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A Mobile Field Extractor for Extracting Water Samples While Driving between Sampling Sites

J. D. Mattice · E. E. Gbur · B. A. Greer · B. W. Skulman

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Solid phase extraction (SPE) of water samples has become a common analytical practice. A search of the literature for ''solid phase extraction'' using SciFinder Scholar (http://www.cas.org./SCIFINDER/SCHOLAR/) resulted in 26,745 hits on October 5, 2006.

Senseman et al. (1993) showed that twelve pesticides were as stable on Empore C18 disks as they were in water, and some compounds were more stable. The most pronounced example of enhanced stability on disks was for captan. When water samples were stored for 3 days at 4°C, the recovery was 28%, whereas when equivalent samples were extracted onto disks, and the disks were stored under the same conditions, recovery was 114%.

The purpose of sampling and analyzing water was to determine what was present in the water at the time of sampling. It was necessary to minimize any degradation of analytes between the time of sampling and the time of instrumental analysis. Therefore, it was desirable to extract the samples onto the SPE material as quickly as possible after they were collected. One way to do this would be to take a conventional apparatus to the field along with a table and a portable pump and to extract the samples at the sampling sites.

Unfortunately, a common problem when filtering environmental samples through SPE disks is that particulates can clog the disk, which means that several hours would be required to filter a sample. This can be partially remedied by prefiltering the sample through a glass microfiber filter. However, for some samples prefiltering will only reduce, not eliminate, the problem. The researcher may have to stay at one site for several hours until the sample has filtered before moving to the next collection site. Also, a conventional apparatus often has glass reservoirs that can break.

It would be preferable to have a durable apparatus that would be powered by a battery, which could be placed in the back of a van or a pickup truck. The researcher could pour the sample into the reservoir, turn on the pump, and be extracting the sample while driving to the next collection site or back to the laboratory. The driving time would also be used for filtering. At the laboratory, all that would be required would be to elute the samples with 10 to 20 mL of organic solvent, and to reduce the volume for instrumental analysis.

We reported the construction and testing of this type of apparatus using Empore disks (Mattice et al., 2002). Although the apparatus worked well, we felt that it could be improved. The reservoir was constructed of stainless steel with a threaded end that attached to the support for the disk. This required threading the stainless steel at a machine shop. We felt that this lack of convenience might prevent some people from making the reservoir. Also, when C18 disks are being used, a thin film of methanol is to be left on the disks when they are conditioned. It was difficult to determine how much methanol was left when looking down the stainless steel reservoir. Another problem was that when the compounds were eluted from the disk, if the disk was not exactly realigned on the support, the exposed area of the disk was not the same as for extraction from water, which could affect recovery.

J. D. Mattice (✉) · B. W. Skulman
Crop, Soil, and Environmental Sciences Department,
University of Arkansas, Altheimer Laboratory,
1366 West Altheimer Drive, Fayetteville, AR 72704, USA
e-mail: jmattice@uark.edu

E. E. Gbur · B. A. Greer
Agricultural Statistics Laboratory, University of Arkansas,
Fayetteville, AR 72704, USA

SPE media are now available in a plastic housing (Speedisk) which also contains a built-in prefilter. The entire cartridge can be removed and placed back on a manifold so that the same area is exposed for eluting as was exposed for extracting. We report here the construction and testing of a mobile field extractor using Speedisks, which is easily made with a commercially available manifold and rigid polyvinyl chloride (PVC). PVC is durable, will not sorb most compounds from water (Jones and Miller, 1986; Koskinen et al., 1999; Schuh et al., 1997), and therefore can be used in place of glass for the reservoir.

