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Development of an Analytical Method for White Phosphorus (P_4) in Water and Sediment Using Solid-Phase Microextraction

Marianne E. Walsh, Susan Taylor and Philip G. Thorne

August 1996

Abstract: Headspace solid-phase microextraction (SPME) methods were developed for white phosphorus in water and sediment/soil to minimize waste generated by methods based on solvent extraction. Headspace SPME provided a rapid, non-exhaustive extraction, based on equilibrium, of white phosphorus. Comparison of results obtained by headspace SPME and solvent extraction shows that headspace SPME may be used quantitatively for some water matrices and qualitatively for more complex matrices such as sediment/soil. Because detection limits appear to be similar to those obtained by solvent extraction, headspace SPME can be used to rapidly screen samples for contamination, eliminating the need to solvent-extract most samples.

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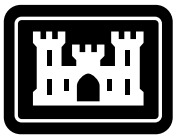
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Prepared for
U.S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION

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PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, Applied Research Division; Susan Taylor, Research Physical Scientist, and Philip G. Thorne, Research Physical Scientist, Geological Sciences Division; Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire. Funding for this work was provided by the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, through Environmental Quality Technology Project AF25, Ann Strong, Project Monitor.

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Development of an Analytical Method for White Phosphorus (P_4) in Water and Sediment Using Solid-Phase Microextraction

MARIANNE E. WALSH, SUSAN TAYLOR AND PHILIP G. THORNE

INTRODUCTION

Analytical methods have been developed for white phosphorus (P_4) residues in sediment and water (Walsh and Taylor 1993, Walsh 1995, USEPA 1995). Both methods rely on solvent extraction prior to gas chromatographic analysis. The extracting solvents are isooctane and diethyl ether for soils/sediments and water, respectively. The method for soils/sediments has been performed successfully in field laboratories (Racine et al. 1993), but the safety hazards associated with diethyl ether restrict the analysis of water samples to laboratories with fume hoods. In this study, we describe methods that minimize or eliminate the use of organic solvents.

Solid-phase microextraction (SPME) is a new alternative to traditional techniques for extracting volatile or semivolatile organics (Belardi and Pawliszyn 1989, Boyd-Boland et al. 1994, Zhang et al. 1994). First developed to analyze for volatile chlorinated organics, PCBs (polychlorinated biphenyls) and BTEX (benzene, toluene, ethylbenzene, xylene) in water (Arthur and Pawliszyn 1990; Arthur et al. 1992a, b, d; Potter and Pawliszyn 1992, 1994; Buchholz and Pawliszyn 1993), the method has been successfully used for a wide variety of analytes in environmental, food and pharmaceutical matrices (Hawthorne et al. 1992, Otu and Pawliszyn 1993, Buchholz and Pawliszyn 1994, Horng and Huang 1994, Yang and Peppard 1994, Zhang et al. 1994). The technique has several advantages (fast, simple, precise, sensitive), and requires no solvent (Arthur et al. 1992e). For this technique, a thin fused silica fiber coated with a stationary phase is exposed to a sample, either by immersion in a water or air sample or to headspace above an aqueous or solid sample (Fig. 1). Analytes sorb to the stationary phase, then the fiber is transferred directly to a heated injection port of a gas chromatograph for thermal desorption and analysis. The method can be automated and an SPME autosampler is available commercially (Arthur et al. 1992c, Berg 1993).

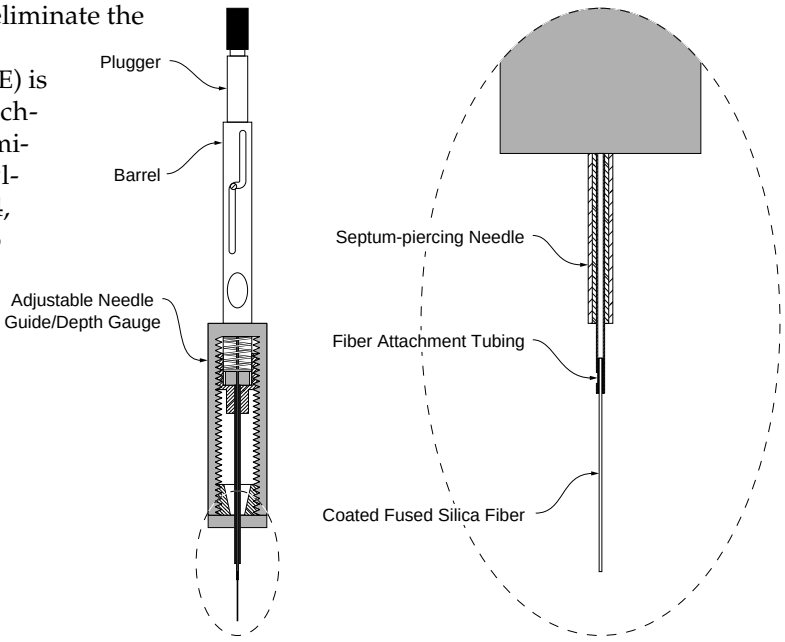


Figure 1. SPME device.

Headspace sampling works well for analytes with a Henry's Law constant, the equilibrium partition coefficient for a chemical between water and the headspace above it, above 90 atm-cm^3/mole (Zhang and Pawliszyn 1993a, b). Since Henry's Law constant for white phosphorus is over 2000 atm-cm^3/mole (Spanggord et al. 1985), headspace SPME is feasible. We were particularly interested in headspace sampling because environmental matrices containing white phosphorus are potentially complex (surface waters, wastewater, sediments), and the SPME fiber would be damaged or fouled by immersion into these matrices. Headspace sampling relies on the equilibrium partitioning of the analyte among the matrix, headspace and SPME phase (Zhang and Pawliszyn 1993a, b). The extraction is not exhaustive, and for semi-volatiles only a small portion of the total analyte present becomes associated with the fiber. If depletion of the analyte is negligible, the same aliquot of a sample can be analyzed first by headspace, then by solvent extraction. Analysis of the same sample aliquot by headspace SPME followed by solvent extraction allows direct comparison of the two methods without the confounding effect of heterogeneity, and makes SPME a valuable tool for screening samples for contamination. Because the majority of samples sent to analytical labs for the analysis of volatiles or semi-volatiles tend to be blank (devoid of the analytes of interest at analytical detection limits), considerable time and solvent could be saved by screening samples for contamination prior to solvent extraction and analysis.

The objectives of this study were to

1. Determine if headspace SPME provides a detection capability similar to solvent extraction methods for white phosphorus in water and sediment matrices.
2. Test the feasibility of calibrating headspace SPME for the quantitative analysis of water samples.
3. Evaluate the performance of headspace SPME with field-contaminated water and sediment samples.
4. Compare concentration estimates obtained via headspace SPME with estimates obtained by solvent extraction.
5. Evaluate the suitability of headspace SPME for use in a field laboratory.

