Time-Weighted Average Water Sampling with a Solid-Phase Microextraction Device

ARTICLE *in* ANALYTICAL CHEMISTRY · DECEMBER 2005

Impact Factor: 5.64 · DOI: 10.1021/ac051035q · Source: PubMed

3 AUTHORS, INCLUDING:

Gangfeng Ouyang
Sun Yat-Sen University
109 PUBLICATIONS **2,295** CITATIONS
SEE PROFILE

Janusz Pawliszyn
University of Waterloo
516 PUBLICATIONS **25,077** CITATIONS
SEE PROFILE

Article

Time-Weighted Average Water Sampling with a Solid-Phase Microextraction Device

Gangfeng Ouyang, Yong Chen, and Janusz Pawliszyn

Anal. Chem., **2005**, 77 (22), 7319-7325• DOI: 10.1021/ac051035q • Publication Date (Web): 08 October 2005

Anal. Chem. **2005,** *77,* 7319−7325

Time-Weighted Average Water Sampling with a Solid-Phase Microextraction Device

Gangfeng Ouyang,† Yong Chen, and Janusz Pawliszyn*

Department of Chemistry, University of Waterloo, Ontario N2L 3G1, Canada

A fiber-in-needle SPME device was developed and investigated for time-weighted average water sampling. The device was designed so that the overall mass-transfer resistance is contained within the static water inside the needle, which ensures that mass uptake could be predicted with Fick's first law of diffusion and the sampling rate is less affected by water turbulence. The device possesses all of the advantages of commercialized devices, in addition to needle filling and replacement ease. Laboratory calibration with deployment of the device to a flow-through system demonstrated that there was a linear mass uptake for up to 12 days, and the linear range could be longer. PDMS coating is assumed to be a perfect zero sink for most polycyclic aromatic hydrocarbons, except naphthalene. The effect of water temperature was also investigated. Under normal field conditions, the change of mass uptake rate with temperature was negligible. To facilitate the convenience for long-term water sampling, a new standard aqueous generator was introduced. This study extended the application of SPME technology for long-term water sampling.

Conventional solid-phase microextraction (SPME) is performed by exposing a fiber coated with a liquid polymeric coating to a sample matrix or its headspace until an equilibrium is reached between the analyte partitioned in the fiber coating and the analyte dissolved in the sample matrix. The amount of the analyte extracted onto the fiber is linearly proportional to its initial concentration in the sample matrix.[1] To date, the equilibrium extraction method is the most widely used method for SPME. To address long equilibrium times for liquid coatings and the intermolecular displacement effect for solid porous coatings, a preequilibrium extraction method is an alternative approach for quantification with SPME.[2] In both equilibrium and preequilibrium extraction approaches, the fiber is extended outside its needle to facilitate fast mass transfer to shorten the equilibrium time, enhance the sensitivity, or both. Spot or grab sampling using equilibrium or preequilibrium SPME allows for the rapid analysis of various airborne, waterborne, and solid samples.[3] In addition, it allows for the rapid on-site monitoring, which can be used to determine time-weighted average (TWA) concentration. However, the determination of TWA concentration by grab sampling turns is cost prohibitive, due to the large number of grab samples that must be collected.

For convenience and cost, one sample is preferred for a TWA concentration. This is achieved by withdrawing the fiber coating a known distance into its needle during the sampling period. Analyte molecules access the fiber coating only by means of diffusion through the static air gap between the needle opening and the fiber coating. The well-defined geometry of the diffusion zone allows for the diffusion-based calibration of the mass uptake, thus eliminating the requirement for calibration curves, which simplifies analytical procedure and makes SPME TWA sampling more adaptable in the field.[4−6] The most attractive aspect of SPME TWA sampling is that the sampler performance is independent from the face velocity of air across the needle opening, due to the extremely small inner diameter of the fiber needle, causing the overall mass-transfer resistance to be contained within the static air gap inside the needle. This means that SPME devices can be used for TWA sampling without considering the convection conditions of air.[6,7] The further development of this technique involved a systematic study of environmental factors,[6] field sampling, and development of a new portable and user-friendly field sampler.[8] All these works demonstrate the usefulness of TWA sampling with a SPME device, especially for volatile organic compounds in air. In this work, the application of this technique for aqueous samples was investigated.

The existing techniques for TWA water sampling are mainly based on passive sampling, because it is economical and not practical to operate a pump for long periods of time (weeks or months) to determine a TWA concentration. The currently available passive samplers for water sampling are based on either permeation or diffusion,[9] including solvent-filled devices,[10−12]

* Corresponding author. Tel.: +1-519-888-4641. Fax: +1-519-746-0435. E-mail: janusz@uwaterloo.ca.

† Permanent address: School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China.

