

EPA Method 8081: Automated Solid Phase Extractions of Organochlorine Pesticides from Water Using Certified for Automation Atlantic SPE Disks

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Introduction

Solid Phase Extraction (SPE) is an increasingly popular method to analyze trace contaminants in water samples. Benefits of the technique include less solvent usage and exposure, less time, and less effort than liquid-liquid extraction. SPE disks are a common media used to adsorb and elute analytes. In this study the effectiveness of the Atlantic SPE Disk in extracting organochlorine pesticides from water samples was investigated, and an optimized method of extraction developed.

Pesticide pollution is a subject of global concern and although many countries have now banned the use of organochlorine pesticides, they linger in the environment and can contaminate water sources. Organochlorine pesticides can be toxic to animals and humans, so methods which accurately and easily quantify them are essential. The organochlorine pesticides analyzed in this study were part of a standard mix consisting of alpha-, beta-, gamma- and delta-benzene hexachloride (BHC), 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, endosulfan (I, II and sulfate), heptachlor, heptachlor epoxide, and methoxychlor.

The Atlantic Disk uses divinyl benzene (DVB) adsorbent and is designed and certified for automation with the SPE-DEX® 4790 Automated Extractor from Horizon Technology. The extractors pass a 1 liter sample of water that has been spiked with standard, through the disk to collect the analytes, and are then eluted in a small volume of solvent into a VOA vial - all in one automated procedure. In this study the eluents were then dried and concentrated in another automated procedure using the DryDisk™ along with the DryVap® System and the Reclaimer System, which captures harmful solvent vapors from the atmosphere. Automation through the SPE-DEX® 4790 allows increased levels of productivity and precision, making the SPE disk an efficient alternative to liquid-liquid extraction, as well as to other SPE methods.

Experimental Methods

SPE-DEX® 4790 Technique

A purge method was executed before the first extraction of each day. This is important to ensure that there is no air in the solvent lines. The spiked samples were adjusted to pH 2 prior to extraction. The method program is outlined in Tables 1 and 2.

Table 1. Outline of purge method parameters.

Purge Method		
SPE-DEX Conditions	Soak Time (min:sec)	Dry Time (min:sec)
No Pre-Wet Step.		
No Sample, purged with empty vial. No Wash Step.		
Rinse		
Hexane	0:00	0:05
Hexane	0:00	0:05
Hexane	0:00	0:05
Acetone	0:00	0:05
Acetone	0:00	0:05
Acetone	0:00	0:05

Table 2. Outline of extraction method parameters.

SPE-DEX Conditions	Soak Time (min:sec)	Dry Time (min:sec)
Pre-Wet		
Hexane	1:00	0:10
Acetone	1:00	0:10
Reagent Water	1:00	0:10
Process Sample, 1 Liter		
Air Dry, 0:30		
Rinse		
Acetone	3:00	0:10
Hexane	3:00	0:10
Hexane	1:00	0:10
Hexane	1:00	0:10
Hexane	1:00	0:10
Hexane	1:00	0:30

DryVap® System Method

The parameters on the DryVap® are outlined in Table 3.

Table 3. DryVap® settings.

Dry Volume	20 ml
Heat Power	5
Heat Timer	Off
Rinse Mode	Off
Sparge Heat	Off
Vacuum Level	15" Hg
N2 Gas Pressure	25 psi

The sample eluent was taken from the SPE-DEX® 4790 extractor and poured slowly into the DryDisk™ holder as the start button was being pushed to ensure the top organic layer was in contact with the disk membrane. The VOA vial was washed out with a small volume of hexane, as were the sides of the DryDisk™ holder. The sample was concentrated automatically to 0.9 ml and transferred by Pasteur pipette to a GC vial (2ml). The DryDisk® holder was washed down with two 100µl aliquots of hexane to ensure a quantitative transfer into the GC Vial.

The final analysis was done by gas chromatography (GC). An internal standard surrogate which was a 1:1 tetrachloro-*m*-xylene: decachlorobiphenyl mixture in hexane (1µg) was added to each GC vial. This allowed for the comparison of the sample with the Response Factor (RF) vial which contained 1µg of each organochlorine pesticide and internal standard dissolved in 1 ml of hexane. In every case, at least 3 injections of the RF vial were performed before running samples to create a calibration table.

The instrument used was an Agilent 5890 Series II Gas Chromatograph. Hydrogen with a column head pressure of 21 psi and a split flow of 75 ml/min served as the carrier gas. The injector was an Agilent model 7673, and each injection was 1.0µl. A splitless injection was used with a purge on time of 0.75 min. The injection temperature was 220°C. The column used was a 30m x 0.25mm x 0.25µm Restek CL Pesticide column. The oven temperature program was set to an initial temperature of 110°C and raised at 30°C/minute to a final value of 280°C. The run time was 9.1 min. The detector was an Electron Capture Detector (ECD), at a temperature of 300°C, and data points were taken at a rate of 20 Hz.

Results

The results are summarized in Table 4 and a sample chromatogram is given. All of the average recoveries fall within the standard range set forth by the Environmental Protection Agency (EPA) of 70 – 130 percent recovery.

Those recoveries of heptachlor and heptachlor epoxide were affected. This effect was lessened by increasing the sensitivity of the integration of the peaks which can be noted in the baseline. The recoveries noted for these compounds are still high, over 100 percent. However, these remain well under the 130 percent limit set by the EPA.

The results demonstrate the Atlantic Disk is able to quantify a wide array of organochlorine compounds in a single extraction; each at a better rate than the standard which has been set by the EPA. The success in analyzing a range of 20 organochlorine pesticides illustrates the breadth of analytes the Atlantic Disk is able to accurately quantify.

Table 4. Percent recovery results and statistics associated with organochlorine pesticides. The number of trials included was seven.

	Compound Name	AVG	SD	%RSD
1	α-BHC	86.5	3.6	4.2%
2	γ-BHC	83.8	4.0	4.8%
3	β-BHC	78.7	3.4	4.3%
4	δ-BHC	88.5	4.2	4.7%
5	Heptachlor	88.9	14.7	16.5%
6	Aldrin	72.6	4.0	5.5%
7	Heptachlor epoxide	92.1	11.1	12.0%
8	γ-Chlordane	81.1	4.8	5.9%
9	α-Chordane	78.7	3.1	4.0%
10	Endosulfan I	85.4	3.3	3.9%
11	4,4'-DDE	76.8	4.5	5.9%
12	Dieldrin	83.0	3.0	3.6%
13	Endrin	83.5	2.7	3.3%
14	4,4'-DDD	82.1	5.5	6.6%
15	Endosulfan II	81.3	3.2	3.9%
16	4,4'-DDT	81.4	6.0	7.4%
17	Endrin Aldehyde	82.8	8.5	10.3%
18	Methoxychlor	76.2	3.8	4.9%
19	Endosulfan Sulfate	78.1	3.1	4.0%
20	Endrin Ketone	81.3	3.0	3.7%