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Potential Passive Empore C18 Disk Extraction for Analysis of Water Samples Containing Fine Particulates

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Over the past few years, using Solid Phase Extraction (SPE) by filtering water through C18 disks has become a commonly used technique for extraction of water samples. A recent bibliography from 3M Corporation lists 172 articles since 1990 (Price, 1995) dealing with Empore membrane applications.

The pioneering article was by Hagen, Markell, and Schmitt (1990). Other articles that followed dealt with using disks for the analysis of environmental samples for organochlorine pesticides (O'Donnell, 1991) organophophorous and triazine pesticides (Durand, 1991), sulfonyl ureas (Klaffenbach, 1993), thiobencarb (Redondo, 1994) and other pesticides in soil or water samples (Redondo, 1993; Chiron, 1993).

Although the conventional methodology works well for extracting and concentrating organic chemicals from clean water, actual water samples taken in the field are often more difficult to filter because they contain tine particulates that clog the pores in the filter disk. Occasionally such samples may require all day to pass through the disk. Analysis of samples containing particulates or suspended solids was addressed by Dirksen (1993).

A possible way to reduce the time necessary for extraction of these types of samples would be to passively extract the sample by shaking the water and disk together rather than filtering the water through the disk. If satisfactory recovery results can be obtained, then the problem of having the disks clogged with the fine particulates can be avoided. This approach has been tried by Reagan and Vo (1994) using a 90 mm Empore Disk and EPA Method 608 pesticides. They emphasized that process variables for their procedure had not been optimized, but average recoveries were within 75-80% of recoveries using liquid-liquid extraction procedures.

Since our laboratory commonly encounters water samples that are difficult to filter, we investigated using Empore disks to passively extract nine pesticides from water. We particularly wanted to investigate the effect on extraction efficiency of different shaking speeds, different shaking times, and different disk areas and the relative importance of these variables. Our objective was to see if passive extraction has

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the potential to be applied to samples that contain fine particulates that preclude conventional filtration extraction. In addition, we looked at the effect of shaking method and initial conditioning of the disk with methanol on recoveries.

MATERIALS AND METHODS

The compounds we investigated and the two concentration levels are listed in Table 1. Other parameters are listed below.

Disk area - a complete 47 mm disk (17.4 cm^2), ½ disk (8.7 cm^2), ¼ disk (4.35 c^2) and 1 cm^2

Shaking speed - 100 rpm and 150 rpm on an orbital shaker and 3-4 shakes per second on a wrist-action shaker

Shaking time - 16 hours and 30 hours

Disk conditioning - 1 minute and 30 minutes

Water - deionized and local stream

Pesticide concentrations - 0 ng/ml, approximately 1 ng/ml and approximately 50 ng/ml (see Table 1 for exact amounts)

Replications - 4 for each disk area/speed/time/water/concentration combination

Water samples were prepared by placing 800 ml of water in 1 L amber bottles with Teflon lined caps. The samples were fortified with 1 ml of a mixture of pesticides in methanol. An additional 6 ml of methanol was then added. Controls were prepared by adding 7 ml of methanol instead of the pesticide mixture.

The Empore disk was conditioned by shaking with approximately 30 ml portions of 1: 1 dichloromethane:ethyl acetate for two minutes two times. The disks were allowed to air dry and were then soaked in methanol for either 1 minute or 30 minutes prior to dropping them into the water sample.

After shaking the water samples for the selected time, the disks were removed and patted dry with a Kimwipe. They were then placed in culture tubes equipped with Teflon lined screw caps and 2, 5, or 10 ml of ethyl acetate was added, depending on the size of the disk. The tubes were capped and shaken on a wrist action shaker for 15 minutes at 3-4 shakes per second. An aliquot of the ethyl acetate extract was placed in a 2 ml GC vial to which a small amount of anhydrous sodium sulfate had been added to remove any residual water. The samples were analyzed by gas chromatography/mass spectrometry (GC/MS).

RESULTS AND DISCUSSION

Although five factors were evaluated, major differences in pesticide recovery were related to disk area, shaking speed, and shaking time. Therefore, the results for both water types and for both concentrations were pooled, resulting in 16 replications which were used to investigate the major effects of disk area, shaking speed, and shaking time.

