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ORIGINAL ARTICLE

Magnetic Solvent Bar Liquid-Phase Microextraction Followed by Gas Chromatography-Flame Ionization Detection for the Trace Determination of Selected Polycyclic Aromatic Hydrocarbons in Environmental Water Samples

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KEYWORDS

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Polycyclic aromatic hydrocarbons

ABSTRACT: A novel and efficient hollow fiber-based method, viz. magnetic solvent bar liquid-phase microextraction (MSB-LPME) combined with gas chromatography-flame ionization detection (GC-FID) was successfully developed for the trace determination of selected polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. The target analytes were extracted from sample solution to the organic solvent immobilized in a fiber. After extraction, the analyte-adsorbed magnetic solvent bar could be readily isolated from the sample solution by a magnet which could greatly simplify the operation and also decline the total pretreatment time. The bar was first eluted with methanol, evaporated to dryness while the residue was dissolved in toluene and finally injected into GC-FID. Begin with, effective parameters controlling the performance of the microextraction were evaluated and optimized. The values of the detection limit of the method were in the range of 0.05-0.08 µg L^{-1} and the RSD% values for the analysis of 10.0 µg L^{-1} of the analytes was below than 5.8% (n= 6). A good linearity ($0.998 \geq r^2 \geq 0.994$) and a broad linear range (0.1-200 µg L^{-1}) were obtained. The method was eventually utilized for the preconcentration and determination of the PAHs in environmental water samples and satisfactory results were obtained.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are classified as parlous chemical compounds mainly consisted of multiple fused benzene rings originated from the partial combustion of organic materials and have recently received ample concerns owing to their high lipophilicity, recalcitrant and prevalent in the environment [1, 2]. Low molecular weight PAHs are acutely toxic while high molecular weight PAHs are highly carcinogenic and mutagenic; they could even induce oxidative stress and oxidative DNA damage over the metabolic activation and the production of reactive oxygen species [3, 4]. On the accounts, some regulatory bodies such as the US Environmental Protection Agency and the European Union have classified some PAHs as "priority organic pollutants" [5]. Thus, the development of novel methods for separation and trace determination of PAHs among complex matrices are yet dominant issue.

Gas chromatography (GC) and high-performance liquid chromatography (HPLC) [6, 7] have been commonly applied for the

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analysis of PAHs in different media. Nonetheless, when the concentration levels are low, a prior enrichment step is usually needful. The extraction techniques applied before the instrumental analyses are liquid-liquid extraction (LLE) and solid phase extraction (SPE) [8, 9]. Though, these sample pretreatment methods require either significant amount of sample and often employed high-priced, not recyclable organic solvents while they are considered as time-taking and labor-intensive which frequently results in substantial blank values.

The liquid-phase microextraction (LPME) is a sample pretreatment technique that utilizes small volumes of organic solvents to extract a broad kind of analytes from various matrices before instrumental analysis [10]. The development of these methods focuses on providing easy, low-priced and environmentally friendly extraction approaches for sample preparation [11, 12]. Among the various modes of LPME and to improve its capabilities, hollow fiber liquid-phase microextraction (HF-LPME) is reported [13, 14]. It uses an HF to keep steady and protect the extraction solvent, and the small pore size of the fiber prevents large molecules and particles from entering into the acceptor phase, resulting in a clean-up of sample matrix in addition to the extraction [15]. Since very little amounts of the solvent are used, consumption of toxic organic solvents is minimized while the technique simply combines extraction and concentration as well as sample introduction into a single step [16, 17].

Recently, a simple, efficient and novel HF-LPME based method was developed, named magnetic solvent bar liquid-phase microextraction (MSB-LPME) initially applied for the determination of organophosphorus pesticides in fruit juice samples [18]. In MSB-LPME, some modifications of HF-LPME were introduced for simplifying the practical operation as well as improving the extraction efficiency.

