

Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

EPA Method 1613, Revision A (October 1990)

Table 1A. Summary of Holding Times and Preservation for Dioxins and Furans by Isotope Dilution HRGC/HRMS

Analytical Parameter ^a	Technical and Contract Holding Times	Preservation
Tetra- through octa-chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in Water ^b	<u>Technical for Extraction:</u> 7 days from collection; <u>Contract for Extraction:</u> 5 days from receipt at laboratory; <u>Technical and Contract for Analysis:</u> 40 days from extraction	Amber glass; Cool to 4EC ±2EC; Keep away from light;
Tetra- through octa-chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in Soil	<u>Technical for Extraction:</u> 14 days from collection; <u>Contract for Extraction:</u> 10 days from receipt at laboratory; <u>Technical and Contract for Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC; Keep away from light

^a Individual target compounds are listed in Table 1B.

^b Aqueous samples must be filtered prior to extraction as outlined in Sections 10.3 and 10.4 of EPA Method 1613A.

Data Calculations and Reporting Units:

Calculate the response factor (RF) and the sample concentrations of target compounds following Sections 7.6.1 and 16 of EPA Method 1613A.

Report water sample results in concentration units of picogram per liter (pg/L). Report soil sample results on a dry-weight basis in concentration units of nanogram per kilogram (ng/kg). Report percent solid and percent moisture to the nearest whole percentage point.

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

Table 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits for Dioxins and Furans by EPA Method 1613A

COMPOUND	CAS No.	CRQL Water (pg/L) ^a	CRQL Soil (ng/kg) ^a
2,3,7,8-TCDD	1746-01-6	10	1
Total-TCDD	41903-57-5	10	1
2,3,7,8-TCDF	51207-31-9	10	1
Total-TCDF	55722-27-5	10	1
1,2,3,7,8-PeCDD	40321-76-4	50	5
Total-PeCDD	36088-22-9	50	5
1,2,3,7,8-PeCDF	57117-41-6	50	5
2,3,4,7,8-PeCDF	57117-31-4	50	5
Total-PeCDF	30402-15-4	50	5
1,2,3,4,7,8-HxCDD	39227-28-6	50	5
1,2,3,6,7,8-HxCDD	57653-85-7	50	5
1,2,3,7,8,9-HxCDD	19408-74-3	50	5
Total-HxCDD	34465-4608	50	5
1,2,3,4,7,8-HxCDF	70648-26-9	50	5
1,2,3,6,7,8-HxCDF	57117-44-9	50	5
1,2,3,7,8,9-HxCDF	72918-21-9	50	5
2,3,4,6,7,8-HxCDF	60851-34-5	50	5
Total-HxCDF	55684-94-1	50	5
1,2,3,4,6,7,8-HpCDD	35822-46-9	50	5
Total-HpCDD	37871-00-4	50	5
1,2,3,4,6,7,8-HpCDF	67562-39-4	50	5
1,2,3,4,7,8,9-HpCDF	55673-89-7	50	5
Total-HpCDF	38998-75-3	50	5
OCDD	3268-87-9	100	10
OCDF	39001-02-0	100	10

^a In order to achieve these CRQLs, sample extracts may require removal of sample interferences by one or more of the cleanup procedures listed in EPA Method 1613A prior to analysis, including gel permeation chromatography (GPC) (Section 12.2), silica gel cleanup (Section 12.3), alumina cleanup (Section 12.4), AX-21/Celite (Section 12.5), and high performance liquid chromatography (HPLC) (Section 12.6).

Table 2. Summary of Calibration Procedures for Dioxins and Furans by EPA Method 1613A

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points) (ICAL) ^{a, b, c}	Initially; whenever required, due to failure of CCV	RSD for RFs #30%	1. Terminate analysis 2. Re-calibrate and verify before sample analysis
RT window defining standard mixture ^d	As part of ICAL and when RT shifts are observed during daily calibrations which are significant enough to hinder identification of isomers within individual descriptors	Guidance provided in EPA Method 1613A	1. Identify the problem. 2. Criteria must be met before any samples, blanks, or QC samples are analyzed
Isomer specificity test standards ^e	Analyzed daily at beginning of 12-hour period	Separation between adjacent peaks must be 75% or greater.	1. Identify the problem. 2. Criteria must be met before any samples, blanks, or QC samples are analyzed
Continuing Calibration Verification (CCV) (mid-point concentration for each analyte)	Beginning of each day, after each group of 10 samples	%D between RF of CCV and avg RFs from ICAL #25%; RT for all analytes within the RT windows established in the ICAL	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV
High Resolution Mass Spectrometry (HRMS) tune ^f	Beginning of each 12-hour period during which standards and samples are analyzed	Criteria specified in EPA Method 1613A	1. Identify the problem. 2. Criteria must be met before any calibration standards, samples, blanks, or QC samples are analyzed
Internal Standards ^g	All calibration standards, samples, method blank, and QC samples	IS area within a factor of two of the IS area in the associated CCV (-50% to +100%)	1. Investigate the system for malfunction; 2. Re-analyze all samples analyzed during a system malfunction