METHODS

Standards and spiking solutions

An analytical standard for white phosphorus was obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin). The white phosphorus was supplied as a 5-g stick. It came immersed in water and had a white coating on its surface. Pieces (100–300 mg) of white phosphorus were cut from the stick under water. Care was taken to ensure that the surfaces of each piece of white phosphorus were freshly cut, lustrous in appearance, and showed no evidence of white coating. These translucent, colorless pieces were transferred under water to a test tube, and the test tube was placed in a beaker filled with water. The water with white phosphorus pieces was heated to 54°C to melt the white phosphorus, which remains as a separate phase. A Gilson Microman Positive Displacement Pipet was used to obtain 25-µL (45 mg) droplets of white phosphorus, which were placed in separate test tubes under water. The water was cooled to solidify the droplets.

A stock solution for calibration standards was prepared under nitrogen by dissolving 90 mg of white phosphorus in 250 mL of toluene (Aldrich Chemical Co.). Standards over the range 7.2 to 7200 µg/L were prepared by diluting the stock solution with methanol. Aqueous standards over the range of 0.0072 to 0.72 µg/L were prepared by adding 25 µL of a methanol standard to individual 25-mL aliquots of water in 40-mL glass vials sealed with a septum.

Aqueous solutions of white phosphorus were prepared by placing pieces of white phosphorus into an amber jug containing 4 L of reagent-grade water (Type I) (MilliQ, Millipore) with no headspace, and agitating the jug for more than 60 days.

Matrices

Blank matrices used to prepare spiked samples were reagent-grade (Type I) water (MilliQ, Millipore); groundwater from a domestic well in Weathersfield, Vermont; surface water from a pond in Hanover, New Hampshire; surface water from a salt marsh in Anchorage, Alaska; Ottawa sand purchased from U.S. Silica (Ottawa, Illinois); a loamy soil from the U.S. Army Environmental Center (Aberdeen Proving Ground, Maryland); and a sandy silt from Lebanon, New Hampshire. Soil samples were wetted to 100% moisture (dry weight basis, i.e., equal parts water and soil) prior to spiking.

Field-contaminated samples were obtained from Eagle River Flats, Fort Richardson, Alaska. Water samples were collected in 1-L amber glass bottles and sediment samples were collected in 120-mL wide-mouth jars filled so that there was no headspace. Samples were maintained at 4°C until extracted.

SPME

SPME fiber assemblies were obtained from Supelco (Bellefonte, Pennsylvania) (Fig. 1). These assemblies are composed of a fused silica fiber coated with a stationary phase (we purchased the 100-µm polydimethylsiloxane-coated fibers). The fiber is attached to a holder with a septum-piercing sheath that protects the fiber. The holder also allows precise positioning of the fiber in samples and the injection port of the gas chromatograph. In general, the fiber is exposed to a sample for a short period, during which time analytes sorb to the stationary phase. Then the fiber is placed into the injection port of a gas chromatograph to thermally desorb the analytes. We used the SPME fibers as follows: for each water sample, a 25-mL aliquot was placed in a 40-mL vial. The vial was either allowed to stand statically at room temperature or was placed in a sonic bath for five or ten minutes, during which time the SPME phase was exposed to the headspace (Fig. 2a). The SPME phase was immediately transferred to a heated (200°C) injection port of the gas chromatograph (Fig. 2b) described below.

For each sediment/soil sample, a 40-g subsample was placed in a 120-mL jar containing 10.0 mL of reagent-grade water. The jar was sealed with a cap equipped with a septum. Each sample was shaken manually for 15 seconds, and then the SPME phase was exposed statically to the headspace for five minutes such that there was no physical contact between the fiber and the sample. The SPME phase was thermally desorbed as described for the water samples.

Solvent extraction

For water samples with white phosphorus concentrations less than 0.1 µg/L, preconcentration of the solvent extracts is required. A non-evaporative approach is used since white phosphorus is volatile and air-sensitive (Walsh 1995). A 500-mL aliquot of water was mixed with 50 mL of diethyl ether by shaking in a 500-mL separatory funnel for five minutes. After phase separation, all of the ether layer was collected. The volume of the ether layer recovered varied depending on the temperature and the ionic strength of the samples; it generally ranged from 3 to 10 mL. The volume of the ether layer was further reduced to 0.5–1.0 mL by adding the ether extract to approximately 50 mL of reagent-grade water in a 125-mL separatory funnel and shaking for one minute. After phase separation, the ether layer was collected in a 5.0-mL graduated cylinder and the exact volume measured. This procedure resulted in a preconcentration factor of 500 to 1000. White phosphorus concentration in the extract was then determined by gas chromatography. Extracts were analyzed immediately to minimize loss due to solvent evaporation.

For samples with white phosphorus concentrations greater than 0.1 µg/L (Walsh 1995), simple solvent extraction provides sufficient concentration. A 25-mL aliquot of water was shaken for five