(1) Pawliszyn, J. *Solid-Phase Microextraction: Theory and Practice*; Wiley-VCH: New York, 1997.
(2) Ai, J. *Anal. Chem.* **1997**, *69*, 1230−1236.
(3) Pawliszyn, J., Ed. *Applications of Solid-Phase Microextraction*; Royal Society of Chemistry: Cornwall, U.K., 1999.
(4) Martos, P. A.; Pawliszyn, J. *Anal. Chem.* **1999**, *71*, 1513−1520.
(5) Khaled, A.; Pawliszyn, J. *J. Chromatogr., A* **2000**, *892*, 455−467.
(6) Chen, Y.; Pawliszyn, J. *Anal. Chem.* **2003**, *75*, 2004−2010.
(7) Lestremau, F.; Andersson, F. A. T.; Desauziers, V.; Fanlo, J. *Anal. Chem.* **2003**, *75*, 2626−2632.
(8) Chen, Y.; Pawliszyn, J. *Anal. Chem.* **2004**, *76*, 6823−6828.
(9) Kot, A.; Zabiegata, B.; Namieœnik, J. *Trends Anal. Chem.* **2000**, *19*, 446−459.
(10) Kot-Wasik, A. *Chem. Anal. (Warsaw)* **2004**, *49*, 691−705.
(11) Sodergren, A. *Environ. Sci. Technol.* **1987**, *21*, 855−859.
(12) Peterson, S. M.; Apte, S. C.; Batley, G. E.; Coade, G. *Chem. Speciation Bioavailability* **1995**, *7*, 83−88.

10.1021/ac051035q CCC: $30.25
Published on Web 10/08/2005

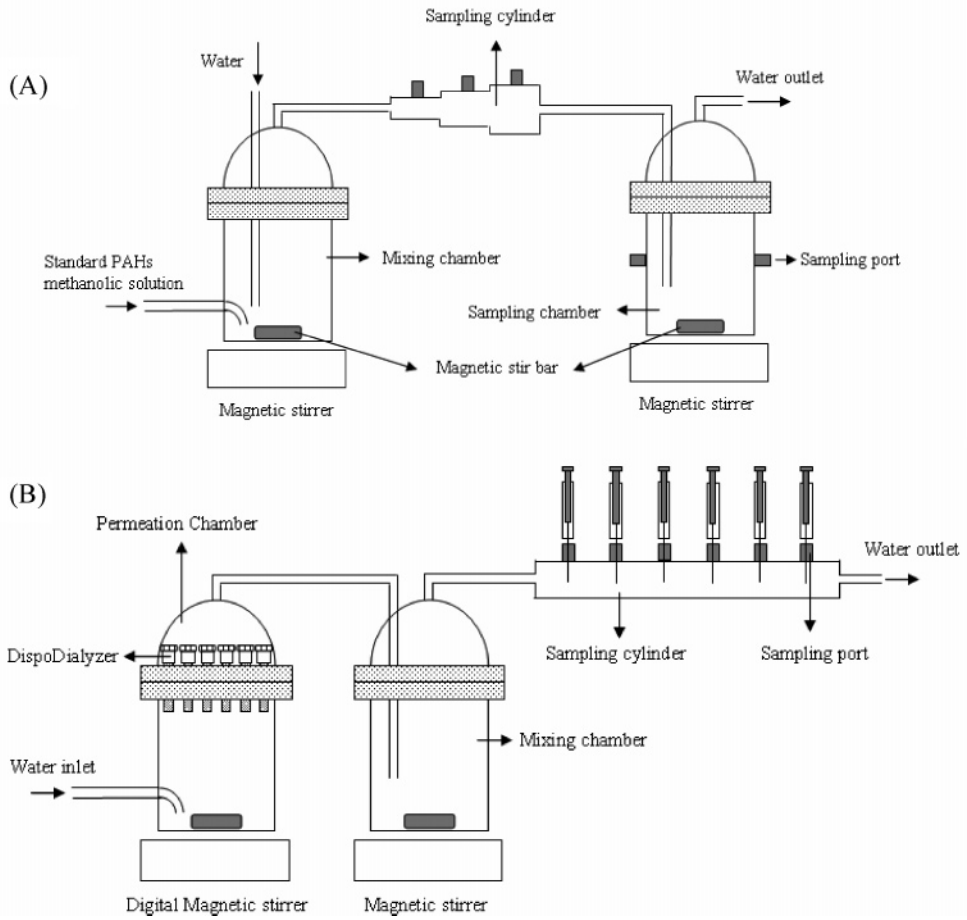

Figure 1. (A) Schematic diagram of the flow-through system based on dilution. (B) Schematic diagram of the new flow-through system based on permeation.

semipermeable membrane devices,[13] passive in situ concentration/extraction samplers,[14] and sorbent-filled devices.[15] Permeation devices utilize a diffusion-limiting membrane inside which a collecting medium with a high affinity for organic pollutants is held.[10,13,16,17] The main advantages of membrane-based devices are their high sensitivity and bioavailability. Diffusion devices utilized diffusion of analyte molecules through a static water gap between a collecting medium and the opening of the diffusion channel.[15] The main advantage of diffusion devices is that mass uptake can be calibrated based on the diffusion coefficient. However, most permeation and diffusion devices still utilize solvent as the collecting medium or for analyte desorption. The main disadvantage of these devices is that their performance is dependent on the convection conditions of water,[17,18] which limits laboratory calibrations for field applications where the convection of water is variable and unpredictable.

