Solid-Phase Microextraction and Headspace Solid-Phase Microextraction for the Determination of High Molecular-Weight Polycyclic Aromatic Hydrocarbons in Water and Soil Samples

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Abstract

The feasibility of direct-immersion (DI) solid-phase microextraction (SPME) and headspace (HS) SPME for the determination of high-ring polycyclic aromatic hydrocarbons (PAHs) (4- to 6-ring PAHs) in water and soil samples is studied. Three SPME fibers—100- and 30-µm polydimethylsiloxane (PDMS) and 85-µm polyacrylate (PA) fibers—are compared for the effective extraction of PAHs. Parameters affecting the sorption of PAHs into the fiber such as sampling time, sampling volume, and temperature are also evaluated. The extracted amounts of high-ring PAHs decrease with the decreasing of film thickness, and the 100-µm PDMS has the highest extraction efficiency than 85-µm PA and 30-µm PDMS fibers. Also, the extraction efficiency decreases with the increasing molecular weights of PAHs. Of the 10 high-ring PAHs, only fluoranthene and pyrene can reach equilibrium within 120 min at 25°C for DI-SPME in a water sample. Increasing the temperature to 60°C can increase the sensitivity of PAHs and shorten the equilibrium time. A 0.7- to 25-fold increase in peak area is obtained for DI-SPME when the working temperature is increased to 60°C. For HS-SPME, the extraction efficiency of PAHs decrease when the headspace volume of the sampling system increases. All high-ring PAHs can be detected in a water sample by increasing the temperature to 80°C. However, only 4- and 5-ring PAHs can be quantitated in a CRM soil sample when HS-SPME is used. The addition of a surfactant with high hydrophilic property can effectively enhance the sensitivity of high-ring PAHs. HS-SPME as well as DI-SPME with 100-µm PDMS or 85-µm PA fibers are shown to be suitable methods for analyzing high-ring PAHs in a water sample; however, this technique can only apply in a soil sample for PAHs having up to 5 rings.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and primarily occur as a result of incomplete combustion processes. These compounds are considered to be hazardous to the environment. On the basis of their properties and molecular masses, two classes (the 2- and 3-ring and 4- to 6-ring) of PAHs can be distinguished. The low molecular-weight 2- and 3-ring PAHs have a significant acute toxicity, and some of the high molecular-weight PAHs show high carcinogenic and mutagenic potentials. Of the 21 most often found PAHs, the US Environmental Protection Agency has promulgated 16 unsubstituted PAHs in their list of 129 priority pollutants. Because of their high partition coefficients and low water solubilities, PAHs can easily absorb onto the organic phase of solid particles. Therefore, the development of effective extraction and enrichment techniques for PAHs to be administered prior to an analytical procedure is necessary.

The most commonly used methods for the extraction of semivolatile organic compounds from aqueous and solid phases are liquid–liquid extraction (LLE), Soxhlet extraction, and solid-phase extraction (SPE) (1). However, LLE and Soxhlet extraction require large amounts of solvents and is tedious and time-consuming, and SPE is prone to interference from impurities. Recently, a new solvent-free technique—solid-phase microextraction (SPME)—has been introduced for the extraction of many volatile and semivolatile organic compounds (2–5). SPME uses coated fused-silica fibers to extract analytes from gaseous or liquid phases. After equilibrium is reached or after a well-defined extraction time, the absorbed compounds are thermally desorbed by exposing the fiber in the injection port of a gas chromatograph (GC).

Two strategies of SPME—direct-immersion (DI) SPME and headspace (HS) SPME—have been applied to the analysis of a wide variety of pollutants. DI-SPME has been used to analyze volatile organic compounds (6), pesticides (7–9), polychlorinated biphenyls (PCBs) (10), and PAHs (11–14) in water and soil samples. HS-SPME has also been used to determine organophosphorus pesticides in soil (15), PCBs in soils and sediments (16), and low molecular-weight organic compounds in biological fluids (17,18). Sampling in the headspace presents a significant advantage in terms of selectivity because only volatile and semivolatile organic compounds can be released into the headspace. Because

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the fiber is not in contact with the sample, background adsorption and the matrix effect are reduced, which also enhances the life expectancy of SPME fibers. However, the application of SPME for the determination of high molecular-wieght organics in aqueous and solid matrices has received less attention.

In this study, high molecular-weight PAHs (including 4- to 6-ring PAHs) have been analyzed in water and soil samples. Different strategies such as DI-SPME and HS-SPME using different SPME fibers—100- and 30-µm polydimethylsiloxane (PDMS) and 85-µm polyacrylate (PA) fibers—were compared for the extraction of high-ring PAHs. Extraction time profiles and the temperature effect on the extraction efficiency were performed for optimizing the extraction conditions. Moreover, the addition of surfactants to a soil sample for enhancing the extraction efficiency of analytes was evaluated.