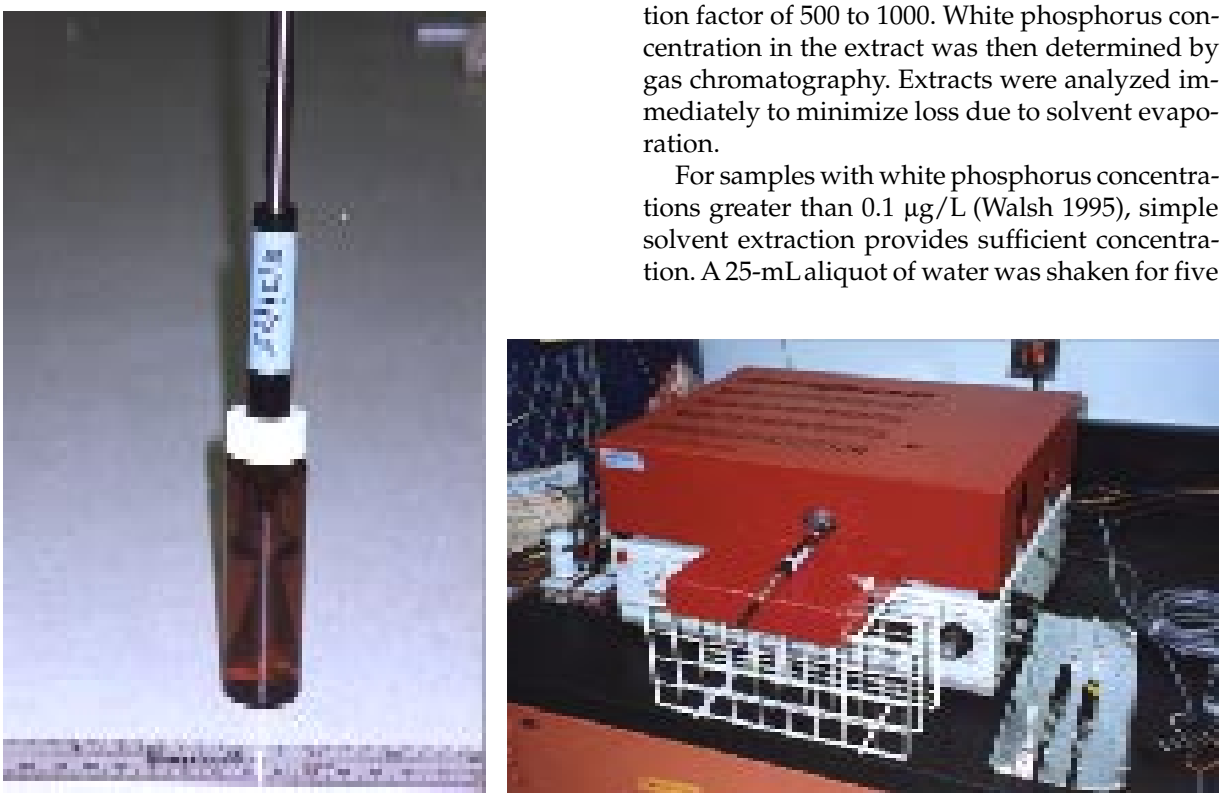


Figure 2. (left) Headspace SPME followed by (right) thermal desorption in injection port of gas chromatograph.

minutes with 2.00 mL of isooctane. Following phase separation, the isooctane extract was analyzed.

Wet sediment samples were extracted by placing a 40-g subsample into a 120-mL jar containing 10.0 mL of reagent-grade water. Then, 10.0 mL of isooctane was added. Each jar was tightly sealed with a Teflon-lined cap and vortex-mixed for one minute, and then placed horizontally on a platform shaker for 18 hours. The sample then was allowed to stand undisturbed for 15 minutes, and, if necessary, centrifuged for five minutes, to permit phase separation. Extracts were analyzed within a few hours.

Gas chromatograph

For solvent extracts or calibration standards, white phosphorus was determined by injecting a 1.0-µL aliquot on-column into an SRI Model 8610 gas chromatograph equipped with a nitrogen–phosphorus detector. SPME fibers were thermally desorbed at 200°C in the injection port of the same GC, and, for convenience, the SPME fiber was left in the injection port for the entire run time (five minutes).

The methylsilicone fused silica column (J and W DB–1, 0.53-mm-i.d., 15-m, 3.0-µm film thickness) was maintained at 80°C. The carrier gas was nitrogen set at 30 mL/minute. Under these conditions, white phosphorus eluted at 2.7 minutes.

RESULTS AND DISCUSSION

Detection capability

We evaluated the detection capability of SPME while gathering validation data for analytical methods for white phosphorus by solvent extraction and gas chromatography (Walsh et al. 1995). For each matrix (Table 1), ten replicate spiked samples (1 L for water and 40 g for wet soil) were prepared by adding an aqueous solution of white phosphorus to yield concentrations near the method detection limits for the solvent extraction methods (0.01 µg/L for water and 1 µg/kg for soil). Headspace SPME was performed and peak height data were obtained.

For those water samples that had white phosphorus concentrations near 0.01 µg/L, the peak heights obtained by headspace SPME were small, but white phosphorus was consistently detectable in all spiked samples (signal-to-noise ratios were greater than 7). Therefore the detection capability of the SPME appeared to be comparable to solvent extraction. In addition, the SPME response factors (means of the peak heights normalized to spiked concentration for each water matrix) were similar. The similarity in response with different water matrices was further studied in terms of calibration, as described below.

In contrast, SPME peak heights varied with the different soil matrices. Peak heights were lowest in the sample with the highest organic content and grain size distribution. However, in all cases, the peak heights were much larger than those obtained by solvent extraction, indicating that detection capability of the headspace SPME might be better than that for solvent extraction. Further studies were performed with field-contaminated samples as described below.

Depletion of total analyte present

White phosphorus may be present in sediment samples as heterogeneously distributed particles of different masses. Due to potential loss of white phosphorus by sublimation and oxidation, traditional homogenization methods involving drying, grinding, sieving, mixing, and subsampling are not applicable for white phosphorus-contaminat-

Table 1. Mean peak heights obtained following headspace SPME/GC for water and soil samples spiked at white phosphorus concentrations near the detection limit for solvent extraction methods.

		Peak height				
Matrix	*Spiked conc.*	*n*	*Mean*	*Standard deviation*	*RSD (%)*	*Response factor**
Reagent-grade water	0.012 µg/L	10	1,465	252	17	122,000
Well water	0.0097 µg/L	10	1,119	106	9.5	115,000
Pond water	0.010 µg/L	10	1,013	235	23	101,000
Sand	1.9 µg/kg	9	270,481	20,356	7.5	142,000
Lebanon (Sandy silt)	0.97 µg/kg	10	97,063	10,486	11	100,000
USAEC (Loam)	0.84 µg/kg	9	74,381	6,157	8.3	88,500

* (Peak height)/(Spiked concentration [µg/L]).

ed sediments. As a result, wide variations are routinely observed in concentration estimates of subsamples from individual field-contaminated sediment samples. This heterogeneity complicates the comparison of different analytical methods.

One potential attribute of headspace SPME is the ability to detect the presence of an analyte without altering a sample. Provided that headspace SPME does not remove a significant amount of analyte, the same subsample of sediment can be analyzed by headspace SPME followed by solvent extraction and GC determination. Using the same subsample for both determinations, the results of the two methods can be compared without the confounding effects of heterogeneity. Since heterogeneity between subsamples of bulk water samples has not been observed, we are primarily concerned with soil/sediment samples.

To see if concentration estimates based on the amount of white phosphorus in solvent extracts would be biased if headspace SPME was performed, we used the peak height data in Table 1 and peak height data from direct injections of calibration standards to calculate the mass of white phosphorus detected by SPME. Less than 0.4% of the initial white phosphorus present was removed by headspace SPME from each soil matrix, and less than 1% from each water matrix. Thus the amount of white phosphorus removed by one headspace SPME extraction is negligible.

Calibration

Calibration, which is necessary for quantitation, has been achieved for other analytes by spiking a known amount of analyte, generally dissolved in a water-miscible solvent, into a clean water matrix, then performing SPME as is done for regular samples (Zhang et al. 1994). Calibration for a complex matrix such as soil is more complicated since matrix–analyte interactions are much more pronounced. While methods such as standard additions or internal standards have been suggested and work well for some analytes (Zhang et al. 1994), the difference in extractability between spiked and native analyte can have a profound influence, unless the extraction is exhaustive. Recently, exhaustive headspace SPME extraction of some volatiles was achieved by simultaneous heating of the sample and cooling of the fiber coating (Zhang and Pawliszyn 1995). Prior to that study, quantitative results by SPME were reported primarily for water samples, and results for soil samples have been predominantly qualitative.

