

EVALUATION OF SOLID PHASE EXTRACTION DISKS FOR THE DETERMINATION OF PCBs, PESTICIDES, PCDFs, AND PCDDs

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ABSTRACT

Solid phase extraction disks, consisting of reverse phase particulate enmeshed in a PTFE network, were evaluated as a replacement for the conventional liquid-liquid extraction technique. This technology requires smaller volumes of solvent, reduced the time required for extraction, and is not subject to emulsion formation. Recoveries of selected target analytes, including PCBs, pesticides, PCDDs and PCDFs, spiked into reagent water were quantitative, ranging typically from 70-130%. SFE was also evaluated for the desorption of the extracted analytes from the disks.

INTRODUCTION

EmporeTM extraction disks consist of 8 μm C₈ or C₁₈ bonded phase silica (90 Wt %) enmeshed in a network of PTFE fibrils. The disks which are 47mm X 0.5 mm and have flow-through pores of approximately 1 μm were designed for use in a standard laboratory filtration apparatus. They contain 500 mg of the particulate and have a target analyte capacity of approximately 25 mg.

Extraction based on the disk technology offers several significant advantages over the conventional liquid-liquid extraction technique typically employed for water analyses. It reduces the time required for extraction, reduces the volume of solvent required for extraction, and provides a concentration step without the necessity of removing a large volume of solvent. Since the sample is filtered through the disk, suspended particulate material is collected on the disk and is more effectively extracted by the eluting solvent. Emulsion formation is also prevented, since the aqueous sample is not in contact with

The solid phase extraction disks were evaluated using 1 liter aliquots of reagent water containing known concentrations of selected target analytes. The extraction apparatus was a 47-mm vacuum filtration unit attached to a one-liter side-arm flask. The side-arm flask was connected to an Edwards roughing pump rated at 50 l/s. The disk was mounted in the holder and washed with 10 ml of methylene chloride using the vacuum pump to draw the solvent through the disk and to dry it. The disk was then conditioned by pulling 10 ml of methanol through it, followed by 10 ml of water, with care being taken to prevent the disk from drying as this would cause non-reproducible results. The one-liter aliquot was then poured into the reservoir and pulled through the disk by means of the vacuum pump. After the extraction and a 10 minute drying period, the disk was transferred to a clean, dry extraction apparatus for elution. The elution was accomplished under a slight vacuum using two 5 ml portions of methylene chloride. The first 5 ml portion of solvent was allowed to soak on the surface of the disk for two minutes to facilitate a more efficient extraction. The 10 ml solution of eluted target analytes was then dried using sodium sulfate, and evaporated to a final volume using dry nitrogen gas. Extracts for PCB/pesticide analysis were analyzed by combined gas chromatography/mass spectrometry¹(GC/MS) without additional analyte enrichment, while extracts for PCDD/PCDF analysis were processed through several liquid chromatography columns². All PCDD/PCDF analyses were carried out using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS)².

RESULTS AND DISCUSSION

PCB/PESTICIDE EVALUATION

The results from the evaluation of the disk for the extraction of PCBs and pesticides are summarized in Table 1. Includes are the target concentration, the concentration of each analyte that was determined, and the relative standard deviation of seven replicates.

Table 1. Results of Using Solid Phase Extraction Disks For The Extraction of Selected PCBs and Pesticides

Analyte	Target Concentration	Accuracy	Relative Standard Deviation
Alachlor	2 ppb	77%	3.5%
Alachlor	0.2 ppb	55%	15%
Aldrin	2 ppb	107%	15%
Aldrin	0.2 ppb	130%	13%
Endrin	2 ppb	98%	6.1%
Endrin	0.2 ppb	117%	25%
Heptachlor	2 ppb	105%	15%
Heptachlor	0.2 ppb	139%	23%
Lindane	2 ppb	134%	21%
Lindane	0.2 ppb	110%	6.5%
PCB-Cl ₁	2 ppb	126%	11%
PCB-Cl ₁	0.2 ppb	78%	7.2%
PCB-Cl ₂	2 ppb	117%	19%
PCB-Cl ₂	0.2 ppb	87%	9.7%
PCB-Cl ₃	2 ppb	82%	29%
PCB-Cl ₃	0.2 ppb	95%	21%
PCB-Cl ₄	2 ppb	106%	7.4%
PCB-Cl ₄	0.2 ppb	107%	28%
PCB-Cl ₅	2 ppb	106%	15%
PCB-Cl ₅	0.2 ppb	84%	16%
PCB-Cl ₆	2 ppb	102%	26%
PCB-Cl ₆	0.2 ppb	96%	32%
PCB-Cl ₇	2 ppb	123%	32%
PCB-Cl ₇	0.2 ppb	141%	38%
PCB-Cl ₈	2 ppb	49%	38%
PCB-Cl ₈	0.2 ppb	99%	21%

EXTRACTION OF PCDD/PCDF ISOMERS

The PCDD/PCDF solid phase extraction experiments were designed to evaluate the ability of the disks to absorb PCDDs and PCDFs, as well as to compare three methods of desorbing the PCDDs and PCDFs from the disks. A total of nine aliquots of reagent water spiked with representative Cl₄-Cl₅isomers were prepared and extracted as described above. Three of the disks were desorbed using three 5 ml rinses with methylene chloride. Three of the disks were transferred to Soxhlet extractors and extracted for 18 hours with benzene, while the remaining three disks were transferred to supercritical fluid extraction (SFE) vessels and desorbed using supercritical carbon dioxide.

The SFE extractions were carried out using a Suprex Model SFE 150 instrument. The extraction time was 15 minutes for all experiments using SFE operating conditions previously optimized by analyzing EmporeTM disks that were directly spiked with known amounts of selected PCDD and PCDF isomers. Pressure regulation was provided by an integral restrictor located at the end of the extraction vessel under the collection solvent.

The SFE conditions were optimized using a statistical experimental design approach. The design employed two factors, temperature and pressure, at two levels (a 2² design). This approach allowed the data to be fit to a linear first-order model in each factor. The factorial design provided information on the primary effect of each factor, as well as the possible existence of an interaction term.

Conclusions

The EmporeTM disk was found to highly efficient for the extraction of selected chlorinated compounds from water. This paper provides not only data from the first evaluation of EmporeTM disks for the extraction of chlorinated compounds of environmental concern, but also information from one of the first systematic investigations of the use of SFE for desorbing organic analytes from an inert matrix. The results demonstrate the general utility of the disk and some insight into the competing effects of solubility and volatility.

¹ EPA Method 525

² EPA Method 1613