^a The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio 5:1. If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

^b ICAL and CCV standards must contain all target analytes listed in Table 1B. Calibration standards must include, in addition to the native compounds, all labeled compounds, a cleanup standard and the internal standards listed in Table 4 of EPA Method 1613A.

^c Calibration standards that do not compare acceptably with reference standards must be replaced (refer to the standard solution acceptance criteria specified in Section 6.17 of EPA Method 1613).

^d RT window defining standard mixture should be prepared as specified in Section 6.15 of EPA Method 1613A. This mixture should contain the PCDD/PCDF isomers indicated in Table 5 of EPA Method 1613A. Sections 7.2.4, 7.3 and 13 of EPA Method 1613A should be followed for establishing RT windows, using Table 2 for guidance.

^e Isomer specificity test standards should be analyzed according to Sections 6.16 and 7.4 of EPA Method 1613A to demonstrate adequate separation between TCDD and TCDF isomers.

^f High Resolution Mass Spectrometry (HRMS) tune should be performed according to Sections 14.2 of EPA Method 1613A.

^g The internal standard compounds to be used are ¹³C₁₂-1,2,3,4-TCDD and ¹³C₁₂-1,2,3,7,8,9-HxCDD (see Sections 6.12 and 13.2 of EPA Method 1613A)

The laboratory must either demonstrate the ability to achieve chromatographic separation of 2,3,7,8-substituted isomers or analyze all samples on two chromatographic columns with different liquid phases.

RFs for native compounds with corresponding labeled analogs are quantitated using isotope responses. RFs for native compounds without labeled analogs are quantitated using internal standard responses. Sample quantitation is to be done using the RRFs from the daily continuing calibration.

Table 3. Summary of Internal Quality Control Procedures for Dioxins and Furans by EPA Method 1613A

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Each 12-hour time period, minimum of one per SDG ^a (After each CCV and after the analysis of unusually concentrated samples)	< CRQL for each compound	1. Investigate the source of contamination and document. 2. Re-analyze all samples processed with a blank that is out of control.
Surrogate Spike ^b	One per batch or SDG	Recoveries of 40-120% for water and soil samples.	1. Re-analyze all samples with non-compliant surrogate spike recoveries.
Cleanup Standard ^{c, d}	Whenever sample extracts requires cleanup procedures	Recoveries of 40-120% for water and soil samples.	1. Re-analyze all samples with the recoveries outside the QC limits.

^a SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

^b All calibration standards, samples and QC samples must be spiked with a labeled compound spiking solution as indicated in Sections 6.10, 8.1.4, 10.3.2, and 10.4.2 of EPA Method 1613A. The spiking solution must contain ¹³C₁₂-tetra- through ¹³C₁₂-octa-CDDs and ¹³C₁₂-tetra- through ¹³C₁₂-hepta-CDFs as indicated in Table 4 of EPA Method 1613A, at the listed concentrations.

^c All sample extracts requiring cleanup procedures must be spiked with a cleanup standard containing ³⁷Cl₄-2,3,7,8-TCDD prepared in nonane as noted in Sections 6.11 and 11.1.3.1 of EPA Method 1613. All calibration standards must be spiked with the cleanup standard as discussed in Section 8.a.1 in Sections 6.13 and 7.7 of EPA Method 1613A. The cleanup standard must contain ³⁷Cl₄-2,3,7,8-TCDD at the concentrations listed in Table 4 of EPA Method 1613A.

^d If sample extract cleanup by GPC and/or HPLC methods is performed, standards recoveries of >85% for GPC and 75-125% for HPLC must be demonstrated as specified in Sections 12.2 and 12.6 of EPA Method 1613A.

All positive sample results must meet the qualitative identification criteria specified in Section 15 and the isotopic ratio criteria listed in Table 3A of EPA Method 1613A.

Dilute and re-analyze samples which contain one or more target analytes at concentrations above the initial calibration range. Results for such re-analyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.