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Commercial polymeric fiber as sorbent for solid-phase microextraction combined with high-performance liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water

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ABSTRACT

A novel microextraction method making use of commercial polymer fiber as sorbent, coupled with high-performance liquid chromatography-fluorescence detection for the determination of polycyclic aromatic hydrocarbons (PAHs) in water has been developed. In this technique, the extraction device was simply a length (8 cm) of a strand of commercial polymer fiber, Kevlar (each strand consisted of 1000 filaments, each of diameter ca. 9.23 μm), that was allowed to tumble freely in the aqueous sample solution during extraction. The extracted analytes were desorbed ultrasonically before the extract was injected into HPLC system for analysis. Extraction parameters such as extraction time, desorption time, type of desorption solvent and sample volume were optimized. Each fiber could be used for up to 50 extractions and the method showed good precision, reproducibility and linear response within a concentration range 0.05–5.00 μg L^{-1} with correlation coefficients of up to 0.9998. Limits of detection between 0.4 and 4.4 ng L^{-1} for seven PAHs could be achieved. The relative standard deviations ($n = 3$) of this technique were between 2.9% and 12.1%.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of fused aromatic ring hydrocarbons that derived from endogenous and anthropogenic sources. These ubiquitous environmental pollutants usually arise from incomplete combustion or high-temperature pyrolytic processes involving organic materials. The main sources of PAH emissions include volcanic eruptions, wildfires, combustion of fossil fuels, motor vehicle exhaust, oil spills, waste incineration, food processing, coke production, oil refining and many other industrial activities [1,2].

It has been estimated that 230×10^6 kg of PAHs enter the global environment annually [3]. Based on their properties and molecular mass, some low polarity and low molecular mass (two and three aromatic rings) PAHs have a significant acute toxicity, whereas many non-polar and high molecular mass (four or more aromatic rings) PAHs show high carcinogenic and mutagenic potential [4,5]. Due to their potential or proven carcinogenic, mutagenic and even endocrine disrupting [6,7] properties, some PAHs have been designated by the US Environmental Protection Agency (EPA) and European Union (EU) as priority pollutants for monitoring purposes [2,8].

As persistent organic pollutants (POPs), PAHs usually accumulate in soil, sediments, surface water, atmosphere as well as organisms. Numerous books and review articles have reported the occurrence and distribution of PAHs in the environment [1,2,9,10]. In order to evaluate and monitor the environmental fate and impacts of trace levels of PAHs, it is necessary to extract them from these matrices. PAHs are regularly measured in the atmosphere for air quality assessment, in biological tissues for health effects monitoring, in sediments and mollusks for environmental monitoring and in foodstuffs for safety reasons [11].

The traditional pretreatment techniques for the extraction of these semi-volatile organic compounds from aqueous samples are liquid–liquid extraction (LLE) [12–14] and solid-phase extraction (SPE) [12,15,16]. These multistep sample preparation methods do have some drawbacks; they are time-consuming, labor-intensive, involve moderate to heavy use of toxic solvents, and are prone to loss of analytes [17]. However, these procedures are still popular and are routinely implemented in EPA test methods [18,19], EU standard methods [20–22] and many laboratories worldwide.

Alternative sample preparation techniques have been established over recent years to address the limitations inherent in LLE and SPE. These include solid-phase microextraction (SPME) [4,5,23,24], liquid-phase microextraction (LPME) [25–27] and stir bar sorptive extraction (SBSE) [28–30]. Among these techniques, SPME is the method of choice and has been widely used for the

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sampling and analysis of environmental, food, aroma, pharmaceutical and forensic samples [17,31].

SPME is a very simple, efficient and solvent-free sample preparation technique, developed by Pawliszyn's group [32], which successfully integrates sampling, extraction, concentration and sample introduction into a single step using a single device. The analytes of interest are extracted from the samples by the polymeric phase according to their affinity towards the fiber coating and then can either be thermally desorbed for gas chromatography (GC) or solvent desorbed for high-performance liquid chromatography (HPLC) [17,33].

