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Solid-phase microextraction under controlled agitation conditions for rapid on-site sampling of organic pollutants in water

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ABSTRACT

An electric drill coupled with a solid-phase microextraction (SPME) polydimethylsiloxane (PDMS) fiber or a PDMS thin film was used for rapid sampling of polycyclic aromatic hydrocarbons (PAHs) in aqueous samples. Laboratory experiments demonstrated that the sampling rates of SPME fiber and thin film can be predicted theoretically. Compared with the SPME fiber, the PDMS thin film active sampler exhibited a higher sampling rate and much better sensitivity due to its higher surface-to-volume ratio and its larger extraction phase volume. The amount of the analytes extracted by the thin film was around 100 times higher than those obtained by fiber, for both 5 min rapid sampling and equilibrium extraction. A new thin film active sampler was then developed for rapid on-site water sampling. The sampling kit included a portable electric drill, a copper mesh pocket, a piece of thin film, and a liner. Laboratory experiments indicated that the sampling remained in the linear uptake phase with this sampler to 8 min for the PAHs. Field test illustrated that this novel sampler was excellent for rapid on-site water sampling due to its short sampling period, high sampling efficiency and durability The thin film sampling kit facilitates on-site sampling, sample preparation, storage and transport. This new sampler is more user-friendly and easier to commercialize than previous samplers.

1. Introduction

Solid phase microextraction (SPME) is a solvent-free technique for sampling and sample preparation [1]. In the SPME process, the movement of analytes follows a concentration gradient according to Fick's first law of diffusion. The fluid contacting the extraction phase's surface is always stationary. To model mass transport, the gradation in fluid motion and convection of molecules in the space surrounding the extraction phase can be simplified by Prandtl boundary layer [1], as shown in Fig. 1(A).

With the commercialization of SPME fiber coatings and the development of SPME field samplers, SPME has become suitable for different types of analytes and samples in both laboratory and field applications [2–5].

Recently, thin film, a new format of SPME that differs from the coated fiber format, was developed [6]. PDMS thin films have a high surface-to-volume ratio, which gives them a high extraction efficiency and sensitivity without sacrificing analysis time [6,7]. The thin film technique has been evaluated by determining the time weighted average (TWA) concentrations of PAHs in Hamilton Harbor. The study showed that the thin film sampler is simple, durable, cost-effective and can easily be used for field sampling [8,9].

Significant analytical chemistry effort is currently directed at developing suitable methods to facilitate on-site analysis [10]. Performing sample preparation on-site has some advantages, since analytes are more stable in the extraction phase compared to the natural matrix [10]. As a sampling technique used to load samples on-site, passive sampling is based on the free flow of analyte molecules from the sampled medium to a collecting medium as a result of a difference in chemical potential [11]. Passive sampling devices allow long-term monitoring of pollutant levels in aquatic systems [12–14]. An alternative approach to environmental analysis involves performing spot sampling to measure contaminant levels in water at the moment of sampling [10]. Rapid sampling and sample preparation are therefore necessary. When rapid spot sampling is performed, the amount collected by the sampler depends on both sampling rate and exposure time [11]. If exposure time is short (in contrast with 1 week or 1 month in long-term monitoring), the sampling rate should be fast enough to achieve high sensitivity for analysis. In passive sampling, because the flow of analytes from the sample into the trap is completely free and follows Fick's first law of diffusion, the sampling rate is controlled by the molecular diffusion coefficient of the analyte and the parameters of the sampler device [9,15,16]. Compared with passive sampling, active sampling uses electrically powered equipment and thus requires an energy

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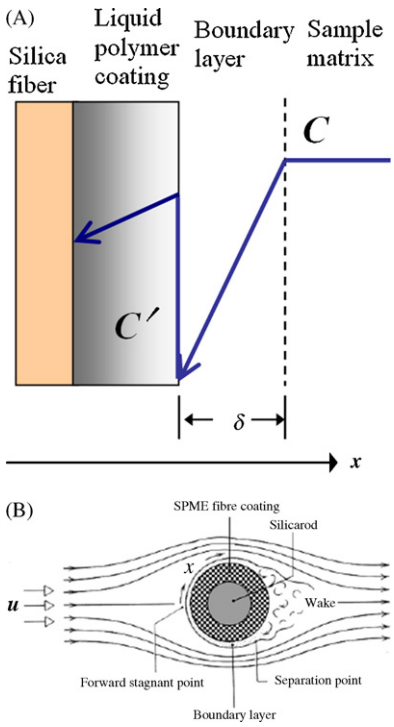

Fig. 1. (A) Boundary layer model in the SPME procedure. C is the concentration of the analyte in the sample matrix and C' is the concentration of the analyte in the boundary layer at the interface of the boundary layer and fiber. (B) Cross-flow model in the SPME procedure [21].

source. Although an active sampler is more complicated and costly, it is an attractive option because it allows for better control of the sampling rate and is more suitable for rapid sampling.

