Solid-Phase Microextraction of Organophosphate Pesticides in Source Waters for Drinking Water Treatment Facilities

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Abstract

The rapid detection of contaminants in our nation's drinking water has become a top homeland security priority in this time of increased national vigilance. Real-time monitoring of drinking water for deliberate or accidental contamination is key to national security. One method that can be employed for the rapid screening of pollutants in water is solid-phase microextraction (SPME). SPME is a rapid, sensitive, solvent-free system that can be used to screen for contaminants that have been accidentally or intentionally introduced into a water system. A method using SPME has been developed and optimized for the detection of seven organophosphate pesticides in drinking water treatment facility source waters. The method is tested in source waters for drinking water treatment facilities in Mississippi and Alabama. Water is collected from a deepwater well at Stennis Space Center (SSC), MS, the drinking water source for SSC, and from the Converse Reservoir, the main drinking water supply for Mobile, AL. Also tested are samples of water collected from the Mobile Alabama Water and Sewer System drinking water treatment plant prior to chlorination. The method limits of detection for the seven organophosphates were comparable to those described in several Environmental Protection Agency standard methods. They range from 0.25 to 0.94 µg/L.

Introduction

Recently, there has been an increasing interest in the development of rapid detection methods for pollutants that might be introduced into source waters for drinking water treatment plants. Monitoring for many pesticides at drinking water treatment facilities can be expensive, even cost prohibitive, for smaller laboratories using conventional pesticide analyses. Currently, liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are widely used in water analyses for pesticides (1). Both techniques employ solvents to attain the separation of analytes from the matrix. In the case of LLE, the solvent use is particularly excessive. Extractions also require a large amount of glassware and additional equipment, such as rotary evaporators. Extraction times run from 1 to 2 workdays.

The purpose of this work is to investigate the benefits of using a solid-phase microextraction (SPME) fiber to extract organophosphate (OP) pesticides that would present contamination concerns were they to be accidentally or deliberately introduced into a drinking water system. SPME, in contrast to LLE and SPE procedures, uses no solvent. This reduces safety concerns inherent to solvent use and represents a significant reduction in laboratory costs for both the purchase and disposal of solvents. In addition, SPME techniques require significantly less time as compared with LLE and SPE procedures (2). Another advantage of SPME is the reduced sample size. Sample sizes of 3 to 30 mL are typically used as compared with a 1-L sample size for other techniques. The equipment requirements were also minimized as a result of the use of the SPME method.

SPME consists of a length of fused-silica fiber coated with a polymeric material and, in some cases, mixed with a solid adsorbent. The fiber is immersed in the water sample, in which equilibrium is established between the fiber and the analytes in the stirred or agitated sample. The amount of analyte adsorbed onto the fiber is determined by the distribution ratio of the analyte between the sample matrix and the coating material. After a predetermined amount of time, the fiber is removed from the sample and inserted into a heated gas chromatographic (GC) inlet for desorption onto a chromatographic column.

The concept for SPME originated in the late 1980s from work by Pawliszyn et al. on laser desorption–GC (3). Although the work resulted in rapid separation times, the preparation of samples for the experiment took hours. In 1990, the work evolved into SPME, as it is known today, with extraction by a fused-silica fiber coated with a polymeric phase and desorption of the fiber in a heated GC inlet (4).

The SPME device was commercialized in 1993 by Supelco (Bellefonte, PA) in a reusable microsyringe form. Since then, many different matrices (water, soils, food, or biological fluids) have been analyzed by SPME using GC and high-performance liquid chromatography (HPLC) analyses coupled with various detection systems. Fiber coatings have multiplied from the initial polydimethylsiloxane (PDMS) and polyacrylate (PA) to other coatings based on solid sorbents such as PDMS–divinylbenzene

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(DVB), carboxen–PDMS, and carbowax–DVB (5). The expansion of available coatings has given analysts a wider range of choices, enabling them to use compound affinities for a particular fiber based on such characteristics as polarity and molecular size to select the optimum fiber for extraction. As a result, SPME can now be used to extract a much broader array of compounds.

