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Ionic Liquid-based Ultrasound-assisted In-situ Solvent Formation Microextraction and High-performance Liquid Chromatography for the Trace Determination of Polycyclic Aromatic Hydrocarbons in Environmental Water Samples

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Abstract

A green and efficient ionic liquid-based ultrasound-assisted in-situ solvent formation microextraction (IL-UA-ISFME) in combination with high-performance liquid chromatography-ultraviolet detection (HPLC-UV) has been successfully developed for the trace determination of five selected polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. In this method, a hydrophobic ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) was formed by addition of a hydrophilic ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) to sample solution containing an ion-pairing agent ($NaPF_6$). The analytes were extracted into the ionic liquid phase while the microextraction solvent was dispersed through the sample by utilizing ultrasonic radiation. The sample was then centrifuged and extracting phase retracted into the microsyringe, diluted with acetonitrile, and injected to HPLC. In the beginning, effective parameters controlling the performance of the microextraction process were studied in detail and optimized. The limit of detections (LOD, S/N = 3) were in the range of 0.32-0.79 $\mu g\ L^{-1}$ while the RSD% values were below than 5.2% (n = 6). A good linearity (0.997 ≥ r^2 ≥ 0.992) and a broad linear over the concentration ranges from 1 to 500 $\mu g\ L^{-1}$ were achieved. The method was ultimately applied for the preconcentration and sensitive determination of the PAHs in several environmental water samples. The accuracy of the method in the real samples was tested by the

relative recovery experiments with results ranging from 90-106%, which confirmed that complicated matrixes had almost little effect on the developed analytical procedure.

Keywords: *Environmental water samples, High-performance liquid chromatography, Ionic liquid, Microextraction, Polycyclic aromatic hydrocarbons.*

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) indicate an important category of hazardous chemicals including of two or more fused benzene rings in linear, cluster or angular arrangements [1, 2]. They are widespread pollutants existing in all parts of the environment (atmosphere, soil and water) and released from both anthropogenic and natural origins that involve incomplete burning of fossil fuels, disposal of coal, industrial cracking and the deterioration of manufactured materials such as detergents, plastics, lubricating oils and dyes [3, 4].

PAHs have nonpolar characteristics while their polarity drops as the number of aromatic rings rises. Low molecular weight PAHs are mostly acutely toxic, whereas high molecular weights are extremely mutagenic and carcinogenic [5, 6]. Owing to their toxicity, possible or proven carcinogenicity and mutagenicity, bioaccumulation and persistent and features, PAHs exhibit a risk to the environment and human health [7, 8]. The regulatory bodies like the US Environmental Protection Agency and the European Union have classified some PAHs as "priority organic pollutants" [9]. Thus, the development of new sample preparation method for sensitive determination of PAHs in complex matrixes is still of great importance.

High-performance liquid chromatography (HPLC) [10] and Gas chromatography (GC) [11] have commonly been utilized for the analysis of PAHs in various media. Furthermore, when the concentration levels are low, a previous enrichment step is usually needed. The extraction techniques, which are generally applied before the instrumental analysis, are liquid-liquid extraction (LLE) [12, 13] and solid-phase extraction (SPE) [14, 15]. Nevertheless, these sample pretreatment methods need either large amount of sample and toxic organic solvents while they are considered as time-consuming, labor-intensive and expensive with frequently result in strong blank values [16, 17]. Therefore, a variety of microextraction techniques that use no or small amounts of solvent have been developed in last years.

Ionic liquids (ILs) are non-molecular solvents with low melting points, negligible vapor pressures, and high thermal stability [18, 19]. Their exclusive solvation properties giving ILs unique selectivity and diverse separation mechanism, coupled to the fact that they can be structurally tailored for specific applications [20, 21]. There have been climbed interests for using the physicochemical characteristics of ILs in different analytical chemistry schemes [22, 23].Recently, Zeeb et al. has been developed a novel microextraction technique as a high performance and powerful preconcentration method, viz. ionic liquid-based ultrasound-assisted in-situ solvent formation microextraction (IL-UA-ISFME) [24, 25]. This approach is based on the dissolution of a hydrophilic IL in an aqueous solution containing analytes of interest, followed by the addition of an ion-exchange reagent which undergoes an in-situ metathesis reaction forming an insoluble IL.

