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Development of a novel ultrasound-assisted surfactant-enhanced emulsification microextraction method and its application to the analysis of eleven polycyclic aromatic hydrocarbons at trace levels in water

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ABSTRACT

A novel ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) technique has been proposed by using low-density extraction solvents. In the proposed technique, Tween 80 and cyclohexane were injected into 5-mL glass test tubes with conical bottoms, containing 5.00 mL of a water sample that was located inside the ultrasonic bath. When the extraction process was finished, the glass test tube was sealed with a rubber plug and then placed upside down in a centrifuge. The finely dispersed droplets of cyclohexane collected at the conical bottom of test tube because the density of cyclohexane is less than of water, and the PAHs were concentrated in the cyclohexane. Next, 5 μL of the cyclohexane that collected at the conical bottom was removed using a 10-μL microsyringe and injected into high performance liquid chromatography coupled with fluorescence detection (HPLC-FLD) for analysis. The proposed method avoided the use of chlorinated solvents, which have been widely used as extraction solvents in a normal UASEME assay. Parameters that affected the extraction efficiency, such as the type and volume of the extraction solvent, the type and concentration of the surfactant, and the ultrasound emulsification time and salt addition, were investigated and optimised for the method. Under the optimum conditions, the enrichment factors ranged between 90 and 247. The limits of detection of the method were 0.6–62.5 ng L^{-1}. Good recoveries and repeatability of the method for the eleven PAHs were also obtained. The proposed UASEME technique has been demonstrated to be simple, practical and environmentally friendly for the determination of PAH residues in real water samples.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants. Such persistent compounds damage the entire ecosystem, especially the aquatic environment [1]. The carcinogenic effect of many PAHs has attracted worldwide concern [2]. Many environmental agencies have established very low levels of PAHs for potable and natural waters, intending to protect the environment and human health [3]. For instance, for the quality of water for human consumption, the U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) have proposed routine monitoring for benzo[a]pyrene (B[a]P). According to the EPA, maximum concentration of B[a]P should not exceed 200 ng L^{-1} [4], whereas the WHO has established the maximum permissible concentration of B[a]P to be 700 ng L^{-1} [5]. In addition to B[a]P, the European Union, in Directive 98/83/EC, has regulated fluoranthene (Flt), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[g,h,i]perylene (B[g,h,i]P) and indeno[1,2,3-c,d]pyrene (I[1,2,3-c,d]P). Maximum values for contaminant levels were set at 10 ng L^{-1} for the highly toxic B[a]P and 100 ng L^{-1} for the sum of remaining PAHs [6]. The European Union has also fixed very restrictive limits for these compounds in different types of superficial waters [7,8]. The limits for B[a]P were fixed at 50 ng L^{-1} as an annual average value and 100 ng L^{-1} as the maximum admissible concentration for different types of superficial waters.

Most of the problems linked with the analysis of PAHs in water are associated with their low concentration levels fixed by the EPA and EU as well as the extraction steps. These compounds are generally extracted from water samples either by liquid–liquid extraction (LLE) [9–11] or solid-phase extraction (SPE) [12]. They are often analysed by high performance liquid chromatography coupled with fluorescence detection (HPLC-FLD) [13]. However, modern trends in analytical chemistry can be used for the sim-

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plification of sample preparation. For example, in the last few years, microextraction techniques are playing an important role in the determination of PAHs. Solid-phase microextraction (SPME) [14], stir-bar sorptive extraction (SBSE) [15] and liquid-phase microextraction (LPME) [16,17] have been developed as alternative techniques to the classical LLE and SPE methods.

Recently, much attention is being paid to the development of miniaturized, more efficient and environmentally friendly extraction techniques, which could greatly reduce organic solvent consumption [18,19]. For this purpose, several different types of LPME techniques have emerged for sample preparations. More recently, a relatively new mode of LPME, the dispersive liquid–liquid microextraction (DLLME), has also been developed [20–26]. The advantages of the DLLME method include rapidity, low cost, simplicity of operation and a high enrichment factor. However, to enhance the dispersion of the extraction solvent in the aqueous sample phase, the use of a water-miscible organic dispersive solvent is required in DLLME, although its use could decrease the partition coefficient of analytes into the extraction solvent. Another disadvantage of DLLME is that a majority of the extraction solvents used in the reported DLLME methods are halogenated hydrocarbons, which are environmentally hazardous.