Experimental

Chemicals and materials

Organophosphate pesticides with purities greater than 98% were supplied by the Enivornmental Protection Agency National Pesticide Standard Repository at Fort Meade, MD and used as received. Individual stock standard solutions of sulfotepp, phorate, terbufos, disulfoton, methyl parathion, ethyl parathion, and methidathion were prepared by dilution of 10-mg amounts of each pesticide with acetone. The solvents used were Optima grade acetone, hexane, and reagent water supplied by Fisher Scientific (Pittsburg, PA).

Portions of each of the seven stock standards were combined and diluted with acetone to create mixed fortification standards at 0.5 and 2.5 µg/mL. The individual stocks were also diluted with hexane to prepare standards to determine retention times on the GC.

Procedure

Water samples, including reagent water control samples and drinking water treatment plant source waters, were placed in 4-mL screwcap vials (15 × 4 mm) preassembled with polytetrafluorethylene–silicone septa (No. 27136, Supelco). A microstir bar (No. 14-511-69, Fisher) was added to the sample, and the sample vial was placed into a 4-mL vial puck (No. 57333-U, Supelco) on a heated stir plate. The SPME fiber consisted of a length of fused-silica fiber with a 65-µm PDMS–DVB (No. 57310-U, Supelco) coating. The fiber was mounted in an SPME fiber holder for manual sampling (No. 57330-U, Supelco). The stainless steel sheath on the fiber holder was used to puncture the septa on the sampling vial, and then the fiber was pushed out of the sheath and into the sample. After the prescribed amount of time, the fiber was retracted into the sheath and removed from the sample.

Fibers were preconditioned prior to first use by being left in a hot GC injection port (280°C) overnight. Prior to each day's analyses, the dry fiber was placed in the injection port for 3 min at 280°C, removed, and analyzed by GC in a manner identical to the sample analyses. If no interferences were observed, the experimental analyses with the water samples began.

Chromatographic analyses were carried out on a Hewlett-Packard 6890 GC with a nitrogen phosphorus detector (NPD) (Palo Alto, CA). The injection port was equipped with an SPME 0.75-mm i.d. splitless injection liner (No. 26375, 01, Supelco) and a predrilled Thermogreen LB-2 septum (No. 23168, Supelco), which was specifically designed for SPME. An SPME inlet guide (No. 57356-U, Supelco) was used to support the manual holder and its fiber during the desorption process. The splitless injection inlet temperature was set for 3.0 min at 280°C with a purge flow of 60 mL/min. The instrument was equipped with an Equity J-5 fused-silica analytical column (30 m × 0.32-mm i.d. × 0.25-µm film thickness) (No. 28097-U, Supelco). The oven temperature was held at 70°C for 3 min, then programmed to 170°C at 20°C/min, then raised to 250°C at 4°C/min, and held for 10 min. The flow rates were 1.0 mL/min for helium, 60 mL/min for air, and 4.1 mL/min for hydrogen.

Calibration was achieved by fortifying reagent water with known amounts of standards at 1.0, 2.5, 5.0, and 12.5 µg/L. The aqueous standards were then extracted in a manner identical to that used for the samples. The standard extracts were then used to calibrate the GC–NPD using a linear regression, and the water samples were measured against that regression. The calculations were done using the Hewlett-Packard Chemstation Revision A. 06.01 software. An aqueous standard was used to monitor the calibration. It was prepared by fortifying reagent water with the organophosphates near the level of the samples in the set. It was then extracted and analyzed along with the samples. The calibration verification standard recovery should be within ± 30% of the initial calibration curve. If this criterion is not met, a new calibration curve should be analyzed and the instrument calibrated with it before any sample analysis can proceed.

In order to optimize the extraction procedure, deionized water was fortified with seven organophosphates at sample sizes of 3 and 11 mL. The SPME fiber was exposed to the water samples for 15-, 30-, 45-, 60-, and 120-min intervals before desorption on the GC inlet. Water samples were also prepared with varying amounts of sodium chloride to determine the effect of salt on the adsorption of the OPs from the water onto the fiber. Aqueous solutions of NaCl (Ultrapure Bioreagent Grade, J.T. Baker, Phillipsburg, NJ) were prepared at 0%, 5%, 10%, 15%, and 20%. To establish the optimum temperature for extraction, the fiber samples were exposed at 30°C, 40°C, 50°C, and 60°C.

