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Determination of polycyclic aromatic hydrocarbons in water samples using online microextraction by packed sorbent coupled with gas chromatography–mass spectrometry

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ABSTRACT

A fully automated microextraction by packed sorbents (MEPS) coupled with large volume injection gas chromatography–mass spectrometry (GC–MS) has been developed for the determination of eight polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. Naphthalene (Nap), pyrene (Pyr), anthracene, acenaphthylene, phenanthrene, fluoranthene (Flr), fluorene and acenaphthene were the PAHs studied. The performance of the microextraction-GC–MS protocol was compared with solid phase extraction (SPE) and GC–MS analysis. Under optimized experimental conditions, the methods were linear for all analytes in the following ranges: 0.05–2.0 μg L^{-1} (MEPS) and 0.25–10.0 μg L^{-1} (SPE). The correlation coefficients (R^2) were in the range 0.9965–0.9997 (MEPS) and 0.9978–0.9998 (SPE) for all the analytes. Limits of detection (LODs) for 2 mL samples (MEPS) ranged from 0.8 ng L^{-1} to 8.2 ng L^{-1}. LODs for 50 mL samples (SPE) were between 4.8 ng L^{-1} and 35.9 ng L^{-1}. The two methods were successfully applied to the determination of the 8 PAHs in environmental waters, with recoveries in the range of 70–117% (MEPS) and 72–134% (SPE) for a real spiked sample. The two sample preparation processes showed good repeatabilities with intra-day relative standard deviations below 14.0% (MEPS) and 14.6% (SPE). Nap, Flr and Pyr were found in a river water sample.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds that consist of two or more fused aromatic rings and they make up a group of ubiquitous environmental pollutants. PAHs have attracted growing attention due to their potential mutagenic and carcinogenic properties [1,2]. Many research findings have suggested that frequent exposure to PAHs is associated with increased risks of lung, skin and bladder cancer [3]. Some regulatory bodies such as the US Environmental Protection Agency and the European Union have classified some PAHs as priority contaminants [4,5]. The PAHs introduced into the environment originate from natural or anthropogenic sources, such as incomplete combustion of organic matter [6], industrial processes and vehicle emissions [7,8]. Because of their water-solubility, some PAHs can also be found in the aquatic environment [9,10]. For this reason, it is important that selective and sensitive analytical methodologies are developed for PAHs in the aqueous environment.

However, the determination of PAHs in environment water samples such as lake water is a challenging task due to their very low concentrations in the environment water. So efficient clean-up and enrichment procedures prior to analysis of PAHs are required when the complex water matrix is analyzed. Solid-phase extraction (SPE) is a conventional extraction and preconcentration method for PAHs from aqueous samples [11,12]. The main drawbacks of the SPE technique are its high organic solvent consumption and sample consumption. What is more, SPE is known as being difficult to automate [13], so that a long extraction time is required. Microextraction in packed sorbents or syringes (MEPS) is a recently developed sample pretreatment technique based on the miniaturization of conventional SPE. MEPS can be fully automated, the sample preparation procedure is performed online using the same syringe and the whole extract is injected into a chromatographic system [14]. The MEPS system is constructed as a barrel/insert/needle (BIN) containing an SPE packed bed. The BIN is fixed and sealed to the syringe (100 or 250 μL) and sample pretreatment takes place on the sorbent bed (about 3 mg). In recent years, this microextraction technique has been developed

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to connect online to liquid or gas chromatography (GC) separation [15,16]. Also, Morales-Cid et al. [17] reported a method using MEPS–nonaqueous capillary electrophoresis–mass spectrometry to detect anesthetic drugs in human plasma. MEPS can be used for various matrices. For example, Abdel-Rehim et al. [18] reported a specific and sensitive liquid chromatography–mass spectrometry method combined with MEPS to characterize olomoucine in plasma. Also Matysik and Matysik [19] reported the extraction of metabolites of monoterpenes from urine by an MEPS sample preparation technique. Compared to conventional SPE, MEPS can be used for smaller samples (10 μL), and with shorter sample preparation times and lower solvent volumes. In this experiment, the volumes of sample and organic solvent needed were only 2 mL and 50 μL, respectively; in our sample processing procedure and the time required was about 18 min.

