INVESTIGATING THE EXTRACTION EFFICIENCY OF DIOXINS IN SEVERAL TYPES OF AQUEOUS MATRICES BY AUTOMATED SOLID PHASE EXTRACTION UTILIZING DISKS

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Introduction

Dioxins are of great environmental concern due to their teratogenic, mutagenetic, and carcinogenic impact. These lipophilic compounds bioaccumulate in humans and wildlife and can have half lives of up to 132 years. Traditional SPE requires a filtration step to remove particulates when using SPE cartridges, because of clogging issues. The filtered particulates then require another extraction step, such as soxhlet extraction. Liquid-liquid Extraction (LLE) often has issues with emulsions that can adversely affect the proper extraction of the particulate matter.

Using the automated 47 mm SPE disk approach allows for the extraction to take place without the problems such as clogging, filtration or emulsions. The SPE Disk allows for the dioxin compounds in the water to be retained to the divinylbenzene (DVB) disk packing while the water passes through. It also allows the particulate matter to sit on the top of the disk. This way, when the elution solvents are delivered to extract the disk, they can also extract any dioxin compounds that may have attached to suspended particulates or sediment, allowing for extraction of the "whole sample". The disks combine fast flow rates without compound breakthrough, allowing efficient extraction of particulate laden samples larger than 1 liter with great recoveries and low detection limits. This presentation will focus on SPE extraction techniques, results and recoveries of dioxins in deionized and particulate laden river water samples and waste water.

Materials and Methods

Extractions of samples were accomplished using Horizon Technology's SPE-DEX 4790 with the Envision platform controller.   SPE extraction disks were Atlantic DVB disks 47 mm, and pre-filters. Extraction solvents were methylene chloride, acetone, methanol, reagent water, hexane, and nonane. Samples were dried using sodium sulfate and then cleaned up using a coupling column, containing silica gel, alumina and florisil. Samples were concentrated on a Genivac mi vac, and analytical analysis was carried out by high resolution gas chromatography (HRGC) / high resolution mass spectroscopy (HRMS).

Results and Discussion:

Due to the persistent nature of these compounds great care needs to be taken to ensure all glassware and extraction system components are clean in order to assure no cross contamination between samples or interferences in method blanks or low level samples. A cleaning procedure was developed using organic solvents and mild detergent that assures the extractors liquid flow path is free of contaminants between samples.

12 samples were prepared, extracted, and analyzed in order to demonstrate the effectiveness of the SPE method and to compare matrix effects. Two samples were distilled water 500 mls each acting as Laboratory Control Spikes (LCS's), six very fine particulate laden river samples 500 mls each, two river samples 300mls each containing fine particles and sediment, and finally two waste water influent samples 500mls each.   All sample sizes were reduced due to the use of the 47 mm extraction disks. Dioxins and furans are known to bind to sediment or suspended particles so these types of samples were ideal as reference matrix spikes. Each of the 12 samples was spiked with 25uL of a 20pg/µl solution containing CDDs and CDFs and a 40 pg/µl for OCDD and OCDF. The following method in Table 1 was programmed into the envision controller for a 47mm disk and was used for all of the runs in this study.

Table 1 Envision Platform Extraction Method

Steps	Solvent	Soak	Air-Dry
Pre-Wet 1	DCM	1 Min	1 Min
Pre-Wet 2	Acetone	1 Min	1 Min
Pre-Wet 3	MeoH	1 Min	4 sec
Pre-Wet 4	Water	5 sec	2 sec
Pre-Wet 5	Water	0 sec	0 sec
Sample Introduction			
Air-Dry Time 5 min			
Rinse 1	Acetone	1 min 30 sec	30 sec
Rinse 2	DCM	1 min 30 sec	30 sec
Rinse 3	DCM	1 min 30 sec	30 sec

The clean LCS samples were processed very quickly up to 150 mls/minutes. A sample pre-filter was used with the particulate laden river samples and the sediment laden samples. The flow rates through these samples were slower than the LCS samples. Additionally, it was determined that increasing the soak times with the multiple rinse steps in the particulate laden samples will optimize the extraction efficiency of the automated extractor. One of the unique features in the design of this extraction system is that the original sample bottle is automatically rinsed.

25 mls of extracts consisting of methylene chloride and acetone 80:20 were collected, dried with sodium sulfate and concentrated to 100 uL on the Genivac Mi Vac. Solvent extracts were exchanged with 3.0 mls of hexane, 2 times to ensure complete solvent exchange takes place. The Sample extracts were then brought up to 1 ml volume and cleanup was carried out with a coupling column with silica gel, alumina and florisil. Final concentration was carried out on the Genivac mi vac to 100 uL, 25 uL of Nonane is added and placed back on the concentrator until a final volume of 25 uL is reached. Results for these samples are shown in tables 3, 4, 5, and 6.