Ultimately, the optimum conditions were determined to be a 3-mL sample size heated to 50°C and rapidly stirred, while the PDMS–DVB fiber was exposed to the sample for 60 min. No NaCl was added.

Source waters from two water treatment facilities in Mississippi and Alabama were fortified with the organophosphates of interest, extracted by SPME, and analyzed by GC–NPD to determine the applicability of the optimized method to "real world" samples. The source waters included water from a deep well at Stennis Space Center, MS. Also tested were source waters from the Mobile Area Water and Sewer System (MAWSS). They included water from the Converse Reservoir in Mobile, AL and water taken at the MAWSS drinking water treatment facility sampled after flocculation, sedimentation, and filtration but prior to chlorination.

Results

Extraction time profiles using 3- and 11-mL sample sizes

Typically, extraction by SPME is not exhaustive. It is a process based on an equilibrium established between the analyte in solution and that adsorbed onto the fiber coating.

Although it is not necessary for sample analytes to reach equilibrium with those adsorbed on the fiber if extraction conditions (time, temperature, and sample agitation) are held consistent, it has been observed that precision/accuracy improves as equilibrium is approached (6). In order to determine the effects of sample volume and time of fiber exposure on the equilibrium, the SPME fiber was exposed to 3- and 11-mL water samples fortified with the organophosphates of interest and held for increasing amounts of time. Triplicate analyses were performed for each extraction time. Organophosphate adsorptions on the SPME fiber immersed in 3-mL samples showed indications of reaching an equilibrium between analyte adsorbed on the fiber and that in solution as the exposure time approached 60 min (as indicated by a gradual leveling out of most detected analyte responses at 60 min). Conversely, organophosphate adsorptions in the 11-mL samples maintained a near linear response because of the additional compound available in the 11-mL sample. Figure 1 shows the contrast between the two sample sizes.

A sample size of 3 mL with a fiber exposure of 60 min was established for these experiments. The 3-mL sample size was selected for two reasons; first, because most of the analytes were approaching equilibration at 60 min (as mentioned earlier, a fiber exposure time and sample size that approaches equilibrium has been shown to improve precision/accuracy results) (6). Second, a 3-mL sample size would accommodate samples with higher concentrations without overwhelming the capacity of the fiber. High concentrations might be encountered in cases of deliberate contamination. The 60-min exposure time was selected because 60 min was enough time for most compounds to approach equilibrium, and, at the same time, it was short enough to allow for multiple extractions within a 1 day period.

Ionic strength effects on fiber adsorption

It has been observed that the addition of NaCl to aqueous samples results in increased fiber adsorption for some compounds because the greater the affinity for a compound to water the lower the affinity for some SPME fibers. In 1998, Beltran and colleagues (7) observed that compounds with higher water solubilities ranging from 145 to 400 mg/L showed an increase in extraction yield with a rise in NaCl concentrations.

To determine if the addition of NaCl would result in a "salting out" effect, which would enhance the extraction of the seven organophosphates by the PDMS–DVB SPME fiber, 3-mL water samples were prepared with 5%, 10%, 15%, and 20% NaCl. The results, as illustrated in Figure 2, reinforced the findings by Beltran et. al. (7). The organophosphates with water solubilities below 145 mg/L (disulfoton, phorate, terbufos, disulfoton, methyl parathion, and ethyl parathion) responded to the NaCl additions with a decrease in recoveries. Only recoveries for methidathion with a reported water solubility of 240 mg/L were enhanced by the addition of NaCl. Therefore, it was decided not to add NaCl to the water samples for this experiment. The impact of NaCl on the SPME adsorption process should be further studied because of salinity differences found in natural drinking waters sources.