Linearity

To determine the feasibility of calibrating headspace SPME for water contaminated with white phosphorus, a series of aqueous calibration standards over the range 0.0072 to 7.2 µg/L (Table 2) was prepared in duplicate. Linearity of response (peak heights) with respect to white phosphorus concentration was tested for water from four sources (a MilliQ purification system, a well water, a pond water and a salt marsh) (Table 3). These aqueous standards were prepared by adding 25 µL of standards prepared in methanol to 25 mL of water, which resulted in a methanol concentration of 0.1%. Previous studies with BTEX showed that a methanol of less than 1% did not effect peak areas obtained by SPME (Arthur et al. 1992c). Peak heights obtained by headspace SPME-GC were converted to mass (pg) of white phosphorus from response factors based on syringe injections of standards in methanol (Zhang and Pawliszyn 1993a).

Table 2. Concentration of calibration standards prepared for headspace SPME of water samples.

Conc. of methanol std. (µg/L)	*Conc. of aqueous std. (µg/L)**	*Mass of white phosphorus in each aqueous std. (ng)*
7.2	0.0072	0.18
14.4	0.0144	0.36
28.8	0.0288	0.72
72	0.072	1.8
144	0.144	3.6
1440	1.44	36
7200	7.2	180

* Prepared by adding 25 µL of methanol standard to 25 mL of water.

Table 3. Water quality measurements for matrices used for aqueous white phosphorus standards.

Matrix	*Conductivity (mmho/cm)*	*pH*	*Redox (mV)*
Reagent-grade water	0		
Well water	0.277	7.6	163
Pond water	0.201	7.4	14
Salt marsh water	23	7.9	133

For data for each water matrix, a linear regression model with intercept (Fig. 3) and a linear regression model through the origin were tested for lack of fit. In all cases, linear models adequately described the data over the concentration range 0.0072 to 0.144 µg/L (the F ratio for lack of fit was less than the critical value for 95% confidence)

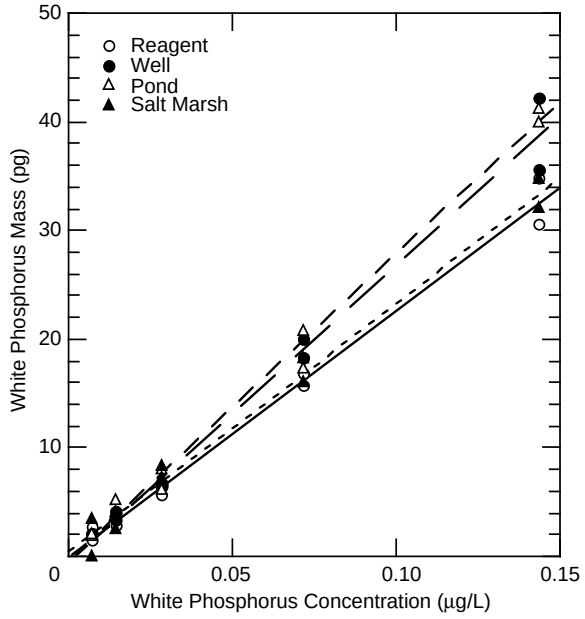


Figure 3. Mass of white phosphorus (pg) detected by headspace SPME vs. aqueous concentration over range of 0.0072 to 0.144 µg/L. Lines represent least squares regression models.

Table 4. Regression coefficients for linear calibration models of white phosphorus (pg) detected by headspace SPME vs. aqueous concentration over range of 0.0072 to 0.144 µg/L.

	Model with intercept*			*Model through origin*		*Zero-intercept hypothesis*
Water matrix	*Slope*	*Intercept*	*Lack of fit F ratio†*	*Slope*	*Lack of fit F ratio***	*Calculated F††*
Reagent grade	226	–0.0067	0.15	226	0.11	0.00014
Well	272	–0.42	0.16	268	0.16	0.26
Pond	280	–0.27	0.88	278	0.71	0.21
Salt marsh	230	0.41	0.24	234	0.25	0.41

* $y = mx + b$, where y = mass of WP (pg) and x = aqueous WP concentration (µg/L)
† Critical $F_{0.95\,(3,5)} = 5.41$
** Critical $F_{0.95\,(4,5)} = 5.19$
†† Critical $F_{0.95\,(1,8)} = 5.32$

Table 5. White phosphorus mass (pg) detected by headspace SPME for replicate 0.144 µg/L aqueous standards prepared in four water matrices and analyzed on the same day.

	White phosphorus mass (pg)			
Rep	*Reagent*	*Well*	*Pond*	*Salt marsh*
1	31.8	36.5	41.3	39.6
2	35.8	39.1	31.5	32.1
3	37.6	32.9	36.7	33.1
4	32.9	36.2	36.6	34.3
5	32.3	34.1	35.6	36.8
Mean	34.1	35.8	36.3	35.2
Std dev	2.5	2.4	3.5	3.0
% RSD	7.4%	6.8%	9.6%	8.6%
Mass (pg) / Conc. (µg/L)	237	249	252	244

(Table 4). Higher concentrations were beyond the linear range of the detector. The slopes for the regression models for the four different waters were not compared statistically because the data were not generated on a single day; however, they appeared to be similar.

Matrix effects

To confirm the similarity in response (mass of white phosphorus detected by headspace SPME) among the four different matrices, five replicate 0.144-µg/L aqueous standards were prepared for each matrix and analyzed on a single day. The means of the responses obtained (Table 5) were compared by ANOVA and were not significantly different ($p = 0.65$) despite the fairly wide range

of conductivities (0 to 23 mmho/cm) between the matrices. These results, however, are consistent with those observed for BTEX where salt concentrations below 1% did not significantly affect results (Arthur et al. 1992c). However, salt saturation has been used successfully to enhance response for BTEX by headspace SPME (MacGillivray et al. 1994).

The mean mass of white phosphorus detected by headspace SPME for the combined data set (Table 5) is 35.4 pg. To prepare each 25-mL aqueous standard at 0.144 µg/L, 3600 pg of white phosphorus was added. Therefore, the mass removed by headspace SPME was 0.98% of the initial mass. These data provide further confirmation that headspace SPME may be performed on the same sample prior to solvent extraction without biasing the concentration estimates obtained by solvent extraction. For water samples, sequential SPME–solvent extraction of the same aliquot would be appropriate for samples with white phosphorus concentrations greater than 0.1 µg/L. For water samples with lower concentrations, a larger aliquot (500 mL) of water is needed to provide adequate preconcentration using ether extraction. Results using these various extraction options will be discussed later in relation to field samples.