Samples were analyzed by HRGC/HRMS under the following conditions
Instrument Conditions: HRGC/MS
- Column = DB5 (60m)
- Flow = 1mL/min
- Column Temp = 180°C to 190°C at 2°C/min then 190°C to 240° C at 5°C/min
- Sample Injection Volume = 1.8μL
- Run Time: 52 minutes

In order to know how much recovery would be lost to the drying and concentration steps, 25 mL methylene chloride was spiked with 25uL of a 20pg/µl solution containing CDDs and CDFs and a 40 pg/µl for OCDD and OCDF. These spikes were dried, treated with florisil, silica gel, and alumina and concentrated. The following table reports losses in recovery associated with these steps. Results for dried down methylene chloride spike is shown in Table 2

Table 2 Methylene Chloride Spike (Dried, treated and concentrated)

Compounds	%Recovery	% Loss
2,3,7,8-TCDF	93.7	6.3
1,2,3,7,8-PeCDF	87.9	12.1
2,3,4,7,8-PeCDF	95.6	4.4
1,2,3,4,7,8-HxCDF	107.0	0
1,2,3,6,7,8-HxCDF	106.6	0
2,3,4,6,7,8-HxCDF	105.7	0
1,2,3,7,8,9-HxCDF	102.1	0
1,2,3,4,6,7,8-HpCDF	60.0	40.0
1,2,3,4,7,8,9-HpCDF	61.8	38.2
OCDF	65.4	34.6
2,3,7,8-TCDD	91.4	8.6
1,2,3,7,8-PeCDD	94.6	5.4
1,2,3,4,7,8-HxCDD	102.4	0
1,2,3,6,7,8-HxCDD	109.9	0
1,2,3,4,6,7,8-HpCDD	60.4	39.6
OCDD	41.8	58.2

Table 3 DI Water LCS

Compounds	Sample 1 %Recovery	Sample 2 %Recovery	RSD
2,3,7,8-TCDF	74.2	91.7	12.37
1,2,3,7,8-PeCDF	78.6	87.6	6.36
2,3,4,7,8-PeCDF	70.4	85.0	10.32
1,2,3,4,7,8-HxCDF	85.2	76.4	6.22
1,2,3,6,7,8-HxCDF	85.3	76.2	6.43
2,3,4,6,7,8-HxCDF	72.6	82.9	7.28
1,2,3,7,8,9-HxCDF	74.6	83.0	5.94
1,2,3,4,6,7,8-HpCDF	70.1	52.4	12.52
1,2,3,4,7,8,9-HpCDF	65.5	56.0	6.72
OCDF	63.6	55.0	6.08
2,3,7,8-TCDD	70.9	82.8	8.41
1,2,3,7,8-PeCDD	98.6	85.0	9.62
1,2,3,4,7,8-HxCDD	75.4	79.4	2.83
1,2,3,6,7,8-HxCDD	70.5	87.3	11.88
1,2,3,4,6,7,8-HpCDD	70.0	53.3	11.81
OCDD	69.2	36.6	23.05

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Table 4 River water with fine particulates

Compounds	1 %Recovery	2 %Recovery	3 %Recovery	4 %Recovery	5 %Recovery	6 %Recovery	RSD
2,3,7,8-TCDF	94.0	91.8	115.3	85.1	91.4	86.9	10.91
1,2,3,7,8-PeCDF	94.2	92.7	100.4	84.2	81.2	78.8	8.46
2,3,4,7,8-PeCDF	101.2	96.0	104.6	85.8	87.3	83.3	8.82
1,2,3,4,7,8-HxCDF	80.5	81.5	111.3	80.0	84.0	86.5	12.01
1,2,3,6,7,8-HxCDF	79.6	80.4	107.9	78.1	81.8	82.7	11.29
2,3,4,6,7,8-HxCDF	82.7	85.3	114.9	81.3	88.1	90.6	12.44
1,2,3,7,8,9-HxCDF	83.5	83.1	101.3	83.0	89.4	94.7	7.55
1,2,3,4,6,7,8-HpCDF	71.9	70.0	97.3	76.7	75.5	76.1	9.85
1,2,3,4,7,8,9-HpCDF	83.5	83.3	112.9	84.7	91.0	90.5	11.27
OCDF	96.4	87.9	123.9	95.0	107.0	100.7	12.53
2,3,7,8-TCDD	81.4	79.9	110.7	75.2	89.9	85.1	12.61
1,2,3,7,8-PeCDD	99.7	91.8	104.2	77.6	88.2	82.9	10.03
1,2,3,4,7,8-HxCDD	79.6	81.8	117.6	81.2	86.7	87.1	14.34
1,2,3,6,7,8-HxCDD	79.9	84.0	114.3	79.4	85.1	85.0	13.15
1,2,3,4,6,7,8-HpCDD	78.7	71.3	102.6	73.8	76.7	81.5	11.28
OCDD	74.7	67.9	99.5	72.4	73.9	70.1	11.58