Thereupon, analytes are extracted and preconcentrated once the IL is insolubilized while mass transfer process is speed-up significantly by ultrasound wave. This dominant and environmentally friendly method is an efficient and adequate analytical procedure, for which excellent accuracy and precision are demonstrated, being simple and sensitive enough for the screening purposes.

The aim of present study is to assess IL-UA-ISFME technique suitability for the determination of nine selected PAHs in environmental water samples. The factors affecting the microextraction efficiency were studied in detail and the optimum conditions were established. The method was finally validated for quantitative purposes and applied to real sample analysis in combination with high-performance liquid chromatography-ultraviolet detection (HPLC-UV).

Experimental

Chemicals

All five PAHs (fluorene, phenanthrene, anthracene, fluoranthene and pyrene) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Analytical grade of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$], sodium hexafluorophosphate (NaPF$_6$), HCl and NaOH were obtained from Merck Company (Darmstadt, Germany). 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF$_4$] was purchased from Fluka Company (Steinheim, Switzerland). HPLC grade of acetonitrile and methanol were purchased from Riedel-de Haën Company (Germany). Ultrapure water (Millipore, Bedford, MA, USA) was used for preparing standards and dilutions. All solutions were stored at 4 °C and protected from light.

Apparatus

A HPLC system (Shimadzu, Kyoto, Japan) including a pump, an automatic injector equipped with 20 µL sample loop and a UV detector (set at 254 nm) was applied for the analysis of the PAHs. The analytical column chosen for the separation was a RP-C$_{18}$ (LiChrospher, Merck Millipore, Darmstadt, Germany) with 5 µm particle size and dimensions of 250 mm × 4.6 mm i.d., at room temperature of 22 ± 0.5 °C. Isocratic mobile phase consisted of acetonitrile/water (80:20) at a flow rate of 1.5 mL min^{-1} was run through the column. A GS-6 centrifuge (Beckman, CA, USA) was utilized for accelerating the phase separation. The hydrophobic ionic liquid (as the extraction solvent) was dispersed through the aqueous media via Sonorex ultrasonic baths (Bandelin, Berlin, Germany). The mobile phase was filtered using a 0.2 µm membrane filter (Millipore, Bedford, MA, USA) and it was degassed continuously using an online degasser.

Preparation of solutions

A stock solution of five PAHs at concentration levels of 1.0 mg L^{-1} was prepared in methanol. Working standard solutions were prepared by diluting the stock solution with water at known concentrations. A 1.0 g mL^{-1} solution of [Bmim][BF$_4$] as hydrophilic IL was prepared in methanol. A solution of 200 mg mL^{-1} of NaPF$_6$ as an ion-exchange reagent was obtained by dissolving required amount of this salt in ultra-pure water. All the stock and working solutions were stored at 4 °C.

Real samples collection

The performance of the proposed method was evaluated by analyzing the PAHs in four environmental water samples including: Caspian Sea (Sari, Iran), Persian Gulf (Mahshahr, Iran), Jajroud River (Tehran, Iran) and Amirkabir Dam (Karaj, Iran). The samples were collected in amber glass bottles (1000 mL). The bottles were rinsed several times with the water to be analyzed and filled till overflow to prevent loss of 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 at 4 °C until their analysis time.