Generally, PAHs have been analyzed by high performance liquid chromatography–fluorescence detection (HPLC–FLD) [20] or HPLC coupled with mass spectrometry (HPLC–MS) [21]. In addition, GC–MS is an appropriate tool for PAHs analysis [22].

The aim of this work was to optimize a fully automated method utilizing MEPS coupled with a large volume injection-gas chromatographic mass spectrometer to determine PAHs in environmental water samples. Several potential factors affecting sorption of the analytes were studied in detail. A common SPE method was also used for comparison with the MEPS protocol.

2. Experimental

2.1. Reagents and materials

Eight PAHs standards were delivered by Sigma–Aldrich (St. Louis, MO, USA) including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flr) and pyrene (Pyr). The deuterated internal standard (2000 mg L^{-1} in methylenechloride, 98% purity) phenanthrene-d10 was purchased from o2si smart solutions (Charleston, SC, USA). All solvents, including methanol, acetone, dichloromethane and *n*-hexane were of HPLC grade and were supplied by Merck (Darmstadt, Germany). The water used in the experiments was supplied by Watson's (Quchenshi, Shanghai, China) and had been treated by passing through a Millipore system (USA). The C18 SPE extraction column (1 g/6 mL) was purchased from Shanghai Anpel Scientific Instrument Co. (Shanghai, China). The MEPS syringe and cartridge were donated by SGE Analytical Science (Griesheim, Germany). Lake water samples were collected from two lakes in Tianshan park and Xujiahui park in Shanghai (China) and a river water sample was collected from the SuZhou river in Shanghai.

Table 1
Retention time and ions selected for analysis of the target polycyclic aromatic heterocycle.

Compounds	Retention time (min)	Quantification ions (*m*/*z*)
Nap	6.470	128.127.129
Acy	8.610	152.151.76
Ace	8.970	153.154.152
Flu	10.140	166.165.82
Phe-d10	12.915	188.80.189
Phe	12.999	178.176.179
Ant	13.140	178.176.89
Flr	17.560	202.200.101
Pyr	18.455	202.200.101

Ions used for quantification are underlined and remaining ions were used for confirmation.

2.2. Preparation of standard solutions

Individual stock solutions were prepared at a concentration of 200 mg L^{-1} in methanol. From these solutions, a working mixture (10 mg L^{-1}) was prepared in methanol on a monthly basis. An internal standard stock solution was prepared at 2000 μg L^{-1} in methanol and from this, a concentration of 200 μg L^{-1} was prepared in methanol on a monthly basis. Standard working solutions of different concentrations were prepared daily by appropriate dilution of the stock solutions with water before use. All stock and working solutions were stored in the dark at 4 °C.

2.3. Instrumentation

Chromatographic analyses were performed on a Shimadzu GCMS-QP2010 Plus gas chromatograph–mass spectrometer