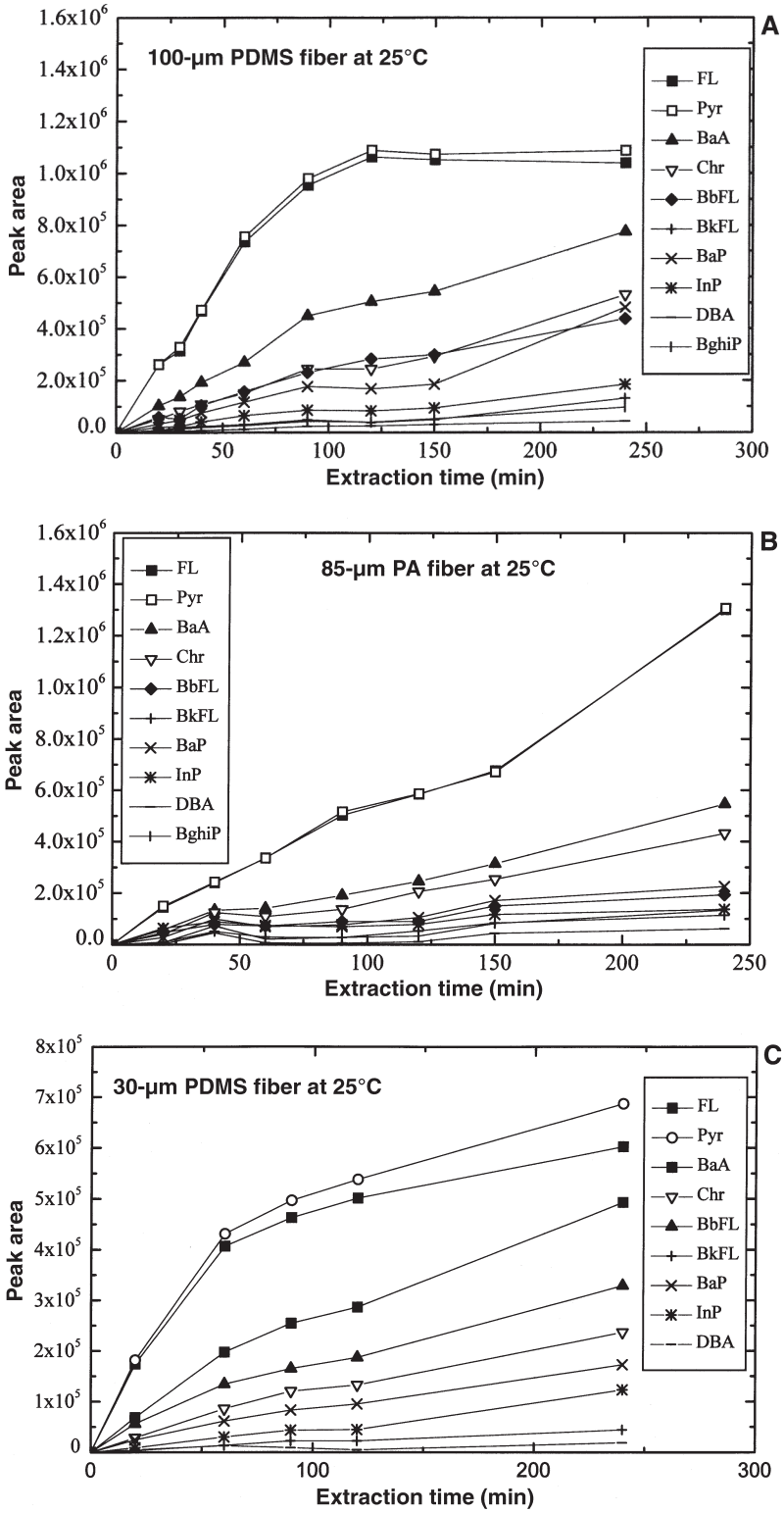

Figure 1. The extraction time profiles of high-ring PAHs using three different SPME fibers: 100-µm PDMS fiber, A; 85-µm PA fiber, B; and 30-µm PDMS fiber, C. PAH abbreviations: fluoranthene, FL; pyrene, Pyr; benz[a]anthracene, BaA; chrysene, Chr; benzo[b]fluoranthene, BbFL; benzo[k]fluoranthene, BkFL; benzo[a]pyrene, BaP; indeno[1,2,3-cd]pyrene, InP; dibenzo[a,h]anthracene, DBA; benzo[ghi]perylene, BghiP.

Experimental

Reagents and materials

The standard mixtures of PAHs at a concentration of 2000 µg/mL in methylene chloride–benzene (1:1, v/v) were purchased from Supelco Co. (Bellefonte, PA). These standards were stored at 4°C and used for the preparation of working standard solutions (20 µg/mL in acetone). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA). Methanol, dichloromethane, acetone, and *n*-hexane were obtained from Mallinckrodt Co. (Phillipsburg, NJ). Toluene was purchased from Redial de Haen Co. (Seelze, Germany).

Three kinds of different fibers (a 100- and 30-µm PDMS and a 85-µm PA fiber) were also obtained from Supelco. All fibers were conditioned in the hot injector part of the GC for 0.5 to 2 h and at 250 to 300°C according to the instructions provided by the manufacturer.

The glassware used in this study was first washed with detergent and deionized water, followed by placing them in a cleaning solution overnight to remove the trace amounts of organics on the surface of the vials. The glassware was then rinsed with deionized water, methanol, acetone, and hexane in sequence, dried in the oven at 105°C, and wrapped with aluminum foil before use. For SPME procedures, the vials were further silanized by soaking the glassware overnight in a 10% (v/v) mixture of dichlorodimethylsilane (Supelco) in toluene. Finally, the vials were rinsed with toluene and methanol and oven-dried at 105°C.