The present study aimed to appraise the MSB-LPME technique suitability for the determination of selected PAHs in the aquatic environment. The factors affecting microextraction efficiency were considered in detail, and the optimum conditions were set. The method was validated for quantitative purposes and employed to real samples analysis in combination with gas chromatography-flame ionization detection (GC-FID).

MATERIALS AND METHODS

Chemicals and materials

Eight PAHs analyzed including naphthalene (Nap), acenaphthylene (Acl), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flr) and pyrene (Pyr) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Analytical reagent grade acetone, ethyl acetate, hexane, carbon tetrachloride, 1-octanol and toluene were obtained from Merck Company (Darmstadt, Germany). Q3/2 Accurel PP hydrophobic polypropylene HF membrane (600 µm inner diameter, 200 µm wall thickness and 0.2 µm pore size) was purchased from Membrana GmbH (Wuppertal, Germany). The extraction procedure was performed in the 22 mL screw top vials (Sigma-Aldrich, Steinheim, Germany) with dimension of 23 mm (outer diameter) × 85mm (height) × 18mm (inner diameter). The stainless-steel wire (505 µm outer diameter) was just fit HF membrane. HPLC-grade methanol (Fisher Chemicals, Fair Lawn, NJ, USA) and ultrapure water (Millipore, Bedford, MA, USA) were used in all experiments. All solutions were stored at 4°C and protected from light.

Instruments

An Agilent 6890N gas chromatograph (Wilmington, DE, USA) equipped with a split/splitless inlet and flame ionization detector (FID) was used for the determination of the PAHs. Helium (99.999%) was employed as carrier gas at the flow rate of 2.0 mL min^{-1}. The chromatographic data were recorded using a HP Chemstation, controlled by Windows NT (Microsoft). The analytes were separated on a 30 m × 0.25 mm i.d. × 0.25 m film thickness DB-5 gas chromatographic column (J&W Scientific, Folsom, CA, USA) with the following oven temperature program: initial 80 °C, from 80 °C (held 2 min) to 180 °C at 5 °C min^{-1}, increased at 10 °C min^{-1} to 280 °C and held for 5 min. Analysis employed a 1.0 µL sample injection in a 5:1 split ratio while the injection port and detector were operated at 260 °C and 280 °C, respectively.

Real samples collection

The performance of the proposed method was evaluated by analyzing the PAHs in four environmental water samples including Caspian Sea (Noushahr, Iran), Persian Gulf (Assaluyeh, Iran), Jajroud River (Tehran, Iran) and Latian Dam (Tehran, Iran). The samples were taken in September 2017 and were collected in amber glass bottles (1000 mL). The containers were rinsed several times with the water to be analyzed and filled till overflow to prevent loss of the volatile organic compounds in the presence of the headspace. The water samples were filtered before the analysis using a 0.45 µm nylon membrane filter (Whatman, Maid-stone, UK) to eliminate the particles. All the samples were transported and stored at the refrigerator in 4 °C until their analysis time.

Extraction procedure

Schematic of the presented microextraction is shown in Figure 1. It contained a HF and stainless-steel wire with magnetic properties; they were manually cut into segments of 1.5 cm length. These segments were ultrasonically cleaned to remove impurities and dried in the air. To prepare the extraction set-up, the stainless steel wire was inserted into the HF. The resulting fiber piece was immersed in an organic solvent for one min to impregnate pores of the fiber wall. With regard to remove the extra amount of the organic solvent from the surface of the fiber, it was carefully rinsed with water. To start the procedure, five MSBs were placed into the 22 mL screw top vial containing 20 mL of aqueous sample. The vial was closed and put into a water bath with temperature of 40 °C on the magnetic stirrer for 20 min at 600 rpm. After the extraction, with the help of an external magnet, the MSBs were separated rapidly from the sample solution. Then the bars were eluted with 400 µL of methanol in an ultrasonic bath for 3 min. The eluate was separated from the MSBs also by a magnet. The eluate obtained was evaporated to dryness under a nitrogen stream and the residue was dissolved in 100 µL of toluene. At last, a 1.0 µL of the extracting phase was injected into GC-FID.