The key component of SPME is the fiber coating. However, almost all commercially available SPME fibers are prepared with fused-silica as the support material. Such fibers are fragile and require careful handling during the extraction and desorption processes. In addition, an appropriate polymer fiber coating and its thickness is generally required to achieve the desired sensitivity and high sample loading [34]. Decreasing the coating thickness usually increase the extraction kinetics, but the thinner coating will increase the fragility of the fiber. To address these issues, devising novel sorbents which is robust and versatile is an essential part in the development of SPME technology.

Downsizing of extraction approaches (to micron or submicron scale) has become the trend in analytical chemistry in the past two decades. The merits of miniaturization are not only in terms of environmental friendliness but also for effective hyphenation to microcolumn separation techniques without causing any overload and poor resolution during chromatographic separation. Furthermore, downsizing also enhances the development and application of various materials as novel sorbents in extraction and separation science [35,36].

One interesting miniaturized sample preparation method, termed fiber-in-tube solid-phase extraction (FIT-SPE) [36–39], was introduced by Jinno and co-workers for microscale liquid-phase separation. In this technique, the extraction was carried out using a short capillary into which a bundle of fine polymeric fiber filaments (e.g. Zylon, Kevlar, Nomex and Technora) serving as the extraction medium, was packed longitudinally. Analytes were extracted onto the surfaces of the filaments by passing the aqueous sample into the extraction capillary. The extracted analytes were then desorbed by pumping a small amout of organic solvent through the capillary.

Based on FIT-SPE, the same authors further developed a fiber-packed in-needle extraction device [40,41] for gas chromatographic (GC) analysis of trace organic compounds in aqueous and gaseous samples. These sample preparation devices possess most of the merits of SPME plus additional advantageous features, such as increased sorbent surface area of the fiber, reduced pressure drop through the extraction tube, good storage performance, and enhanced extraction selectivity with different types of coatings on the fiber filaments [41,42]. All of the applications mentioned above revealed that polymeric fibers have great analytical potential as an effective sorbent for extracting pollutants from various sample matrices.

The most common techniques used for PAHs determination are high-performance liquid chromatography with fluorescence detection (HPLC-FLD) and GC–mass spectrometry (MS) [43,44]. HPLC offers several advantages in PAH analysis, including good separation for isomers, high fluorescence detection selectivity and avoidance of thermal decomposition of the analytes as analysis is usually carried out at ambient temperature [45].

Different polymeric fibers have been used as sorbent for SPME. To the best of our knowledge, Jinno's group was the first to use Kevlar fiber for microextraction [46]. In Jinno's work [47], the surface derived Kevlar fiber and the parent fiber were used in FIT-SPE, where the separation column was prepared by packing a bundle of 160–170 fibers into a fused-silica capillary and conditioned at 200 °C for more than 5 h before installation to a GC system as extraction and separation media. Furthermore, the FIT-SPE also been developed as a miniaturized sample preparation technique for microcolumn LC [36–38,42]. Similarly, in Marcus's work [48], bundles of 1000–3000 polypropylene and polyester fibers were packed into a stainless steel tubing as stationary phases in LC separations of various mixtures. In both cases, some fabrication of specific extraction or separation apparatuses was involved. Moreover, insoluble particles must be removed from sample solutions by filtration before extraction to prevent plugging of the capillary column and flow lines [49], and this could be practically be more labor-intensive overall.

In the present project, we aimed to develop a simple, robust and sensitive SPME methodology coupled with HPLC-FLD for the determination of trace PAHs in water samples by using a polymeric fiber directly as sorbent. In contrast to FIT-SPE or a fiber-packed in-needle extraction device, the polymeric fiber, i.e. Kevlar, as a strand, is used as is; it is free-moving and tumbles continuously throughout the stirred sample solution during extraction in order to enhance the extraction efficiency. This approach avoids the need for fabricating specific devices to support the fibers for extraction. Besides, no filtration is necessary for the sample solutions. The advantages of using a single fiber directly, compared to FIT-SPE or fiber-packed in-needle extraction device, are simplicity of operation and convenience. This novel approach is, it is believed, more accessible to the analytical community. The use of HPLC with FLD, instead of ultraviolet (UV) detection was expected to increase the sensitivity and selectivity for the determination of PAHs, since FLD is inherently more sensitive than the latter, and PAHs have strong fluorescent characteristics [44]. Also, no further cleanup of the extract was required. The effects of various extraction parameters on the efficiency of extraction were investigated. After optimization of the microextraction conditons, the developed methodology was applied to determine trace PAHs in local rainwater samples.