Instrumental conditions

A Hewlett-Packard 6890 GC equipped with a flame ionization detector (FID) was used for the experiments in order to determine the optimized SPME conditions. The carrier gas was nitrogen

with a flow rate of 3 mL/min. The GC was operated in a splitless mode with a 5-min splitless time. The injector was maintained between 270°C and 320°C depending on the fiber used. The temperature of the detector was at 350°C. A 30-m Ultra Alloy-5 stainless steel capillary column (0.5-mm i.d., 0.5-µm film thickness) (Quadrex Co., New Haven, CT) was used for separating PAHs. The column was held at 40°C for 5 min, increased to 180°C at a rate of 20°C/min, ramped at 4°C/min to 250°C, increased to 270°C at a rate of 2°C/min and held for 2 min, and finally ramped to 320°C at a rate of 10°C/min and then held for 10 min.

The analysis of PAHs on soil by GC–mass spectrometry was performed with a Hewlett-Packard 5793 mass-selective detector equipped with a 6890 GC and a split/splitless injection port (splitless mode). The column used was a 30-m HP-5 (0.25-mm i.d., 0.25-µm film thickness). Helium was used as the carrier gas, and the flow rate was maintained at 1.3 mL/min (linear velocity 41 cm/s). The ionization was carried out in the electron impact mode (70 eV). The electron multiplier voltage and automatic gain control target were set automatically. The transfer line and ion-trap manifold were set at 280°C and 230°C, respectively. The mass range scanned was from 50 to 550 amu under full-scan acquisition mode.

SPME procedures

The SPME extractions were performed either by placing 10 mL of deionized water (water sample) or 0.1 g of CRM soil and 10 mL of deionized water (soil sample) into 15-mL amber vials capped with polytetrafluoroethylene-coated septa. Aqueous standards were prepared by spiking an appropriate amount of the working standard to a final concentration of 10 ng/mL. Magnetic stirring with a 1-cm long Teflon-coated stir bar was used to agitate the solution at approximately 1000 rpm. The SPME equilibrium was conducted by immersing the fiber into the aqueous phase (DI-SPME) or headspace (HS-SPME) of the sample with stirring at room temperature for an appropriate time period, during which analytes absorbed on the stationary phase of the fibers. After extraction, the fiber was thermally desorbed for 5 min into the glass liner of the GC injector port at 270°C (30- and 100-µm PDMS fibers) or 300°C (PA fiber). Possible carryover was removed by keeping the fiber in the injector for an additional time with the injector in the split mode. Reinserting the SPME fiber after the run did not show obvious carryover.

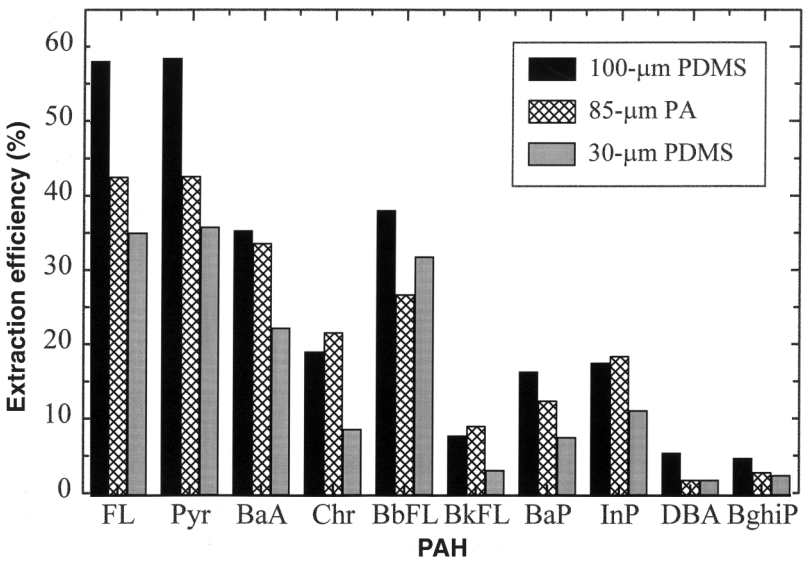

Figure 2. The extraction efficiency of PAHs extracted by three different SPME fibers with an extraction time of 90 min. PAH abbreviations same as Figure 1.

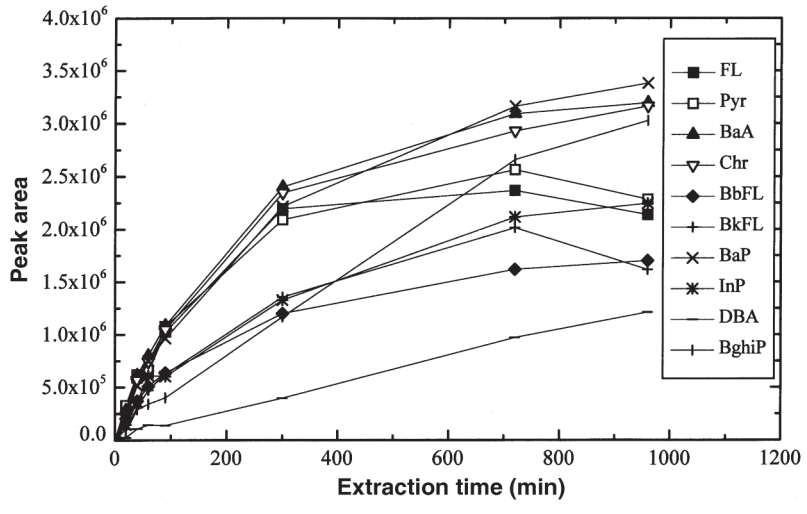

Figure 3. The extraction time profiles of PAHs for DI-SPME at a working temperature of 60°C using an 85-µm PA fiber. PAH abbreviations same as Figure 1.