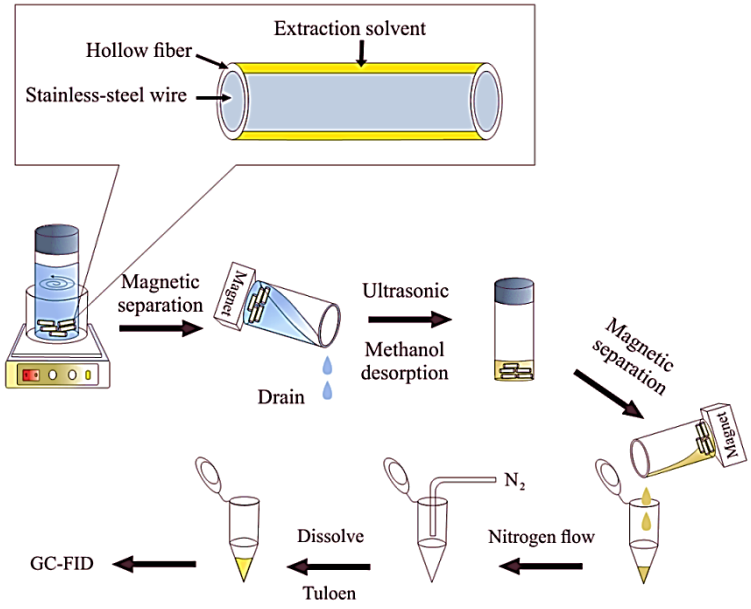

Figure 1. The schematic diagram of MSB-LPME-GC

RESULTS AND DISCUSSION

A one variable at a time approach was employed to optimize the affecting parameters on the microextraction efficiency including the type of extraction solvent, extraction temperature, salt concentration, stirring speed, extraction time and desorption conditions. A fixed concentration (100.0 µg L^{-1}) of the analytes was used in the optimization process. All the quantifications were performed from the average of three replicate measurements. Blank samples were periodically run to confirm the absence of interference.

The selection of extraction solvent

The selection of an appropriate organic solvent in HF-LPME is of great importance for efficient analyte preconcentration [19]. There are some criteria for organic solvent selection as follow. Firstly, it should be easily immobilized in the HF pores. Second, it needs to be almost nonvolatile to avoid solvent loss during the extraction. Third, the organic solvent should be immiscible with water because it serves as a barrier among the two aqueous phases, the source and the receiving phases. Besides, the organic solvent is used to promote analyte diffusion from the source phase into the receiving phase via the pores of the HF [20]. Depending on these considerations, 1-octanol, carbon tetrachloride, toluene and hexane were investigated in preliminary experiments. The highest extraction efficiency for all the analytes was obtained with toluene. Therefore, it was selected as the extraction solvent (Figure 2).

