



Determination of Chlorinated Dioxins and Furans in Four Types of Wastewater by EPA Method 1613 Rev. B

Application Note

Environmental

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Abstract

CDS Empore™ C18 (Formerly 3M™ Empore™ C18) SPE Disks help ensure rapid and reliable sample preparation and provide excellent analyte recovery in the screening or monitoring of Dioxins and Furans in 4 types of wastewater samples for EPA Method 1613 Rev. B.

Introduction

EPA Method 1613 was developed by the United States Environmental Protection Agency's Office of Science and Technology for isomer-specific determination of the 2,3,7,8-substituted, tetra through octa-chlorinated, dibenzo-p-dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS). EPA Method 1613 contains extraction directions for several matrices including aqueous, solid, and tissue samples. The CDS Empore™ disk extraction procedure is applicable to aqueous matrices in Method 1613^{1,2}.

CDS Empore™ C18 SPE Disks are compatible with the specified requests from this method: large sample volume (1 liter) and low pH (pH 2). Empore™ C18 Disks can consistently work with large samples and low pH without loss of C18 phase from the silica support in the membrane disks. EPA specially emphasizes that the potential damage of phase stripped from the extraction disk packing at pH 2 is to complicate the chromatographic analysis with high background, which could obscure compounds of interests.

In this application note, the one-liter aqueous samples from 4 types of wastewater, including Publicly Owned Treatment Works (POTW) final effluent, petroleum refinery American Petroleum Institute (API) separator and secondary treatment effluent, and a river water, were spiked with isotopically labeled analogs of the Chlorinated Dibenzo Dioxins/Chlorinated Dibenzo Furans (CDDs/CDFs). Those samples containing sediment can either be filtered off-line or in-situ (a prefilter placed above the Empore™ disk in the extraction glassware) with the extraction disk. Samples (pH 2, 5 mL methanol) were extracted with a C18 disk. Both the prefilter and the C18 disk were placed in a Soxhlet thimble and extracted 16-24 hours with toluene. The extract was subjected to the standard clean-up and concentration techniques as in the previous version of Method 1613. The detection method was Isotope Dilution HRGC/HRMS.

The validation data presented herein were determined on three independent lots of C18 disks. MDLs were not determined as part of this validation.

Experimental Setup

1. This extraction option is applicable only to aqueous samples. Measure sample volume. Add isotopically labeled analogs, 5 mL methanol, and pH to 2. Allow the sample to sit and the sediment settle as much as is practical.

2. Assemble an all glass filtration assembly using a 90 mm CDS Empore™ extraction disk containing C18. For samples with no particulates, a 47mm disk can be used. Use of a manifold for multiple extractions is acceptable.



If samples contain significant quantities of particulates, the use of an in-situ glass micro-fiber prefilter (Whatman GMF 150, 1-micron pore size or equivalent) is advisable. The glass fiber prefilter is placed on top of the Empore disk prior to placement of the glass reservoir and clamp.

3. Prewash. Wash the extraction apparatus and disk by adding 15 mL of toluene to the reservoir washing down the sides of the glass reservoir in the process. Pull a small amount through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry. Repeat the wash step using 15 mL of acetone.

4. Condition. Pre-wet the disk by adding 15 mL methanol (MeOH) to the reservoir, pulling a small amount through the disk then letting it soak for about one minute. Pull most of the remaining MeOH through the disk, leaving 3-5 mm on the surface of the disk, which should not be allowed to go dry from this point until the sample extraction has been completed. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY. The disk is composed of hydrophobic materials. To make them amenable to a water solution, they must be pre-wetted with a water miscible solvent (MeOH) or they will not allow water to pass through the materials. Should the material accidentally dry before the sample is added, simply repeat the pre-wetting step.

5. Rinse the disk by adding 50 mL of reagent water to the disk and drawing most through, again leaving 3-5 mm of water on the surface of the disk. Repeat using a second 50 mL aliquot of water.