The performance of SPME devices for TWA passive sampling was found to be independent of the convection of air.[6] Further studies were designed to identify whether this is also true for TWA water sampling, while validating diffusion calibration.

EXPERIMENTAL SECTION

Chemicals and Supplies. All chemicals were of analytical grade. HPLC grade methanol was purchased from BDH (Toronto, ON, Canada). Naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, and pyrene were from Supelco (Oakville, ON, Canada). The SPME holders and the 30- and 100-μm poly(dimethylsiloxane) (PDMS) fibers were also obtained from Supelco. The fibers were conditioned at 250 °C for 1 h prior to their use. Deactivated needles and Silcosteel-treated tubing were purchased from Restek (Bellefonte, PA). The 500-μL gastight syringes were purchased from Hamilton (Reno, NV). DispoDialyzers of 2000 molecular weight cutoff (MWCO) were purchased from Spectrum Laboratories (Rancho Dominguez, CA).

Flow-Through System. Two flow-through systems were used for the TWA water sampling experiment. One was a typical flow-through system based on dilution (Figure 1A). The system was modified from the parameters described by Shurmer.[19] This flow-through system consisted of a water delivery pump, a polycyclic aromatic hydrocarbon (PAH) standard injection syringe pump, a mixing chamber, a long sampling cylinder with three different diameters, and a sampling chamber. Ultrapure water from a Nanopure filter (Barnstead, Dubuque, IA) was delivered by a LC

(13) Huckins, J. N.; Tubergen, M. W.; Manuweera, G. K. *Chemosphere* **1990**, *20*, 533−552.
(14) Litten, S.; Mead, B; Hassett, J. *Environ. Toxicol. Chem.* **1993**, *12*, 639−647.
(15) Digiano, F. A.; Elliot, D.; Leith, D. *Environ. Sci. Technol.* **1988**, *22*, 1365−1367.
(16) Vrana, B.; Popp, P.; Paschke, A.; and Schûûrmann, G. *Anal. Chem.* **2001**, *73*, 5191−5200.
(17) Kingston, J. K.; Greenwood, R.; Mills, G. A.; Morrison, G. M.; Persson, L. B. *J. Environ. Monit.* **2000**, *2*, 487−495.
(18) Vrana, B.; Schûûrmann, G. *Environ. Sci. Technol.* **2002**, *36*, 290−296.
(19) Shurmer, B.; Pawliszyn, J. *Anal. Chem.* **2000**, *72*, 3660−3664.

pump (Spectra-physics, San Jose, CA) to the mixing chamber, to which PAH standards in methanol were injected by a syringe pump (Razel, Stamford, CT). Water and PAH standards in methanol were mixed by vigorous magnetic stirring (model 400S digital magnetic stirrer from VWR Scientific, West Chester, PA). The generated aqueous PAH standards then entered the long sampling cylinder where the effect of the face velocity was studied. The main sampling chamber was installed the downstream of the sampling cylinder, where routine TWA sampling was carried out.

The concentrations of the aqueous PAH standards were validated by headspace SPME:[1] 25 mL of the effluent was collected in a 40-mL vial capped with a phenolic screw cap and PTFE-coated silicone septa (Supelco), and a 1-in. (2.54 cm) PTFE-coated stirring bar (Supelco) was used to agitate the solution at 1200 rpm (VWR Scientific). The solution was agitated for 20 min before a PDMS 30-μm fiber was used to sample the PAHs in the headspace for 20 min, and the fiber was then introduced into a GC injector for desorption, separation, and quantification.

The results of the 20-month experiment illustrate that the change in concentrations of naphthalene, acenaphthene, and fluorene generated in the flow-through system was ~15%. Although the dilution method can generate stable concentrations of PAH compounds, the disadvantages for this system are obvious. The first disadvanatage is that the syringe must be periodically be refilled with the standard solution, since the syringe volume is limited. Although refilling the syringe does not affect the system significantly, it is not convenient as a long-term solution. Another disadvantage of this dilution method is that the solvent used for the dilution is subsequently added into the standard system with the test chemicals. These disadvatanges limit the ability of the system to achieve high concentrations of analytes by the dilution method, due to the presence of a high concentration of solvent and the frequent need to refill the system. A high concentration of analytes in the flow-through system is very important, because it will shorten the testing time for passive samplers. Therefore, an alternative approach is needed.