2. Experimental

2.1. Chemicals and materials

The PAHs, naphthalene (Nap), fluorene (Flu), anthracene (Ant), pyrene (Pyr), chrysene (Chr), benzo[*k*]fluoranthene (Ben) and dibenz[*a*,*h*]anthracene (Dib) were purchased from Supelco (Bellefonte, PA, USA). The stock solutions of each analyte (1 mg mL^{-1}) were prepared separately in acetone. A fresh working solution containing a mixture of each analyte (5 μg mL^{-1}) was prepared weekly by stepwise diluting the stock solutions with acetone. Both stock and working solutions were stored in the dark at 4 °C. Appropriate volumes of the working solution were spiked into deionized water to give sample solutions of the desired analyte concentrations.

All solvents used were of HPLC-grade. Acetone, acetonitrile and methanol were purchased from Tedia (Fairfield, OH, USA). Doubly deionized water (18 MΩ cm^{-1}) obtained from a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout this study.

The commercial polymeric fiber, Kevlar 29 (poly(*p*-phenylene terephthalamide)) with filament diameter ca. 9.23 μm [50] was kindly provided by Professor Kiyokatsu Jinno from Toyohashi University of Technology (Toyohashi, Japan) and used as received without modification. It has 1500 denier (g per 9000 m) and is made up of 1000 filaments [50]. The chemical structure of Kevlar is given in the Supplementary Material, Fig. 1 [47].

Rainwater samples were collected from several locations in the campus of National University of Singapore and stored in precleaned glass bottles (thoroughly pre-washed with detergent, water, methanol and doubly deionized water in sequence, oven-dried and wrapped with aluminum foil). The collected samples

were stored in the dark at 4 °C and processed within 24 h of collection without any prior treatment or filtration. Quantification of the analytes was done by external calibration where a series of standard solutions was prepared by dilution of the stock solution and analysis by HPLC-FLD to obtain linear calibration plots for each analyte based on the chromatographic peak areas.

2.2. Instrumentation

Separation of the PAHs was carried out using a Waters (Milford, MA, USA) HPLC system. The chromatographic system consisted of a Rheodyne (Cotati, CA, USA) 7125 manual injector equipped with a 200-μL sample loop, a Waters 600E quarternary pump and a Waters 470 scanning fluorescence detector.

Separations of PAHs were achieved on a Merck (Darmstadt, Germany) monolithic C18 reversed-phase column (Chromolith Performance RP-18, 100 mm × 4.6 mm I.D., 2 μm particles size) which inlet is capped with a guard column (Chromolith RP-18E, 10 mm × 4.6 mm I.D.). Analytes were eluted with the following binary solvent (acetonitrile–water) gradient programme: initial 50% acetonitrile for 2 min, then a linear ramp to 60% in 10 min, another linear ramp to 90% in 10 min, then follow by another linear ramp to 100% within 5 min, and held at 100% acetonitrile for 5 min until the end of the analysis. The system mobile phase flow rate was 2.0 mL min^{-1} and column temperature was maintained at 25 °C (ambient).

Optimized parameters of the fluorescence detector program used are tabulated in Table 1. The excitation and emission wavelength pairs [51] were programmed to change according to the elution time of each PAH during the analytical run to optimize the detection of each analyte with minimal interference. The Waters Empower software version 5.0 was used for spectral acquisition and chromatographic data processing.

Scanning electron microscopy (SEM) micrographs were obtained with JSM-5800 scanning electron microscope (JEOL, Tokyo, Japan) to observe the morphology of Kevlar fiber. To prepare samples for SEM, the fiber was fixed on the stub by a double-sided sticky tape and then coated with gold by a JEOL JFC-1600 Auto Fine Coater at 10 mA for 100 s. The diameter of fiber was measured on the basic of SEM micrographs, using an image analysis software, ImageJ (National Institues of Health, Bethesda, MD, USA).