Results and Discussion

Extraction time profile of DI-SPME

The characteristics of the fiber used can affect the sorption behavior of the analytes in the sample. Three SPME fibers (100- and 30-µm PDMS and 85-µm PA fibers) were compared in this study for effectively determining high molecular-weight PAHs. Because SPME is an equilibrium process in which analytes partition between the sample matrix and a polymeric stationary phase of the fiber, the determination of the extraction time required for all PAHs to equilibrate with the fiber is needed. Figure 1 illustrates the time profile of high-ring PAHs using three different SPME fibers. Pyrene and fluoranthene can reach equilibrium after a 120-min extraction at 25°C when a 100-µm PDMS fiber is used, and the remaining high molecular-weight PAHs need more than 240 min to reach equilibrium. This is because of the low water solubilities and diffusion coefficients of high-ring PAHs. The diffusivities of high molecular-weight PAHs in the aqueous phase range from 6.3×10^{-6} to 7.4×10^{-6} cm^2/s, and the apparent diffusivities can be decreased from 10^{-8} to 10^{-9} cm^2/s in polymeric material (19,20). Therefore, a longer extraction time is needed for high-ring PAHs to reach equilibrium.

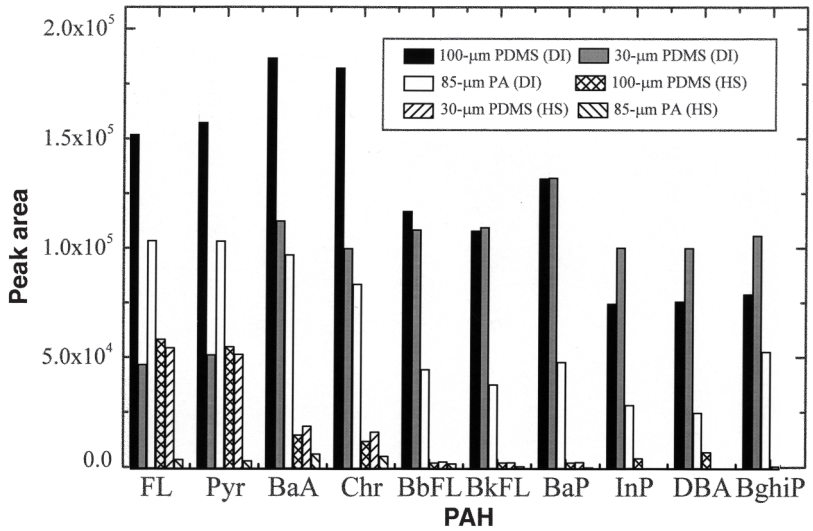

Figure 4. The peak areas of PAHs extracted by three different SPME fibers at a working temperature of 60°C with an extraction time of 30 min. PAH abbreviations same as Figure 1.

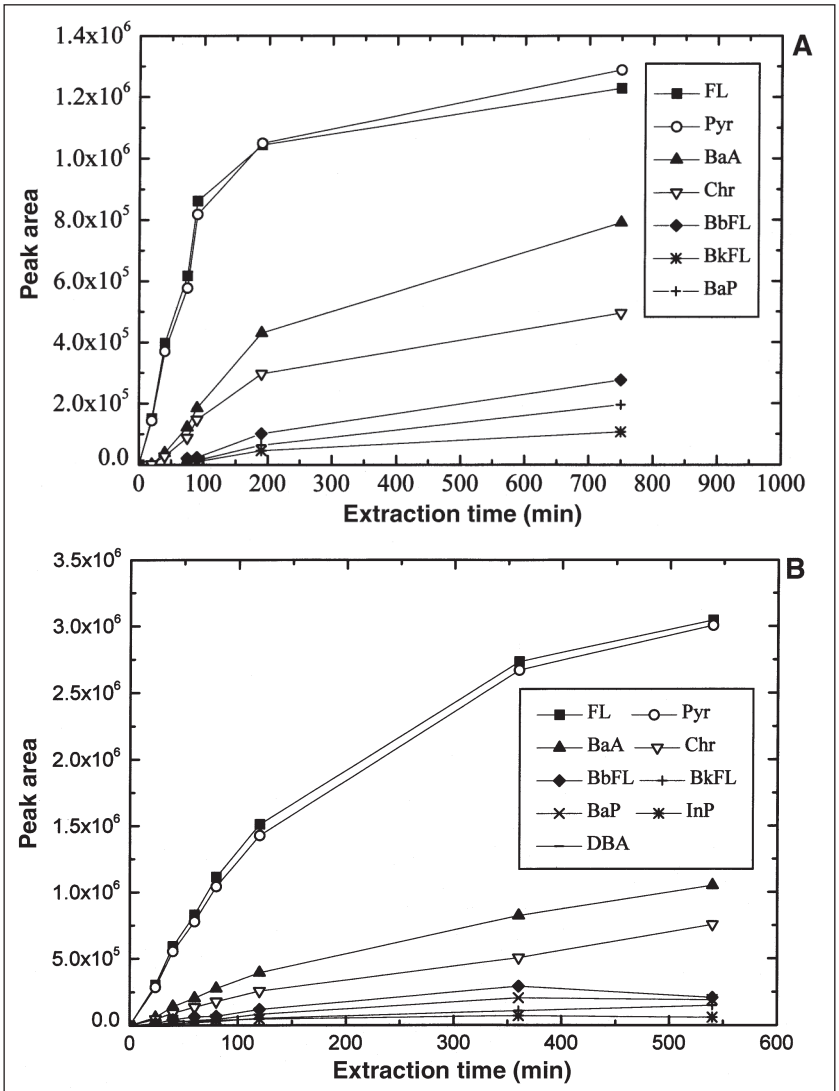

Figure 5. The extraction time profiles of PAHs for HS-SPME using a 100-µm PDMS and 85-µm PA fiber at 60°C. PAH abbreviations same as Figure 1.