Model predictions

Zhang and Pawliszyn (1993a) derived the following equation for the mass of analyte sorbed by the SPME phase at equilibrium during headspace SPME of water samples:

$$n = \frac{K_1 K_2 C_0 V_1 V_2}{K_1 K_2 V_1 + K_2 V_3 + V_2}$$

where K_1 = SPME phase/gas partition coefficient
K_2 = gas/water partition coefficient
C_0 = initial concentration of the analyte in the aqueous solution
V_1, V_2, and V_3 = volumes of the SPME phase, aqueous solution and the headspace.

The gas/water partition coefficient (K_2) is derived from the Henry's Law constant (K_H)

$$K_2 = \frac{K_H}{RT}.$$

The SPME phase/gas partition coefficient (K_1) can be estimated from the relationship

$$K = K_1 K_2$$

where K is close to the octanol water partition coefficient (K_{ow}) for many analytes (Zhang and Pawliszyn 1993a, Louch et al. 1992, Dean et al. 1996). For BTEX compounds, the ratios of K_{ow}/K ranged from 0.9 to 2.7 (Zhang and Pawliszyn 1993a). K_{ow} and K_H have been measured for white phosphorus (Spanggord et al. 1985). The estimates are K_{ow} = 1200 and K_H = 2100 atm-cm^3/mole. Using these estimates for K_{ow} and K_H, the predicted mass of white phosphorus sorbed to the SPME phase was computed for equilibrium with a 0.144-µg/L aqueous solution and the two size vials used in these studies (Table 6).

Table 6. Predicted mass (pg) of white phosphorus sorbed to the SPME phase during headspace SPME based on model by Zhang and Pawliszyn (1993) and estimates of K_{ow} and K_H by Spanggord et al. 1985.

Size of vial (mL)	*Volume (mL)*		*Theoretical mass sorbed (pg)*
	Headspace	*Aqueous solution*	
40	1	39	104
	5	35	102
	10	30	100
	15	**25**	**97**
	20	20	93
	25	15	87
	30	10	77
	35	5	57
120	1	119	105
	10	110	104
	20	100	103
	30	90	102
	40	80	100
	50	70	98
	60	60	95
	70	**50**	**92**
	80	40	87
	90	30	80
	100	20	69
	110	10	49

Predictions are shown for two sizes of extraction vials used for these studies and various volumes of headspace. Numbers in bold correspond to volumes used in this study.

$n = \frac{K_1 K_2 C_0 V_1 V_2}{K_1 K_2 V_1 + K_2 V_3 + V_2}$ = mass of analyte sorbed by the SPME phase at equilibrium during headspace SPME.

V_1= volume of SPME phase = 6.12×10^{-4} mL*
V_2= volume of aqueous solution
V_3= volume of headspace
C_0= 0.144 µg/L
K_1= SPME phase/gas partition coefficient
K_2= gas/water partition coefficient = K_H/RT = 0.09
$K_1 K_2 \approx K_{OW}$ = 1200.

* Personal communication, Supelco, 1996.

For 25 mL of 0.144 µg/L aqueous solution in a 40-mL vial, the predicted mass of white phosphorus sorbed by the SPME phase is 97 pg. We found approximately 35 pg, or about one-third of the predicted mass. Assuming that K_2 is accurately predicted from K_H, the amount of mass sorbed corresponds to a K of 410. The ratio between K_{ow} and K equals 2.9, which is slightly outside the range reported for BTEX. Therefore the model predictions and experimental results are in fair agreement.

The model also predicts the effect of variable volumes of headspace. Predicted mass sorbed increases as headspace volume shrinks, but the effect is minimal for the size vials we used when the vials are at least half full. This characteristic is very useful in a field laboratory since sample volumes need to be measured with a precision of approximately ±1 mL. Sample aliquots could be obtained by gentle pouring into graduated vials, eliminating the need for volumetric pipets and associated glassware washing and rinsing.

Agitation

During headspace SPME, agitation of the sample hastens equilibrium (Arthur et al. 1992c). We used a sonic bath (Motlagh and Pawliszyn 1993), but found that temperature had to be carefully controlled. Fluctuating temperatures decrease precision. Higher temperatures increase the analyte vapor phase concentration but decrease analyte sorption into the fiber (MacGillivray et al. 1994, Zhang and Pawliszyn 1995) since sorption is an exothermic process (Arthur et al. 1992c). Stirring was not tested, but has been used by previous investigators (MacGillivray et al. 1994, Zhang and Pawliszyn 1995). The most convenient and least labor-intensive setup is static extraction for five minutes (length of the GC run) at room temperature.

Zhang and Pawliszyn (1993a) predicted equilibration time for headspace SPME using a model based on one-dimensional diffusion described by Fick's second law. Equilibration time was controlled by the gas/water and SPME phase/water partition coefficients (K_2 and K_1 described above). Extraction time profiles of analytes by headspace SPME are characterized by a three-part curve: first, by a rapid increase in mass sorbed within the first minute of exposure of the SPME phase to the headspace, followed by a much slower increase, then no change at equilibrium. The initial increase corresponds to the sorption of analyte initially present in the headspace, and the slower increase is due to the mass transfer of analytes from the aqueous phase (Pawliszyn 1995). The transition between the initial rapid rise and equilibrium is reduced by agitation. Based on this model and the physical properties of white phosphorus (K_{ow} = 1200, K_H = 2100 atm-cm^3/mole), equilibration time for white phosphorus should be only a few minutes for well-agitated samples. Even though equilibrium may not be reached within a few minutes when the sample is not agitated, the mass absorbed should approach the mass at equilibrium because of the shallow slope of the extraction profile.

To see if the elimination of the sonication significantly decreased the mass of white phosphorus sorbed to the SPME phase, four replicate 0.144-µg/L aqueous standards were prepared in reagent-grade water and extracted and analyzed in random order by headspace SPME by three methods: five minutes of sonication, ten minutes of sonication, and five minutes static. One sample was extracted statically for 20 minutes, then 80 minutes. The results (Table 7) were compared by blocked ANOVA (Table 8), and a significant difference was found indicating that equilibrium was not reached during five minutes of static headspace SPME. However, the difference was small for practical purposes, 30.6 pg vs. 34.0 pg (90% recovery). For the one sample extracted statically for 20 minutes and 80 minutes, the masses detected were 31.5 and 35.2 pg, respectively. Since sonication or lengthy static extractions resulted in only modest increas-

Table 7. Mass of white phosphorus (pg) found by headspace SPME for samples extracted with sonicated and static aqueous phases.

