each test protocol will be different and will have different types of records.

1. Complete records of field sampling

   - Field sampling logbook pages or sampling forms giving the sample identifiers, the person conducting the sampling, the location of the samples, the sampling method, the data, and the time of sampling
   - Calibration records of sampling equipment, before and after sampling
   - Shipping forms
   - Preparation, manufacturer, lot number, and expiration date of any reagents used in sampling
   - Any sampling problems

2. Sample shipment records

   - Sample traceability forms
   - Field inventory sheets
   - Documentation of laboratory receipt indicating who received the samples, when, and the conditions upon receipt

3. Complete standard preparation records for reference standards for both internal standard addition and instrument calibration

   - Standard preparation notebook pages or forms giving the standard identifier, the person preparing the standards, the amount weighed, and all subsequent dilutions
   - Balance calibration records
   - Supplier, lot number, purity, and expiration dates for reference materials and all reagents
   - Verification of standards by comparison to independently prepared standard or certified standards

4. Sample preparation records

   - Sample preparation notebook pages or forms giving the name of the analyst, the date, the samples prepared, all sample preparation operations, and reference to the approved test protocol
   - All additions of internal standards
   - All sample preparation problems
   - Initial sample size and all subsequent dilutions and concentrations
   - Balance calibration records for the balance used in sample weighing
   - All reagents and their preparation

5. Sample analysis records

   - Complete information on the instrumental system including manufacturer, model number, chromatographic column, chromatography conditions, data system, and pertinent maintenance which affects the sample results
   - Complete list of all standards and samples in the order of analysis
   - Instrument logbook pages for the days on which sample analyses were conducted
   - All chromatograms, peak areas, ion masses (m/z) etc., needed to calculate the calibration information (e.g., relative retention times, ion abundance ratio factors, etc.), and the sample results
   - Complete traceable documentation of data reduction and validation procedures including formulas, tables of mass area ratios, hand calculations for situations where the data system was inadequate, explanations for rejected data, calculations of internal standard recoveries, etc.

IV. CONCLUSION

A description of the information needed for a submittal of test data in response to the Rule should help the regulated community prepare a complete document resulting in an efficient and timely review of the information. If the submittal follows the format given in the Section II, the data should be clearly presented and address all the testing objectives of the Rule.

Table 1. Example of Sample Results
PCDDs/PCDFs in Commercial Product (ng/g)

Analytes	Blank[a]	Sample identification number 109	234	573	638	552	698	226	Average	SD[b]	RSD[c]	Range
2,3,7,8-TCDD	< 0.05	1.6	1.2	1.1	0.8	1.5	1.1	1.4	1.2	0.3	22.2	0.8-1.6
1,2,3,7,8-PeCDD	< 0.1	2.2	3.1	2.6	1.9	.17	2.1	2.4	2.3	0.5	20.4	1.7-3.1
1,2,3,4,7,8-HxCDD	< 1.2	25.1	33.5	20.1	23.6	30.9	28.2	27.6	27.0	4.5	16.7	20.1-33.5
1,2,3,6,7,8-HxCDD	< 1.2	ND[d]	ND	ND	ND	ND	ND	ND	NA[e]	NA	NA	NA
1,2,3,7,8,9-HxCDD	< 1.2	66.3	52.3	44.1	89.3	50.1	93.2	33.4	61.2	22.8	37.2	33.4-93.2
1,2,3,4,6,7,8-HpCDD	< 14	56.4	88.3	103	64.1	22.3	98.5	55.6	69.7	28.6	41.1	22-3-103
2,3,7,8-TCDF	< 0.05	1.9	2.2	1.6	2.6	1.8	4.5	3.4	2.6	1.0	40.6	1.6-4.5
1,2,3,7,8-PeCDF	< 2.2	36.4	64.5	46.3	12.6	55.3	33.6	52.1	43.0	17.1	39.9	12.6-64.5
2,3,4,7,8-PeCDF	< 2.2	22.6	36.1	15.8	25.9	21.6	33.3	19.8	25.0	7.3	29.3	15.8-36.1
1,2,3,4,7,8-HxCDF	< 12.6	950	725	668	852	645	889	753	783	116	14.8	645-950
1,2,3,6,7,8-HxCDF	< 12.6	260	225	146	360	259	189	230	238	67.0	28.1	146-360
2,3,4,6,7,8-HxCDF	< 12.6	460	523	356	498	550	390	462	463	69.7	15.1	356-550
1,2,3,7,8,9-HxCDF	< 12.6	382	399	363	264	346	452	299	358	62.7	17.5	264-452
1,2,3,4,6,7,8-HpCDF	< 25.0	1310	1560	1450	1340	1220	1610	1460	142	140	9.8	1220-1610
1,2,3,4,7,8,9-HpCDF	< 25.0	2250	2190	2400	2110	2560	2890	2360	2400	260	11.0	2110-2890
Internal standard	Spike level ng/g	Percent recovery										
^{13}C-2,3,7,8-TCDD	10	63.2	92.1	93.6	49.5[f]	81.6	123	95.2	166[f]	100.1	36.3	36.2	49.5-166
^{13}C-1,2,3,7,8-PeCDD	50	92.1	83.6	125	95.2	92.5	88.6	66.1	102	93.3	18.0	19.3	66.1-125
^{13}C-1,2,3,6,7,8-HxCDD	50	96.2	114	134	149	131	87.6	74.2	89.3	111.3	28.1	25.2	74.2-152
^{13}C-1,2,3,4,6,7,8-HpCDD	50	87.4	96.2	90.6	73.5	87.4	99.4	123	87.2	93.9	15.3	16.2	73.5-123
^{13}C-2,3,7,8-TCDF	10	117	83.4	53.1	72.3	74.9	134	88.4	99.5	86.5	25.5	29.4	53.1-134
^{13}C-1,2,3,7,8-PeCDF	50	104	80.2	63.2	64.5	43.9[f]	59.3	96.2	114	74.4	24.0	32.2	43.9-114
^{13}C-1,2,3,6,7,8-HxCDF	50	104	93.6	63.8	94.9	86.4	78.2	101	77.1	85.0	12.8	15.1	63.8-101
^{13}C-1,2,3,4,6,7,8-HpCDF	50	109	124	112	101	107	112	115	88.3	108.5	11.4	10.5	88.3-124

[a]Blank results are not included in statistics. Values are limits of quantitation (ng/g) based on a 1.0-g sample size.
[b]SD = Standard deviation
[c]RSD = Relative standard deviation
[d]ND = Not detected above LOQ required by 40 CFR 766.27.
[e]NA = Not applicable -- values are beneath LOQ.
[f]Outside 50%-150% range specified by Rule.

Table 2. Example of Limit of Quantitation Determination

Limit of Quantitation Determination--Sample 573

Internal standard	Spike level (ng/g)	Signal:noise	% Recovery First sample	% Recovery Second sample	Average	%R[a]
$^{13}C_{12}$-2,3,7,8-TCDD	0.1	12:1	63.1	72.4	67.8	13.7
$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.5	50:1	90.2	115	102	24.3[b]
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	2.5	50:1	123	145	134	16.4
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	1000:1	62.4	72.6	67.5	15.1
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50:1	61.6	63.4	62.5	2.9
$^{13}C_{12}$-1,2,3,7,8-PeCDF	5.0	50:1	45.6[c]	51.2	48.4	11.6
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	25.0	100:1	105	89	97.1	16.3
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1000	1000:1	102	121	112	16.9

[a]%R = Range percent = [(high-low)/average)] x 100.
[b]Outside the QA objective of ±20%.
[c]Outside the QA objective of 50%-150% recovery.