2.3. Extraction procedures

A schematic of the extraction apparatus used is given in the Supplementary Material, Fig. 2. The fiber was cut into ca. 8 cm long segments which were preconditioned and ultrasonically cleaned in acetone and water for 10 min prior to use.

During extraction, the fiber tumbled freely under stirring in the sample solution (20 mL). For optimization experiments, aqueous samples were spiked with PAHs (final concentration 2.5 μg L^{-1} of each). The stirring speed of 500 rpm was applied using Vibramax 100 (Heidolph, Kelheim, Germany) magnetic stirrer. The highest stirring speed of 500 rpm was used (the maximum speed of the stirrer is 1250 rpm) because at this rate the fiber tumbled freely without any noticeable problems or negative impact on the extraction. Fiber integrity was maintained throughout the extraction. Beyond 500 rpm, formation of bubbles was observed and caused extraction efficiency to be reduced. After 30 min extraction, the fiber was removed with a pair of tweezers (ultrasonically cleaned in acetone and deionized water for 10 min before use to prevent cross-contamination) and dab-dried with lint-free tissue. The extracted analytes on the fiber were desorbed in 100 μL of acetonitrile in a Chrompack (Palo Alto, CA, USA) crimper vial via sonication for 20 min. Finally, 50 μL of extract was directly injected into the HPLC system for analysis. Possible carryover was minimized or eliminated by ultrasonically cleaning the fiber in acetone for 10 min before it was used for another extraction.

Table 1
Optimized fluorescence detection program used for PAHs determination.

Step	Time (min)	Excitation wavelength (nm)	Emission wavelength (nm)	Analyte determined	Retention time (min)
1	0.0–6.8	280	330	Nap	3.7
				Flu	5.9
2	6.8–8.5	250	375	Ant	7.3
3	8.5–11.0	270	390	Pyr	9.4
4	11.0–14.0	265	380	Chr	12.3
5	14.0–17.0	290	430	Ben	15.7
6	17.0–20.0	290	410	Dib	17.7

3. Results and discussion

3.1. Properties of Kevlar fiber

Kevlar is a high-performance para-aramid fiber developed by DuPont Company in 1965 for industrial and advanced technological applications [52]. It is a long-chain synthetic polyamide in which at least 85% of the amide (–CO–NH–) linkages are attached directly to two aromatic rings. It has a molecular weight equal to or greater than 60,000. Kevlar is highly crystalline, does not melt, and have extremely low combustibility. Kevlar also has very good resistance to heat and chemicals. It can retain useful properties at temperatures up to 260 °C and is resistant to most organic solvents and chemicals except hot, concentrated acid and alkali. Kevlar has an extremely high tenacity, i.e. 22 g $denier^{-1}$, which is five times the strength of a steel wire at the same weight, and twice the strength of industrial nylon, polyester and fiberglass [53]. As the first synthetic fiber that combines high strength with light weight, Kevlar is applied to broad range of uses, including automotive brakes and tires, body armor and protective clothes, aerospace and airplane components, and building materials [54].

Recently, Kevlar was employed as a sorbent in sample preparation taking into account their unique properties, such as excellent stability to organic solvents and chemicals, mechanical strength, and excellent thermal stability [50]. In addition, the fiber surface is easily modifiable with different functional groups, such as butyl, octyl, benzyl and phenylethyl for enhancing the extraction efficiency and selectivity in FIT-SPE or fiber-packed in-needle extraction device, particularly by Jinno's group [47,55]. PAHs are lipophilic; the larger compounds are less water-soluble and less volatile. Kevlar is a lipophilic polymer. Thus, the compatibility between the analytes and the fiber conceivably contributed to the efficient extraction of PAHs from aqueous solutions. It is conceivable that π–π interactions and hydrophobic interactions with analytes and the large surface area of the fiber also facilitate the adsorption of target analytes. In this approach, we investigated the usability of Kevlar fiber as an extraction device directly without modification or integration with other apparatus for the extraction of PAHs from aqueous samples.

Fig. 1 shows the SEM micrograph of an aligned Kevlar fiber at 2000× magnification. Each fiber filament, as mentioned above, has a uniform diameter of 9.23 μm.