Effect of temperature variations in aqueous samples on fiber adsorption

Raising temperatures in water samples has two opposing effects on the adsorption of an analyte onto an SPME fiber. First, it increases the diffusion of the analyte in the aqueous environment, enhancing the mass transfer of the compound to the fiber. However, the higher temperatures have a negative effect on the analyte partition coefficient between the fiber and the sample matrix (8).

To determine the effect of sample temperature on SPME fiber adsorption of the organophosphates being studied, an adsorption temperature profile was prepared. Triplicate sets of water samples fortified with the seven organophosphates of

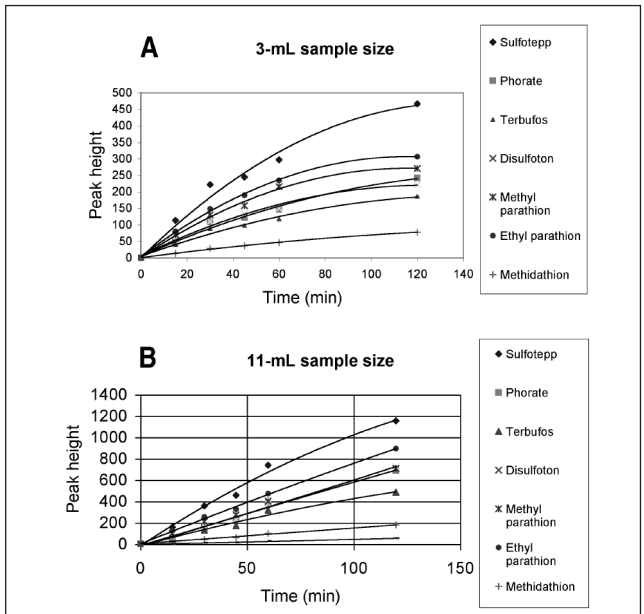

Figure 1. SPME adsorption time profiles for seven organophosphates fortified at 1 µg/L in 3-mL (A) and 11-mL reagent water samples (B) as illustrated by NPD response (B).

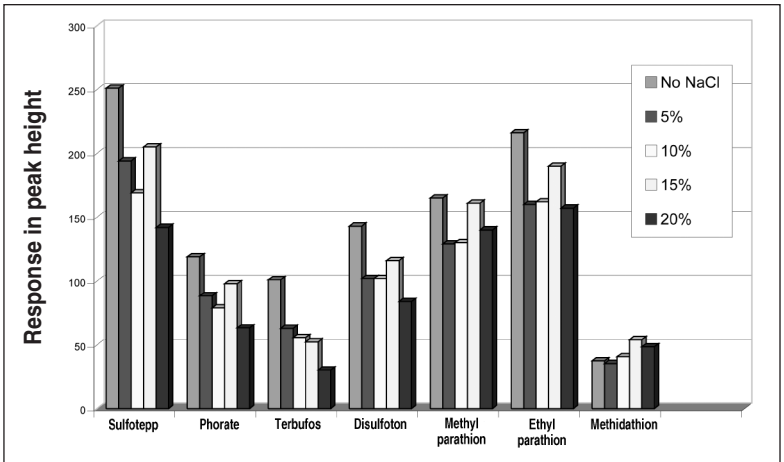

Figure 2. Effect of varied NaCl concentrations on OP fortified in reagent water at 1 µg/L, extracted by SPME, and analyzed by GC–NPD.

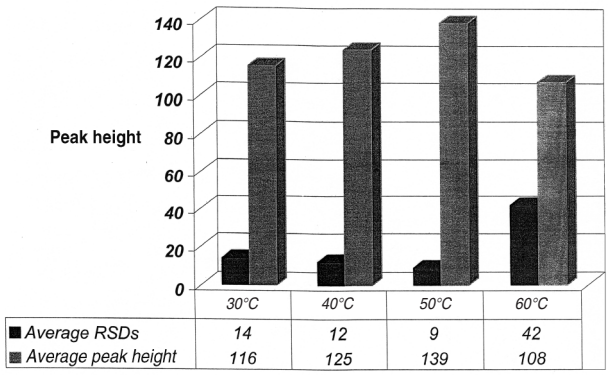

Figure 3. Effect of sample temperature on OP fortified in reagent water at 1 µg/L, extracted by SPME and analyzed by GC–NPD.