Materials and Methods

The equipment consists of a supporting frame, a Millipore 6 place stainless steel 876 mm × 152 mm × 152 mm vacuum manifold with an independent valve for each position. Vacuum is applied with a 12 v DC Vacuum pump Barnant Air Cadet (Thermo Fisher Scientific, Barrington Facility, 28W092 Commercial Avenue, Barrington, IL 60010), Single Head model 400–1903 or equivalent, which plugs into an electrical outlet in the rear of the van. A backpack spray tank is used as the reservoir for filtered water. Bungee cords are used to help hold the reservoirs to the frame, and tygon tubing is used from the outlet of the manifold to the reservoir and from the reservoir to the pump. The reservoir is made of commonly available PVC (Fig. 1).

The apparatus was tested using environmental water from three sites. One site was Lake Fayetteville (LF), AR, USA. The other two sites were on Clear Creek downstream from LF. Greathouse Springs (GHS), AR, USA, is approximately 7 km downstream from LF and Wheeler (W), AR, USA, is approximately 6 km downstream from GHS. The first two km of Clear Creek downstream from LF flow through a residential area in the small town of Johnson, AR, USA. After Johnson, the land is primarily pasture.

Hydrophobic divinylbenzene (DVB) speedisks were conditioned on the morning of sampling by drawing through 10 mL of dichloromethane followed by 10 mL of methanol. At each sampling site, a set of six, 900-mL samples were prepared in erlenmeyer flasks, and a set of six were prepared in amber-colored bottles. One sample from each set was fortified with 1 mL of methanol as a blank. The other five samples in each set were fortified with 1 mL of a mixture of pesticides in methanol that included 1.8 μg/mL in each compound to yield a fortification concentration of 2 ng/mL in each compound. Teflon-lined caps were placed on the samples in the bottles, and they were placed in an ice chest with cold packs.

Speedisks were attached to the manifold, and 10 mL of deionized water was pulled through. The PVC reservoirs

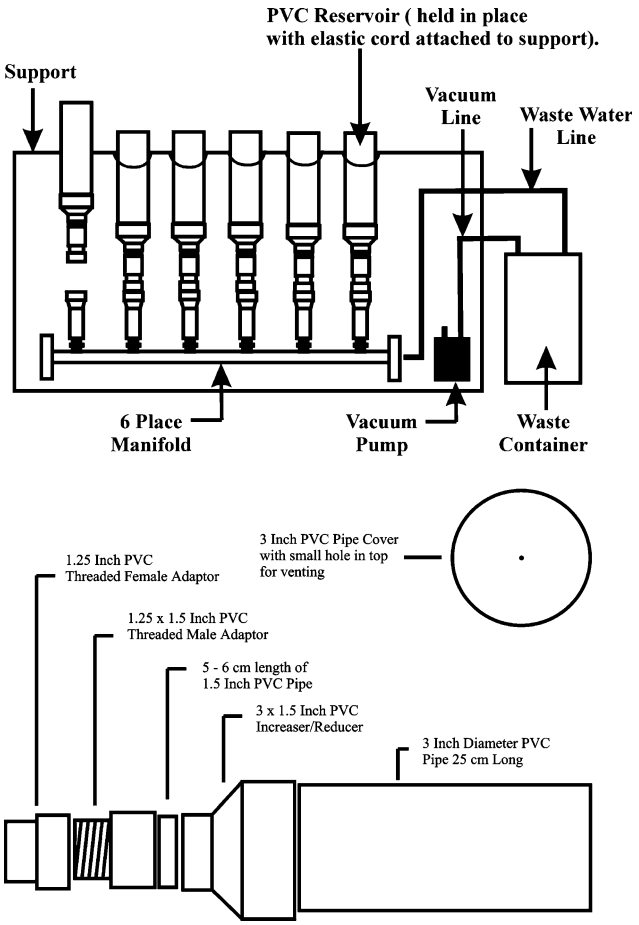

Fig. 1 Construction of apparatus (top) and reservoir (bottom)

were attached to the speedisks, the samples were poured into the reservoirs, the pump was turned on, and the samples were filtered while driving to the next sampling site. All samples had filtered during the time it took to reach the next site. The disks were removed, were wrapped in aluminum foil, and were placed in an ice chest with cold packs. New sets of samples were prepared as described previously.