Figure 1B presents the schematic diagram of the new flow-through system of the standard aqueous solution based on permeation.[20] It consists of a permeation chamber, a mixing chamber, and a long sampling cylinder with six sampling ports. Ultrapure water was delivered by an ISO-1000 digital pump (Chrom. Tech., Apple Valley, MN). The flow rate was set at 1 mL/min. The key part of the generator is the DispoDialyzers (Spectrum Laboratories) in the permeation chamber. Each DispoDialyzer was partially filled with pure standards (naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene) and pure water. The DispoDialyers were then tightly sealed and placed into a 400-mL beaker (filled with 300 mL of water) and sonicated for ~30 min. The prepared DispoDialyzers were deployed in the permeation chamber with an inlet close to its bottom and an outlet near its top. A small amount of air was left inside the DispoDialyzers for suspension at the top of the chamber. A magnetic stir bar was placed in the bottom of the permeation chamber, and a 400S digital magnetic stirrer (VWR Scientific) was used for agitation. Analytes were dissolved in the water inside the DispoDialyzer. The dissolved analyte molecules further diffused through the membrane of the DispoDialyzer and were transported via the water to the sampling cylinder and the sampling chamber. As the solids (PAHs) and liquid (water) coexist inside of the Dispodialyzer, the concentrations of the analytes inside the Dispodialyzer will remain constant (saturated concentration) if the temperature remains constant. If the flow rate of water is maintained constantly, the diffusion of the analyte molecules, from inside of the Dispodialyzer to the outside water, will reach steady state, creating constant analyte concentrations.

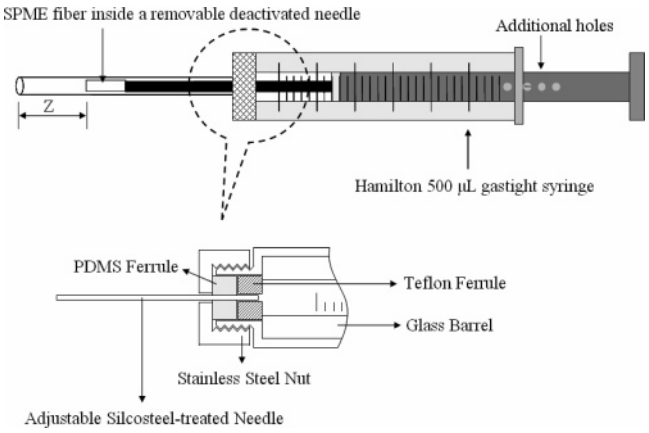

Figure 2. Schematic diagram of the fiber-in-needle SPME device for TWA water sampling and the adjustable/removable needle.

After an initial induction period of 1 week, the permeation rate reached a constant value. When the room temperature was maintained at 24 ± 1 °C, the average concentration was about 680, 150, 110, 8, 20, and 12 ppb for naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, and pyrene, respectively. The observed changes in the concentration of the six PAH compounds are comparable to those obtained by the use of the syringe pump (less than 20% over 3 months) and satisfy the requirement for long-term water sampling. A total of 20−50 mg of each compounds was added to each Dispodialyzer, and the lifetime of the generator is greater than 1 year.

Fiber-In-Needle SPME Device. In order for a SPME device to act as a diffusive sampler in water, all of the air in the SPME needle must be replaced with water before sampling begins. The use of commercialized fiber assemblies does not satisfy this requirement. Even if the fiber was repeatedly extended outside and withdrawn inside the needle many times with the opening of the needle dipped into pure water, or the fiber assembly was boiled in water for an extended period, it still remained difficult to remove all air bubbles inside the needle. This is because the diameter of the needle is very small. To solve this problem, a new design was developed to remove all air from the needle and set the fiber retraction length, as shown in Figure 2. A PDMS-coated fused-silica fiber connected with the fiber attachment tubing was obtained from a commercially available fiber assembly. The color-coded screw hub was cut from the tubing. Then, the empty end of the attachment tubing was inserted into a small hole predrilled on the center of the plunger of a Hamilton 500-μL gastight syringe. High-temperature epoxy glue was used to permanently mount the fiber. The position of the fiber coating in the needle could be precisely controlled by a stainless steel tubing by the positioning holes borne in the plunger and adjusting the Silcosteel-treated needle (Figure 2). Repeated exposure and retraction of the plunger in the degassed ultrapure water allowed for the removal of air

(20) Ouyang, G.; Chen, Y.; Pawliszyn, J. Submitted to *J. Chromatogr., A*, in press.

from the needle, while it filled with water. When the needle was inserted in the water, the plunger was pushed down and the sampling was initiated. After sampling, the stainless steel tubing was removed from the plunger and the needle and the PDMS ferrule were removed from the syringe. The plunger was pushed completely to expel the water inside the needle, and any remaining water on the opening was gently dried with Kimwipes. Then, a clean stainless needle (original needle of Hamilton 500-μL gastight syringe) was fixed on the syringe. Finally, the fiber was retracted into the syringe needle and introduced to the hot injector of a GC to thermally desorb the analytes from the coating to the GC column for separation and quantification.