IL-UA-ISFME procedure

In IL-UA-ISFME, 5.0 mL of sample solution was poured into a centrifuge tube with a conical bottom. Then, 0.5 mL of NaPF$_6$ (200 mg mL^{-1}) as an ion-exchange reagent was dissolved into the solution. To form water-immiscible [Bmim][PF$_6$] IL, 70 mg of water-miscible [Bmim][BF$_4$] IL was added to the aqueous sample solution. In order to disperse the hydrophobic IL through the sample, the test tube was transferred into an ultrasonic bath and sonicated for 5 min. Under this condition, the in-situ formed water-immiscible [Bmim][PF$_6$] IL was entirely dispersed into the aqueous media and hence, the analytes were immediately extracted into the fine drops of [Bmim][PF$_6$] IL. To accelerate phase separation and moving IL to the bottom of the test tube, the sample solution was centrifuged for 4 min at 4000 rpm. The upper phase was decanted-off and the enriched phase (approximately 10.0 μL) was diluted with acetonitrile to a final volume of 25 μL and then injected into HPLC-UV. Schematic of the presented microextraction is shown in Figure 1.
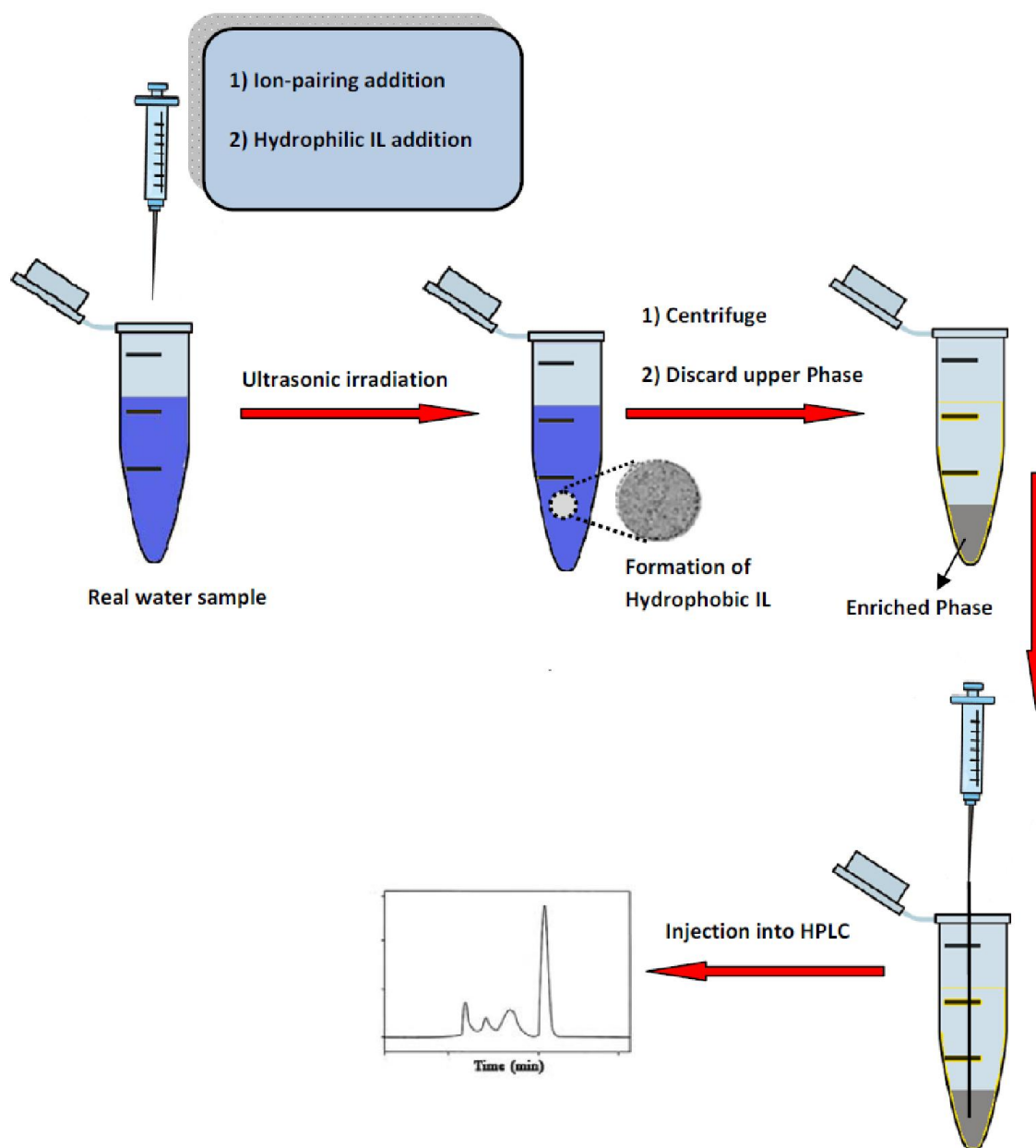
Figure 1. Schematic diagram of the proposed method for quantification of the PAHs.

Results and discussion

A one at a time approach was used to optimize the influential parameters within this work. A fixed concentration of all PAHs (25.0 μg L^{-1}) was performed in the optimization process. Quantifications were accomplished by calculating the peak areas from the average of three replicate measurements while blanks were run periodically to confirm the absence of contaminations.