6. Extraction. Add the water sample to the reservoir and, under full vacuum, filter as quickly as the vacuum will allow. Drain as much water from sample bottle as possible. Particulate-free water may pass through the disk in as little as 10 minutes without reducing analyte recoveries. Allow the entire sample to pass through the disk then dry the disk by maintaining vacuum for about 3 minutes.

With heavily particle-laden samples, allow the sediment to settle, decant as much liquid as is practical into the reservoir. Allow most of the liquid to filter then swirl the sediment portion and add it to the reservoir. Before the entire sample has filtered, rinse the sample bottle with reagent water and add to the reservoir to transfer any particulates remaining in the bottle to the extraction. Drain as much water as possible from the sample bottle.

7. Disassemble the extraction glassware and carefully transfer both the Empore™ disk and the particle-laden GMF filter to the thimble of a Soxhlet Dean-Stark apparatus. Place a glass wool plug over the filters. Add about 50 mL toluene to the sample bottle, replace the cap and agitate well to rinse all remaining

residues into the toluene. Transfer the toluene to the Soxhlet apparatus. Repeat the bottle rinse three times. Using 10 mL toluene, rinse the extraction glassware reservoir and transfer to the Soxhlet.

8. Soxhlet extract for 16-24 hours. The data for this validation was generated using a 16-hour Soxhlet extraction.

9. Concentrate sample and proceed to clean-up and analysis as per the Method 1613 directions.

Results and Discussions

Validation studies for this method were performed on four types of wastewater provided by EPA. The effluents included POTW final effluent, petroleum refinery API separator and secondary treatment effluent, and a river water. Validation data on these samples were generated in a single laboratory with additional recovery data provided by pulp and paper mills on various matrices from their respective plants. The study was performed on triplicate samples of each matrix. One liter of each wastewater type was also analyzed for background levels. In addition, the post-extraction filtrate from the triplicate spikes was combined and liquid/liquid extracted to document the efficiency of extraction. In all cases, the combined filtrates were “not detected” for all analytes. Using the in-situ prefilter, settle/decant method described herein, all sample extractions were completed in under 20 minutes.

The spike level is from 200 pg/L to 2000 pg/L with 3 repeats. For 4 types of wastewater in this study, all 16 targeted dioxins and furans native compounds have the recovery rate between 85%-123%, and only one recovery for 12378-PeCDD at POTW effluent is below 90% (88%), and only one recovery for 123678-HxCDD at river water is over 120% (123%). All other recovery rates of the 16 monitored compounds fall in 90%-120% range. Together all of recovery rates of the 16 monitored compounds in all 4 types of wastewater in this study fall in 75-125% range per EPA Method 1613B requirement. The average recovery for native compounds from these 4 types of wastewater are 109%, which are much better than those from internal standards.

Conclusions:

A simple and effective method to extract organic compounds from large volume wastewater samples (1000 ml) by CDS Empore™ C18 47mm disks has been developed. 16 tetra-to-octa chlorinated, dibenzo-p-dioxins and dibenzofurans listed in EPA Method 1613 have been studied in this experiment. They have been extracted from 4 types of wastewater samples (including POTW final effluent, petroleum refinery API separator and secondary treatment effluent, and a river water), and then quantified by high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS) with concentration at 0.2 ppb to 2.0 ppb. With our extraction procedures, recovery exceeded 90% for most native compounds in the wastewater samples, and only 1 compound has the recov-

ery of 88% in POTW effluent, and 1 compound has the recovery of 123% in river water sample. Together all of recovery rates of the 16 monitored compounds in all 4 types of wastewater in this study fall in 75-125% range per EPA Method 1613B requirement. The average recovery of native compounds from these 4 types of wastewater is 109%.

Excellent analyte recovery and very clean chromatograms can be obtained by using CDS Empore™ C18 disks. If you are screening wastewater samples according to EPA Method 1613 Rev. B – or monitoring chlorinated dibenzo-p-dioxins and dibenzofurans in wastewater – CDS Empore™ C18 disks will help to ensure rapid, economical, reliable sample preparation for you.

