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Portable System for Extracting Water Samples for Organic Analysis

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Extraction of water samples using Solid Phase Extraction (SPE) disks has become a commonly used technique. A bibliography from 3M Corporation (Price, 1995) lists 172 articles since 1990 that deal with Empore disk applications.

Senseman (1993) investigated the stability of various pesticides on Empore C18 disks. Twelve pesticides in water were filtered through the disks and stored at different temperatures, one of which was 4 °C, for 3, 30, 90, and 180 days. Water samples were stored at 4 °C for the same periods of time. Senseman found that for most pesticides the stability on the disks was as good as or better than the stability in water for the same period of time. The most pronounced example was for captan where recovery from water stored for 3 days at 4 °C was 28% whereas recovery from the disks stored at 4 °C was 114%.

Since the compounds are stable on the disks, it should be possible to construct an apparatus to extract samples in the field. This would have the advantage of preserving or enhancing the stability of the pesticides by transferring them to the C18 membrane rather than keeping them in water. It would also eliminate the need for glass storage bottles which could break and also reduce the size of a storage container. The volume required to keep a certain number of glass bottles cold would be replaced by the volume needed to keep the same number of disks in plastic bags cold.

A conventional apparatus that is used in the lab could be taken to the field, used at a sampling site, packed up, and moved to the next sampling site. However, since the extraction apparatus is mainly glass, care would have to be taken to ensure that it did not break during transit. Also, since some samples may take an hour or two to filter, personnel might have to spend that amount of time at one location waiting for the samples to filter.

It would be preferable to have an apparatus that would be durable and could be loaded with the water samples such that the filtration could be performed while the researchers were driving to the next collection site. At that point the disks would be removed, new samples loaded, and the researchers could again be on the way to the

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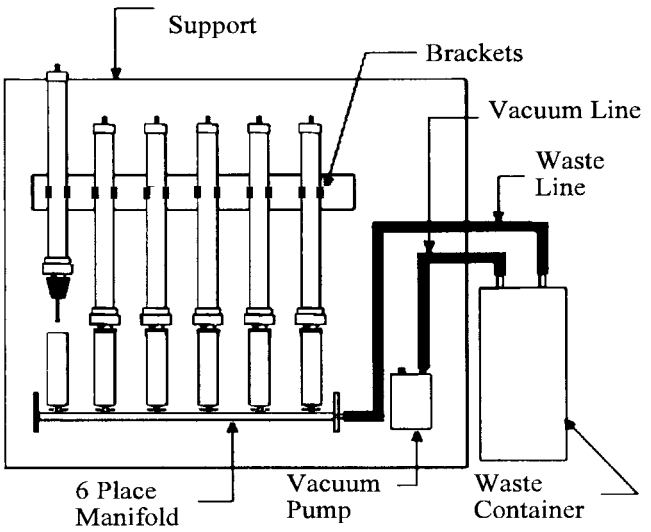

Figure 1. Extraction manifold

next site while those samples were being filtered. This paper reports the construction and results of testing such a system.

MATERIALS AND METHODS

The equipment consisted of a supporting frame of aluminum and steel, six pressure holders, vacuum manifold, and vacuum pump assembled at the Agricultural Engineering Research Laboratory of the Biological and Agricultural Engineering Department, University of Arkansas. Six identical stainless steel pressure holders, 340 mL capacity and 3.5 cm id, with Viton seals and neoprene stoppers held 47 mm filters. Each pressure holder was held in vertical position by a spring clamp about 35 cm above the filter holder. The lower (stopper) end of each holder was fitted into a six-branch vacuum manifold (similar to Cole-Parmer E-02924-30) with an independent valve for each branch. Vacuum was applied by a 12VDC pump (Barnant 400-1903). Electrical power, controlled with a toggle switch, was provided by a car battery. The pump and manifold were connected with 3/8 inch ID vacuum tubing. A reservoir for waste consisted of a backpack spray tank with adapters to connect the tank to the vacuum manifold. See figure 1.

The apparatus was bolted to the side of a pickup immediately behind the cab and the truck was equipped with a camper shell.

The apparatus was tested by collecting and filtering water from five sites. The Empore disks were conditioned the previous day by soaking them in a 1/1 methylene

chloride/ethyl acetate solution for two minutes, removing them, soaking them for an additional two minutes in a fresh solution, and allowing them to air dry. Prior to leaving the lab for the first site, three C18 disks were placed in a bottle with a small amount of methanol. On arrival at each site, duplicate 900 mL water samples were collected in amber bottles. One sample was placed on ice for return to the laboratory; the other sample was prefiltered through a glass microfiber filter. Three 250 mL subsamples were measured into erlenmeyer flasks. Two of the subsamples were fortified with 1 mL of a mixture of the pesticides in methanol to give a water sample that was fortified at 4 ng/mL. An additional 1 mL of methanol was added to each of the fortified subsamples and 2 mL of methanol was added to the blank subsample. The disks were removed from the methanol with a forceps, placed on the filter support, and the steel reservoirs clamped in place. The samples were immediately poured into the reservoirs, and the vacuum was turned on to begin pulling the samples through the disks. Three new cleaned disks were placed in methanol for conditioning, and the researchers proceeded to the next site. On arrival at the next site the disks were removed from the apparatus, placed in plastic bags, and the bags placed on ice in a cooler. Extraction of a new set of samples was then started.