	White phosphorus mass (pg)		
Rep	*5 min sonic*	*10 min sonic*	*5 min static*
1	30.3	32.7	29.1
2	36.8	34.5	31.5
3	36.8	35.1	30.8
4	31.2	33.6	31.0
Mean	33.8	34.0	30.6
Std dev	3.52	1.06	1.02
% RSD	10.4%	3.1%	3.3%

Table 8. Blocked ANOVA comparing means of sonicated and static samples.

	ss	*df*	*MS*	*F*
Total	12971.74	12		
Correction factor	12899.92	1		
Between block	28.02	3	9.34	3.58
Between treatment	28.14	2	14.07	5.39
Error	15.66	6	2.61	

$F_{0.95(2,6)} = 5.14$

es in response, simple five-minute static extraction should provide satisfactory precision and sensitivity if timing and extraction conditions are consistent. When analyzing samples in a field lab, eliminating the need for extra equipment and steps in the method will save time and money.

Field samples

Water

Water samples were collected from a salt marsh that was contaminated by white phosphorus munitions (Racine et al. 1993). Each of the five samples plus a blank were analyzed first by headspace SPME and concentrations estimates obtained using aqueous calibration standards. Triplicate measurements were made on some samples to estimate precision with real samples. White phosphorus was detectable by headspace SPME in three of the five water samples (Table 9).

Solvent extractions were then performed, either with isooctane or diethyl ether, depending on the concentration. One sample had an estimated concentration of 0.1 µg/L, which is barely detectable by isooctane extraction, so both types of extractions were performed, with the isooctane extraction performed on the same subsample as the headspace SPME. One sample was overrange using the headspace SPME method. The sample was diluted by a factor of 1:100 with reagent-grade water, and headspace SPME was repeated, followed by isooctane extraction of the same aliquot of sample.

Agreement between the methods was good, as was the precision of the headspace SPME method (Table 9). Regression of the mean of the headspace SPME determinations with those by solvent extraction yielded a linear model with slope of 1.07 and R^2 of 0.997 (Fig. 4). Although the data set is small and more samples need to be analyzed for confirmation, these initial results showed good agreement between the different methods.

Sediment

A much larger number of sediment samples were available for analysis. A total of 92 sediment samples was analyzed by headspace SPME followed by solvent extraction. We used the same subsample for both types of extractions. Of these samples, 30 were blank and 62 were positive by both methods; therefore, there were no false positives or false negatives for the headspace SPME method. The sediment samples varied widely in salt and organic matter content, and this matrix heterogeneity resulted in a poor correlation between the amount of white phosphorus detected by headspace SPME and the concentration found by solvent extraction (Fig. 5a, b). Nonetheless, headspace SPME proved to be an excellent screen-

Table 9. Estimates of white phosphorus concentrations by headspace SPME and solvent extraction in field-contaminated water samples.

	Estimated concentration (µg/L)		
	Headspace	*Solvent extraction*	
Sample	*SPME*	*isooctane**	*Ether*
1	<d		0.003
	<d		
	< d		
2	< d		<d
	< d		<d
	<d		
3	0.0348		0.0149
	0.0354		0.0187
	0.0355		
4	0.109	0.0834	0.0759
	0.106		
	0.0972		
5	>17.2 (overrange)	39.7	
		38.7	
5 ($^1/_{100}$ dilution)	0.399	0.369	
Blank	<d		<d

* Isooctane extraction of the same subsample as headspace SPME.

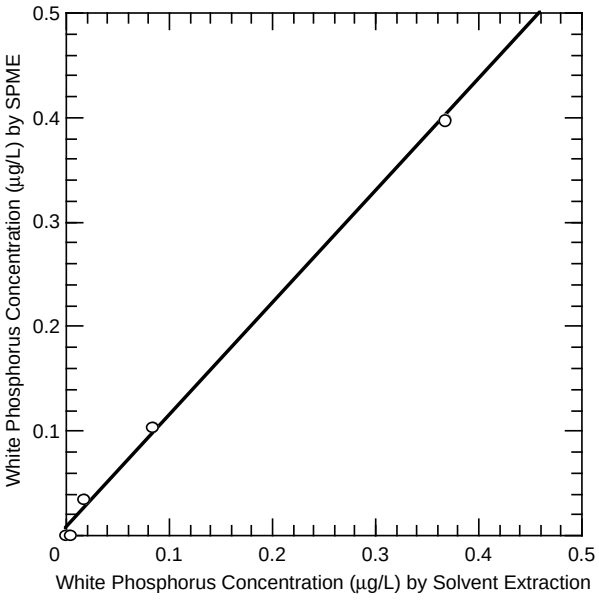
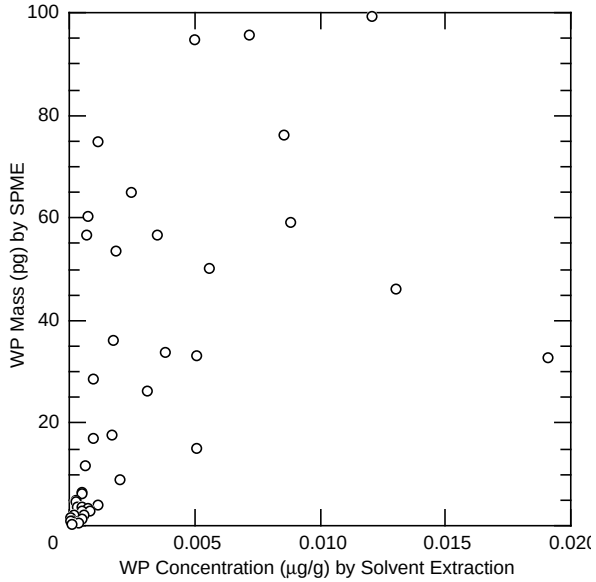
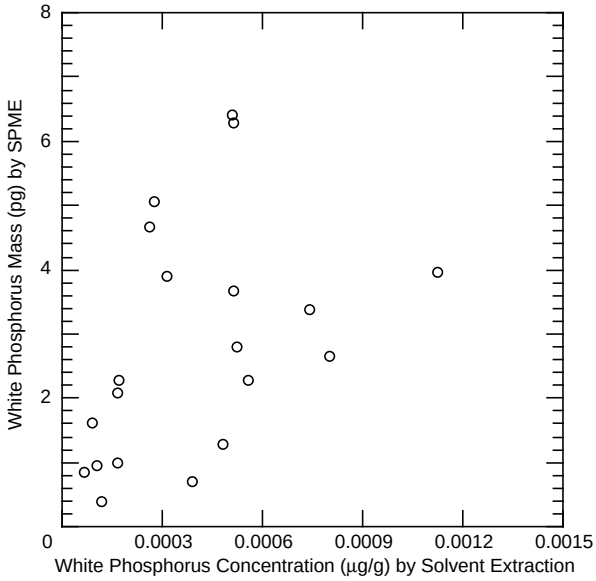


Figure 4. Concentration (µg/L) of white phosphorus estimated by headspace SPME vs. solvent extraction for field-contaminated water samples.