Table I. MDLs for OPs Extracted by SPME from Fortified Reagent Water

OP	MDL (µg/L)
Sulfotepp	0.46
Phorate	0.73
Terbufos	0.94
Disulfoton	0.42
Methyl parathion	0.25
Ethyl parathion	0.25
Methidathion	0.45

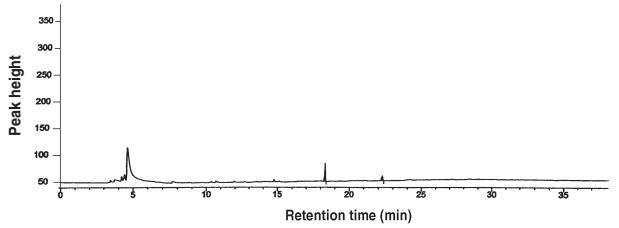

Figure 4. Chromatogram of control water from the Converse Reservoir, extracted by SPME with analysis by GC–NPD.

Table II. Recoveries and Precision in Source Waters for Drinking Water Treatment Facilities Fortified with OP at the LOQ

	SSC ground water		Converse reservoir water		MAWSS-treated water	
Compound	Recovery	%RSD	Recovery	%RSD	Recovery	%RSD
Sulfotepp	98.0	10.4	86.5	28.6	91.5	21.8
Phorate	92.9	10.9	76.9	21.6	85.6	18.8
Terbufos	88.3	11.9	77.5	15.8	88.4	15.5
Disulfoton	104	5.81	82.9	16.4	93.2	8.44
Methyl parathion	71.9	11.7	79.1	12.7	82.2	3.15
Ethyl parathion	90.3	7.71	86.9	12.4	96.2	5.07
Methidathion	69.7	13.4	71.2	7.09	65.5	6.20
Average recovery/RSD	87.9	10.3	80.1	16.4	86.0	11.3

interest at concentration levels of 1 µg/mL and heated to 30°C, 40°C, 50°C, and 60°C were prepared. The SPME fiber was exposed to each for 60 min to determine the effect of heating on the recovery and precision of the extraction and analyses. To compare overall recovery and precision data, the peak height and relative standard deviations (RSDs) for the seven OPs were averaged for all the compounds and graphed as shown in Figure 3. As can be seen, the average peak height was greatest at the same temperature that resulted in the best precision (lowest RSD); that temperature was 50°C. Temperatures greater than 50°C resulted in a significant decrease in both precision and recovery.

Analytes eliminated from method

Initially, it was intended that the method be used to extract 10 organophosphates, but, ultimately, three of the 10 had to be eliminated from the method. They were methamidaphos and azinphos methyl because of low recoveries and malathion because of poor reproducibility.

Linearity and detection limits

Method linearity was determined by analysis of aqueous standards prepared in reagent water fortified at 1.0, 2.5, 5.0, and 12.5 µg/L and extracted using the same method used for sample extraction. Regression analysis was used to determine linearity. Typical correlation coefficients for the analytes ranged from 0.98840 for sulfotepp to 0.99947 for methidathion. The linear dynamic range was limited not by the SPME extraction but by the NPD. This was demonstrated by the analysis of external standards that were prepared in hexane and analyzed on the NPD.

Method detection limits (MDLs) for the seven OPs were determined by analyzing seven replicates of reagent water fortified at 1 µg/L. The MDL was calculated by multiplying the average standard deviation for each of the analytes by the student t value for $(n - 1)$ analyses at the 99% confidence level as described in 40 CFR Appendix B, Part 136 (9). The MDLs ranged from 0.25 to 0.95 µg/L. MDLs for all the analytes are listed in Table I.