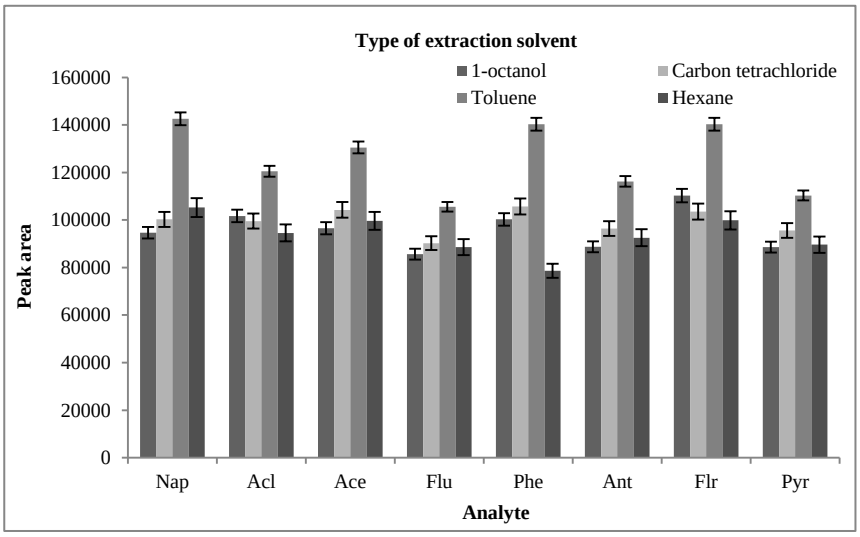

Figure 2. The effect of extraction solvent type on MSB-LPME efficiency

The effect of extraction temperature

The extraction temperature could obviously influence the extraction efficiency in two opposing ways; to begin with, it could improve the mass transfer of the analytes and secondly, it could decline the partition coefficients (K_{ow}) between the organic and aqueous phase [21, 22]. Hence, the extraction efficiency will be higher or lower depending on the dominant factor. The effect of sample solution temperature was studied in the range of 20-50 °C. The extraction efficiency for all the target analytes was raised with the increase of temperature and maximum analytical signals were obtained at 40°C (Figure 3). However, increasing the extraction temperature upper the mentioned value would result in the dissolution and volatilization loss of the extracting solvent and formation of air bubbles adhering to the HF, which would influence on the extraction operation and precision. Thereupon, to achieve better extraction efficiency and reproducibility, temperature of 40°C was used for further studies.

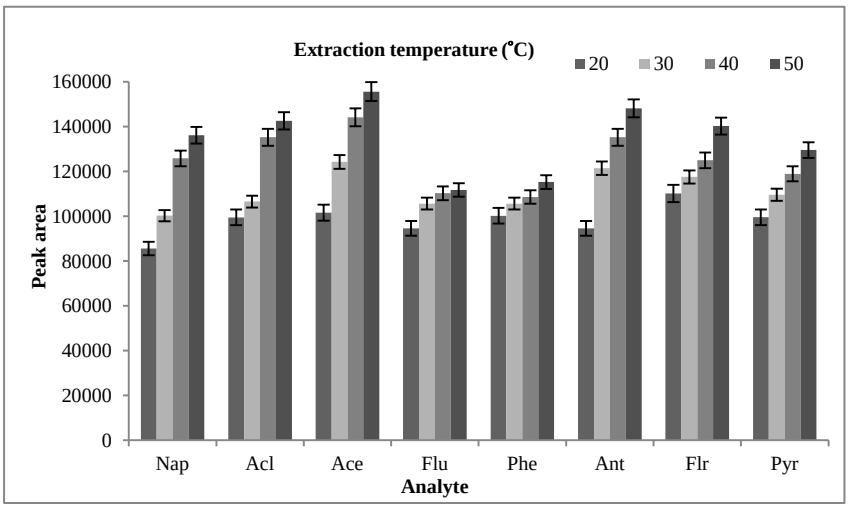

Figure 3. The effect of extraction temperature on MSB-LPME efficiency

The effect of salt concentration

The salt addition to sample solution often increases the ionic strength, and therefore improves the extraction efficiency because of the salting out effect [23, 24]. This effect has been accounted to decline the solubility of target analytes in the aqueous phase and increasing partitioning into the organic phase. For this purpose, different concentrations (0%-20% w/v) of NaCl were added to the sample solution to evaluate its effect on the extraction efficiency (Figure 4). Salt addition has no considerable effect on the preconcentration factors. Therefore, the factor is nearly steady by increasing the amount of NaCl, and the extraction experiments were carried out without adding salt.