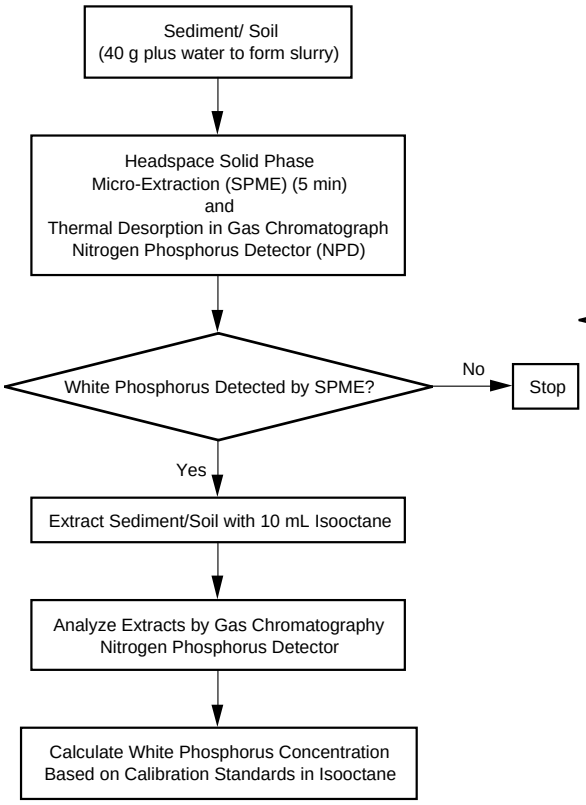


a. Data within linear range of detector.

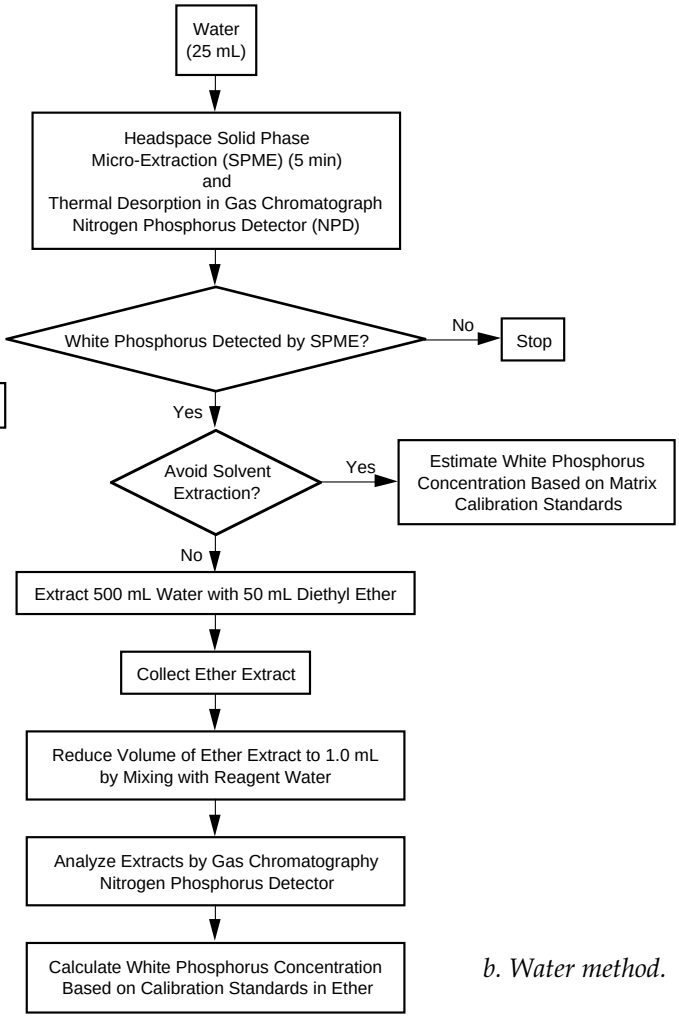


b. Same data as a, showing results at lowest concentrations detected.

Figure 5. Mass of white phosphorus detected by headspace SPME and concentration found in same sediment sample following solvent extraction.



a. Sediment/soil method.



b. Water method.

Figure 6. Flow chart of analytical methods for white phosphorus with headspace SPME used to screen samples for white phosphorus.

ing method. Based on the results from these field-contaminated sediment samples, the detection limit of the headspace SPME appeared to be similar to that of the solvent extraction (Fig. 5b).

The samples used for this experiment were collected from an area that was known to be contaminated, thus the high percentage of positive samples. Typically, most samples submitted for analysis are blank. We suggest that solvent extraction be used only for those sediment and soil samples where quantitative results are desired (Fig. 6).

Advantages of headspace SPME

When samples are analyzed for white phosphorus, headspace SPME provides the following advantages over the methods based on solvent extraction:

1. Time required for extraction/preconcentration is reduced to five minutes for water samples.
2. Water samples may be analyzed easily in a field laboratory.
3. Sediment/soil samples can be screened for the presence of white phosphorus.
4. Solvent extraction of blank samples can be eliminated, reducing the production of hazardous laboratory waste and reducing costs.

Further studies

Beyond these initial studies, the following experiments will be performed.

1. Gather more data to validate quantitative results for field-contaminated water samples.
2. Determine if salt saturation, which generally increases response of headspace SPME for BTEX, is appropriate for white phosphorus.
3. Explore ways to calibrate headspace SPME for sediments/soils.

SUMMARY AND CONCLUSIONS

Using the spiked and field-contaminated water and sediment samples, we tested headspace SPME for the analysis of white phosphorus. The SPME fiber was simply exposed to the headspace above a sample and then thermally desorbed in the injection port of the gas chromatograph. We calibrated the method to obtain quantitative results for water samples. Matrix dissimilarities confounded quantitation for sediment samples; however, headspace SPME successfully detected the presence of white phosphorus in sediment. Using headspace SPME of water and sediment matrices, detection limits appear to be similar to those obtained by solvent extraction.

LITERATURE CITED

Arthur, C.L. and J. Pawliszyn (1990) Solid-phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry*, **62**: 2145–2148.

Arthur, C.L., L.M. Killam, S. Motlagh, M. Lim, D.W. Potter and J. Pawliszyn (1992a) Analysis of substituted benzene compounds in groundwater using solid-phase microextraction. *Environmental Science and Technology,* **26**: 979–983.

Arthur, C.L., D.W. Potter, K.D. Buchholz, S. Motlagh and J. Pawliszyn (1992b) Solid-phase microextraction for the direct analysis of water: Theory and practice. *LC•GC*, **10**: 656–661.