A record was kept of the departure location, departure time, odometer reading, arrival location, arrival time, and odometer reading in order to determine the time and distance between each location. In addition, the pH of the water and the time required for prefiltering were recorded.

On the following day the disks were placed on a conventional glass manifold in the lab and extracted using conventional Empore extraction techniques. Additionally, the duplicate 900 mL water sample from each location was prefiltered, and two fortified and one blank sample were prepared as in the field. The samples were extracted using the conventional glass system. All samples were analyzed using a Varian Saturn 2 gas chromatograph mass spectrometer (GCMS).

One sampling trip involved going from the lab to Greathouse Springs (GHS1), Hickory Creek (HC), Lake Fayetteville (LF), Twin Bridges (TB), Greathouse Springs (GHS2), and back to the lab. The entire process was duplicated a week later.

Comparisons were made between the recovery from the samples extracted in the field and eluted in the lab and the ones that were both extracted and eluted in the lab. The analysis determined the number of samples (n) that would have to be extracted in the field and in the lab in order to detect a difference in recovery for the two procedures. The information needed to determine n was the difference in the mean recoveries for the compounds of interest, the probability of detecting this difference (power), and estimates of variance for each population.

We assumed that the same number of observations (n) would be taken from each population (field and lab). If $1-\beta$ is the power and δ is the difference in mean recoveries, then

$$n \geq (t_{\alpha/2} + t_{\beta})^2[(S_L^2 + S_F^2)/\delta^2]$$

where $t_{\alpha/2}$ and t_{β} are from the t-table with 2(n-1) degrees of freedom (df) and S_L^2 and S_F^2 are the mean square error terms for the lab and field extractions taken from the ANOVA for each extraction location separately.

Since $t_{\alpha/2}$ and t_{β} depend on df, which is defined in terms of the unknown n, a preliminary n was calculated using critical values from the normal table instead of the t-table. This preliminary n was used to calculate df and then to get t-values, from which final n was calculated. We did not iterate this step because there was little change in the value of n.

The compounds that were used to fortify the water were alachlor, atrazine, carbofuran, chlorpyrifos, DCNA, DCPA, diazinon, malathion, metalaxyl, methyl parathion, metolachlor, molinate, pendimethalin, simazine, and thiobencarb. The standards were obtained from Chem Service, AccuStandard, FMC, Dow Elanco, and EPA, and purity ranged from 97 - 99.9%.

RESULTS AND DISCUSSION

Table 1. Travel time (min) and mileage between locations, time at each location, and prefiltering time for trips 1 (T1) and 2 (T2)

Depart	Arrive	Mileage[a]	Travel time (min)		Prefilter time (min)		Time at arrival site (min)	
			T1	T2	T1	T2	T1	T2
Lab	GHS1	4	9	8	2	3	44	27
GHS1	HC	22	39	32	3	4	33	28
HC	LF	17	39	27	3	3	31	30
LF	TB	13	62*	64*	3	3	21	27
TB	GHS2	14	28	25	3	3	31	22
GHS2	Lab	4	7	7				

[a] GHS1 - Greathouse Springs 1, HC - Hickory Creek, LF - Lake Fayetteville, TB - Twin Bridges, GHS2 - Greathouse Springs 2, Lab - Altheimer Laboratory
* includes lunch

Since the reservoirs are stainless steel, it is difficult to look down through them to determine when only a thin film of solvent is left when drawing solvent through as is normally done to condition the disk. This was overcome by preconditioning the disks before the trip and soaking them in methanol for approximately 15 minutes before use. We recommend not leaving the disks in methanol for an extended period of time. When all the disks were put in methanol at the beginning of the day, by the end of the day the shape of some of them was beginning to be distorted. Putting the disks in

methanol immediately on arriving at a sampling site allows them to become sufficiently solvated in the time it takes to remove the disk from the previous site,

Table 2. Percent recovery from 250 mL of water fortified at 4 ppb and extracted in the field or lab and the number of samples (n) required to detect the difference in recovery with $\alpha = 0.05$ and a power of 0.9.