The selection of hydrophilic ionic liquid and ion-exchange reagent

In IL-UA-ISFME, a water-immiscible IL is formed by addition of a water-miscible IL to sample solution containing an ion-exchange reagent. To select a desired water-miscible IL, significant points must be considered as follow: (1) hydrophilic property of IL (2) density of the in-situ formed hydrophobic IL (3) expense of IL (4) extraction capability of target analytes and (5) chromatographic behavior. In the point of hydrophilic feature, the ILs containing Cl^-, BF_4^- and $CF_3SO_3^-$ are water-miscible and ILs containing PF_6^- and $(CF_3SO_2)_2N^-$ are water-immiscible. It is well known that ionic compounds containing $(CF_3SO_2)_2N^-$ are approximately pricey while those containing BF_4^- are fairly low-priced [26]. As a result, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] and 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF$_4$] ILs, which match the discussed necessities, were selected for the evaluation. These ILs present reasonable hydrophilic characteristics, which is fitted with fundamentals of ISFME, however, in the case of [Hmim][BF$_4$] IL, the extraction recovery was lower than [Bmim][BF$_4$] IL. Hence, [Hmim][BF$_4$] IL was omitted in the assessment. Moreover, the density of the in-situ formed hydrophobic IL must be greater than water, conducive to be collected at the bottom of the test tube. Ultimately, to fulfill a bargain between all the points, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF4] IL was selected as an optimum hydrophilic IL. By dissolving this IL in aqueous media including NaPF$_6$ (ion-exchange reagent),it is feasible to acquire hydrophobic 1-butyl1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF$_6$] IL, which plays as the extraction solvent.

The effect of hydrophilic IL amount

The influence of [Bmim][BF$_4$] IL amount on the method performance was investigated in range of 20-110 mg. As shown in Figure 2, reproducible and sensitive signals were attained using 70 mg of [Bmim][BF$_4$] IL. It is clear that by growing the content of [Bmim][BF$_4$] IL, the volume of the hydrophobic IL (formed under these conditions) meaningfully enlarges, which causes a decline in analytical response. Consequently, a value of 70 mg was employed for the following experiments.
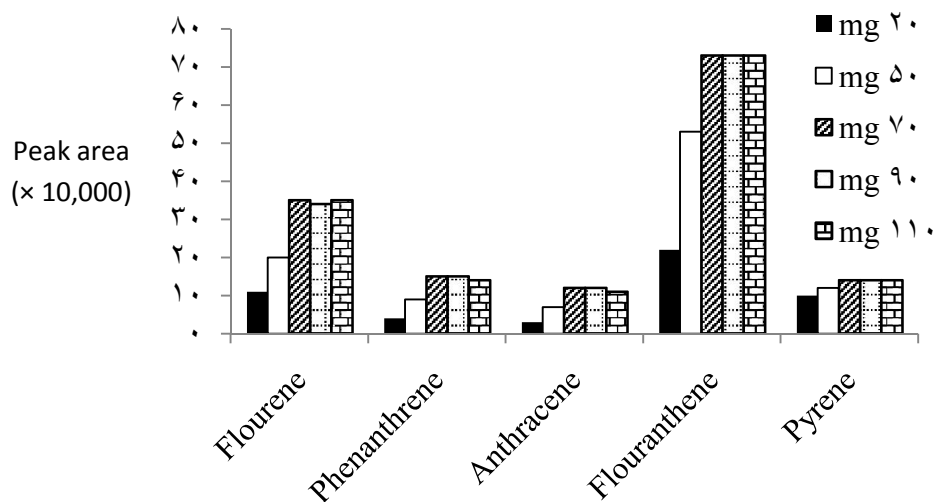
Figure 2. Influence of hydrophilic IL ([Bmim][BF$_4$]) amount on the extraction efficiency.