Disks were eluted in the laboratory with ethyl acetate, which was then taken to just dry under a stream of nitrogen at 40–45°C. The residue was dissolved in 200 μL of methanol, and then 800 μL of deionized water was added and the test tube was shaken. The samples were placed in vials for HPLC analysis. The water samples that were brought back to the laboratory were refrigerated and extracted and eluted within 36 hr.

The entire process of collecting samples and preparing them for HPLC analysis was repeated one week later.

An additional study was done in which water was brought to the laboratory from LF. Fifteen 900-mL samples were fortified as described previously but at 1.8 ng/mL. Three samples were extracted and eluted immediately. Six samples were extracted with Speedisks, and 3 replications

were stored at 7°C for 24 hr, and 3 replications were stored for 48 hr prior to elution with ethyl acetate. The six water samples were stored at the same temperature for the same time interval before extraction with Speedisks and elution with ethyl acetate.

The test compounds were carbofuran, cyhalofop-butyl, diazinon, diuron, fluometuron, methyl parathion, metribuzin, propanil, and simazine.

The experiment was designed as a three factor factorial with place (Field/Lab) and location (GHS/LF/W) as fixed effects, and trip as a random effect. There were five replications for each treatment combination. A separate analysis of variance was performed on the recovery concentration for each of the nine pesticides. Variance components were estimated using the method of moments. A protected, least significant difference (LSD) at $\alpha = 0.05$ was used to separate means when appropriate.

Results and Discussion

Travel time between sites ranged from 10 to 35 min. Recovery results are given in Table 1 along with the number of samples required to detect the observed difference with the power equal to 0.75, 0.80, and 0.90, and $\alpha = 0.05$. For example, a power of 0.90 means that if the true difference is as stated in Table 1, by taking the indicated number of samples we would statistically detect that difference 90% of the time. For most compounds recovery was good, and there was no significant difference in recoveries between lab/lab and field/lab.

As seen in Table 2, unexplained variability accounted for approximately one-half (41.0% to 58.8%) of the variation in the recovery concentrations for all pesticides except diazinon (21.6%) and propanil (79.0%). The trip effect and its interactions accounted for the remaining variability. Hence, except for diazinon, extraction in the field instead of the laboratory did not have a greater effect on the total variability than did the experimental error.

Recovery was the same, but poor, for metribuzin for both lab/lab and field/lab, indicating that the DVB was not a good matrix for extraction of metribuzin. Except for cyhalofop-butyl, for differences of the magnitude that we observed, an impractically large number of samples would have to be taken to declare the differences to be statistically significant.

There was a large difference in recovery of cyhalofop-butyl from field/lab (95.1%) and lab/lab (47.3%) samples. Cyhalofop-butyl has an aerobic aquatic half-life of 2.4 to 4.4 hr (USEPA, 2002). Since the water samples were extracted in the laboratory after the field samples were eluted, it is possible that we were observing a time effect. The storage study was done to determine if this was the case. The results are shown in Table 3. Recovery at time zero was 86%, and after two days of storage on the disks at 7°C, recovery was 82%. Recovery from water stored for one day at 7 C was 13%. It would not be unusual to collect water samples, return to the laboratory, refrigerate the samples, and then extract them the following day. In this case, most of the cyhalofop-butyl would have degraded, whereas if the samples had been immediately extracted onto the disks, there would have been little degradation, or none at all.

If there is a situation where there is a steady inflow of a compound that is unstable in water, the inflow rate and degradation rate may result in a continuous presence of the compound. If a sample is removed and analyzed later, even though it is kept cold, the amount found may be much lower than is actually present in the water source.