3.2. Optimization of extraction procedures

In order to achieve maximum analyte recovery and low detection limits in a relatively short extraction time, analytical factors affecting the extraction efficiency such as extraction time, desorp-

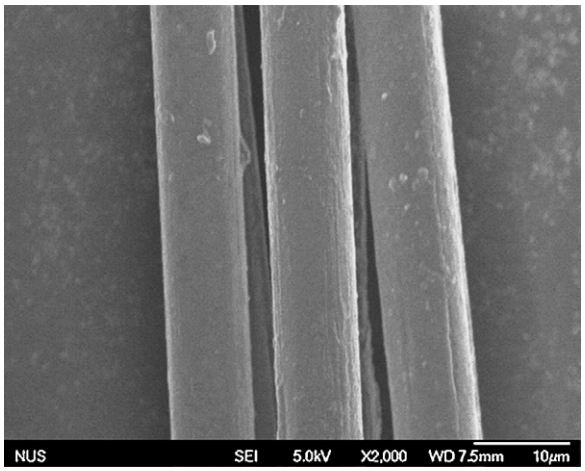

Fig. 1. SEM micrograph of Kevlar fiber at 2000× magnification.

tion time, desorption solvent and sample volume were optimized. All optimization experiments were performed in triplicate. The extraction efficiency was evaluated by measuring the HPLC-FLD peak areas.

Extraction of PAHs using the Kevlar strand is an equilibrium-dependent process. The amount of analyte that can be extracted depends on the partition coefficient of the analyte between the aqueous sample and the fiber surface [47]. The extraction equilibrium was generally established within the range of 5–50 min, as shown in Fig. 2. The PAHs exhibited different extraction time profiles because based on their molecular masses, they likely have different diffusion coefficients. The higher molecular mass PAHs have lower diffusion coefficients and would take a longer time to reach equilibrium [4]. Most of the analytes achieved the highest extraction efficiency up to 30 min. For some analytes (for example, Chr, Ben and Dib), extraction efficiency decreased slightly after 20 min. It is conceivable that after reaching equilibrium, prolonged extraction time would effect back-extraction. The reduction in extraction efficiency may be attributed to the issue of solubility of these analytes in water, or it may also be due to the movement of analytes into the headspace that would in turn lead to reduced sample concentrations [23]. The equilibrium time is usually selected as extraction time, but it is not practicable to prolong an extraction to achieve maximum extraction efficiency for all analytes, since no common time to equilibrium was exhibited. Hence, 30 min was selected as the optimal extraction time, since this appeared to be the equilibrium extraction period for most of the analytes.

After extraction, solvent desorption efficiency was evaluated. Fig. 3 shows that a 20-min desorption time appeared to be the optimum for all analytes. After the first desorption, the fiber was further desorbed and analyzed under the same conditions to test carryover. That no peaks were observed in the resulting HPLC-FLD chromatogram confirmed that the absence of carryover, or at least the carryover was negligible. Besides, the reusability of the fiber was tested. Each fiber could be reused for up to 50 extractions (results not shown) without carryover effects and deterioration in extraction capability.

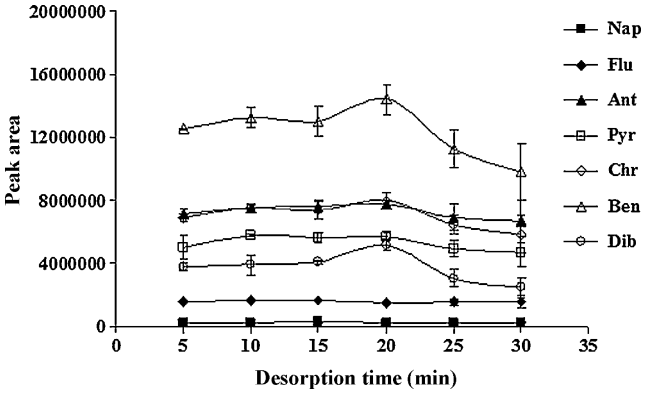

Fig. 3. Effect of desorption time on extraction efficiency.