Although a thinner PDMS fiber coating has been reported to be suitable for the determination of high molecular-weight PAHs (21), no equilibrium was reached within 240 min when a 30-µm PDMS fiber was used for extracting PAHs. Further SPME extractions showed that only fluoranthene and pyrene can reach equilibrium when the extraction time is prolonged to 540 min. A similar extraction profile was observed when the SPME fiber was changed to an 85-µm PA fiber. No equilibrium was observed for all high-ring PAHs within 240 min. Although several studies have demonstrated that more-polar fibers can extract more-polar analytes (22–24), a PA fiber can also extract high molecular-weight PAHs as well. However, a longer time to reach the equilibrium is needed when using a PA fiber to extract nonpolar compounds (25).

Figure 2 illustrates the extraction efficiency of PAHs for the three different SPME fibers with an extraction time of 90 min. The extraction efficiency was compound- and fiber-dependent. Four-ring PAHs such as fluoranthene and pyrene were the most extensively absorbed compounds with an extraction efficiency of 35.3 to 58.7%. Increasing the molecular weights of PAHs decreased the extraction efficiency. Less than 10% of the extraction efficiency was observed for 6-ring PAHs. Also, the extraction efficient decreased with decreasing the film thickness. The extracted amount of PAHs by a 100-µm PDMS fiber was higher than those by 85-µm PA and 30-µm PDMS fibers.

Effect of temperature

Because the extraction efficiency of high-ring PAHs in the DI-SPME system at 25°C was low, an increase in the working temperature could decrease the partition coefficients and increase the diffusion coefficients of PAHs and then enhance the absorbed amounts of PAHs in a fiber (28). Figure 3 illustrates the extraction efficiencies of PAHs at a working temperature of 60°C using a 85-µm PA fiber. Increasing the temperature can significantly increase the absorbed amounts of 5- and 6-ring PAHs. The equilibrium time was 300 min for fluoranthene and pyrene and 720 min for benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene. However, no equilibrium was observed for 6-ring PAHs. It should be noted that the peak areas of fluoranthene and pyrene decreased after an extraction of 960 min. This may be attributed to the fact that the elevated temperature significantly increased the mass transfer at the water–gas interface. Therefore, the amounts of 4-ring PAHs in the headspace were higher than

those in the aqueous phase, thus decreasing the extraction efficiencies of PAHs in the aqueous phase.

An increase of temperature can also change the extraction efficiencies of high-ring PAHs using different SPME fibers. Figure 4 illustrates the peak areas of PAHs with different fibers at 60°C with an extraction time of 30 min. Similar to the extraction profiles of PAHs at 25°C, 4-ring PAHs were the most extensively absorbed compounds when a 100-µm PDMS fiber was used. However, the extraction amounts of 5- and 6-ring PAHs followed the order: 30-µm PDMS > 100-µm PDMS > 85-µm PA fibers. This means that an SPME fiber with a thin coating is more suitable for the extraction of high molecular-weight PAHs at a high temperature and short extraction time.

Comparison between HS-SPME and DI-SPME

The possibility of sampling the headspace over the water sample instead of directly immersing the fiber in the water was evaluated in this study. The preliminary study showed that only fluoranthene and pyrene could be extracted using HS-SPME at 25°C. Therefore, we used the working temperature of 60°C for extracting PAHs in the headspace phase. Figure 5 illustrates the extraction time profiles of high-ring PAHs in the headspace phase using 100-µm PDMS and 85-µm PA fibers at 60°C. All of the high-ring PAHs could be detected at 60°C by a 85-µm PA fiber. However, the response of 6-ring PAHs was low and could only be detected when the extraction time was longer than 75 min. Also, no equilibrium was observed for all PAHs within 540 min. Unlike the PA fiber, only 7 of the 10 high-ring PAHs could be detected with an extraction time of 560 min when the fiber was changed to a 100-µm PDMS fiber. The 6-ring PAHs (indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[ghi]perlyene) could not be extracted. By further increasing the working temperature to 80°C, the six-ring PAHs could thus be extracted; however, the extraction efficiency was less than 5%.

Table I. The Enhancement of PAH at 60°C for Different SPME Methods and Fibers*

PAHs	PDMS fiber		PA fiber	
	DI-SPME	HS-SPME	DI-SPME	HS-SPME
Fluoranthene	0.71	0.90	2.04	2.22
Pyrene	0.92	0.84	2.09	2.03
Benzo[a]anthracene	1.85	0.41	5.70	1.23
Chrysene	0.29	0.60	7.67	1.06
Benzo[b]fluoranthene	2.24	0.10	7.12	0.59
Benzo[k]fluoranthene	10.48	0.21	22.59	0.68
Benzo[a]pyrene	4.42	0.08	12.57	0.44
Dibenzo[a,h]anthracene	6.05	–†	8.71	0.53
Benzo[ghi]perylene	6.47	–	25.33	0.07
Indeno[1,2,3-cd]pyrene	8.73	–	14.27	0.13

* Enhancement ratio = peak ratio of each PAH at 60°C/peak area of PAH at 25°C using DI-SPME.
† No peak area determined.