In the sampling process, analytes of interests are mass loaded in direct proportion to the bulk analyte concentration for the specific sampling period. In the initial phase of sampler exposure, the rate of desorption of analytes from the receiving phase into water is negligible, and the sampler works in the linear uptake regime [17–20]. Rapid sampling happens in this regime. The mass of analyte accumulated in the extraction phase after an exposure time (t) can be calculated as [17]

$$M_s(t) = C_w R_s t, \tag{1}$$

where C_w is the concentration of analyte in the water phase, and R_s is the proportionality constant (sampling rate) and may be interpreted as the volume of water cleared of analyte per unit of exposure time by the sampler. When the sampler is used for on-site sampling, the sampling rate can be determined in the laboratory. If R_s is known, C_w can be calculated from the sampling rate (R_s), the exposure time (t) and the amount ($M_s(t)$) of the analyte trapped by the receiving phase.

Coupling an electric drill with a thin film to control the agitation conditions when the sample solution is static has been experimentally demonstrated to be an effective method for active sampling [7]. This study investigates, both theoretically and experimentally, the application of this agitation technique coupled with both SPME fiber and thin film as active samplers. This study also addresses some limitations of previous works on thin film technique. The previous holder for thin film was not user-friendly and not suitable for commercialization [7]. The present study aims to design a more convenient and effective SPME device as an active sampler for rapid and low-cost on-site sampling.

2. Theoretical considerations

2.1. Mass transfer associated with SPME fiber extraction in fluid samples

2.1.1. Cross-flow model

When the motion of the fluid sample is normal in relation to the axis of the fiber, heat transfer can be translated into a mass transfer solution by replacing temperatures with concentrations, heat with flux of mass, and thermal conductivity with molecular diffusion coefficient [21,22]. Fig. 1(B) illustrates this model.

The average Nusselt number Nu can be calculated with Eq. (2) [23,24]

$$\overline{Nu} \equiv \frac{\bar{h}d}{D} = ERe^m Pr^{1/3} \tag{2}$$

where $\bar{h}$ is the average mass transfer coefficient (cm/s), d is the outside diameter of the fiber (cm), and D is the diffusion coefficient (cm^2/s). Re is Reynolds number ($Re = ud/\nu$), u is the linear velocity of the sample (cm/s), and ν is the kinematic viscosity of the matrix media at the extraction temperature (cm^2/s). The fluid's linear speed is calculated as the angle speed of the rotation $\omega \times$ rotating radius. Pr, the Prandtl number of the liquid, equals ν/D. Constant E is 0.989 and constant m is 0.33 under the experimental conditions [23,24]. Once $\bar{h}$ is known, the amount of extracted analytes n during sampling period t can be calculated by the following equation:

$$n = \bar{h}AC_{bulk}t \tag{3}$$

where A is the surface area of the fiber (cm^2), and C_{bulk} is the bulk analyte concentration (ng/mL). Eq. (3) is used to calculate the theoretical values of the amount extracted by the fiber based on the cross-flow model.

2.1.2. Boundary layer model

The agitation conditions and the viscosity of the sample determine the thickness of the boundary layer δ (cm) [1]:

$$\delta = 2.64\frac{b}{Pr^{0.43}\sqrt{Re}} \tag{4}$$

where b is radius of the fiber (cm).

The theoretical values of the initial extraction rate by fiber, based on the boundary layer model, can be estimated with

$$\frac{dn}{dt} = \left(\frac{DA}{\delta}\right) C_{bulk} \tag{5}$$

Table 1 presents the theoretical calculation of the extracted amount by the 100 μm PDMS fiber based on the cross-flow model and boundary layer model in a 10 mL sample. The fiber is rotated in the sample with an electric drill at 600 rpm. The surface area of the fiber is 10 mm^2.

2.2. Mass transfer associated with thin film extraction in fluid samples

When the 5 cm^2 thin film is rotated around its axis vertically below the fluid surface (Fig. 2(A)), the relative motion of the thin film and fluid can be regarded as the composite result of both parallel and perpendicular directions. If a little portion of the thin film at any time t is considered, then the fluid flows past it at a velocity vector $\vec{u}$. In Fig. 2(B), when thin film rotates a small angle,

$$\vec{u} = \vec{u}_{pa} + \vec{u}_{pe} \tag{6}$$

where $\vec{u}_{pa}$ is the velocity vector parallel to the thin film plane, and $\vec{u}_{pe}$ is the velocity vector perpendicular to the thin film plane.

The mass transfer in the thin film extraction process is associated with the relative motion of the thin film and the fluid. For this

Table 1
Theoretical calculations of fiber extraction of PAHs in a 10 mL sample, based on the boundary layer model and the cross-flow model (for 5 min extraction).