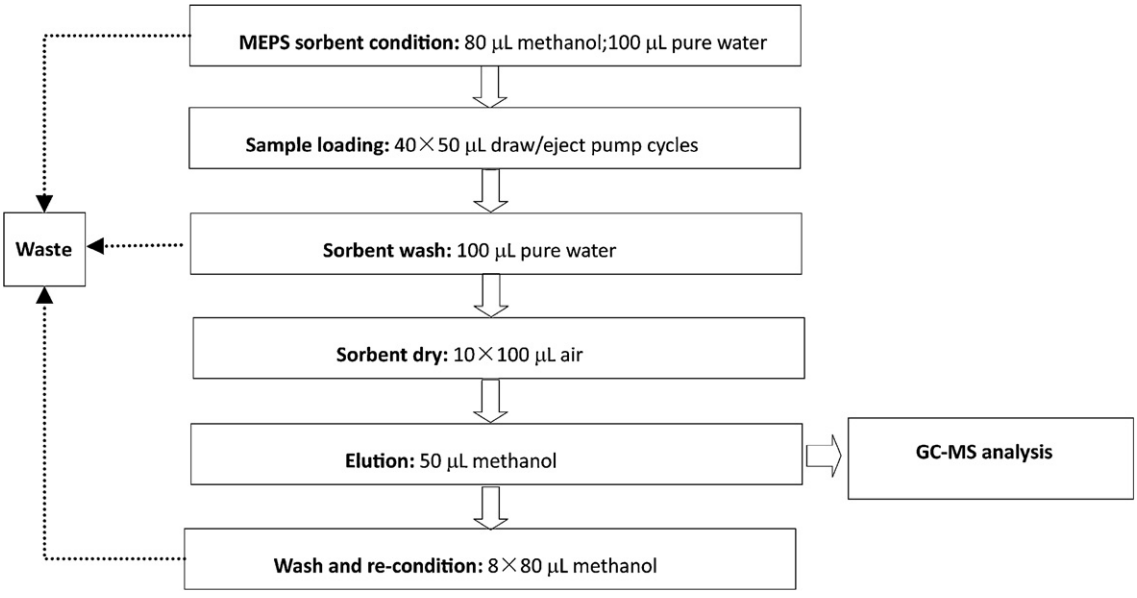

Fig. 1. Schematic diagram of the optimized MEPS–GC–MS method with 100 μL syringe for the determination of target compounds.

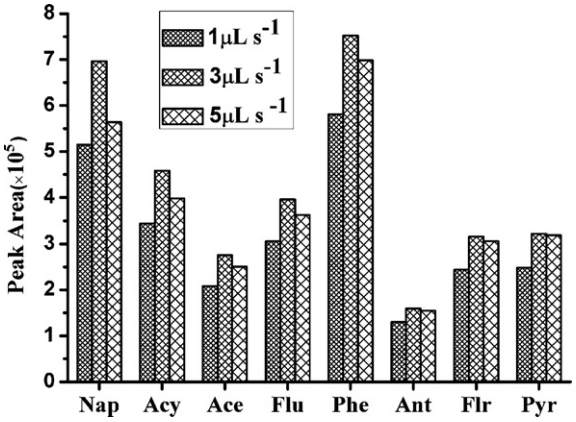

Fig. 2. Optimization of draw-eject speed of elution solvent (MEPS). Sample spiked concentration, 2 μg L^{-1}; eluent, methanol; pump cycles of sample loading, 40 × 50 μL; draw-eject speed of sample loading, 5 μL s^{-1}; eluent volume, 50 μL.

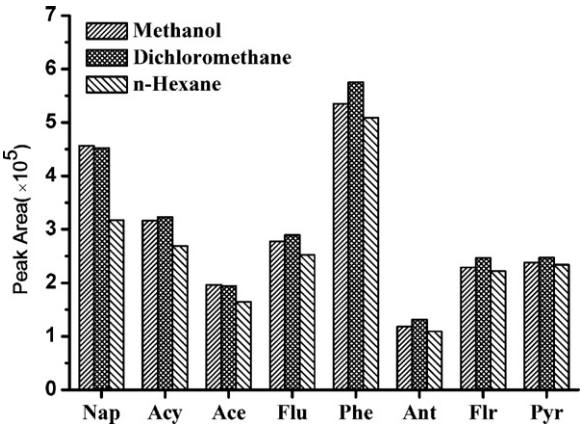

Fig. 4. Selection of eluent (MEPS). Sample spiked concentration, 2 μg L^{-1}; pump cycles of sample loading, 40 × 50 μL; draw-eject speed of sample loading, 5 μL s^{-1}; eluent volume, 50 μL; draw-eject speed of elution solvent; 3 μL s^{-1}.

system (Shimadzu Corporation, Kyoto, Japan) with a programmed temperature vaporizer injector (PTV) and an AOC-20i autosampler. A personal computer equipped with the Shimadzu Labsolution GCMS 2.6 system was used to process the MS data. The column used was an Rxi-5ms fused-silica capillary column (30 m × 0.25 mm internal diameter, 0.25 μm film thickness) obtained from Shimadzu (Kyoto, Japan).