The enhancement of PAH responses at 60°C is fiber- and method-dependent. The enhancement ratio is defined as the ratio of the peak area of each PAH at 60°C to that at 25°C obtained from DI-SPME. As depicted in Table I, an enhancement of a 2- to 25-fold increase in peak area was obtained by the 85-µm PA fiber for DI-SPME. The enhancement of the 100-µm PDMS fiber was lower than that of the 85-µm PA fiber, and only a 0.7- to 10.5-fold increase was obtained. In the HS-SPME system, the peak areas of PAHs obtained at 60°C by the 100-µm PDMS fiber were lower than those obtained at 25°C. However, the enhancement ratios of PAHs were all less than normal. For the PA fiber, the extraction of 4-ring PAHs in the headspace was better than that in the aqueous phase at 25°C. The low enhancement ratios for 6-ring PAHs may be attributed to their extremely low vapor pressures. This implies that the application of HS-SPME can only be used for up to 5-ring PAHs.

Effect of sample volume

Sample volume is an important parameter affecting the quantitative results. In this study, different aqueous and headspace volumes for the mass extraction were carried out using 15-mL vials. The water volumes were 7.5 and 10 mL and the headspace volumes were 7.5 and 5 mL, respectively. The added concentration of PAHs was 10 ng/mL. Figure 6 illustrates the influence of the sample volume on the extracted amounts of PAHs absorbed by a 100-µm PDMS fiber at a working temperature of 60°C. The 4-ring PAHs (fluoranthene, pyrene, benz[a]anthracene, and chrysene) had higher responses for both DI-SPME and HS-SPME. In general, the FID responses of PAHs slightly increased with the increasing water volume for DI-SPME, and the peak areas decreased with the increasing headspace volume when HS-SPME was used. Pawliszyn et al. (29,30) proposed a theoretical consideration of the effect of sample volume on the quantitative determination of analytes by SPME. According to the theory and model prediction, the extracted amounts of analytes increases with the increasing sample volume in a two-phase system, and the sample volume has a significant effect on the amount extracted by an

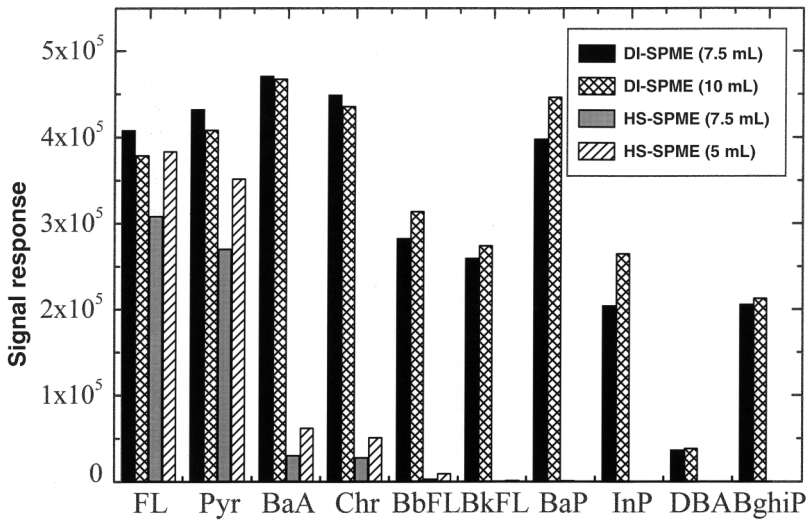

Figure 6. Effect of sample volume on the extraction of PAHs by a 100-µm PDMS fiber at 60°C. PAH abbreviations same as Figure 1.

SPME fiber only when the partition coefficient of the analyte is low. However, the extracted amounts of analytes decreases when the headspace volume of the sampling system increases in a three-phase system. This predicted data are similar to our results, which shows that the sample volume is an important factor influencing the quantitation of high-ring PAHs using HS-SPME.