Analyte	D (cm^2/s)	Re	Pr	δ (cm)	$\bar{h}$ (cm/s)	n_1 (theoretical, ng)	n_2 (theoretical, ng)	n (experimental, ng)
Ace	0.0000064	3.533	1406	0.000989	0.00374	0.194	0.112	0.225 ± 0.018
Fl	0.0000061	3.533	1475	0.000969	0.00362	0.189	0.109	0.221 ± 0.0049
Anth	0.0000059	3.533	1525	0.000955	0.00354	0.185	0.106	0.220 ± 0.010
Fla	0.0000056	3.533	1607	0.000934	0.00342	0.180	0.103	0.217 ± 0.012
Pyr	0.0000056	3.533	1607	0.000934	0.00342	0.180	0.103	0.197 ± 0.014

n_1: boundary layer model; n_2: cross-flow model.

reason, at any time t, the mass loaded from fluid to the little portion of film can be divided into parallel and perpendicular parts (Eq. (7)):

$$M = M_{pa} + M_{pe} \tag{7}$$

where M_{pa} is the mass loaded into the little portion of film by parallel motion of the fluid to the thin film plane, and M_{pe} is the mass loaded into the little portion of film by perpendicular motion of the fluid to the thin film plane. Therefore, the total mass uptake from the fluid to the whole thin film can be expressed as:

$$\sum M = \sum M_{pa} + \sum M_{pe} \tag{8}$$

In other words,

$$n = n_{pa} + n_{pe} \tag{9}$$

where n is the amount extracted by the thin film after extraction time t, n_{pa} is the total mass uptake by parallel mass transfer, and n_{pe} is the total mass uptake by perpendicular mass transfer.

The theoretical descriptions of separate perpendicular mass transfer process and parallel mass transfer process are complicated. However, empirical correlations are readily available [24]. The mathematics of diffusion and heat transfer are equivalent because both processes are described by Laplace's equation. The formula for heat transfer can be used for mass transfer by substituting diffusion coefficients for thermal conductivity and diffusivity constants [25].

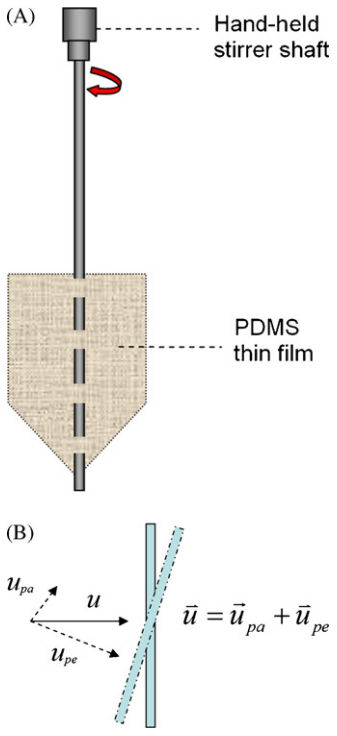

Fig. 2. (A) Thin film sampler. (B) Rotated thin film sampling.

The relationships for predicting Nusselt numbers for laminar flow and turbulent flow parallel to the film plane are described as follows [24]

$$\overline{Nu}_{laminar} = 0.648Re^{1/2}Pr^{1/3} \tag{10}$$

$$\overline{Nu}_{turbulent} = 0.0366Re^{4/5}Pr^{1/3} \tag{11}$$

where Re is Reynolds number (Re = ud/ν), u is the linear velocity of the sample, and ν is the kinematic viscosity of the matrix media. Pr, the Prandtl number of the liquid, equals ν/D.

Substituting Eq. (2) into Eq. (3),

$$n = \left(\frac{\overline{Nu}D}{d}\right) AC_{bulk}t \tag{12}$$

The above equation in combination with Eqs. (10) and (11) can be used to calculate the mass loaded into the thin film by parallel mass transfer process after extraction time t:

$$n_{pa} = \left[(0.648Re^{1/2}Pr^{1/3} + 0.0366Re^{4/5}Pr^{1/3})\frac{D}{d}\right] AC_{bulk}t \tag{13}$$

The empirical result of the Nusselt number for perpendicular flow to the film plane is [24]

$$\overline{Nu}_{pe} = 0.0921Re^{0.675}Pr^{1/3} \tag{14}$$

Combining Eqs. (12) and (14) gives Eq. (15)

$$n_{pe} = 0.0921Re^{0.675}Pr^{1/3}\frac{D}{d}AC_{bulk}t \tag{15}$$

Using this expression along with Eqs. (9) and (13), Eq. (9) then becomes Eq. (16)

$$n = \left[(0.648Re^{1/2}Pr^{1/3} + 0.0366Re^{4/5}Pr^{1/3})\frac{D}{d}\right] AC_{bulk}t + 0.0921Re^{0.675}Pr^{1/3}\frac{D}{d}AC_{bulk}t \tag{16}$$

Eq. (16) was used to calculate the theoretical mass uptake by the rotated thin film immersed in the aqueous solution. Table 2 gives the predicted amount extracted by the rotated thin film based on the above model in 50 L PAHs solution.