The effect of NaPF$_6$ amount

To generate water-immiscible [Bmim][PF6] IL, an extra amount of NaPF$_6$ was dissolved in an aqueous media. The effect of NaPF$_6$ quantity was examined in the range of 30-150 mg. As it can be seen in Figure 3, with growing the amount of this reagent, the peak area boosts up to 100 mg and after that, analytical signals acquire to steady conditions. Due to the common ion effect, the solubility of the ionic liquid decreases and obtains a stable condition so after a certain value no considerable change in the characteristic of the hydrophobic ionic liquid is occurred which leads to the steady signals. Accordingly, to obtain a balance among with sensitivity and reproducibility, 100 mg of the reagent was chosen as the optimum.
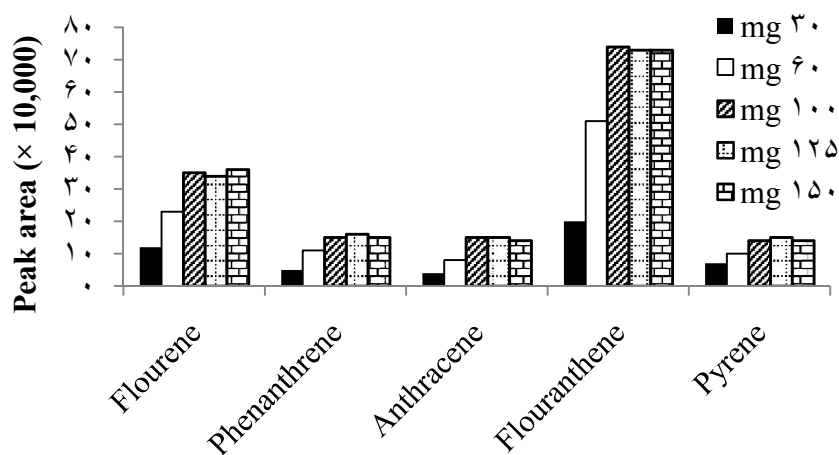

Figure 3. Effect of ion-pairing agent (NaPF$_6$) amount on the extraction performance.

The effect of salt addition

The addition of salt commonly magnifies the ionic strength, and therefore raises the extraction efficiency by the reason of salting-out effect [27]. For this aim, several concentrations (0%-25% w/v) of NaCl were added to the sample solution to examine its effect on the extraction efficiency (Figure 4). This can be clarified that by growing the viscosity of the sample solution, at higher concentrations of NaCl (> 15% w/v), diffusion of the analytes toward the extracting solvent becomes difficult. The maximum signal was achieved at the NaCl concentration of 15% w/v and noticed to decline afterwards. Reasoning from this fact, a fixed concentration of 15% w/v NaCl was applied as the optimum value.
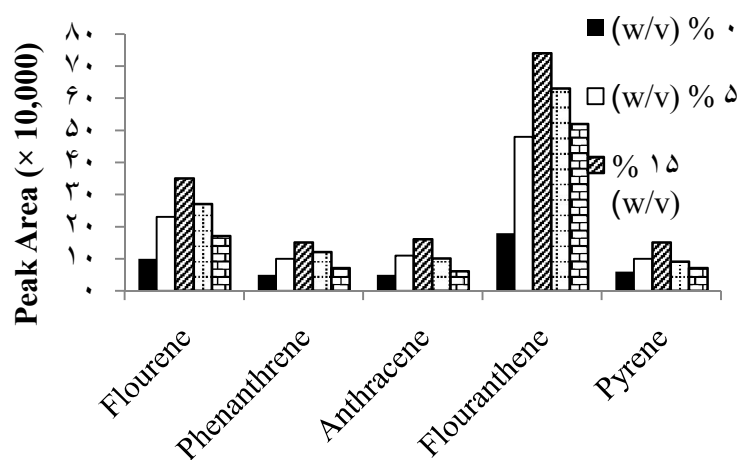

Figure 4. Impact of ionic strength on the extraction phenomenon.

The effect of sonication time

The mass transfer in IL-UA-ISFME is a process depend on equilibrium rather than exhaustive extraction and to obtain acceptable repeatability, it is needful to choose a suitable extraction time [28, 29]. In this context, ultrasound radiation was applied as a disperser agent, which remarkably enhances the extraction yield and the accelerate of the target analytes migration into the tiny droplet of [Bmim][PF6] IL. Herein, the sonication time profiles were investigated in the range of 1-12 min at the power of 50 W. As shown in Figure 5, by raising the values up to 5 min, the extraction efficiencies grow swiftly and afterwards remained nearly stable. It is noteworthy that longer extraction time can result in the loss of the extracting solvent and contraction of the extraction yields. Consequently, the exposure time of 5 min was selected as optimum in the subsequent experiments.
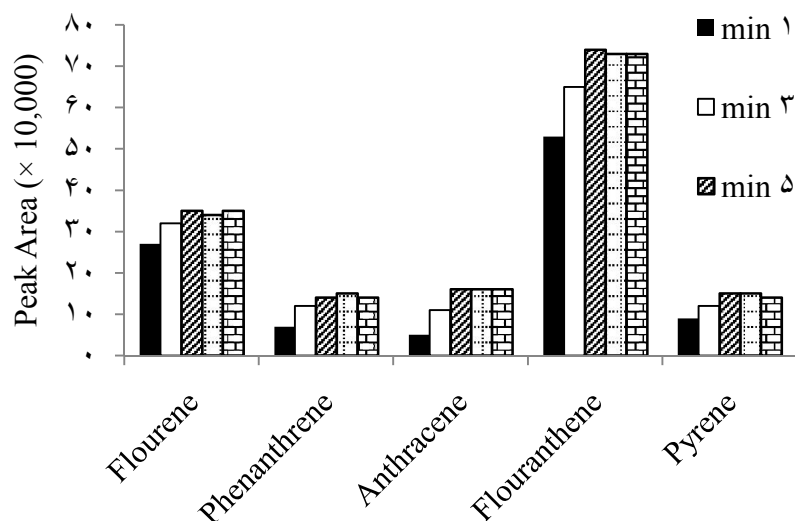
Figure 5. Ultrasonic irradiation time profile on the extraction yield.