2.4. Gas chromatography–mass spectrometry conditions

The PTV injector temperature started at 50 °C for 1 min, increased at 30 °C min^{-1} to 80 °C for 1 min, then increased at 250 °C min^{-1} to 300 °C and held at 300 °C for 17 min. Helium was used as the carrier gas at constant linear velocity conditions of 36.3 cm s^{-1}. The GC oven temperature was programmed as follows: 50 °C for 1 min; 25 °C min^{-1} to 160 °C; 5 °C min^{-1} to 300 °C.

The mass spectrometer operated at 70 eV with electron impact ionization. The transfer liner was maintained at 300 °C and the ion source at 200 °C. The solvent delay time was 4.5 min. A mass range of *m*/*z* 50–500 was recorded in the full-scan mode. Peak identification of targets was based on the retention times and full scan spectra of the standards. The selected ion monitoring mode was employed for quantification of ions. The characteristic ions selected for qualitative and quantitative studies are listed in Table 1.

2.5. Microextraction

The microextraction procedure was carried out with a MEPS system containing a syringe and BIN. A 100 μL syringe equipped with C18 sorbent incorporated in the needle was used throughout this experiment. The MEPS device was suitable for use with an AOC-20i autosampler, which was employed for the whole sample preparation procedure. Before each sample extraction, the MEPS sorbent was conditioned using 80 μL of methanol and 100 μL of ultrapure water. Both methanol and water were discarded into waste vials. The water sample (50 μL each) was pulled/pushed through the syringe 40 times at a speed of 5 μL s^{-1} by the autosampler. Then the sorbent was washed using 100 μL pure water to reduce interference absorption and was dried by 10 cycles of drawing and pressing air. Finally, the analytes were eluted with 50 μL methanol directly into the GC large volume injector. To get rid of any carryover effect, eight 80 μL portions of methanol were used to clean the sorbent after the extraction/elution step. A schematic diagram of the MEPS procedure is shown in Fig. 1.

2.6. Solid-phase extraction

SPE of samples was carried out with Visiprep SPE manifold (GL Sciences, Tokyo, Japan). A C18 cartridge (1 g, 6 ml) was conditioned with 10 ml of methanol, and then the cartridge was washed with 10 mL of ultrapure water to equilibrate the phase. After that, 50 mL

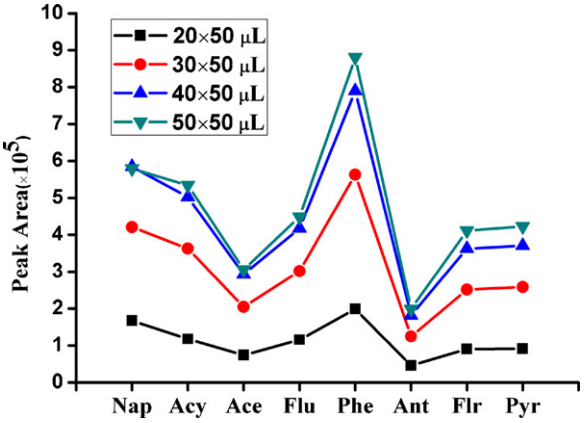

Fig. 3. Optimization of pump cycles of sample loading (MEPS). Sample spiked concentration, 2 μg L^{-1}; eluent, methanol; draw-eject speed of sample loading, 5 μL s^{-1}; eluent volume, 50 μL; draw-eject speed of elution solvent; 3 μL s^{-1}.

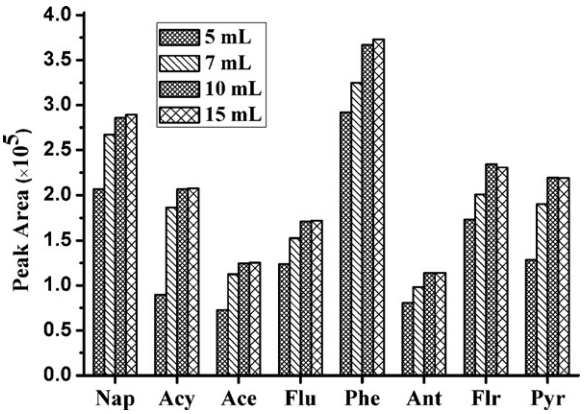

Fig. 5. Optimization of eluent volume (SPE). Sample spiked concentration, 2 μg L^{-1}; eluent, methanol; sample volume, 50 mL.