3. Experimental

3.1. Chemicals and supplies

All chemicals were of analytical grade. Methanol (HPLC grade) was purchased from BDH (Toronto, ON, Canada). Polycyclic aromatic hydrocarbons (acenaphthene (Ace), fluorene (Fl), anthracene (Anth), fluoranthene (Fla) and pyrene (Pyr)) were purchased from Supelco (Oakville, ON, Canada). Praxair (Waterloo, ON, Canada) supplied helium (99.9%), nitrogen (99.9%), liquid nitrogen, and compressed air for the analytical instruments. Nano-pure water from a Barnstead water system (Dubuque, IA) was used for all the experiments. The SPME fibers used in all experiments were 100 μm PDMS metal fibers from Supelco (Oakville, ON, Canada). These fibers were conditioned before use for 30 min at 250 °C in a

Table 2
Theoretical calculations for rotated thin film extraction of PAHs in a 50 L sample (for 5 min extraction).

Analyte	D (cm^2/s)	Re	Pr	n_{pa} (ng)	n_{pe} (ng)	n (theoretical, ng)	n (experimental, ng)
Ace	0.0000064	13,956	1406	17.8	6.7	24.5	23.2 ± 2.04
Fl	0.0000061	13,956	1475	27.7	10.5	38.2	39.7 ± 3.52
Anth	0.0000059	13,956	1525	9.1	3.4	12.5	11.1 ± 0.86
Fla	0.0000056	13,956	1607	85.3	32.4	117.7	113.6 ± 7.71
Pyr	0.0000056	13,956	1607	84.1	31.9	116.0	109.8 ± 5.90

fiber conditioner. PDMS thin films with a thickness of 127 μm were purchased from Specialty Silicone Products Inc (Ballston Spa, NY). A Mastercraft 10 in. bench drill was used at the 600 rpm setting in the following experiments. A portable 7.2 V Makita drill was applied with a constant agitation speed of 600 rpm. These two drills were purchased in Canadian Tire (Waterloo, ON, Canada).

3.2. SPME fiber and thin film samplers

Initial laboratory experiments in a 10 mL sample involved attaching the SPME fiber or thin film to the bench drill like a drill bit. The thin film was also attached in this way. The thin film was cut into the shape of a house (i.e., a 2 cm × 2 cm square with a 1-cm high triangle on top) and secured to the drill like a drill bit. The surface area for one side was 5 cm^2 and the volume of each thin film was 0.0635 cm^3. Such a thin film sampler was designed to be coiled and fitted inside the liner for injection, taking into consideration the length of the heat zone. Before use, the thin film was conditioned for 1 h at 250 °C in a GC injection port. After extraction, the thin film was removed from the solution, dried with a lint-free tissue, and inserted into the liner. The liner containing the thin film was inserted in the thermal desorption unit for automated analysis by thermo-desorption.

For laboratory sampling in the 50 L sample, a special "drill bit" (Fig. 3) was developed for attaching a fiber to the bench drill. Two Teflon disks (created by the University of Waterloo Science Shop, Waterloo, ON, Canada) were attached to a metal shaft using small screws. The fiber could be screwed into the top disk. A small hole in the bottom disk was used to secure the position of the fiber. The top disk was movable and could be adjusted to expose the fiber during sampling or to withdraw the fiber into the needle after use. When the drill was turned on, the fiber rotated and the water was agitated. The Teflon disks prevented the fiber from spinning outward during sampling.

Portable cordless drills are more practical for sampling on-site. The controlled speed drill was deemed suitable for field sampling because it is easier to maintain drill rotation at a constant speed.

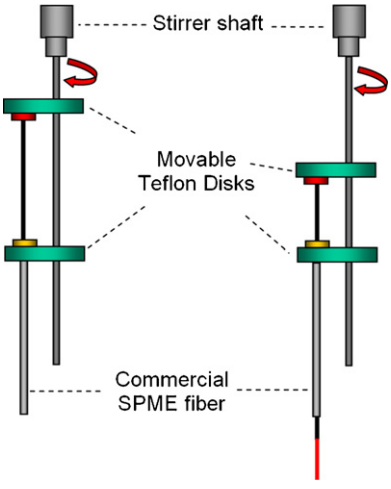

Fig. 3. SPME sampler showing the protected position of the fiber before and after sampling, and the exposed position of the fiber during sampling.

3.3. Application of the thin film sampler for rapid sampling on-site

Laurel Creek, a small river located on the University of Waterloo campus (Waterloo, ON, Canada) was chosen to field test rapid sampling using the thin film sampler. The experimental site was about 1 m offshore.