Gas Chromatography. A Saturn 3800 GC/2000 ITMS system fitted with a SPB-5 column (30 m, 0.25-mm i.d., 0.25-μm film thickness) (Supelco, Mississauga, ON, Canada) was used for the analysis of PAHs. Helium as the carrier gas was set to 1 mL/min. For SPME injection, the 1079 injector was set to 270 °C, and the desorption time was set at 10 min. For liquid injection, the injector was set at 40 °C and then increased to 250 °C at a rate of 100 °C/min. A 1093 SPI liner was used for the 1079 injector to ensure the sample transfer efficiency was the same for both the SPME injection and the liquid injection.[21] The column temperature was maintained at 40 °C for 2 min and then programmed at 30 °C/min to 250 °C, held for 5 min, then programmed at 30 °C/min to 280 °C, and held for 15 min. The total run time was 30 min. The MS system was operated in the electron ionization mode and tuned with perfluorotributylamine. A mass scan from 40 to 300 was obtained, and the base peak of each compound was selected and integrated.

The instrument was checked on a daily basis by calibration with a liquid midpoint calibration standard. Any deviation in the area counts greater than 15% required reinjection of that standard; if the deviation was still greater than 15%, the instrument was recalibrated with a six-point calibration plot. Peak shape quality, resolution, and retention times were also carefully monitored to ensure all chromatography was within the required specifications.

RESULTS AND DISCUSSION

Zero Sink. It was demonstrated that the most important prerequisite for TWA SPME passive sampling is that the fiber coating must be a zero sink for the target analytes.[6] Zero sink ensures constant sampling rate for the entire sampling duration.

Since diffusion in water is very slow, previously reported empirical methods for the test of zero sink cannot be adapted for aqueous samples. In this study, a new approach was used. That is, a 100-μm PDMS fiber (100-μm PDMS fibers were used for all experiments, unless otherwise indicated) was exposed in a standard PAH aqueous solution (4 mL, 1500 rpm) for 30 min, and then the fiber was either analyzed immediately or subsequently exposed to static clean water for another 30 min prior to analysis. The reason to use static water is because when the fiber is withdrawn into the needle, the water surrounding the fiber is static. If the fiber has a high affinity for the analytes, the loss of the analytes during exposure to clean water would be negligible. Otherwise, significant loss of the analytes would occur. However, this is a "worse case" than TWA SPME sampling where the fiber is inside the needle, because the diffusion of analytes desorbed from the fiber in TWA sampling model is limited by the small dimensions of the needle.

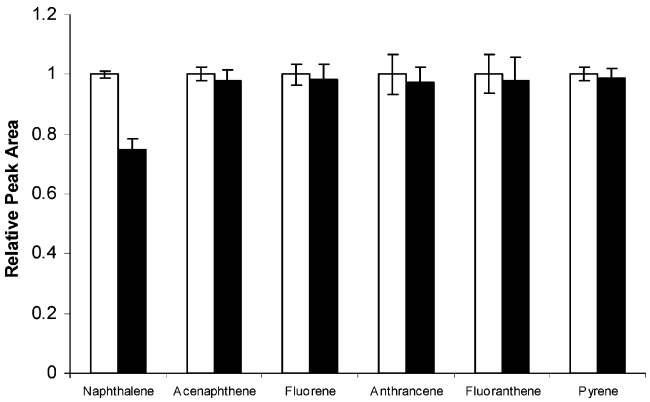

Figure 3. Test of zero sink: □, 30-min exposure of the fiber to standard solution; ■, 30-min exposure of the fiber to standard solution plus 30-min exposure of the fiber to static clean water.

The amounts of PAHs from each routine exposure were compared, as shown in Figure 3, from which PDMS was proved to be a perfect zero sink for acenaphthene, fluorene anthracene, fluoranthene and pyrene. Significant loss of naphthalene during exposure of the fiber to clean water was observed, as the greater solubility of naphthalene in water, which means that PDMS is not a perfect zero sink for naphthalene but it assumes a zero sink for other PAH compounds.

Response Time. The diffusion coefficient of most organic pollutants in water is in the range of 10^{-5}–10^{-6} cm^2/s. The slow diffusion prolongs the response time, which means that the capacity of TWA water samplers for integration of high peak concentrations is not as good as that of TWA air samplers, e.g., TWA sampling of naphthalene in water if diffusion length is 0.5 cm; the response time is ~4 h. However, the response time is still negligible compared with the sampling time, which could be as long as 10 days, for example.

Adsorption of PAHs on Needle. The test of the elimination of adsorption of PAHs on the deactivated needle is important for TWA SPME sampling, because ordinary stainless steel needles adsorb high boiling point compounds that are also introduced into a GC injector after sampling/sample preparation.[6] For conventional SPME, the adsorption on the needle is negligible compared to the absorption/adsorption of analytes on the fiber coating. For TWA SPME, the adsorption is undesirable because the absorption/adsorption of analytes on the fiber coating is small; especially at the beginning sampling phase, the adsorption of analytes on the needle might be a significant fraction of the absorption/adsorption of analytes on the fiber coating, resulting in underestimation (if the needle was replaced before injection, the analytes adsorbed to the wall inside the needle were lost) or overestimation (if the needle was not replaced before injection, the analytes adsorbed to the wall outside the needle were introduced in the injector) of the sampling rate. The use of a deactivated needle is a convenient way to avoid this problem.[6]

The test started with exposure of the fiber in-needle device with a deactivated needle to the flow-through system (Figure 1A) for 7 days, and then the fiber was analyzed. The sampling and analysis were repeated. It was found from the test that there was no adsorption of PAHs on the deactivated needle for the first 10

(21) Ouyang, G.; Chen, Y.; Pawliszyn, J. Submitted to *J. Chromatogr., A*, in press.