Table 5 Fine Particulate and Sediment Laden River Water

Compounds	Sample 1 %Recovery	Sample 2 %Recovery	RSD
2,3,7,8-TCDF	78.4	61.0	12.30
1,2,3,7,8-PeCDF	81.1	60.9	14.28
2,3,4,7,8-PeCDF	82.6	62.5	14.21
1,2,3,4,7,8-HxCDF	67.2	56.9	7.28
1,2,3,6,7,8-HxCDF	70.0	54.3	11.10
2,3,4,6,7,8-HxCDF	69.0	56.1	9.12
1,2,3,7,8,9-HxCDF	66.9	60.4	4.60
1,2,3,4,6,7,8-HpCDF	58.1	49.8	5.87
1,2,3,4,7,8,9-HpCDF	63.2	58.5	3.32
OCDF	75.9	66.4	6.72
2,3,7,8-TCDD	71.1	54.0	12.09
1,2,3,7,8-PeCDD	82.3	59.4	16.19
1,2,3,4,7,8-HxCDD	72.0	54.3	12.52
1,2,3,6,7,8-HxCDD	69.7	54.0	11.10
1,2,3,4,6,7,8-HpCDD	65.9	53.3	8.91
OCDD	61.9	50.9	7.78

Table 6 Waste Water Influent Samples

Compounds	Sample 1 %Recovery	Sample 2 %Recovery	RSD
2,3,7,8-TCDF	88.3	87.6	0.49
1,2,3,7,8-PeCDF	71.3	69.2	1.48
2,3,4,7,8-PeCDF	81.6	77.6	2.83
1,2,3,4,7,8-HxCDF	76.9	74.5	1.70
1,2,3,6,7,8-HxCDF	75.5	72.5	2.12
2,3,4,6,7,8-HxCDF	86.1	84.8	0.92
1,2,3,7,8,9-HxCDF	86.7	81.9	3.39
1,2,3,4,6,7,8-HpCDF	54.8	48.0	4.81
1,2,3,4,7,8,9-HpCDF	75.8	55.8	14.14
OCDF	79.3	28.1	36.20
2,3,7,8-TCDD	91.8	91.9	0.07
1,2,3,7,8-PeCDD	79.5	81.1	1.13
1,2,3,4,7,8-HxCDD	85.1	85.8	0.49
1,2,3,6,7,8-HxCDD	79.5	84.6	3.61
1,2,3,4,6,7,8-HpCDD	64.7	60.1	3.25
OCDD	61.2	54.9	4.45

The faster extraction rate of the LCS water samples yielded lower results (Table 3) due to the high flow rates through the extraction disk. Samples with suspended particles and slower flow rates through the extractor yielded higher recoveries than the LCS (Table 4). The suspended particles and sediment in the bottle did lower the recoveries due to the compounds natural tendency to adhere to soil particles (Table5). Waste water influent samples were analyzed and shown in (Table 6).

We were able to demonstrate an efficient SPE Disk technology for the extraction of several types of known water matrices for the detection of tetra through octa- chlorinated dioxins and furans with analytical sensitivities to PPT (ng/L) levels. We were able to achieve acceptable recoveries with particulate laden water samples without the means of another extraction apparatus such as SDS (Soxhlet/Dean-Stark extractor). This extraction method is very efficient, and provides a fast method of extracting these difficult compounds from water matrices.

Future work on these compounds will involve the extraction of larger volumes of samples (1 L or greater) using the Fast Flow Sediment Disk Holder. These studies will enable the analysis of "Dirtier" matrix type samples to be processed in a timely efficient manor while lowering detection limits to the range of PPQ (pg/L).

References:
EPA Method 1613, Revision B (Tetra- through Octa- Chlorinated Dioxins and Furans By Isotope Dilution HRGC/HRMS, EPA-821-B-94-005)