On-site sampling with thin film sampler was illustrated in Fig. 4. The thin film was positioned in the designed copper mesh pocket attached to the handling rod. The sampler was rotated with the portable drill at 600 rpm vertically 0.2–0.5 m below the surface of the water. An extraction time of 5 min, a short sampling time in the linear range of the uptake by thin film, was used for sampling. After retrieval, the thin film was sealed in the liner and transported to the lab, and then analyzed using the methods described above. To validate the thin film measurement, a water sample from the river was collected separately in a bottle and carried to laboratory. This water sample was treated by SPME fiber direct extraction using the standard addition approach. The concentrations of PAHs were determined by adding a series of known concentrations of PAHs (10, 20, 50 ppb) to 10 mL river samples. The original and spiked samples were agitated at 600 rpm (Gerstel Agitator). Extraction lasted 30 min, followed by fiber desorption in the GC injector.

3.4. Instrumental analysis

3.4.1. Thin film analysis

Gas chromatography was performed on an Agilent 6890 GC and 5973 MSD equipped with a Multipurpose Sampler (MPS 2) system (Gerstel GmbH, Mullheim, Germany). A Thermal Desorption System (TDS-2) unit was mounted on the GC via the Cooled Injection

Fig. 4. On-site sampling of river water using the thin film sampler.

System (CIS-4) inlet for thermal desorption of analytes. The thin film was placed into a liner 187 mm in length, 6 mm O.D., and 4 mm I.D.

A Thermal Desorption Unit (TDU) was used for large volume injection (LVI). The liner with sampler was heated to transfer the compounds of interest into the CIS-4. The CIS acts as cryogenic trapping, focusing and concentrating the compounds to be determined, and then is heated, transferring them to the capillary column. The temperature of the CIS was 0 °C for the first 5 min, during which time the temperature of TDU was increased to 250 °C and the analyte was desorbed. After desorption, the cooled liner with the thin film was removed from the TDU. At last the temperature of CIS was increased to transfer the analyte to the GC column.

An HR-1 capillary column (30 m, 0.25 mm I.D., 0.25 μm film thickness) (Shinwa, Kyoto, Japan) was used with helium as the carrier gas at a flow rate of 1 mL/min. For the analysis of the PDMS thin film, column temperature was maintained at 40 °C for 2 min, then increased at a rate of 15 °C/min to 280 °C, and finally held constant for 2 min. Total run time was 20 min. The MS system was operated in electron ionization (EI) mode and tuned to perfluorotributylamine (PFTBA). A mass scan from 40 to 300 was acquired, and the base peak of each compound was selected and integrated.

3.4.2. SPME fiber analysis

Commercial SPME fibers were analyzed using a Varian 3800 GC coupled with a Saturn 4000 ion trap-MS system. Separation was performed using a RTX-5 column (30 m, 0.25 mm I.D., 0.25 μm film thickness) (Restek, Bellefonte, PA, USA). The column was initially set at 40 °C, held constant for 2 min, then ramped at 15 °C/min to 250 °C, and finally held at this temperature for 4 min; total run time was 20 min.

4. Results and discussion

4.1. Extraction by SPME fiber and thin film under controlled agitation conditions in a 10 mL sample

The PDMS thin films are very solid and reproducible when handled properly. Their lifetime has not yet been determined, but a single thin film can be used more than 20 times with no significant difference in the results. The cost of making each device is very small, so these thin films can even be used for single-use samplers.

Fig. 5(A) and (B) shows the extraction time profiles determined using the bench drill with the fiber and the thin film, respectively. For each extraction, 10 mL of PAHs aqueous solution (1 ppb) was added to a 10 mL vial, which immobilized with ring stands and clamps. The fiber or the thin film was immersed into the solution, rotating with the bench drill at 600 rpm.

The time required to reach equilibrium increased with the thickness of the PDMS extraction phase [1]. The thickness of the thin film device is only 63.5 μm (thin film has two sides, so the extraction thickness is 127 μm/2 = 63.5 μm), and the fiber's extraction phase is 100 μm thick. The results show that the required length of equilibrium time was shorter for the thin film (10 min) than for the fiber (20 min).

The amount of analyte extracted at equilibrium can be expressed by Eq. (17) [1]:

$$n = \frac{K_{es}V_sC_sV_e}{K_{es}V_e + V_s} \quad (17)$$

where n is the amount of analyte extracted, V_e is the volume of the extraction phase, V_s is the sample volume, K_{es} is the analyte's distribution constant between the extraction phase and sample matrix, and C_s is the initial concentration of analyte in the matrix. The amount of analyte in the thin film extraction phase at equilibrium was much greater than that in the fiber (Fig. 4). The thin film has a higher extraction phase volume than the fiber, and therefore the sensitivity of thin film was higher.