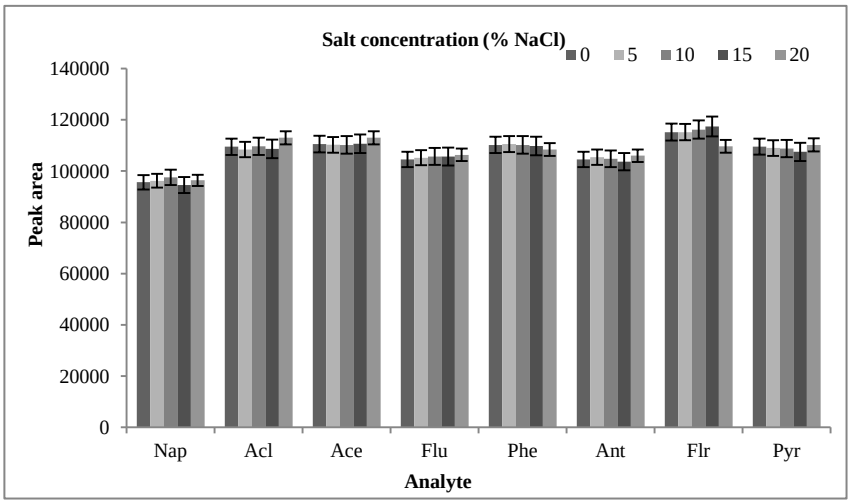

Figure 4. The effect of salt concentration on MSB-LPME efficiency

The effect of stirring speed

The agitation of the sample solution improves the extraction efficiency and thus reduces the extraction time. Meanwhile, it enhances the diffusion of the analytes through the interfacial layer of the HF [25]. The effect of this parameter on the extraction efficiency of the system was studied in the range of 350-750 rpm. The agitation of the sample greatly boosted the extraction efficiency (Figure 5). However, higher stirring rates were not evaluated as they might cause the excessive formation of air bubbles on the surface of HF or would lead to solvent dissolution, which conducted to poorer precision and to exper-

imental failure. Hence, 750 rpm was selected as the optimum condition in the following experiments.

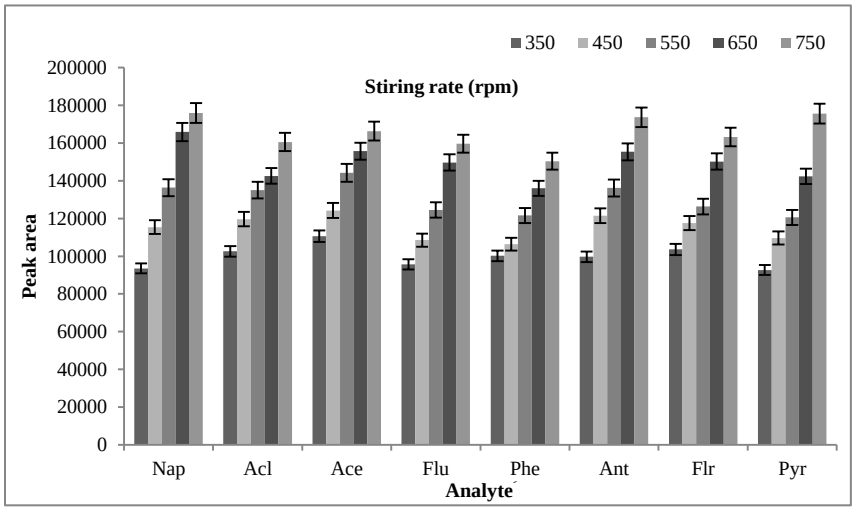

Figure 5. The effect of stirring rate on MSB-LPME efficiency

The effect of extraction time

The mass transfer in MSB-LPME is a process dependent on equilibrium rather than exhaustive extraction and in order to achieve good extraction repeatability, it is necessary to choose a suitable extraction time [26]. In this work, the extraction time profiles were investigated by recording the variation of the analytical signals of the analytes as a function of extraction time, in the range of 10-40 min. By growing the extraction time up to 30 min, the extraction efficiencies rose quickly and afterwards stayed approximately steady (Figure 6). Longer extraction time can result in the loss of the extracting solvent and contraction of the extraction yields. Accordingly, the exposure time of 30 min was selected as optimum value in the subsequent experiments.