Table 1 Recovery from 900 mL water fortified at 2 ng/mL and extracted in the field or laboratory and the total number of samples (n) required to detect the observed difference in mean recovery concentration with $\alpha = 0.05$ and the indicated power

Pesticide	Extract/elute ng/mL (%)		Total variance $(ng/mL)^2$	n		
				Power of test		
	Field/lab	Lab/lab	Field/lab	0.75	0.80	0.90
Carbofuran	1.88* (94.0)	1.69* (84.5)	0.0188	18	20	26
Cyhalofop-butyl	1.71* (85.5)	0.85* (42.5)	0.0298	6	6	6
Diazinon	1.73 (86.5)	1.69 (84.5)	0.0407	710	802	1072
Diuron	1.75 (87.5)	1.73 (86.5)	0.0030	208	236	314
Fluometuron	1.77 (88.5)	1.73 (86.5)	0.0027	34	38	50
Metribuzin	0.73 (36.5)	0.75 (37.5)	0.0032	228	258	344
Methyl parathion	1.73 (86.5)	1.69 (84.5)	0.0179	314	354	472
Propanil	1.66 (83.0)	1.66 (83.0)	0.0265	No difference in means		
Simazine	1.81 (90.5)	1.77 (88.5)	0.0123	216	244	326

*Significantly different mean recovery concentrations for the two places at $\alpha = 0.05$

Table 2 Variance components for each pesticide as a percent of the total variance

Variance component	carb	cy	diaz	diur	flu	met	mp	pro	sim
Trip	51.9	12.6	<0.1	30.6	28.7	30.7	23.6	13.2	3.7
Place × trip	<0.1	<0.1	72.7	27.8	15.7	<0.1	<0.1	<0.1	<0.1
Location × trip	2.7	<0.1	<0.1	0.7	3.9	<0.1	20.8	0.5	<0.1
Place × location × trip	2.6	46.1	5.8	<0.1	<0.1	26.1	<0.1	7.3	37.5
Error	42.8	41.3	21.6	41.0	51.7	43.2	55.6	79.0	58.8

carb, carbofuran; cy, cyhalofop-buty; diaz, diazinon; diur, diuron; flu, fluometuron; met, metribuzin; mp, methyl parathion; pro, propanil; sim, simazine

Table 3 Recovery of cyhalofop-butyl from disks and Lake Fayetteville, AR, USA, water stored at 7°C for 0, 1, and 2 d at an initial concentration of 1.8 ng/mL

Storage time (d)	Disk storage		Water storage	
	Mean recovery (ng/mL)	Standard error (ng/mL)	Mean recovery (ng/mL)	Standard error (mg/mL)
0	1.542	0.00567	–	–
1	1.505	0.01180	0.237	0.09383
2	1.469	0.02123	0.203	0.17977

Mean recovery based on three samples per storage-time combination

This version of the extractor is more easily made than the original, since it uses PVC for the reservoir. The original version used stainless steel that needed to be threaded at a machine shop. Also, the use of Speedisks in the plastic housing eliminates the need to reposition the disk accurately. This use may have been responsible for the higher recoveries of two of the compounds common to both tests when using the present system. Recovery for diazinon was 86.5% using this system as compared to 67.1% for the original, and for simazine recovery was 90.5% as compared to 74.3%. Eliminating the need to reposition a disk accurately also eliminates a source of variability. Transferring labile analytes to the SPE matrix can stabilize labile compounds, which was shown in this study with cyhalofop-butyl.

We have not experienced loss caused by sorption of any of our compounds onto the PVC. Reports in the literature indicate that this is not likely to be a problem (Jones and Miller, 1986; Koskinen et al., 1999; Schuh et al., 1997); however, there are instances where some sorption can occur. It would be prudent to verify that sorption does not occur for the analytes of interest. Also, we have not had problems from compounds leaching from the PVC and interfering with analysis either by HPLC or by GCMS. If one were doing analysis for compounds such as monomers or plasticizers that could leach from PVC, it should be verified that this is not occurring.

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