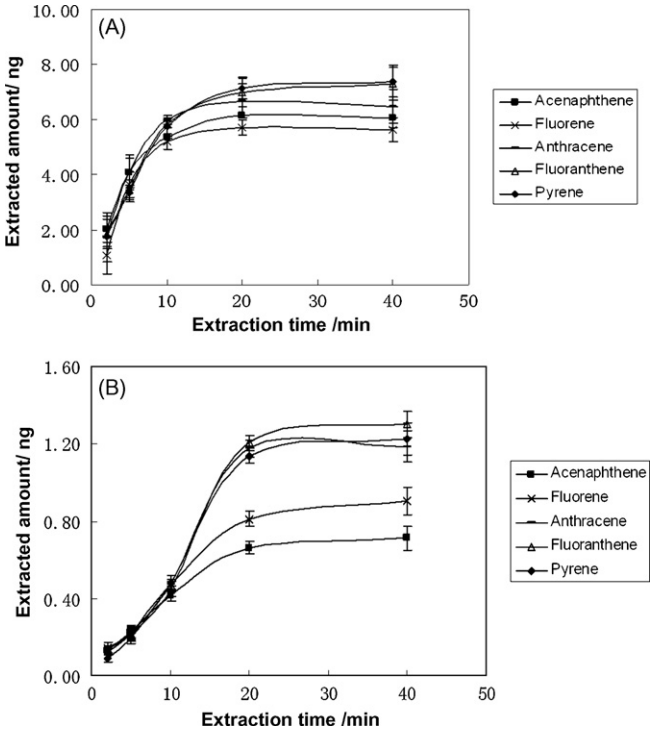

Fig. 5. Extraction time profiles of PAHs in 10 mL samples using a bench drill coupled with (A) a thin film and (B) a fiber.

The volume of a thin film (V_e = 63 μL) is 100 times greater than that of a fiber (V_e = 0.63 μL). However, the amount of analyte extracted by the thin film was less than 100 times greater than that obtained by the fiber. This difference can be explained by the small sample volume and relatively large thin film volume used for extraction. According to Eq. (17), the extracted amount (n) is only directly proportional to the V_e when the $K_{es}V_e$ is negligibly smaller than V_s. Because of the larger extraction phase to sample volume ratio in this study, $K_{es}V_e$ in the denominator of Eq. (17) could not be ignored; thus, the amount (n) was not linearly proportional to the volume of the extraction phase. For the same reasons, analyte concentrations left in the vial during the thin film extraction decreased with extraction time. On the other hand, the fraction of extracted analytes increases with the ratio of $K_{es}V_e$ to V_s. Therefore most of the analytes in the system will be extracted in small sample volume when distribution coefficient of the analyte is relatively high. This was observed in such a small system as the 10 mL sample: two of the PAHs with higher distribution coefficients (fluoranthene and pyrene) were mostly extracted by the thin film.

Table 1 shows theoretical mass uptake by the fiber based on the cross-flow model and boundary layer model. The results of boundary layer model were similar to the experimental values. However, the cross-flow model underestimated the amount of extracted analytes. There are two possible reasons for this low prediction. Firstly, the fiber was vibrating, so a higher sampling rate may have resulted from faster relative movement between the fiber and water. Secondly, the model assumed that the motion of the fluid sample was normal in relation to the axis of the fiber, a condition not observed in the experiments. In the boundary layer model, the extraction rate of a compound is proportional to its diffusion coefficient. In Fig. 5(B), the fiber extracted a slight more amount of the low molecular weight (M_w) PAHs than high molecular weight PAHs after 2 min. The higher diffusion coefficient of the low M_w PAHs might explain this phenomenon.

Because analyte concentrations decreased during sampling, a 10 mL sample was not sufficient for validating the proposed mass uptake model of the thin film.

4.2. Extraction by SPME fiber and thin film under controlled agitation conditions in a 50 L sample

To minimize depletion of analytes during extraction by thin film in a small sample volume, a large spherical bottle filled with 50 L of PAHs aqueous solution was used. The PAH concentrations in the 50 L sample were determined by SPME direct extraction. Ten milliliters of the sample was collected and agitated at 500 rpm (Gerstel Agitator). The extraction was lasted 30 min, followed by fiber desorption in the GC injector. External calibration method was used for the quantitation. The average concentrations of acenaphthene, fluorene, anthracene, fluoranthene and pyrene were 1.1, 1.7, 0.6, 5.7 and 5.6 μg/L, respectively. Fig. 6 shows the extraction time profiles for the SPME fiber (A) and thin film (B). As expected, at equilibrium the amounts of analytes extracted by the thin film are higher than those extracted by the SPME fiber. This occurred because the thin film has a higher extraction phase volume. The equilibration time by thin film extraction was more than 10 min, as with the 10 mL sample.

Sample volume has a significant effect on the extracted amount of the analytes. For the compounds with relatively low K_{es} (acenaphthene, fluorene and anthracene), the thin film extracted around 100 times more analytes at equilibrium than did the fiber. Using a 50 L sample volume instead of a 10 mL sample volume reduced depletion from 50–60% to 0.2–0.4%.