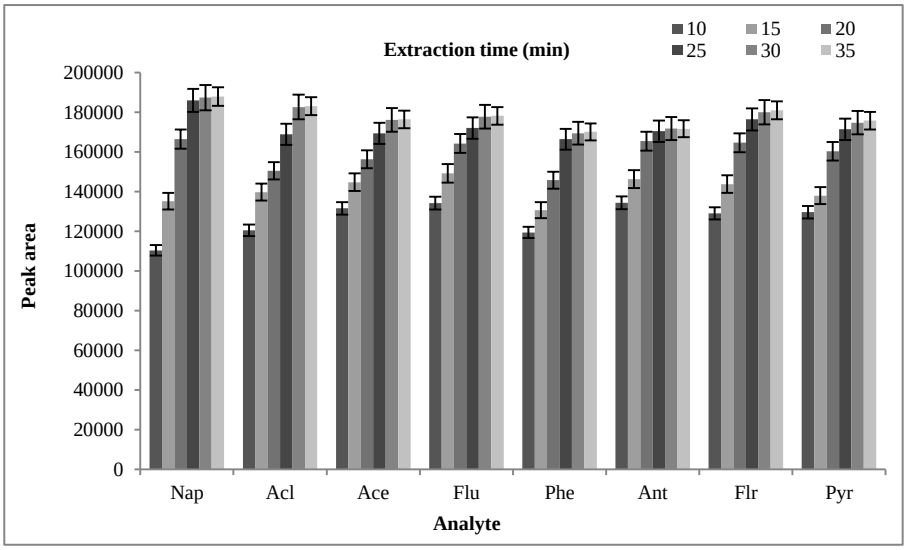

Figure 6. The effect of extraction time on MSB-LPME efficiency.

The effects of desorption solvent and time

Due to the great importance of desorption solvent and time on the extraction efficiency, the parameters were investigated and optimized. When the extraction process was completed, 400 µL of desorption solvents including acetone, methanol and ethyl acetate were applied to elute the analytes from the MSBs. The best desorption efficiencies were obtained with methanol. Therefore, methanol was chosen to be the optimum for extraction of PAHs. To evaluate the other parameter, the analyte-enriched MSB was ultrasonicated in the range of 1-10 min with interval period of one min. Four minutes was enough to get the best analytical signals. However, if the desorption time was too long, the analytes would be lost significantly. Therefore, 4 min was chosen as the appropriate value.

The analytical performance

To assess the applicability of the method, calibration curves were plotted at the optimum conditions using different concentration levels of the analytes. The limits of detection (LODs) based on the signal-to-noise ratio (S/N) of 3, the determination coefficients (r^2), the linear ranges (LRs) and the relative standard deviations (RSDs) were calculated in Table 1. LODs for the PAHs were in the range of 0.05-0.08 µg L^{-1} while linearity values varied in the range of 0.1-200 µg L^{-1} with correlation coefficient of 0.994-0.998. The precision of the method was investigated with 10 µg L^{-1} PAHs mixed standard solution and the RSDs for six replicate measurements varied from 4.8% to 6.8%.

Table 1. Some quantitative data achieved by using MSB-LPME and GC-FID for the determination of the selected PAHs.

Analyte	Nap	Acl	Ace	Flu	Phe	Ant	Flr	Pyr
LOD (µg L^{-1}) [a]	0.06	0.07	0.05	0.08	0.05	0.07	0.07	0.08
r^2	0.995	0.996	0.994	0.998	0.997	0.995	0.995	0.996
LR (µg L^{-1}) [b]	0.1-200	0.2-200	0.1-200	0.2-100	0.1-100	0.2-200	0.2-200	0.2-100
RSD% [c] (n=6)	4.9	5.3	5.7	4.8	5.5	5.8	5.1	5.0

[a] Limit of detection for S/N = 3.
[b] Linear range.
[c] Relative standard deviation at concentration level of 10.0 µg L^{-1} for each PAHs.