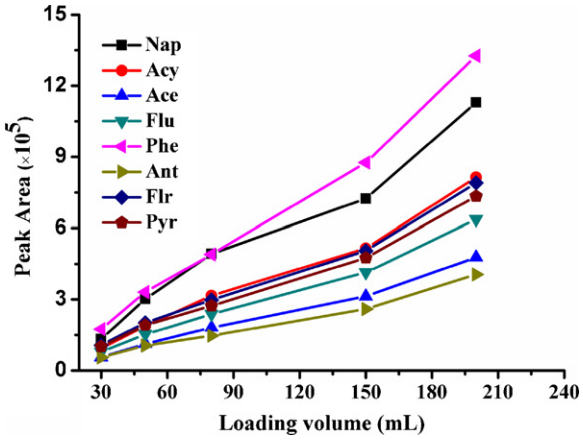

Fig. 6. Selection of sample volume (SPE). Sample spiked concentration, 2 μg L^{-1}; eluent, methanol; eluent volume, 10 mL.

of water sample was loaded, and then 5 mL of water was passed through the cartridge to get rid of the interference absorption. Then the cartridge was dried with nitrogen for 10 min. The analytes were eluted with 10 mL of methanol and the eluent was concentrated by a rotary evaporator system (EYELA, Tokyo, Japan) and finally acetone was added to make up the volume to 1 mL for subsequent PTV–GC–MS analysis, for which 5 μL of this solution was injected.

3. Results and discussion

3.1. Development of microextraction procedure

Various parameters that affect MEPS performance, such as the draw/eject speed, sample loading amount, sort of eluents, elution volume and carry over effects, were examined in this study. All the optimization experiments were conducted using a spiked ultrapure water sample.

Generally, sample preparation times can be reduced by employing a high flow rate, although incomplete adsorptions happen. Complete adsorption can be achieved at a low flow rate but this is time consuming. The draw-eject speeds (1–10 μL s^{-1} range) in the MEPS procedure were optimized for extraction and elution by the MEPS syringe. 5 μL s^{-1} and 3 μL s^{-1} were chosen as the optimal speeds for sample loading and elution/injection (Fig. 2), respectively.

The extract-discard mode and draw-eject mode are available in the sample loading step. In this experiment, the draw-eject mode was adopted and each 50 μL aliquot of sample was pumped through the MEPS cartridge, and 20, 30, 40 and 50 times cycles were tested. An equilibrium in the response of most of PAHs was obtained when 40 × 50 μL of sample was extracted using the MEPS cartridge (Fig. 3), so this was chosen for the extraction step.

Selection of a suitable eluent and optimum volume of elution solvent are essential for the sample pretreatment step. Here, three organic solvents (methanol, dichloromethane and n-hexane) were evaluated as an eluent. As shown in Fig. 4, the best responses of most PAHs were observed when dichloromethane was used as the elution solvent. However, dichloromethane is toxic and environmentally unfriendly. Therefore, methanol was chosen as the most suitable eluent. Moreover, the optimum volume of methanol was examined, and 50 μL of methanol was selected for the following experiments.

In order to evaluate carryover, two, four, six and eight wash-discard cycles were carried out by pumping 80 μL of the eluent through the MEPS syringe after the elution of target analytes. The carryover effect was checked after the cleaning procedure by using eight portions of 80 μL of the elution solvent and was found to be reduced to 0.1–2.1% of the initial analytes. The results were similar to those reported in the literature [15].

Table 2
Linearity, limits of detection (LODs), limits of quantification(LOQs) and repeatability of the proposed method.