Table 2 shows the theoretical and experimental results obtained by rotating thin film sampling in a 50 L sample after a 5 min extraction. Reynolds number (Re) and Prandtl number (Pr) of extraction by thin film were calculated and listed in the table. The predicted mass uptakes were obtained based on Re, Pr and Eq. (16). The theoretical values agree well with the observed experimental uptake. This suggests the model can be used for rotated thin film sampling in a fluid sample. Similar to the boundary layer model in fiber extraction, this thin film model also predicts the higher diffusion coefficients of low M_w PAHs results in their higher concentration rates in the thin film. This prediction was proven in the experiment.

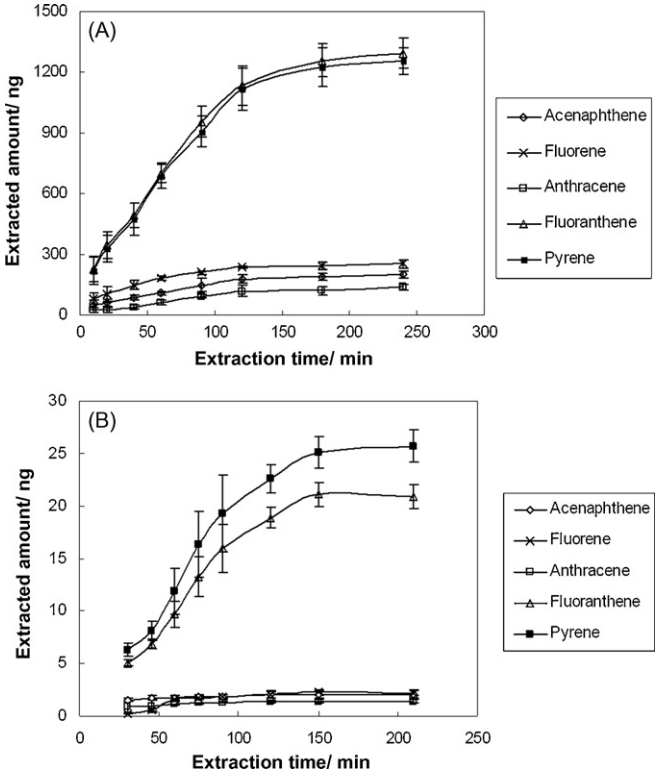

Fig. 6. Extraction time profiles of PAHs in 50 L samples using a bench drill coupled with (A) a thin film and (B) a fiber.

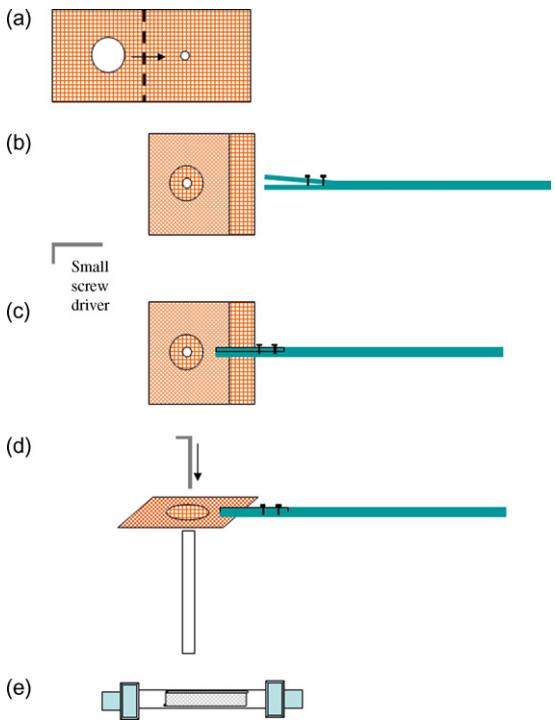

Fig. 7. Schema of a thin film copper mesh sampler. (A) Fold (B and C) fix on a rod (D) push into a liner (E) seal the liner for transportation.

4.3. Design of a thin film sampler for rapid sampling

Because of its higher extraction efficiency, the thin film is more suitable than the fiber for rapid sampling on-site. A copper mesh pocket and handling rod for attaching a drill was designed and manufactured for field-deployed thin film. The thin film was flattened and clamped tightly in the copper mesh pocket. The copper mesh was not prone to clogging by algae or sediment.

Fig. 7 depicts the new thin film sampler. A window was milled in the left part of a piece of copper mesh and another smaller window was milled in the right part. The left window was used to permit analytes access to the thin film for extraction and to allow the thin film to go into the liner after extraction. The smaller window is just big enough to allow the passage of a small screw driver. It is smaller because it needs to support the thin film to prevent it from falling off during rotation and sampling. Step (b) involved folding the copper mesh along the dashed line and sealing the two edges by soldering. A pocket with one opening and two differently sized windows on two sides was thus formed. After placing the thin film in the pocket, the pocket was connected to a metal rod by two small screws. The rod could be extended or shortened depending on the specific requirements for on-site sampling. (c) Represents the final thin film field sampler, which resembles a small racket. When the extraction was completed, the thin film could be pushed from the small window through the big window into the liner by the small screw driver as in step (d). Finally, in step (e), capping two ends of the liner to seal the thin film provided an effective mechanism for preserving the integrity of the sample and for preventing contamination.