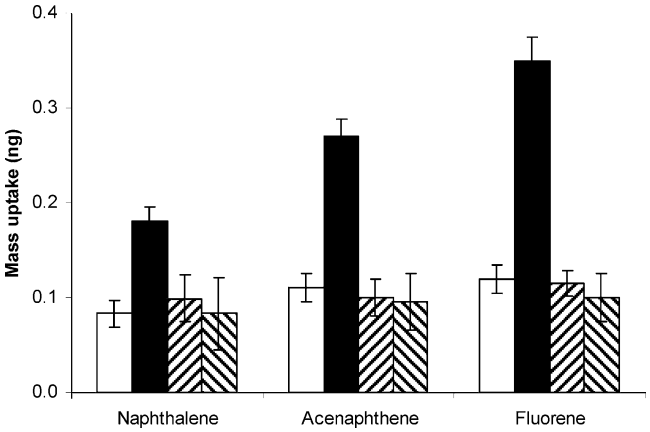

Figure 4. Test of adsorption of the analytes on the needle and the effect of face velocity. □, mean of mass uptake for the first 10 uses of the deactivated needle that was used for sampling and introducing, sampling in the main sampling chamber; ■, mean of mass uptake after the first 10 uses of the deactivated needle that was used for sampling and introducing, sampling in the main sampling chamber; right cross-hatch, mean of mass uptake after the first 10 uses of the deactivated needle that was used for sampling and a new needle was used for introducing, sampling in the main sampling chamber; left cross-hatch, mean of mass uptake after the first 10 uses of the deactivated needle that was used for sampling and a new needle was used for introducing, sampling in the sampling cylinder.

uses of the deactivated needle, but significant adsorption of PAHs on the deactivated needle was found after 10 times usage (Figure 4). This was further confirmed by repeating the TWA sampling with two ways of introducing the fiber into the GC injector. The first method involved using the deactivated needle used for sampling to guide the fiber into the GC injector. The second method involved replacing the deactivated needle that was used for sampling with a new needle just prior to introducing the fiber into the GC injector. This prevented any adsorption of PAHs on the deactivated needle to be introduced into the GC injector. The mass uptake of PAHs obtained from the first introduction method is significantly higher than that obtained from the second introduction method, while the mass uptake with the second approach is still comparable to that obtained from the first 10 uses of the deactivated needle. To ensure that the analytes will not be adsorbed by the needle, a 0.53-mm-i.d. Silcosteel-treated tubing (Silcosteel layer thermally stable to 600 °C) was used as the needle for sampling (Figure 2) and was replaced with a new needle just prior to introducing the fiber into the GC injector for the subsequent experiments.

Effect of Face Velocity. The overall mass-transfer resistance of the transport of analyte molecules from the bulk of samples to the collecting medium of passive samplers consists of mass-transfer resistance from the bulk of samples to the opening of the diffusion channel, which is dependent on the convection conditions of water, the physical dimensions of the sampler, and the mass-transfer resistance in the diffusion channel, which is dependent on the physical dimensions of the diffusion channel. When the mass-transfer resistance from the bulk of samples to the opening of the diffusion channel becomes a significant component of the overall mass-transfer resistance, the change in the face velocity (water turbulence) changes the overall mass-transfer resistance, thus changing the sampling rate. Therefore, the only way to eliminate the face velocity effect is to ensure that the overall mass-transfer resistance is contained within the diffusion channel. The mass-transfer resistance in the diffusion channel is proportional to the diffusion length and inversely proportional to the cross-sectional area of the diffusion channel and diffusion coefficient. If water is used as the diffusion medium, the mass-transfer resistance in the diffusion channel can only be increased by increasing the diffusion length, decreasing the cross-sectional area of the diffusion channel, or both. The physical dimensions of the fiber are very small (1 cm long and 300 μm in diameter), which allows the use of small-diameter needles. Thus, the fiber-in-needle device was designed so that the sampling rate is less affected by the convection conditions of water, in a fashion similar to a microelectrode.

The test of the face velocity effect was carried out in a well-agitated sampling chamber (700 rpm, linear flow rate was $\sim 10^4$ cm/min) and in the sampling cylinder where the linear flow rate was as slow as 0.1 cm/min (Figure 1A). The sampling time was 7 days, and each measurement was repeated seven times. It was found that there was no significant difference in the mass uptake between sampling in the well-agitated sampling chamber and in the sampling cylinder (Figure 4). Sampling in static standard aqueous PAH solutions was not performed, because the concentrations of standard aqueous PAH solutions in a confined container were previously found to consistently decrease,[22] and this was also observed in our experiments.