Generally, when the extraction is coupled with liquid-based analytical techniques, such as HPLC or capillary electrophoresis (CE), analytes are best desorbed in a water-miscible organic solvent. In consideration of the fact that Kevlar is insoluble in common organic solvents [47], and reversed-phase HPLC was used in this work, acetone, acetonitrile and methanol were tested as potential desorption solvents. It may be observed from Fig. 4 that acetonitrile gave the best desorption result in term of analyte peak areas, although acetone could also be considered. If we compare the solvent hydrophobicity in terms of log octanol/water partition coefficient ($\log K_{ow}$), acetonitrile ($\log K_{ow} = -0.34$) and acetone (-0.24) show relatively higher hydrophobicity compared to methanol (-0.82) [56]. Therefore, acetonitrile and acetone should be able to solubilize more highly hydrophobic PAHs ($\log K_{ow} = 3.37–6.75$ [2]) than methanol. Nevertheless, acetonitrile performing as the best desorption solvent may be due to the π–π interactions between its lower unoccupied molecular orbital and the higher occupied molecular orbital of the PAH aromatic rings [57]. The different responses for different PAHs may be due to related to their relative solubilities and response factors under FLD.

The effect of sample volume on extraction efficiency was evaluated using vials with capacities from 5 to 40 mL. Different volumes of identically spiked sample solutions, i.e. at a concentration of 2.5 $\mu g L^{-1}$ of each PAH, were studied. From Fig. 5, it is observed

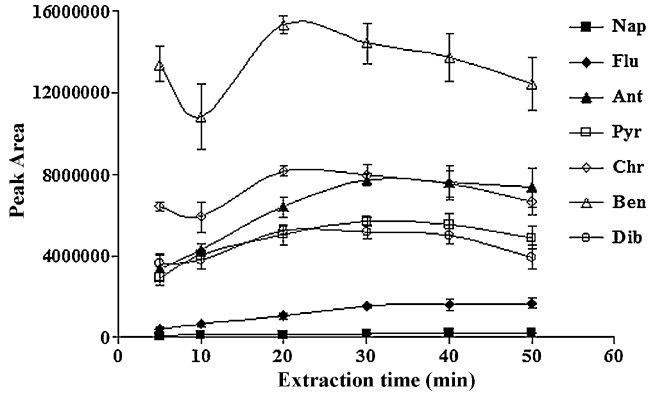

Fig. 2. Effect of extraction time on extraction efficiency.

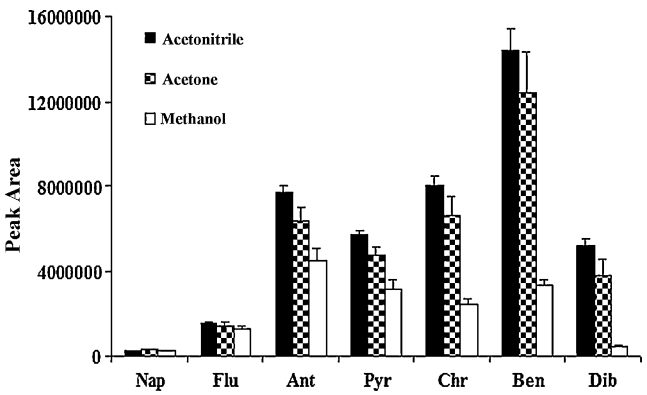

Fig. 4. Effect of desorption solvent on extraction efficiency.

Table 2
Quantitative results of PAH extraction from water samples using Kevlar fiber.

Analyte	Linear range ($\mu g\,L^{-1}$)	r	Calibration curve	RSD[a] (%) ($n=3$)	LOQ ($\mu g\,L^{-1}$) (S/N = 10), this work	LOD ($\mu g\,L^{-1}$) (S/N = 3), this work	LOD ($\mu g\,L^{-1}$), EPA method 610[b]	LOD ($\mu g\,L^{-1}$), SPME[c]
Nap	0.05–5	0.9992	$y = 99{,}813x + 41{,}353$	4.9	0.0090	0.0027	1.8[d]	0.002
Flu	0.05–5	0.9998	$y = 642{,}643x + 9794.3$	10.3	0.0147	0.0044	0.21[d]	0.002
Ant	0.05–5	0.9962	$y = 2E{+}06x + 452{,}055$	12.1	0.0073	0.0022	0.66	0.001
Pyr	0.05–5	0.9978	$y = 2E{+}06x + 327{,}581$	8.2	0.0090	0.0027	0.27	0.001
Chr	0.05–5	0.9985	$y = 2E{+}06x + 212{,}756$	2.9	0.0050	0.0015	0.15	0.001
Ben	0.05–5	0.9984	$y = 4E{+}06x + 328{,}495$	4.2	0.0013	0.0004	0.017	0.001
Dib	0.05–5	0.9968	$y = 884{,}338 + 98{,}116$	11.6	0.0070	0.0021	0.030	0.004