Analytes	R^2		LOD_s (ng L^{-1})		LOQ_s (ng L^{-1})		Precision (RSD%, n = 5)					
	MEPS	SPE	MEPS	SPE	MEPS	SPE	MEPS (μg L^{-1})			SPE (μg L^{-1})		
	0.05–2 μg L^{-1}	0.25–10 μg L^{-1}					0.1	0.5	2.0	0.5	2.0	10
Nap	0.9997	0.9997	1.1	4.8	3.5	15.8	4.5	9.9	8.9	5.0	5.1	3.3
Acy	0.9996	0.9997	8.2	16.2	27.2	53.8	2.9	6.9	2.9	6.1	5.0	4.1
Ace	0.9992	0.9983	6.5	18.1	21.5	60.4	3.7	3.5	4.0	5.7	4.7	3.7
Flu	0.9981	0.9980	3.1	16.3	10.1	54.4	4.2	2.8	1.5	3.6	7.4	4.7
Phe	0.9965	0.9978	0.8	6.4	2.5	21.3	4.4	2.7	0.7	1.5	0.8	7.6
Ant	0.9980	0.9996	8.2	35.9	27.5	119.6	1.0	2.9	1.4	5.0	3.0	9.5
Flr	0.9974	0.9996	2.6	9.0	8.4	29.9	1.6	4.7	1.6	6.3	7.8	4.8
Pyr	0.9993	0.9998	2.5	12.3	8.2	40.9	7.6	6.3	1.3	7.8	8.2	4.9

Table 3
Recovery and repeatability of the method in analysis of real samples.

Analytes	MEPS Intra-day (n = 5)						SPE Intra-day (n = 5)					
	0.1 μg L^{-1}		0.5 μg L^{-1}		1.5 μg L^{-1}		0.35 μg L^{-1}		4.0 μg L^{-1}		8.0 μg L^{-1}	
	RSD(%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD(%)	Recovery (%)	RSD (%)	Recovery (%)
Nap	6.2	116	6.1	85	10.3	74	14.6	100	5.5	78	8.3	93
Acy	9.5	99	5.4	99	8.5	89	9.1	114	4.5	84	3.5	115
Ace	4.8	79	9.2	85	5.7	78	4.7	134	4.5	83	3.9	103
Flu	4.4	72	5.8	76	6.7	74	9.6	72	3.4	84	3.2	98
Phe	1.6	87	2.5	70	7.0	70	4.9	90	4.1	81	2.9	87
Ant	2.5	114	4.1	94	9.5	92	7.9	101	5.9	110	5.5	115
Flr	5.0	117	9.3	82	9.6	83	9.9	96	4.2	85	2.7	86
Pyr	11.6	109	8.0	82	14.0	84	3.3	92	5.1	80	2.9	82

Table 4
Concentrations ($\mu g\,L^{-1}$) found in different environmental water samples.

Analytes	MEPS			SPE		
	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Nap	0.242 (3.8%[a])	n.d	n.d	0.362 (8.1%[a])	n.d	n.d
Acy	n.d	n.d	n.d	n.d	n.d	n.d
Ace	n.d	n.d	n.d	n.d	n.d	n.d
Flu	n.d	n.d	n.d	n.d	n.d	n.d
Phe	n.d	n.d	n.d	n.d	n.d	n.d
Ant	n.d	n.d	n.d	n.d	n.d	n.d
Flr	0.063 (9.4%[a])	n.d	n.d	n.d	n.d	n.d
Pyr	0.119 (9.5%[a])	n.d	n.d	n.d	n.d	n.d

n.d: not detected.
[a] RSD based on four replicates in real sample.

