

VALIDATION OF EMPORE™ SOLID PHASE SORBENT DISKS FOR THE EXTRACTION OF PCDDs AND PCDFs FROM WASTEWATERS - EPA METHOD 1613B

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ABSTRACT

Solid phase extraction (SPE) was evaluated as an alternative wastewater sample preparation technique for the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). In situ or off-line prefiltration can be used in conjunction with SPE to minimize plugging thereby obtaining reasonable extraction times. Both the particulate-adsorbed analytes now isolated on a prefilter and dissolved PCDD/DFs adsorbed to the sorbent disk are eluted by a single Soxhlet extraction. The results confirm that SPE provides equivalent recoveries of both native congeners and labeled standards. In addition, the nature of SPE eliminates emulsion formation and significantly reduces solvent usage and sample preparation time. The revised method, EPA Method 1613 Revision B is published and currently approved for use on drinking waters.¹ Approval for use on wastewaters is anticipated by August 1995.

INTRODUCTION

The conventional wastewater extraction procedure for PCDD/DFs involves phase separation by mechanical filtration followed by Soxhlet extraction of the solids portion. The liquid phase is liquid-liquid extracted (LLE) three times with 200 mL methylene chloride. Both extracts are combined for cleanup and analysis. The liquid phase LLE is commonly subject to emulsion formation which prolongs sample preparation time as techniques are employed to break the emulsion before the LLE can proceed. SPE was evaluated as an alternate sample preparation technique to eliminate emulsion formation thus reduce the labor intensity and consequently sample preparation time.

SPE in packed cartridge format has been used for many years, typically restricted to small volume samples because of flow rate limitations. The introduction of sorbents in a membrane format allows significantly faster flow rates thus rendering SPE practical for one liter (and larger) samples.

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Octadecyl (C18) sorbent functionality is based on hydrocarbon bonding of hydrophobic compounds. The low water solubility of PCDD/DFs makes them ideal candidates for SPE using this mechanism. The affinity of 2,3,7,8-TCDD was initially demonstrated in EPA's proposed Method 513 for drinking waters.² This study incorporated the full congener group monitored in the current EPA wastewater methods. It also focused on sample extraction conditions and corresponding results. Sample clean up and analytical instrument conditions were not varied from the previously approved version of Method 1613.

EXPERIMENTAL SECTION

The EPA provided four types of wastewater for this validation. Each was spiked and analyzed in triplicate. They included POTW final effluent, API separator effluent and secondary treatment effluent from a petroleum refinery, and a river water sample. After each one liter spiked sample was extracted, the filtrates from the triplicate samples were combined and liquid-liquid extracted to document the lack of breakthrough. No additional labeled standards were spiked into this mixture and in all cases, no breakthrough occurred. Additional recovery data using this method on pulp and paper mill effluents was voluntarily provided to EPA by Boise Cascade, Champion International, and International Paper.

Equipment

Extractions for this study were performed on an Empore extraction manifold equipped with three 90mm glassware sets. SPE disks were 3M Empore C18, 90mm size. The in-situ prefilters were multi-grade GMF-150 (1 micron pore size) commercially available from Whatman. All other apparatus and equipment were as outlined in the method. Sample preparation and analyses were performed by an independent contract laboratory. 3M provided the materials for extraction and technical assistance.

Extraction Procedure

The method used for this study was initially developed by Sarah Barkowski for Boise Cascade Corporation use in monitoring mill effluents for 2,3,7,8-TCDD and 2,3,7,8-TCDF.

The samples were prepared by spiking with the native and labeled standards. Five mLs of methanol was added to each and the pH adjusted to 2.0. Each sample was mixed well and allowed to equilibrate at room temperature. The equilibration also allowed the sediment to settle as much as was practical.

A 90 mm C18 Empore disk was placed on the base of the extraction glassware set and Whatman GMF 150 glass microfiber prefilter placed on top. The glass reservoir was then clamped in place and the glassware and both membranes prerinsed with toluene

to remove any background materials from storage and handling. A second prewash using acetone was followed by an air dry step.

The disk and prefilter were then soaked with an aliquot of methanol to precondition the naturally hydrophobic disk materials. Some of the methanol was drawn through using a vacuum, leaving a small amount in the reservoir. Reagent grade water was added to the reservoir to dilute the remaining methanol, and most of it drawn through with the vacuum.

The sample was then added to the reservoir. Rather than agitating the sample, as routinely done in separatory funnel extractions, decanting the liquid and allowing that to filter through the sorbent before adding the sediment was a technique that kept the sorbent disk from plugging. As it neared completion, the remaining liquid was agitated to resuspend the sediment and added to the remaining liquid in the reservoir. The sample bottle was rinsed with a small amount of reagent water to recover any remaining particulate and the rinsate added to the reservoir. This method of sample addition provided the fastest extraction times without having to do off-line prefiltration.

When the entire sample passed through the disk, it was air dried for a few minutes. The reservoir was removed and the prefilter and disk transferred to a precleaned extraction thimble. A glass wool plug was placed over the filters. The sample bottle was rinsed with 50mL toluene and the solvent transferred to the Soxhlet apparatus. A 10 mL toluene rinse of the reservoir was also done and the solvent added to the Soxhlet.

An 18 hour Soxhlet extraction was then done of the prefilter and disk as per the method directions.

RESULTS

Average recovery for spiked native congeners for all samples was 109%. Relative standard deviations for the triplicate sets ranged from 0.6 - 13, with most well under 10. Internal standard recoveries were well within acceptable ranges. Recoveries for native and labeled standards are summarized on Table 1.

The SPE disk extraction method has been shown to perform equivalently to the LLE/Soxhlet sample preparation method for wastewater samples.

DISCUSSION

As part of the validation study, the combined use of the settle/decant technique and GMF 150 prefilter were found to be so effective that none of the samples in this study required off-line filtration. In discussions with the method's originator, since switching to the GMF 150 filters, they no longer prefilter samples as even the worst of their matrices have extraction times of less than 30 minutes.

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TABLE I
EPA Method 1613B
Dioxin/Dibenzofuran Validation Study

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)	112 (4.2)	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 (13)	115 (3.5)	119 (7.2)
Other Standards					
37Cl-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-HpCDF 789		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%