References:

1. Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. Issued October 1994 by US EPA Office of Water. Water Resource Center; Mail Code RC-4100; 401 M Street SW; Washington, D.C. 20460

2. EPA Method 1613. Determination of the 2,3,7,8-substituted, tetra through octa-chlorinated, dibenzo-p-dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/ high resolution mass spectrometry (HRMS) (Revision B). Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH USA 45268.

Validation Data

Analyte	Spike Level pg/L	POTW Effluent %R(RSD)	Refinery Effluent		River Water %R(RSD)
			API %R(RSD)	Final %R(RSD)	
Native					
2378-TCDD	200	101(5.7)	109 (11)	110 (5.6)	112 (2.6)
12378-PeCDD	1000	88(1.0)	110 (9.1)	110 (0.6)	115 (1.5)
123478-HxCDD	1000	99(9.0)	114 (4.9)	108 (2.5)	116 (1.5)
123678-HxCDD	1000	99(9.0)	105 (3.0)	106 (1.5)	123 (2.6)
123789-HxCDD	1000	99(5.6)	118 (15)	109 (1.5)	115 (6.1)
1234678-HpCDD	1000	102(4.9)	108 (0.6)	108(0.6)	110(2.1)
OCDD	2000	111(3.6)	B 119(3.5)	B 119(2.6)	B 116(1.0)
12378-PeCDF	1000	90(1.7)	115 (6.8)	111 (1.5)	116 (0.6)
23478-PeCDF	1000	98(4.0)	113 (6.6)	111 (2.7)	114 (1.0)
123478-HxCDF	1000	100 (3.6)	110(6.0)	108 (6.0)	118 (0.6)
123678-HxCDF	1000	100 (5.0)	110 (2.6)	105 (2.1)	116 (1.0)
234678-HxCDF	1000	94(1.7)	108 (2.5)	101 (1.5)	114 (1.0)
123789-HxCDF	1000	95(4.2)	107 (5.0)	104 (2.1)	118 (2.6)
1234678-HpCDF	1000	B 110 (2.1)	109 (8.6)	100 (3.0)	119 (2.0)
1234789-HpCDF	1000	103 (4.0)	106 (10)	100(1.5)	119 (2.0)
OCDF	2000	105 (9.8)	119 (313)	115 (3.5)	119 (7.2)
Other Standards					
37C1 -TCDD		62(6.2)	64(1.8)	71(9.1)	63(1.5)
Internal Standards					
13C12-2378-TCDD		56(6.7)	64 (2.8)	71 (8.5)	59 (1.9)
13C12-PeCDD 123		82(12)	61 (12)	72 (15)	83 (5.0)
13C12-HxCDD 478		76 (2.9)	87 (18)	99 (5.2)	80 (4.2)
13C12-HxCDD 678		72 (2.3)	70 (12)	76 (5.0)	76 (2.5)
13C12-HpCDD 678		71 (4.2)	87 (6.7)	83 (20)	83 (2.6)
13C12-OCDD		69 (6.0)	80 (14)	86 (4.9)	79 (8.4)
13C12-PeCDF 123		67 (7.2)	61 (9.3)	77 (13)	74 (3.4)
13C12-PeCDF 234		61 (5.3)	63 (9.3)	79 (14)	80 (4.7)
13C12-HxCDF 478		82 (7.2)	81 (14)	96 (1.8)	71 (6.8)
13C12-HxCDF 678		69 (4.0)	72 (6.4)	79 (1.4)	69 (6.3)
13C12-HxCDF 234		80 (2.4)	76(7.3)	85 (1.4)	73 (0.9)
13C12-HxCDF 789		73 (1.6)	78 (7.7)	85 (5.7)	75 (1.4)
13C12-HpCDF 678		63 (2.5)	78(9.4)	77 (14)	69 (11)
13C12-HpCDF789		68 (1.1)	85(5.7)	80 (20)	81 (2.4)

B= Present in blank sample

n=3

2,3,7,8-TCDF Not Determined

Average Recovery Native Compounds = 109%