The analytical performance

In order to ascertain the applicability of the method, calibration curves were plotted at the optimum conditions using spiked 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), the enrichment factors (EFs) and the relative standard deviations (RSDs) were calculated and summarized in Table 1. As shown in Table 1, LODs were in the range of 0.32-0.79 µg L^{-1} while linearity values varied in the ranges of 1 to 500 µg L^{-1} with correlation coefficient of 0.992 to 0.997. The EFs were in the range of103-121 while the precision of the method was investigated with 25.0 µg L^{-1} PAHs mixed standard solution and the RSDs for six replicate measurements varied from 3.8 to 5.2%.

Table 1. Some quantitative data achieved by using IL-UA-ISFME and HPLC-UV for the determination of the selected five PAHs.

Compound	LOD (µg L^{-1})[a]	r^2	LR (µg L^{-1})[c]	RSD%[d] (n = 6)	EF[e]
Fluorene	0.32	0.995	1.0-500	3.8	113
Phenanthrene	0.58	0.992	2.0-400	4.4	103
Anthracene	0.41	0.994	1.5-500	5.0	121
Fluoranthene	0.79	0.997	2.0-500	5.2	108
Pyrene	0.63	0.996	2.0-500	4.9	106

[a] *Limit of detection for S/N = 3.*
[b] *Limit of quantification for S/N = 10.*
[c] *Linear range.*
[d] *Relative standard deviation at concentration level of 25. 0 µg L^{-1} for each PAHs.*
[e] *Enrichment factor.*

A comparison between the proposed technique and the literature values for extraction and determination of PAHs using various methods are presented in Table 2.

Table 2. Comparison of the proposed USAEME method with other methods for determination of PAHs.

Extraction method	Detection System	LOD (µg L^{-1})	LR (µg L^{-1})	RSD%	Reference
FD-LPME[a]	GC-FID	0.07-1.67	0.25-400	1.1-12.6	[30]
HF-LPME[b]	GC-MS	0.005-0.01	0.50–50	≤ 11.3	[31]
SPME[c]	GC-MS	0.001-0.029	0.01–10	≤ 20	[32]
D-LPME[d]	HPLC-UV	0.35-0.6	1.2-12	4.4-6.0	[33]
EPA-8310	HPLC-FL	0.017-0.64	0.1-425	NM[e]	www.epa.gov
IL-UA-ISFME	HPLC-UV	0.32-0.79	1-500	≤ 5.2	Proposed method

[a] Floating drop-liquid phase microextraction.
[b] Hollow fiber liquid phase microextraction.
[c] Solid phase microextraction.
[d] Dynamic liquid phase microextraction.
[e] Not mentioned.

Analysis of environmental water samples

Placed at the optimum conditions, the method performance was verified by analyzing the analytes in the four different environmental water samples. The results showed that the real samples were free of PAHs contamination. To appraise the matrix effects, all the real samples were spiked with PAHs standards at various concentration levels. IL-UA-ISFME is a non-exhaustive extraction procedure and the relative recovery (determined using the ratio of the concentrations found in the real environmental sample and reagent water sample, spiked with the same amount of analytes), instead of the absolute recovery (used in exhaustive extraction procedures), was employed. The relative recovery experiments of the analytes are disposed in Table 3. The attained recoveries were between 90-106%, demonstrating that the method is not affected by the matrix in actual applications. Moreover, satisfactory RSD% values (below than 6.2%, *n* = 6) were obtained in the real sample analysis. The chromatograms obtained after performing IL-UA-ISFME-HPLC-UV for Jajroud River sample before and after spiking are presented in Figure 6 and proved no considerable intervention pointing to the analytical procedure.