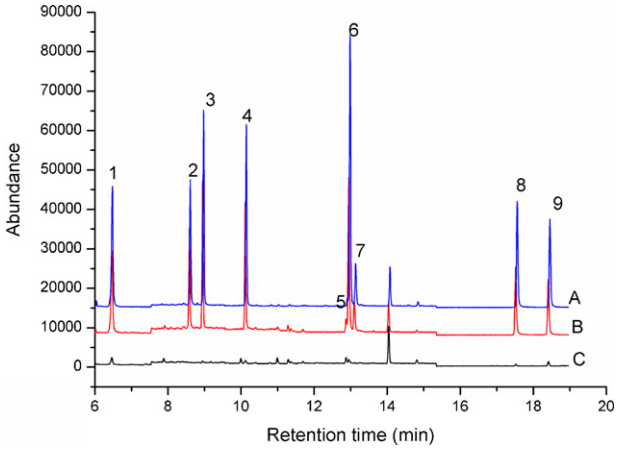

Fig. 7. Chromatograms of Nap, Acy, Ace, Flu, Phe, Ant, Flr and Pyr in real samples. (1) Nap; (2) Acy; (3) Ace; (4) Flu; (5) phenanthrene-d10; (6) Phe; (7) Ant; (8) Flr; (9) Pyr. (A) Concentration of 1 $\mu g\,L^{-1}$ of standard solution and 0.2 $\mu g\,L^{-1}$ of internal standard by MEPS. (B) Spiked with 0.5 $\mu g\,L^{-1}$ of real water sample by MEPS. (C) Real water sample (Sample A) by MEPS.

3.2. Optimization of solid phase extraction

In the preliminary MEPS experiments, methanol was chosen as the elution solvent and it was also used in the SPE method. Moreover, the influence of the volume of methanol was tested with four volumes: 5, 7, 10 and 15 mL. The results (Fig. 5) showed that an equilibrium in the response of most of the analytes happened when 15 mL of methanol was employed; however, the peak area of Flr decreased. In order to ensure the complete elution of the target analytes and the efficient use of solvent, 10 mL of methanol was used to elute the loaded SPE cartridges.

In order to shorten the extraction time, only sample volumes in the 30–200 mL range were evaluated. The results showed that with an increase in the sample volume, increasing analytical responses were obtained and because of the large matrix sample capacity of the sorbents (1 g/6 mL), no breakthrough volume was obtained (Fig. 6). To achieve similar sensitivities of the method compared with MEPS, 50 mL was finally adopted.

3.3. Method validation

Calibration curves were obtained by analyzing standard solutions of the eight PAHs added to the ultrapure water using the above method in the following linear ranges: 0.05–2.0 $\mu g\,L^{-1}$ for MEPS and 0.25–10.0 $\mu g\,L^{-1}$ for SPE. The correlation coefficients (R^2) were in the range 0.9965–0.9997 (MEPS) and 0.9978–0.9998 (SPE) for all the analytes (Table 2). Repeatability was evaluated by extracting pure water samples at the three concentration levels, extracting five replicates for each level. The intra-day precision values expressed as RSD were in the ranges 0.7–9.9% (MEPS) and 0.8–9.5% (SPE) for all analytes (Table 2).

The limits of detection (LODs) and limits of quantification (LOQs) are regarded as the minimum concentrations of target compounds that can be confidently identified and quantified, respectively, by the two methods. The LODs and LOQs were estimated as the analyte concentrations that produced signal/noise ratios of 3:1 and 10:1, and were, respectively, in the ranges of 0.8–8.2 $ng\,L^{-1}$ and 2.5–27.5 $ng\,L^{-1}$ for MEPS, and 4.8–35.9 $ng\,L^{-1}$ and 15.8–119.6 $ng\,L^{-1}$ for SPE, for all analytes.

3.4. Application of methods to real samples

The optimized and validated methodologies were applied to the determination of levels of PAHs in real environmental water samples. The intra-day precision was determined by analyzing spiked real lake water five times a day at three different fortified concentrations (Table 3). The results show that the intra-day RSDs ranged from 1.6% to 14.0% (MEPS) and 2.7% to 14.6% (SPE). At all three fortified concentrations, the recoveries of the eight PAHs were in the range of 70–117% (MEPS) and 72–134% (SPE). The chromatograms of standard solutions, spiked real sample and blank are shown in Fig. 7. Because sample B and sample C were collected from lakes in a park, no PAHs were detected (Table 4). Nap, Flr and Pyr were detected in the sample from the SuZhou river (Sample A).

4. Conclusions

Two sample preparation techniques based on MEPS and SPE combined with GC–MS were developed. Both methods permitted the determination of eight PAHs in environmental water at low levels ($ng\,L^{-1}$). MEPS showed similar recovery results compared to the SPE method. However, a better sensitivity was obtained using the proposed MEPS method. Furthermore, MEPS minimized the volume of organic solvent used for the elution, as well as sample volumes. The proposed MEPS–GC–MS method could be used as a screening method for monitoring PAHs in environmental waters.

Acknowledgments

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