Environmental water sample application

Water samples were collected from two source waters for drinking water treatment facilities. Ground water was collected from a deep well at Stennis Space Center (SSC), MS. This water undergoes chlorination and then serves as the main drinking water source at SSC. Seven 3-mL replicates of the nonchlorinated ground water were prepared and fortified at 3 µg/L [estimated limit of quantitation (LOQ)] and seven replicates were fortified at 30 µg/L (10 × LOQ). At the 10 × LOQ level, the samples were diluted 1:5 to bring the responses into the calibration range. Both were extracted using the optimized SPME method with analysis by GC–NPD. No significant interference was encountered in

the matrix (as seen in Figure 4). Recoveries for the SSC ground water analytes fortified at the LOQ ranged from 69.7% to 104%, with RSDs ranging from 5.81 to 13.4 (as seen in Table II). A typical chromatogram at the LOQ is shown in Figure 5. At the 10 × LOQ level, the recoveries ranged from 102.8% to 123.2% and the RSDs from 6.93 to 10.69.

A second water source, the Converse Reservoir (Mobile, AL), is the primary source of drinking water for Mobile. The sample was collected prior to entering the MAWSS and analyzed using the optimized SPME method. Again, no interference was seen. The seven organophosphates were fortified in 3-mL samples of the reservoir water at the LOQ of 3 µg/L. The precision/accuracy for this matrix is shown in Table II. Recoveries for the seven OPs ranged from 71.2% to 86.5%, with RSDs from 7.09% to 28.6%.

A water sample was also collected from the MAWSS treatment plant. Attempts at the Evironmental Chemistry Laboratyr to extract eight organophosphates, which had been fortified in chlorinated drinking water collected at SSC, MS, resulted in a significant loss in recovery for all compounds. This was the case for both water with chlorine and water in which the chlorine was quenched by the addition of sodium sulfite before extraction with the SPME fiber. It was unclear if the loss in recovery was attributable to the degradation of the organophosphates by chlorine as found in the earlier work by Magara et al. (10) or as a result of some other mechanism associated with the presence of chlorine. Magara found that certain organophosphate pesticides have been shown to convert to oxidative degradates by chlorination during water treatment. The recovery loss for the OPs in chlorinated water was considered an area for future research, but was beyond the scope of this project. It was, therefore, decided to collect the water from the treatment plant prior to chlorination to avoid such interfence. The water had already undergone coagulation, flocculation, sedimentation, and filtration. The water was fortified at the LOQ of 3 µg/L. Results can be seen in Table II. With the exception of methidathion, with a recovery of 65.5%, all other analyte recoveries fell within the range of 70–130%. RSDs of the samples ranged from 3.15% to 21.8%.

Conclusion

SPME using a PDMS–DVB fiber can be used to rapidly identify and quantitate certain organophosphate pesticides that might be deliberately or accidentally introduced into source waters for a drinking water treatment facility. It can also be used to monitor water within a community drinking water treatment facility during the treatment process prior to chlorination to identify possible contaminants (OP).

The advantages of the technique, especially for drinking water treatment facilities that lack resources, include the fact that it requires no solvents and can be performed in as little as 2 h from sample preparation through GC analysis. In contrast, many of the currently used standard methods, using LLE and SPE, take 8 h or more for just the extraction portion of the method. A second advantage is good method sensitivity using very small sample sizes (3 to 30 mL) because the total amount of sample is available for adsorption on the fiber.

The number of analytes that can be extracted via SPME will inevitably expand as the number of new fiber coatings increases as the technology develops.

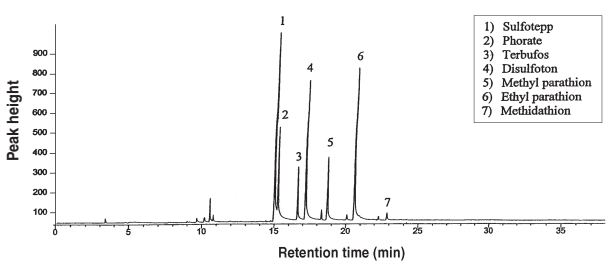

Figure 5. Chromatogram of water from the Converse Reservoir, fortified with seven OPs at 3.0 µg/L (LOQ) and extracted using SPME with analysis by GC–NPD.

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