Although it is a desirable feature that the performance of the device is independent of the face velocity, especially for field sampling, where the convection conditions of water are very difficult to measure and calibrate, the disadvantage of this device is that the amount of analytes acquired is not as high as typical passive samplers because of the low sampling rate. However, this disadvantage is not as important for TWA sampling, because it can be enhanced by increasing the sampling time, which is the ultimate purpose of TWA sampling.

Diffusion Calibration. Laboratory calibrations were carried out by exposing six fiber-in-needle SPME devices to the flow-through system (Figure 1B) simultaneously for different time periods. Calibrations were also performed at different diffusion path lengths. Figure 5 depicts the mass uptake time profiles, indicating, first, that there is a linear relationship between the mass uptake and the sampling time, even up to 12 days of sampling, and the linear range could be longer. In addition, it was observed that the mass uptake changes with the change of the diffusion path length, i.e., the longer the diffusion path length, the smaller the mass uptake. Since diffusion in the static water gap between the fiber and the opening of the needle is assumed to control the overall mass-transfer rate, and diffusion follows Fick's first law of diffusion under steady state; the mass uptake process could be calibrated by the use of Fick's first law of diffusion.

It was found that the ratio of sampling rate R over analyte diffusion coefficient D depended on the physical dimensions of the sampler only, i.e., $R/D = A/Z$, where A is the cross-sectional area of the needle abd Z is the diffusion path length.[6,23] It means $(R/D)/(A/Z)$ should be 1 in theoretically. Table 1 summarizes the experimental results for $(R/D)/(A/Z)$ at two diffusion path lengths ($n = 4-5$). The results show that the values of $(R/D)/$

(22) Futoma, D. J.; Smith, S. R.; Smith, T. E.; Tanaka, J. *Polycyclic Aromatic Hydrocarbons in Water Systems*; CRC Press: Boca Raton, FL, 1981.
(23) Martos, P. A.; Pawliszyn, J. *Anal. Chem.* **1999**, *71*, 1513−1520.

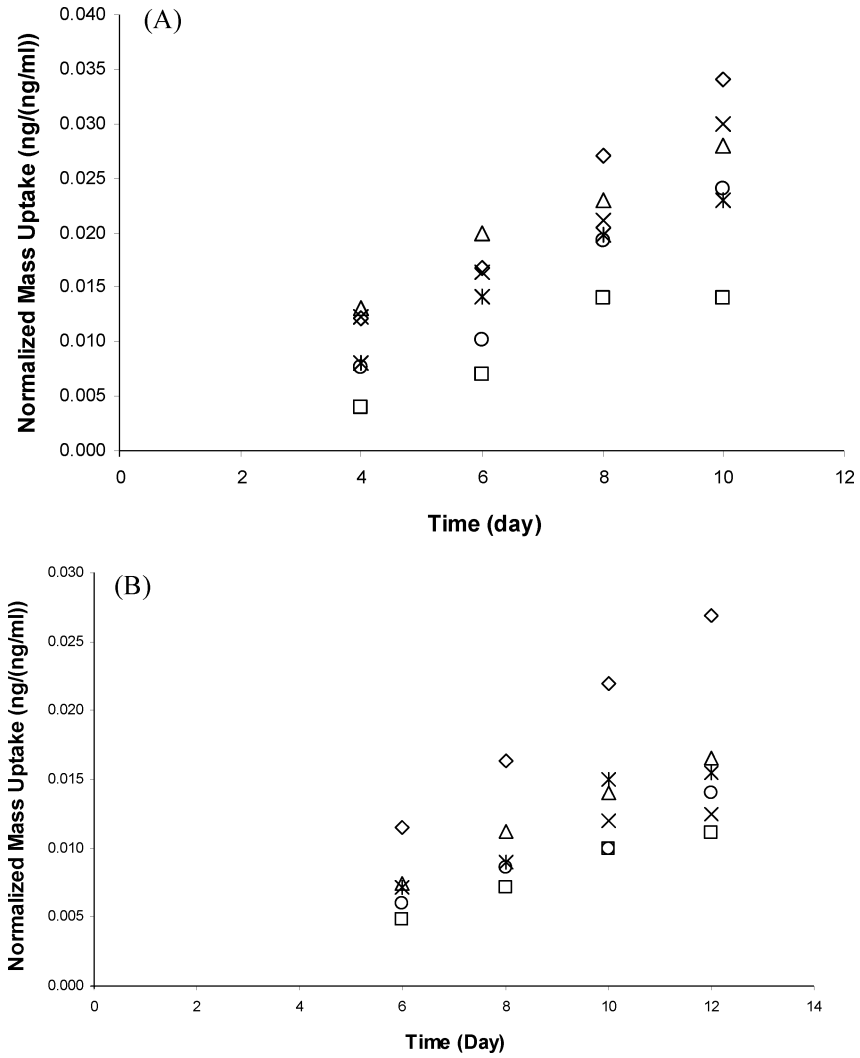

Figure 5. Mass uptake time profiles of PAHs by the fiber-in-needle SPME device. (A) Diffusion path length $Z = 0.5$ cm. (B) Diffusion path length $Z = 1.0$ cm. □, naphthalene; ◇, acenaphthene; ○, fluorene; × , anthracene; *, fluoranthene; △, pyrene.