[a] Water samples containing 1 $\mu g\,L^{-1}$ of each PAH.
[b] LLE of PAHs coupled with HPLC-FLD [59].
[c] PDMS fiber coupled with HPLC-FLD [24].
[d] LLE of PAHs coupled with HPLC-UV [59].

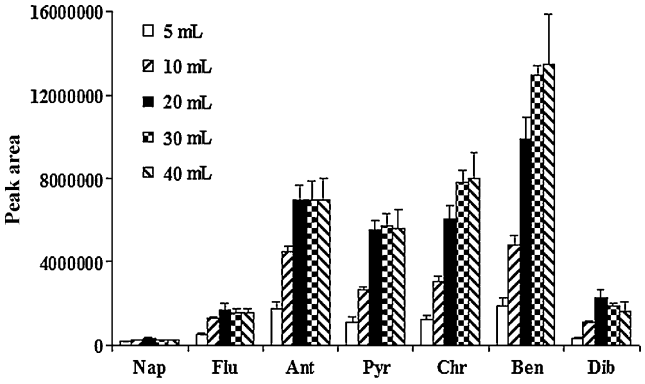

Fig. 5. Effect of sample volume on extraction efficiency.

that except for Ben and to some extent Chr, 20-, 30- and 40-mL volumes gave largely similar results. This seems to suggest that the saturation of adsorption sites of the fiber with analytes occurred when the sample volume was 20 mL [58]; thereafter no increase in extraction was observed. Since, for logistical reasons, smaller sample sizes are preferred, 20 mL was considered to be the most suitable sample volume for extraction.

3.3. Method validation

In order to evaluate the practical applicability of the proposed technique, performance parameters such as linearity, precision and limits of detection (LODs) were measured under optimum extraction conditions using spiked deionized water samples. Results of the validation parameters are given in Table 2.

The linearity of the calibration plots was observed over a concentration range of 0.05–5 $\mu g\,L^{-1}$. All the PAHs showed good linearities with correlation coefficients (r) ranging from 0.9962 to 0.9998. This allowed the quantification of the real water samples by the method