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

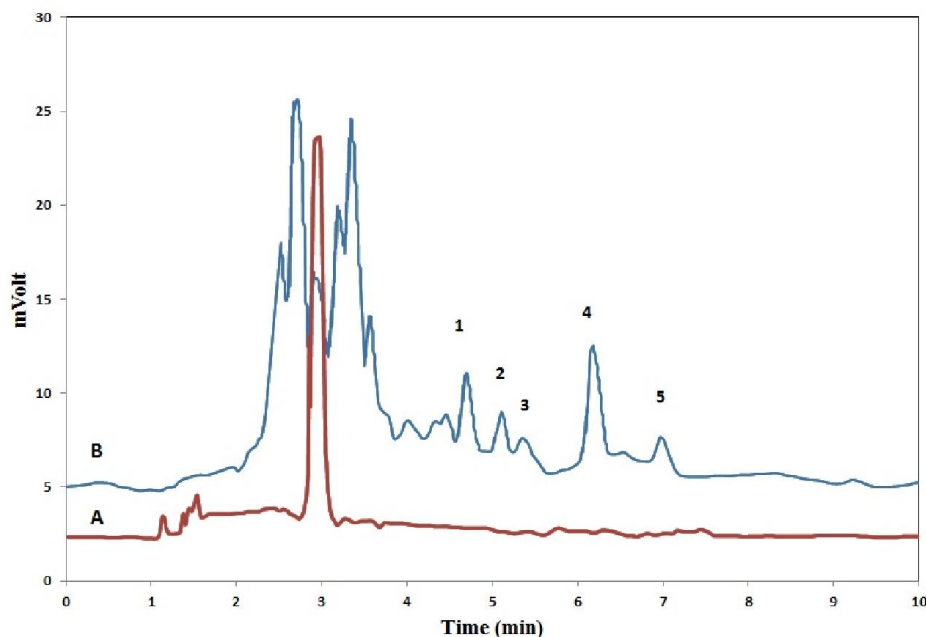| Sample	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
Caspian Sea (Sari, Iran), (2.0 µg L^{-1} added)					
PAHs concentration (µg L^{-1})	ND [a]	ND	ND	ND	ND
Found after spike (µg L^{-1})	2.1	1.8	1.8	1.9	2.1
Relative recovery%	105	90	90	95	105
RSD% (*n* = 6)	4.2	5.1	5.5	6.0	4.0
Persian Gulf (Mahshahr, Iran), (5.0 µg L^{-1} added)					
PAHs concentration (µg L^{-1})	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	4.5	5.3	5.2	4.6	4.7
Relative recovery%	90	106	104	92	94
RSD% (*n* = 6)	5.8	5.1	4.9	5.3	4.7
Jajroud River (Tehran, Iran), (25.0 µg L^{-1} added)					
PAHs concentration (µg L^{-1})	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	26.3	24.0	23.4	25.5	25.9
Relative recovery%	105	96	94	102	104
RSD% (*n* = 6)	5.5	6.2	4.6	5.6	5.4
Amirkabir Dam (Karaj, Iran), (50.0 µg L^{-1} added)					
PAHs concentration (µg L^{-1})	ND	ND	ND	ND	ND
Found after spike (µg L^{-1})	47.0	51.4	47.6	50.5	52.1
Relative recovery%	94	103	95	101	104
RSD% (*n* = 6)	5.0	5.9	4.2	5.5	5.7

[a] Not detected.

Figure 6. The chromatogram of Jajroud River sample (A): before and (B) after spiking PAHs at the concentration level of 25.0 μg L^{-1} of each analyte; (1): Fluorene, (2): Phenanthrene, (3) Anthracene, (4) Fluoranthene and (5) Pyrene.

Conclusion

This study outlined the successful development and application of IL-UA-ISFME method followed by HPLC-UV for the trace determination of selected five PAHs in environmental water samples. 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 matrixes in the real samples analysis. Besides, by applying IL as extracting solvent, the proposed method is a green approach towards sample preparation in analytical chemistry. The entire technique presents a cost-effective and prompt path for the screening purposes. Hence, putting all the advantages together, the method possesses great potential to be employed in the other applications.

Disclosure statement

The authors declared no conflict of interest.

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