	% recovery		Variance		
	Field	Lab	Field	Lab	n
alachlor	71.3	76.2	912.6	237.2	51
atrazine	92.9	104.0	1260.7	464.1	16
carbofuran	93.7	97.8	918.0	292.5	77
chlorpyrifos	70.5	78.0	709.8	300.0	21
DCNA	73.1	75.0	1116.9	224.2	388
DCPA	81.7	86.4	946.0	529.8	72
diazinon	67.1	82.9	842.2	284.5	7
malathion	86.7	92.0	1257.6	330.7	63
metalaxyl	60.4	64.2	548.6	398.2	72
methyl parathion	85.7	88.6	1020.0	204.4	151
metolachlor	84.0	91.4	102.2	369.5	29
molinate	76.5	80.9	919.9	162.2	61
pendimethalin	87.1	93.6	792.1	153.0	13
simazine	74.3	82.7	994.3	203.7	20
thiobencarb	76.8	85.4	1010.6	300.1	20

collect, prefilter, measure, and add methanol to the new water sample.

The apparatus was placed behind the cab to minimize bumping while driving. However, this resulted in cramped quarters for the researchers. A van would provide more room. If the apparatus were bolted to the back of the pickup, the workers could stand outside, but the apparatus would jostle more while driving to the next location.

Table 1 shows the time at each location, travel time and mileage between locations, and time required for prefiltering. The time spent at each site ranged from 21 to 44 minutes. The 44 minutes was for the first stop of the first trip, and it is likely that the work went more slowly since it was the first time that the workers had performed the

procedure in the field. The second longest time at any site was 33 minutes. In each case, when the personnel arrived at the next sampling site, the samples had finished filtering. If the samples had still been filtering, the procedure would have called for the workers to start the next set of samples and drive on to the next location. Since the manifold accommodates 6 samples and two fortified and one blank sample were taken at each location, an additional three samples could be placed on the manifold and the workers could drive to site 3 while the samples from sites 1 and 2 were filtering. The procedure calls for air to be drawn through the disk after the water is pulled through, so there is no problem with letting the pump run until arrival at the next sampling site.

The recovery results are given in Table 2. Since neither trip, sample location, nor sample replication were significantly different, all field extraction samples were pooled as well as all lab extracted samples resulting in 20 replications for each type of extraction. The mean recoveries and associated variance for each compound for field and lab extraction were then determined. These data were used to determine how many field and lab samples would be needed to detect the measured difference in recoveries for the two extraction procedures. The results are given in Table 2 for $\alpha = 0.05$ and power of 0.9. An α value of 0.05 indicates that if there were truly no difference in recoveries we would falsely find a difference 5% of the time. A power of 0.9 means that if the true difference is as stated in the table, by taking the indicated number of samples we would see that difference 90% of the time. For alachlor, if the difference in recovery were truly 4.9%, we would need to take 51 field and 51 lab samples to detect that difference 90% of the time with $\alpha = 0.05$.

Recovery averaged 6.5% higher for samples extracted in the lab, and there was more variability in recovery for samples extracted in the field as indicated by the difference in variance between the lab and field samples. These differences in recovery and variability are likely due at least in part to the necessity of putting the disk back on the filter such that the same area is exposed for elution with organic solvent as was exposed for extraction from water.

Although there is truly a difference in the recoveries between the two methods, the difference is small enough that a relatively large number of samples would need to be taken to detect that difference. Most researchers would likely take one or two samples per site which would not be enough to take advantage of the difference in recovery and variability of the extraction procedures. The field extraction unit may be desirable to use in some instances and not in others. If the field collection trip is of short duration, it may be easier and better to simply take the water sample and return to the lab for complete extraction. However, if it is an extended trip to several locations collecting numerous samples for analysis of a labile analyte, or if the trip requires an overnight stay, then the field extraction unit may be desirable. The labile compound may be stabilized on the disk, there is less danger of breaking bottles, and it would be easier to keep multiple disks cool in plastic bags in a small cooler than to keep the same number of bottles cool.

The difference in the results between the two procedures is small enough that a decision to use the field extraction unit will likely be made based on other factors.

We are presently using the system to extract river water for azoxystrobin, carbaryl, carbofuran, clomazone, fipronil, methyl parathion, molinate, propanil, quinclorac, and thiobencarb using both GCMS and HPLC as the analytical tools. We sample from eight different sites, on a trip that covers 760 miles in two days. The recovery for field fortified samples is comparable to what we have reported in this study with the exception of propanil which has been less than 50% and variable. We collect duplicate disks at each site for a total of 20 disks counting the fortified samples. We have had samples from some locations that were not through filtering by the time we reached the next sampling site; however they were through by the time we got to the following site. Disks are kept cold on frozen cold packs in a small cooler. We eliminate the need for two large coolers with ice. We elute all the disks the day after we return to the lab, concentrate the eluent, and analyze them by GCMS overnight. The next day we evaporate the solvent, reconstitute in HPLC solvent and analyze overnight on HPLC. We are completely through with the analyses within two days. Since some samples are slow to filter, we would require an extra one or two days to complete the analyses if we brought water back to the lab. We also now have a mini van with an auxiliary electrical outlet in the rear that allows us to recharge the battery operating the pump as we are driving.

This equipment and procedure saves time by extracting samples while driving rather than doing it in the lab, can stabilize labile compounds by transferring them to the disk soon after sampling, and removes the necessity of keeping glass containers of water on ice during return to the laboratory.

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