Table 1. Fortification levels of 800 ml of water

Compound	Low (ng/ml)	High (ng/ml)
Alachlor	1.03	51.5
Atrazine	0.97	48.4
Clomazone	1.03	51.4
Diazinon	1.45	72.4
Metolachlor	1.32	65.9
Napropamide	0.93	46.5
Pendimethalin	1.13	56.4
Propanil	1.10	55.0
Trifluralin	1.12	55.9

Usually percent recovery was increased when the disk area, shaking speed, or shaking time was changed to increase the probability of an analyte molecule coming into contact with the Empore surface (Fig 1). At a constant shaking speed and time, recovery increased with increasing disk size. For example, when a water sample was shaken at 150 rpm for 30 hours, percent recovery of atrazine as a function of disk area was 16.1 ± 1.8 (1 cm^2), 50.5 ± 6.7 (4.35 cm^2), 63.5 ± 10.2 (8.7 cm^2), and 70.2 ± 11.3 (17.4 c^2). For a given disk area and shaking speed (100 or 150 rpm), recovery also increased with time (30 hours compared to 16 hours). Recovery for atrazine with a complete disk (17.4 cm^2) at a shaking speed of 150 rpm was 58.3 ± 11.3 percent after 16 hours and 70.2 ± 11.3 percent after 30 hours. For a given disk area and shaking time, recovery also increased with shaking speed (150 rpm compared to 100 rpm). For atrazine using a complete disk and shaking for 30 hours, recovery was 39.4 ± 6.9 percent at a shaking speed of 100 rpm and 70.2 ± 11.3 percent at 150 rpm.

Shaking speed was more important than shaking time for the combinations investigated. Shaking at 150 rpm for 16 hours gave higher recoveries than shaking at 100 rpm for 30 hours (Figs 1 and 2). In some cases the recovery continued to increase with increasing speed and time for a given disk area and also with increasing disk area for a given speed/time combination as exemplified by the data for atrazine where the highest recovery was observed for the largest area at the fastest speed for the longest time (Fig 1). In these cases recovery might be further increased with faster shaking, longer times, or larger disks. In other cases recovery did not continue to increase, as typified by pendimethalin (Fig 2).

Recovery of pendimethalin using 8.7 cm^2 at 150 rpm for 16 hours gave results comparable to using 4.35 cm^2 at 150 rpm for 30 hours Increased disk size at those two speed/time combinations did not increase recovery. For six of the compounds, alachlor, diazinon, metolachlor, napropamide, pendimethalin, and trifluralin, there was no difference in recovery between disk areas of 8.7 cm^2 and 17.4 cm^2 at a shaking speed/time of 150 rpm/30 hrs. For the other three compounds, atrazine,

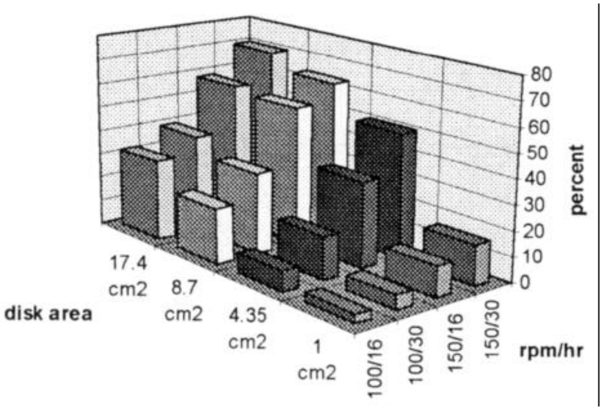

Figure 1. Recovery of atrazine from water as a function of disk area, shaking speed, and shaking time.

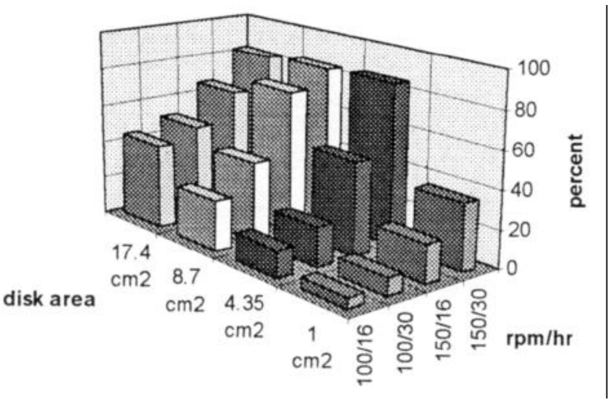

Figure 2. Recovery of pendimethalin from water as a function of disk area, shaking speed, and shaking time.

clomazone, and propanil approximately 10% more recovery was achieved using the 17.4 cm^2 area.

It is possible that in some cases ¼ of a disk might give satisfactory recovery (Fig 2 for pendimethalin with 4.35 cm^2 at 150 rpm for 30 hrs). Typically 8.7 cm^2 or 17.4 cm^2 (a complete disk) would be required, and the small 1 cm^2 disk area never gave or showed the potential of giving satisfactory results.