Table 1. Comparison of the Experimental Values of (*R*/*D*)/(*A*/*Z*) (*n* = 5)

	$(R/D)/(A/Z)$	
analyte	$Z = 0.5$ cm	$Z = 1$ cm
naphthalene	0.42 ± 0.05	0.57 ± 0.12
acenaphthene	1.08 ± 0.13	1.44 ± 0.25
fluorene	0.76 ± 0.11	0.77 ± 0.15
anthracene	1.10 ± 0.18	0.86 ± 0.15
fluoranthene	0.91 ± 0.13	1.01 ± 0.21
pyrene	1.22 ± 0.18	1.04 ± 0.18

(A/Z) for the five compounds are close to 1, except for naphthalene. This is due to the observation that PDMS coating is not a perfect zero sink to naphthalene; thus, the absorbed naphthalene on the PDMS coating decreases the sample rate of available naphthalene in the sample to be absorbed.

Effect of Temperature. The effects of temperature on the sampling are easier to predict because of the simplicity of the device compared to membrane-based passive samplers. Since the diffusion in the static water inside the needle controls the overall mass transfer, if the fiber coating is a perfect zero sink for the analytes, the effects of temperature on the sampling are focused on the temperature dependence of the diffusion coefficient, which can be approximated as linear or, more accurately, the Arrhenius equation.[24,25] Therefore, the mass uptake rate slightly increases

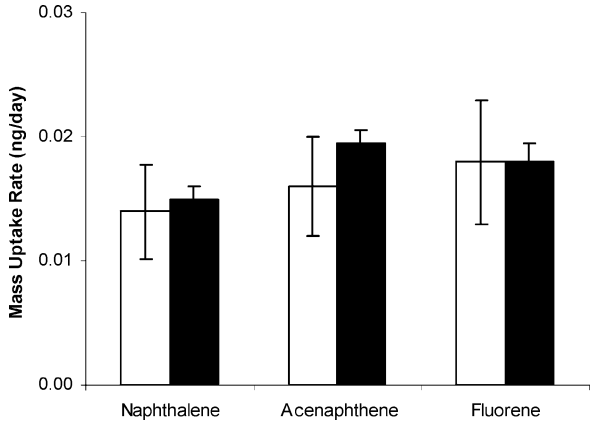

Figure 6. Temperature effect on the mass uptake rate. □, 14 ± 1 °C; ■, 24 ± 1 °C. Error bars signify ±1 standard deviation.

(24) Bonoli, L.; Witherspoon, P. A. *J. Phys. Chem.* **1968**, *72*, 2532−2534.
(25) Poling, B. E.; Prausnitz, J. M.; and O'Conell, J. P. *The Properties of Gases and Liquid*, 5th ed.; McGraw-Hill: New York, 2001.

with the increase of absolute temperature. This suggests that, under normal field conditions, the maximum change of the mass uptake rate is ~10%. Considering that the relative experimental errors are larger than 10%, the temperature effects can be neglected. The investigation of temperature effects was carried out at two temperatures, 24 ± 1 and 14 ± 1 °C, as shown in Figure 6, indicating that the change of temperature does not significantly change the mass uptake rate.

CONCLUSION

A modified fiber-in-needle SPME device was developed and investigated for TWA water sampling. Since the diffusion in the static water gap between the fiber and the opening of the needle controls the overall mass-transfer process, mass uptake could be calibrated with Fick's first law of diffusion. There was good agreement between theoretical prediction and the experimental results for TWA water sampling with the fiber-in-needle SPME device, if the fiber is a zero sink for the target analytes. In addition to all advantages of a conventional SPME device, including its reusability and the solvent-free nature of the method, it is worth noting that this fiber-in-needle SPME device is independent of face velocity, affected only slightly by temperature, and the position of the SPME fiber can be easily adjusted to different diffusion path lengths, to adapt to a large range of analyte concentrations. The advantages are desirable for long-term field water sampling, especially where the convection conditions of water are difficult to measure and calibrate.

In addition, a new flow-through system based on permeation was developed. It can be used to generate stable concentrations for organic pollutants and satisfy the requirement for the experiment of long-term water sampling.

The SPME device has been shown to be a successful passive sampler for both air[6] and water sampling. The SPME field sampler for air sampling had been commercialized.[8] The future work will include the design of a user-friendly SPME field sampler for water sampling and its commercialization.

Received for review June 11, 2005. Accepted September 8, 2005.

AC051035Q