Arthur, C.L., L.M. Killam, K.D. Buchholz, J. Pawliszyn and J.R. Berg (1992c) Automation and optimization of solid-phase microextraction. *Analytical Chemistry*, **64**: 1960–1966.

Arthur, C.L., K. Pratt, S. Motlagh, J. Pawliszyn and R.B. Belardi (1992d) Environmental analysis of organic compounds in water using solid-phase microextraction. *Journal of High Resolution Chromatography*, **15**: 741–744.

Arthur, C.L., L.M. Killam, K. Buchholz, D. Potter, M. Chai, Z. Zhang and J. Pawliszyn (1992e) Solid-phase microextraction: An attractive alternative. *Environmental Laboratory*, **11**: 10–15.

Belardi, R.P. and J.B. Pawliszyn (1989) The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. *Water Pollution Research Journal of Canada*, **24**: 179–191.

Berg, J.R. (1993) Practical use of automated solid-phase microextraction. *American Laboratory*, November, p. 18–24.

Boyd-Boland, A.A., M. Chai, Y.Z. Luo, Z. Zhang, M.J. Yang, J.B. Pawliszyn and T. Gorecki (1994) New solvent-free sample preparation techniques based on fiber and polymer technologies. *Environmental Science and Technology,* **28**: 569A–574A.

Buchholz, K.D. and J. Pawliszyn (1993) Determination of phenols by solid-phase microextraction and gas chromatographic analysis. *Environmental Science and Technology,* **27**: 2844–2848.

Buchholz, K.D. and J. Pawliszyn (1994) Optimization of solid-phase microextraction conditions for determination of phenols. *Analytical Chemistry*, **66**: 160–167.

Dean, J.R., W.R. Tomlinson, V. Makovsdaya, R. Cumming, M. Hetheridge and M. Comber (1996) Solid-phase microextraction as a method for estimating the octanol-water partition coefficient. *Analytical Chemistry*, **68**: 130–133.

Hawthorne, S.B., D.J. Miller, J. Pawliszyn and C.L. Arthur (1992) Solventless determination of caffeine in beverages using solid-phase microextraction with fused-silica fibers. *Journal of Chromatography*, **603**: 185–191.

Horng, J.-Y. and S.-D. Huang (1994) Determination of the semi-volatile compounds nitrobenzene, isophorone, 2,4-dinitrotoluene and 2,6-dinitrotoluene in water using solid-phase microextraction with a polydimethylsiloxane-coated fibre. *Journal of Chromatography A*, **678**: 313–318.

Louch, D., S. Motlagh and J. Pawliszyn (1992) Dynamics of organic compound extraction from water using liquid-coated fused silica fibers. *Analytical Chemistry*, **64**: 1187–1199.

MacGillivray, B., J. Pawliszyn, P. Fowlie and C. Sagara (1994) Headspace solid-phase microextraction versus purge and trap for the determination of substituted benzene compounds in water. *Journal of Chromatographic Science*, **32**: 317–322.

Motlagh, S. and J. Pawliszyn (1993) On-line monitoring of flowing samples using solid-phase microextraction gas chromatography. *Analytica Chimica Acta*, **284**: 265–273.

Otu, E.O. and J. Pawliszyn (1993) Solid-phase microextraction of metal ions. *Mikrochimica Acta*, **112**: 41–46.

Pawliszyn, J. (1995) New directions in sample preparation for analysis of organic compounds. *Trends in Analytical Chemistry,* **14**(3): 113–122.

Potter, D.W. and J. Pawliszyn (1992) Detection of substituted benzenes in water at the pg/mL level using solid-phase microextraction and gas chromatography-ion trap mass spectrometry. *Journal of Chromatography*, **625**: 247–255.

Potter, D.W. and J. Pawliszyn (1994) Rapid determination of polyaromatic hydrocarbons and polychlorinated biphenyls in water using solid-phase microextraction and GC/MS. *Environmental Science and Technology,* **28**: 298–305.

Racine, C.H., M.E. Walsh, C.M. Collins, S. Taylor, B.D. Roebuck, L. Reitsma and B. Steele (1993) Remedial investigation report for white phosphorus contamination in an Alaskan salt marsh. USA Cold Regions Research and Engineering Laboratory, CRREL Report 93–17.

Spanggord, R.J., R. Renwick, T.W. Chou, R. Wilson, R.T. Podoll, T. Mill, R. Parnas, R. Platz and D. Roberts (1985) Environmental fate of white phosphorus/felt and red phosphorus/butyl rubber military screening smokes. USA Medical Research and Development Command, ADA176922.

USEPA (1995) Method 7580: White phosphorus (P_4) by solvent extraction and gas chromatography. Test Methods for Evaluating Solid Waste. U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., SW–846 Update III.

Walsh, M.E. (1995) Analytical method for white phosphorus in water. *Bulletin of Environmental Contamination and Toxicology*, **54**: 432–439.

Walsh, M.E. and S. Taylor (1993) Analytical method for white phosphorus in munitions-contaminated sediments. *Analytica Chimica Acta*, **282**: 55–61.

Walsh, M.E., S. Taylor, D. Anderson, and H. McCarty (1995) Analytical methods for white phosphorus (P_4) in sediment and water. In Proceedings, *Eleventh Annual Waste Testing and Quality Assurance Symposium. 23–28 July 1995, Washington, D.C.,* 380–387.

Yang, X. and T. Peppard (1994) Solid-phase microextraction for flavor analysis. *Journal of Agricultural and Food Chemistry*, **42**: 1925–1930.

Zhang, Z. and J. Pawliszyn (1993a) Headspace solid-phase microextraction. *Analytical Chemistry*, **65**: 1843–1852.

Zhang, Z. and J. Pawliszyn (1993b) Analysis of organic compounds in environmental samples by headspace solid-phase microextraction. *Journal of High Resolution Chromatography*, **16**: 689–692.

Zhang, Z. and J. Pawliszyn (1995) Quantitative extraction using an internally cooled solid-phase microextraction device. *Analytical Chemistry*, **67**: 34–43.

Zhang, Z., M.J. Yang and J. Pawliszyn (1994) Solid-phase microextraction. *Analytical Chemistry*, **66**: 844A–853A.

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13. ABSTRACT (*Maximum 200 words*)

Headspace solid-phase microextraction (SPME) methods were developed for white phosphorus in water and sediment/soil to minimize waste generated by methods based on solvent extraction. Headspace SPME provided a rapid, non-exhaustive extraction, based on equilibrium, of white phosphorus. Comparison of results obtained by headspace SPME and solvent extraction shows that headspace SPME may be used quantitatively for some water matrices and qualitatively for more complex matrices such as sediment/soil. Because detection limits appear to be similar to those obtained by solvent extraction, headspace SPME can be used to rapidly screen samples for contamination, eliminating the need to solvent-extract most samples.

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