Comparing the proposed method with other analytical techniques employed for the determination of PAHs in water samples, the present work has low superiority over the other techniques in term of RSDs and almost the widest LRs and LODs. On the other hand, when it comes to the comparison of the extraction time, the represented method nearly stands in the last order (Table 2).

Table 2. Comparison of various analytical methods for the extraction and determination of PAHs in water samples

Method	LOD (µg L^{-1})	LR (µg L^{-1})	RSD%	Extraction time (min)	Reference
MSB-LPME-GC-FID [(a)]	0.05-0.08	0.1-200	< 5.8	30	Represented method
HF-LPME-GC-MS [(b)]	0.002-0.047	0.5-100	< 13.6	35	[27]
LPME-HPLC	0.35-0.60	1.2-12	< 6.0	20	[28]
DLLME-GC-FID	0.007-0.03	0.02-200	< 10.2	A few seconds	[29]
HLLME-FA-GC-FID	14.0-41.0	50-1000	< 10.3	5	[30]

(a) Magnetic solvent bar liquid-phase microextraction-gas chromatography-flame ionization detection.
(b) Hollow fiber liquid-phase microextraction-gas chromatography-mass spectrometry.
(c) Liquid-phase microextraction-high performance liquid chromatography.
(d) Dispersive liquid-liquid microextraction- gas chromatography-flame ionization detection.
(e) Homogeneous liquid-liquid microextraction via flotation assistance gas chromatography-flame ionization detection.

Analysis of environmental water samples

Set at the optimum conditions, the method performance was verified by analyzing the analytes in the four different environmental water samples. They were free of PAHs contamination (Table 3). MSB-LPME is a non-exhaustive extraction procedure and therefore the relative recovery (determined by the ratio of the concentrations found in the real environmental sample and reagent water sample, spiked with a similar quantity of the analytes), rather than the absolute recovery (used in exhaustive extraction procedures), was utilized. Therefore, in next step and to evaluate the matrix effects, all the real samples were spiked with PAHs standards at different concentration levels and the relative recovery experiments of the analytes are calculated (Table 3). The obtained recoveries were between 93%-108%, indicating that the method is not influenced by the matrix in actual applications while the RSD% values were below than 6.7 (n= 6). An overlay of two chromatograms obtained by performing MSB-LPME-GC-FID for Caspian Sea sample (Noushahr, Iran) before and after PAHs spiking are shown in Figure 7 and demonstrated no significant interference through the analytical procedure.

Table 3. The results acquired from analysis of real environmental water samples.

Sample	Nap	Acl	Ace	Flu	Phe	Ant	Flr	Pyr
Caspian Sea (Noushahr, Iran), (10.0 µg L^{-1} added)								
PAHs concentration (µg L^{-1})	ND [a]	ND	ND	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	10.4	10.8	9.4	9.3	10.2	10.5	10.6	10.1
Relative recovery%	104	108	94	93	102	105	106	101
RSD% (*n* = 6)	5.8	6.5	6.1	5.5	6.7	6.3	6.0	6.4
Persian Gulf (Assaluyeh, Iran), (25.0 µg L^{-1} added)								
PAHs concentration (µg L^{-1})	ND	ND	ND	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	24.1	24.5	23.9	24.3	25.8	25.6	25.9	26.7
Relative recovery%	96	98	96	97	103	102	104	107
RSD% (*n* = 6)	6.1	5.7	6.3	5.9	5.5	6.6	6.0	5.8
Jajroud River (Tehran, Iran), (50.0 µg L^{-1} added)								
PAHs concentration (µg L^{-1})	ND	ND	ND	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	53.1	51.8	49.1	48.4	47.8	46.9	52.5	53.7
Relative recovery%	106	104	98	97	96	94	105	107
RSD% (*n* = 6)	6.0	5.9	6.4	5.4	5.8	5.7	6.3	6.5
Latian Dam (Tehran, Iran), (100.0 µg L^{-1} added)								
PAHs concentration (µg L^{-1})	ND	ND	ND	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	106.1	103.3	94.0	94.9	96.2	105.4	106.8	96.7
Relative recovery%	106	103	94	95	96	105	107	97
RSD% (*n* = 6)	5.8	5.5	5.9	5.7	6.0	6.1	5.5	5.9

[a] Not detected.