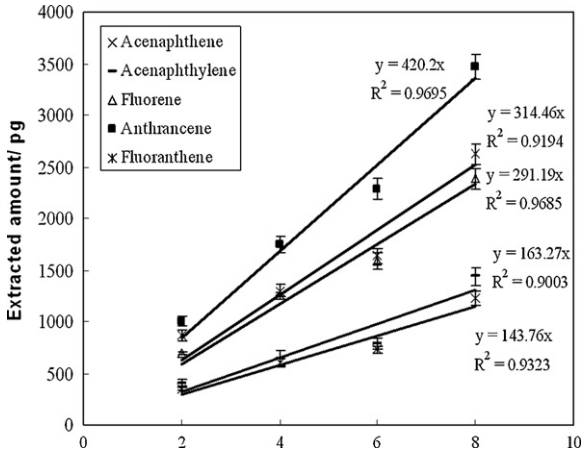

Fig. 8. Uptake by the new thin film sampler over 8 min in a 50 L sample.

Table 3
Sampling rates of PAHs using the new thin film sampler coupled with a portable drill (operated at 600 rpm) and results of field sampling.

Compounds	Sampling rate R_s (mL/min)	Concentration	
		Thin film on-site sampling (ng/L)	SPME off-site sampling (ng/L)
Acenaphthene	1.44	2.0 ± 0.18	2.3 ± 0.15
Acenaphthylene	1.64	5.0 ± 0.57	6.1 ± 0.38
Fluorene	2.91	5.7 ± 0.32	4.9 ± 0.39
Anthracene	4.20	4.2 ± 0.37	3.4 ± 0.22
Fluoranthene	3.14	26.9 ± 2.11	21.8 ± 1.06

4.4. Application of the thin film sampler for rapid sampling in laboratory and on-site

The uptake experiment was conducted in the laboratory in a 50 L aqueous PAHs solution, using the new thin film sampler coupled with a portable drill. Extraction times were 2, 4, 6 and 8 min. Replicate extractions ($n = 3$) were sampled for each extraction period of exposure. Short exposure times reduced the accumulation of chemicals, so detection sensitivity and variability at lower amounts are important. With the PAHs studied here, a 2-min exposure provided sufficient mass to yield reproducible measurements. The longest extraction time was 8 min.

The uptake curve for the PAHs shown in Fig. 8 used linear regression analysis. Because the regression coefficients (R^2) range between 0.9003 and 0.9695, all PAHs remained in the linear uptake phase for the full 8 min. These findings obey first-order uptake kinetics. This is an important verification of the appropriateness of a linear model (Eq. (1)) for deriving thin film sampling rates for all the PAHs. R_s values were determined by rearranging Eq. (1) to solve for R_s (at a fixed C_w) (Eq. (18)) (Table 3).

$$R_s = \frac{M_s(t)}{C_w t}, \tag{18}$$

These calibration data were used to estimate analyte concentrations in the ambient environment.

The results of field sampling in the campus river are shown in Table 3. There was no significant difference in the concentrations measured by the thin film and by the fiber. The approach based on rapid sampling by thin film proved successful.

5. Conclusion

This study demonstrates the advantages and promising applications of a rotated thin PDMS film for rapid analysis of semivolatile compounds in water samples. Unlike the SPME PDMS fiber, the rotated thin film coupled with an electric drill achieved high extraction sensitivity without sacrificing equilibrium time. This is due to its larger surface area to extraction phase volume ratio. We proposed a mass transfer model to quantitatively describe rapid and direct extraction of PAHs with rotated thin film extraction. The mass uptake predicted by the model compares well with experimental mass uptake. Therefore this method would be appropriate for situations in which calibration curves or internal standards are difficult to determine. For SPME fiber extraction, the theoretical prediction based on the boundary layer model is close to the experimental results.

To quantify rapid water sampling with thin film on-site, mass loading rates in the linear uptake regime over 8 min were obtained in the laboratory. A novel and simple copper mesh sampler was used during the rotation of the thin film, thus integrating sampling, sample preparation, storage and transport. This characteristic of the sampler makes it suitable for field sampling. The entire sampling period on-site is only 5 min, which meets the requirement of rapid sampling and shows great potential for future applications. The comparable results using this sampler and the regular SPME fiber prove that this technique is an accurate and reliable method for rapid on-site sampling of organic pollutants in water. Thin film was previously found to be an excellent passive sampler for TWA concentration of a long time period. This study confirms that thin film can also be a successful active sampler for determining the concentration of organic pollutants. Plausible modifications to the thin film sampler could avail it to automation and miniaturization. Application of this sampler in analysis in complex matrix will be investigated in the future.

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