Extraction of PAHs from soil

The extraction of PAHs from soil was performed by adding 0.1 g CRM 104 soil and 10 mL deionized water into a 15-mL amber vial. To minimize the matrix effect and increase the life expectancy of a fiber, HS-SPME with a working temperature of 80°C was used for the extraction of PAHs from soil. Unlike the water sample, only 6 of the 10 high-ring PAHs (fluoranthene, pyrene, benz[a]anthracence, chrysene, benzo[b]fluoranthene, and benzo[k]fluoranthene) were detected with an extraction time of 120 min. Also, the responses of PAHs obtained from soil were low compared to those obtained in the water sample. Preheating is one of the possible methods that can be used for enhancing the extraction of PAHs. Although a longer preheating time can increase the extracted amount of 4- and 5-ring PAHs, no 6-ring PAHs were detected. The extraction may have been mainly hampered by the high partition coefficients and extremely low vapor pressures of 6-ring PAHs. The log K_{ow} values and vapor pressures of 6-ring PAHs are in the range of 5.95- to 6.5-mm and 1.04- × 10^{-10}-mm to 9.78- × 10^{-11}-mm Hg, which falls into the class of nonvolatile hydrophobic organics (19). Therefore, the concentration of 6-ring PAHs in an aqueous phase and headspace are too low to be detected. Several studies have demonstrated that the addition of a surfactant can enhance the apparent water solubilities of hydrophobic organic compounds absorbed on soil when the concentration of a surfactant exceeds the critical micellar concentration (CMC) (31,32). In an attempt to enhance the apparent water solubilities of PAHs, four types of surfactants—Triton X-100, Sodium dodecyl sulfonate (SDS), Tween 80, and Brij 30—were used. The concentration of surfactant used was of CMC value, and the enhancement was surfactant-dependent. As shown in Table II, Brij 30 had the highest enhancement effect for low-ring PAHs, and Tween 80 could effectively enhance the high-ring PAHs. This was mainly attributed to the different number of polyoxyethylenes (POEs) of the surfactants. Brij 30 had the lowest POE number of 4, and Tween 80 had the highest of 20. Therefore, surfactants with a short POE chain have a higher capacity in enhancing the extraction of low molecular-weight PAHs, and surfactants with a high hydrophilic property (long POE chain) are more suitable for the enhancement of high-ring PAHs.

Table II. Peak Areas of PAHs from CRM-104 soil with the Addition of Different Surfactants at Concentrations of CMC Using a 100-µm PDMS Fiber*

PAHs	Triton X-100	SDS	Tween 80	Brij 30
Napthalene	16641	16848	13334	23372
Acenaphthylene	11526	13940	14346	26970
Acenaphthene	204478	209266	286284	346938
Fluorene	89848	63574	58911	90064
Phenanthrene	856666	542219	755714	1052906
Anthracene	44802	21214	40590	297657
Fluoranthene	2108592	1069260	3495873	2855160
Pyrene	920850	44640	1616396	1246210
Benzo[a]anthracene	49182	112187	151990	69815
Chrysene	48912	24752	164706	75232
Benzo[b]fluoranthene	2893	30166	13582	10618
Benzo[k]fluoranthene	900	1693	2766	2024

* Extraction time and working temperature are 120 min and 80°C, respectively.
† Benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[a,h]anthracene, and benzo[ghi]perylene were not detected.

Conclusion

DI- and HS-SPME have demonstrated to be a good determination of high molecular-weight PAHs in water samples. The 100-µm PDMS fiber as well as the 85-µm PA fiber can effectively extract high-ring PAHs. The extraction efficiency decreased with the decreasing film thickness. The extracted amount of PAHs with the 100-µm PDMS fiber was higher than those with the 85-µm PA fiber and 30-µm PDMS fiber. Although the 100-µm PDMS fiber can extract higher amounts of PAHs, more PAHs can be detected using the 85-µm PA fiber. Increasing the working temperature to 60°C can enhance the sensitivity of 5- and 6-ring PAHs, and the extraction efficiency of 4-ring PAHs decreases when using DI-SPME in a water sample. For HS-SPME, the extraction efficiency of PAHs decreases when the headspace volume of the sampling system increases. All PAHs can be detected in water sample when the temperature is increased to 80°C, and only 4- and 5-ring PAHs can be quantitated in a soil sample when HS-SPME is used. Increasing the preheating time or adding a surfactant with a concentration at the CMC value can also enhance the sensitivity of PAHs in a soil sample. In conclusion, HS-SPME as well as DI-SPME with a 100-µm PDMS or 85-µm PA fiber are suitable methods to analyze high-ring PAHs; however, these techniques can only be applied for up to 5-ring PAHs in a soil sample.

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References

1. R.A. Doong and C.Y. Lee. Determination of organochlorine pesticide residues in foods using solid-phase extraction clean-up cartridges. *Analyst* **124:** 1287–89 (1999).
2. J. Pawliszyn. *Solid Phase Microextraction: Theory and Practice*. Wiley-VCH, New York, NY, 1997, pp 141–89.
3. M. Llompart, K. Li, and M. Fingas. Headspace solid-phase microextraction for the determination of volatile and semi-volatile pollutants