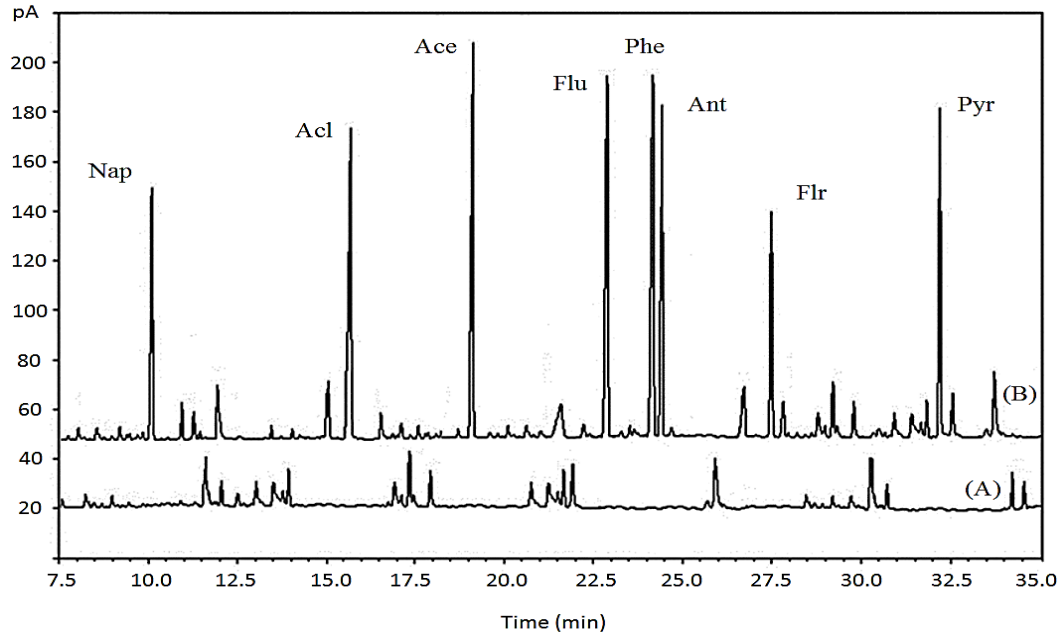

Figure 7. An overlay of two chromatograms obtained by performing MSB-LPME-GC-FID for Caspian Sea sample (Noushahr, Iran) before (A) and after PAHs spiking (B).

CONCLUSIONS

This study outlined the successful development and application of MSB-LPME method followed by GC-FID as a simplified mode of HF-LPME for the trace determination of the selected PAHs in environmental water samples. The magnetic solvent bar was applied utilizing two purposes: the stirring bar of microextraction and extractor of the target analytes. After the microextraction process, it can be simply isolated from the sample solution by a magnetic field to reduce the total analysis time. The satisfactory extraction efficiency, sufficient sensitivity and repeatability along with significant accuracy and linearity over a broad range were achieved, almost independent of the complex matrix in the real applications. Additionally, the developed method needs just a little volume of organic extractants, being consequently an environmentally friendly approach of sample preparation. Besides an efficient sample clean-up, the entire analytical procedure presents a cost effective and quick way for the screening purposes. Hence, putting all the advantages simultaneously, the method possesses great potential to be employed in other analytical applications.

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Conflict of interests

The authors declared no conflict of interests.

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