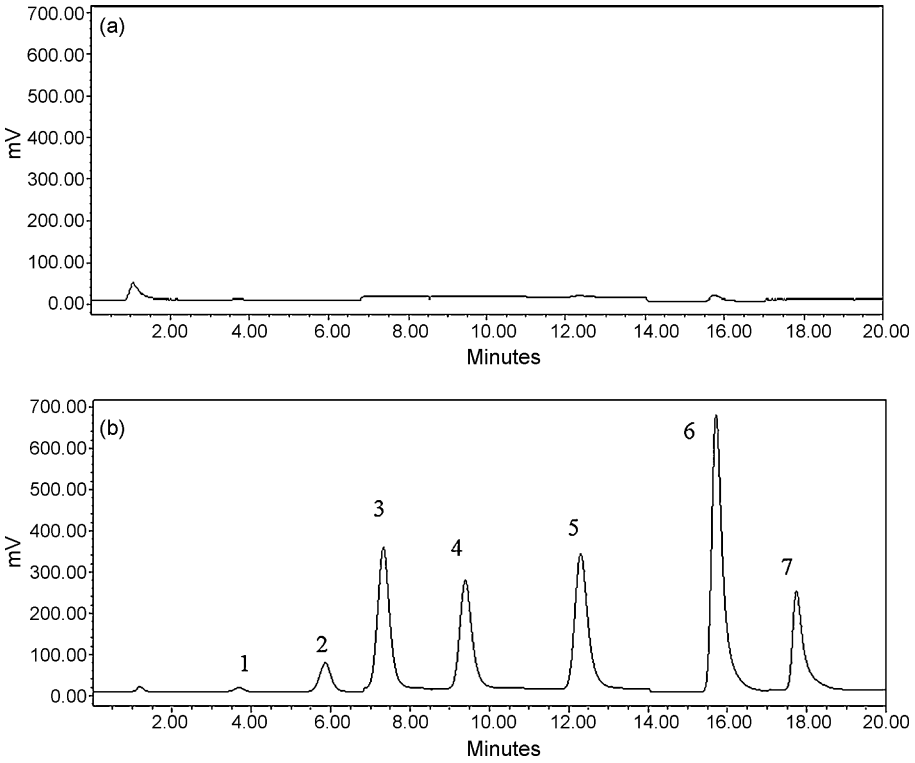

Fig. 6. Liquid chromatogram of the extract of (a) rainwater sample and (b) spiked deionized water sample containing 2.5 $\mu g\,L^{-1}$ of each PAH. Extraction time: 30 min; desorption time: 20 min; desorption solvent: acetonitrile; sample volume: 20 mL. Peaks: (1) Nap, (2) Flu, (3) Ant, (4) Pyr, (5) Chr, (6) Ben and (7) Dib.

Table 3
Concentration of PAHs in rainwater samples.

Analyte	Mean concentration ($\mu g L^{-1}$) (RSD, %, $n = 3$)		
	Site 1	Site 2	Site 3
Nap	0.49 (6.4)	0.55 (13)	0.71 (8.3)
Flu	0.02 (8.8)	0.02 (8.5)	0.02 (11)
Ant	nd[a]	nd	nd
Pyr	0.01 (12)	0.01 (15)	0.01 (9.8)
Chr	0.04 (9.7)	0.01 (7.4)	0.01 (8.9)
Ben	0.07 (13)	0.02 (9.6)	0.04 (15)
Dib	0.03 (13)	0.02 (7.9)	0.02 (9.3)

[a] Non-detected or below the limit of quantification.

of external standardization. The reproducibility studies were carried out by extracting spiked water samples containing 1 $\mu g L^{-1}$ of each PAH. The relative standard deviations (RSDs) were between 2.9% and 12.1% for triplicate extractions.

LODs were calculated based on the signal-to-noise (S/N) ratio of 3 in HPLC-FLD measurements. As Table 2 shows, the LODs achieved in this study ranged from 0.4 to 4.4 $ng L^{-1}$ and were better than or comparable to those reported by EPA Method 610 [59] and other published values [24]. Fig. 6 shows a representative chromatogram of an extract from (a) rainwater and (b) spiked water sample after extraction by Kevlar fiber followed by HPLC-FLD under the optimized conditions.

3.4. Analysis of real samples

The proposed method was applied to investigate the level of PAHs in rainwater samples. The results are shown in Table 3. Since PAHs are ubiquitous environmental contaminants, as expected, they were found in all analyzed samples. Their concentration ranged from non-detected to 0.71 $\mu g L^{-1}$, with Nap as the predominant compound. The levels of other PAHs are in the same general range as determined previously [26]. As rain can behave as a natural ambient trap for air pollutants, the determination of a class of ubiquitous pollutant such as PAHs in this matrix may serve as an initial screening of air quality in an urbanized environment, such as Singapore and other major cities. The method developed here may be applied to routine measurements of PAHs as part of an urban air quality control system [60].

4. Conclusions

The potential of Kevlar fiber as a novel sorbent has been demonstrated as a very simple, robust and sensitive sample preparation technique for extracting and determining trace levels of PAHs in water samples. This is the first report of a commercial polymeric fiber being used as an extraction filament directly, i.e. there is no requirement of a fabricated device or apparatus to support the fiber(s). The developed methodology coupled with HPLC-FLD could achieve quantification limits at low ng per liter levels, good linearity and acceptable reproducibility. In addition, this method is also relatively cost-effective with a single fiber being capable of being used up to 50 times with excellent stability. Preliminary results based on this work for real rainwater samples showed the presence of PAHs, as might be expected. Work is continuing to further develop and apply the procedure to other organic compounds of interest in aqueous environmental samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2009.09.019.

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