With each disk area, with one exception, recovery increased in the order of 100/16 rpm/hr < 100/30 rpm/hr < 150/16 rpm/hr < 150/30 rpm/hr unless it leveled out. The exception was for clomazone, where recovery from the 1 cm^2 area was slightly

Table 2. Percent recovery and relative standard deviation (RSD) from the high concentration samples with ½ of a disk (8.7 cm^2).

		Orbital Shaker* shaking at 150 rpm	Wrist-action Shaker* 3-4 shakes per second
Alachlor	%	31	62
	RSD	6	21
Atrazine	%	29	45
	RSD	6	23
Clomazone	%	21	35
	RSD	8	16
Diazinon	%	39	37
	RSD	10	19
Metolachlor	%	3	76
	RSD	0	16
Napropamide	%	37	50
	RSD	5	18
Pendimethalin	%	32	58
	RSD	4	13
Propanil	%	5	49
	RSD	16	9
Trifluralin	%	28	60
	RSD	19	7

* seven h shaking time

higher for 100/16 than for 100/30 rpm/hr. However, recoveries under those conditions were typically 5 - 10 %, and some of the replications for 100/30 rpm/hr showed no detectable clomazone.

Since recovery correlates with the probability of the analyte coming into contact with the disk, conceivably shaking times could be shortened further if agitation is increased. If shaking time can be decreased to 16 hrs, samples could be put on a shaker at the end of the work day and would be ready for organic solvent extraction at the beginning of the next working day.

We felt that wrist-action shaking might increase the frequency of contact of an analyte with the disk when compared to orbital shaking. The bottles had to be taped to the wrist-action shaker, and were not secure enough to leave overnight; therefore, comparisons were made for a 7 hour period only. The results for the high concentration samples are given in Table 2. Recovery was better with wrist-action shaking compared to orbital shaking for the 7 hour period, but was not as good as either conventional extraction or as shaking at 150 rpm for 30 hrs. Variability in recovery with wrist-action shaking was also greater than passive extraction at 150 rpm for 30 hrs. None the less, it appears possible that wrist-action shaking for 16

Table 3. Percent recovery and relative standard deviation (RSD) for conventional versus passive extraction.

		Passive (1 min condition) 8.7 cm^2		Passive (30 min condition) 8.7 cm^2		Conventional 17.4 cm^2	
		Pesticide Level					
Compound		Low	High	Low	High	Low	High
Alachlor	%	88	74	90	85	78	84
	RSD	3	6	5	3	9	8
Atrazine	%	75	55	72	65	82	88
	RSD	1	3	5	3	10	8
Clomazone	%	77	59	55	52	69	58
	RSD	8	6	2	5	13	11
Diazinon	%	79	72	82	78	72	74
	RSD	5	8	6	4	11	8
Metolachlor	%	111	81	96	90	84	95
	RSD	4	6	3	2	8	10
Napropamide	%	82	67	73	70	50	64
	RSD	12	8	7	3	15	10
Pendimethalin	%	81	77	85	90	59	82
	RSD	21	12	7	4	8	13
Propanil	%	69	62	58	67	73	87
	RSD	3	8	10	3	13	16
Trifluralin	%	68	56	73	96	57	78
	RSD	16	7	5	3	10	14

hours (overnight) might give satisfactory results.

The mean recoveries from deionized water were very similar for passive extraction using either a 1 minute or 30 minute pre-soaking of the disk, however, the precision was better with the 30 minute treatment (Table 3). The relative standard deviation (RSD) was ten or greater in four of the 18 possible situations with the 1 minute treatment and in only one case with the 30 minute treatment. The RSD for that one case was 10 for the low level of propanil. The average RSD for all compounds at both concentrations was 7.6 for the 1 minute treatment and 4.4 for the 30 minute treatment.

Recoveries were similar using passive extraction compared to conventional filtration (Table 3). The noticeable difference was that the precision was better with the passive extraction. The RSD was 10 or greater in 12 of 18 instances for conventional extraction with an average RSD of 10.8.

The better precision achieved using passive extraction may have been a result of limiting the need to concentrate the ethyl acetate used to elute the compounds from the disk. The half-disk was extracted with 5 ml of ethyl acetate and an aliquot of the extract was placed in a GC vial for analysis. With conventional filtration, a total of 20-30 ml of ethyl acetate is collected, which is then reduced in volume to 2 ml in a warm water bath under dry nitrogen. It is possible that there is some loss while transferring solutions to calibrated test tubes or during the evaporation process.

These studies indicate that passive extraction can be used to extract water samples that contain particulates that would clog the filter disk during conventional filtration extraction.

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