in water and air. *J. Chromatogr. A* **824:** 53–61 (1998).
4. Z. Zhang and J. Pawliszyn. Headspace solid-phase microextraction. *Anal. Chem.* **65:** 1843–52 (1993).
5. D.W. Potter and J. Pawliszyn. Rapid determination of polyaromatic hydrocarbons and polychlorinated biphenyls in water using solid-phase microextraction and GC/MS. *Environ. Sci. Technol.* **28:** 298–305 (1994).
6. Z. Zhang and J. Pawliszyn. Sampling volatile organic compounds using a modified solid phase microextraction device. *J. High Resolut. Chromatogr.* **19:** 155–160 (1996).
7. S. Magdic and J. Pawliszyn. Analysis of organochlorine pesticides using solid-phase microextraction. *J. Chromatogr. A* **723:** 111–22 (1996).
8. C. Aguilar, S. Penalver, E. Pocurull, F. Borrull, and R.M. Marce. Solid-phase microextraction and gas chromatography with mass spectrometric detection for the determination of pesticides in aqueous sample. *J. Chromatogr. A* **795:** 105–115 (1998).
9. J. Beltran, F.J. Lopez, O. Cepria, and F. Hernandez. Solid-phase microextraction for quantitative analysis of organophosphorus pesticides in environmental water samples. *J. Chromatogr. A* **808:** 257–63 (1998).
10. M. Llompart, K. Li, and M. Fingas. Solid-phase microextraction and headspace solid-phase microextraction for the determination of polychlorinated biphenyls in water samples. *Anal. Chem.* **70:** 2510–15 (1998).
11. J. Poerschmann, Z. Zhang, F.D. Kopinke, and J. Pawliszyn. Solid phase microextraction for determining the distribution of chemicals in aqueous matrices. *Anal. Chem.* **69:** 597–600 (1997).
12. J.J. Langenfeld, S.B. Hawthome, and D.J. Miller. Quantitative analysis of fuel-related hydrocarbons in surface water and wastewater samples by solid-phase microextraction. *Anal. Chem.* **68:** 144–55 (1996).
13. J. Porschmann, F.D. Kopinke, and J. Pawliszyn. Solid-phase microextraction for determining the binding state of organic pollutants in contaminated water rich in humic organic matter. *J. Chromatogr. A* **816:** 159–67 (1998).
14. R.A. Doong, S.M. Chang, and Y.C. Sun. Solid-phase microextraction for determining the distribution of sixteen US Environmental Protection Agency polycyclic aromatic hydrocarbons in water samples. *J. Chromatogr. A* **879:** 177–88 (2000).
15. W.F. Ng, M.J.K. Teo, and H.A. Lakso. Determination of organophosphorus pesticides in soil by headspace solid-phase microextraction. *Fresenius J. Anal. Chem.* **363:** 673–78 (1999).
16. S.B. Hawthorne, C.B. Grabanski, K.J. Hageman, and D.J. Miller. Simple method for estimating polychlorinated biphenyl concentrations on soil and sediments using subcritical water extraction coupled with solid-phase microextraction. *J. Chromatogr. A* **814:** 151–60 (1998).
17. F.L. Cardinali, D.L. Ashley, J.V. Wooten, J.M. McCraw, and S.W. Lemire. The use of solid-phase microextraction in conjunction with a benchtop quadrupole mass spectrometer for the analysis of volatile organic compounds in human blood at the low parts-per-trillion level. *J. Chromatogr. Sci.* **38:** 49–54 (2000).
18. E. Schimming, K. Levsen, C. Kohme, and W. Schurmann. Biomonitoring of benzene and toluene in human blood by headspace-solid-phase microextraction. *Fresenius J. Anal. Chem.* **363:** 88–91 (1999).
19. R.P. Schwarzenbach, P.M. Gschwend, and D.M. Imboden. *Environmental Organic Chemistry*. John Wiley & Sons, Inc., New York, NY, 1993.
20. M.L. Chang, S.C. Wu, and C.Y. Chen. Diffusion of volatile organic compounds in pressed humic acid disks. *Environ. Sci. Technol.* **31:** 2307–2312 (1997).
21. D. Cam, S. Gagni, L. Meldolesi, and G. Galletti. Determination of polycyclic aromatic hydrocarbons in sediment using solid-phase microextraction with gas chromatography–mass spectrometry. *J. Chromatogr. Sci.* **38:** 55–60 (2000).
22. K. Buchholz and J. Pawliszyn. Determination of phenols by SPME and GC analysis. *Environ. Sci. Technol.* **27:** 2844–48 (1993).
23. P. Bartak and L. Cap. Determination of phenols by solid-phase microextraction. *J. Chromatogr. A* **767:** 171–75 (1997).
24. P. Ferrari, T. Nillson, R. Arena, P. Arlati, and G. Vartolucci. Interlaboratory validation of solid-phase microextraction for the determination of triazine herbicides and their degradation products by SPME and ion-trap GC–MS. *J. Chromatogr. A* **795:** 371–76 (1998).
25. R.A. Doong, S.M. Chang, and Y.C. Sun. Solid-phase microextraction for determining the distribution of sixteen US Environmental Protection Agency polycyclic aromatic hydrocarbons in water samples. *J. Chromatogr. A* **879:** 177–88 (2000).
26. M.R. Negrao and M.F. Alpendurada. Solvent-free method for the determination of polynuclear aromatic hydrocarbons in waste water by solid-phase microextration–high-performance liquid chromatography with photodiode-array detection. *J Chromatogr. A* **823:** 211–18 (1998).
27. A.A. Boyd-Boland, S. Magdic, and J. Pawliszyn. Simultaneously determination of 60 pesticides in water using solid-phase microextraction and gas chromatography–mass spectrometry. *Analyst* **121:** 929–38 (1996).
28. J. Ai. Solid phase microextraction for quantitative analysis in nonequilibrium situations. *Anal. Chem.* **69:** 1230–1236 (1997).
29. T. Gorecki and J. Pawliszyn. Effect of sample volume on quantitative analysis by solid-phase microextraction. 1. Theoretical considerations. *Analyst* **122:** 1079–1086 (1997).
30. T. Groecki, A. Khaled, and J. Pawliszyn. Effect of sample volume on quantitative analysis by solid-phase microextraction. 2. Experimental verification. *Analyst* **123:** 2819–24 (1998).
31. C.C. West and J.H. Harwell. Surfactants and subsurface remediation. *Environ. Sci. Technol.* **26:** 2324–30 (1992).
32. D.A. Edwards, R.G. Luthy, and Z. Liu. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions. *Environ. Sci. Technol.* **25:** 127–33 (1991).

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