Very recently, a novel microextraction technique, named ultrasound-assisted emulsification microextraction (UAME), has been developed by Garcia-Jares and co-workers [27]. In UAME, a microvolume of water-immiscible extraction solvent is dispersed into an aqueous sample solution by ultrasound-assisted emulsification without using any dispersive solvent. The ultrasound-assisted emulsification is usually carried out either at 25 °C for 10 min [27,28] or at 35 °C for 5 min [29].

Lately, using surfactants as emulsifiers in the above UAME technique, Wang et al. introduced a new sample pre-treatment method called ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) for the determination of certain carbamates in water samples [30]. In the UASEME technique, the extraction procedure took place under the combined action of ultrasound waves and surfactant, thus the analysis time was greatly shortened. It is well known that surfactants, or surface-active agents, are amphiphilic molecules. Their heads are polar, or hydrophilic, and their tails are hydrophobic. The tail is generally a hydrocarbon chain with a different number of carbon atoms, which may be linear or branched, and may also contain aromatic rings. Surfactant could serve as an emulsifier to enhance the dispersion of the water-immiscible phase into the aqueous phase. The application of a surfactant as an emulsifier in UASEME would combine the advantages of both DLLME and UAME. The surfactant will accelerate the formation of fine droplets from the extraction solvent in an aqueous sample solution under ultrasound radiations, thus decreasing the extraction time. After extraction, the two phases can be readily separated by centrifugation. However, in both UASEME and DLLME, due to the difficulty of collecting microvolumes of flouted organic solvents, the selected extraction solvent must be denser than the aqueous samples [31,32]. Some common LLE solvents [33] and their densities, including alkanes, cyclanes, alcohols, ethers, ketones and acetates, are less dense than water, and their application in UASEME and DLLME methods would be problematic.

In the present study, a simple and fast UASEME method based on the dispersion of microvolumes of low-density organic solvents (e.g., cyclohexane,1-octanol,1-dodecanol and tetradecane) in aqueous samples is reported below. The microvolumes of organic solvents and emulsifier were withdrawn using a microsyringe and injected into the sample solution. After emulsification, the centrifuge vial was sealed and turned upside down and then centrifugated, the two phases can be readily separated. The conical top of the centrifuge vial makes it suitable for easy collection of microvolumes of the organic solvent that floats on the surface of the aqueous sample. The applicability of the proposed method was studied for the determination of PAHs in real water samples. Meanwhile, in all UASEME methods, solvents of higher density than water (i.e., chlorinated solvents) have been used, and there are no reports describing the use of solvents of lower density than water.

2. Experimental

2.1. Reagents and materials

Naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), benzo[a]anthracene (B[a]A), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P) and dibenzo[a,h]anthracene (D[ah]A) were obtained from Accu Standard Inc. (New Haven, USA). Cyclohexane, 1-octanol, 1-dodecanol, and tetradecane were analytical grade and purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Surfactants (Triton-10, SDS, CTAB, Tween 80) were chemically pure and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HPLC-grade methanol was obtained from Tedia Company Inc. (OH, USA). Sodium chloride (Zhanyun Chemical Co., Ltd., Shanghai, China) was used in the subsequent experiment. Deionized water was purified on a Milli-Q water purification system (Millipore Corporation, Billerica, MA, USA).

Tap water was collected from our laboratory. Rainwater was collected on October 13th, 2010 (Wuhan, China) and waste water was from Central China Normal University (Wuhan, China). All the solvents and water samples were filtered through a 0.45-μm membrane to eliminate particulate matter before analysis.

A mixture stock solution containing the above-mentioned PAHs at 10 ng mL^{-1} was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with double-distilled water in a 10-mL volumetric flask. All the standard solutions were stored at 4 °C, protected from the light, and were prepared daily by dilution of stock solutions with distilled water to the required concentrations.

2.2. Apparatus

A 40-kHz and 0.138-kW ultrasonic water bath with temperature control (Kunshan Ultrasonic Instrument Co., Ltd., Jiangsu, China) was applied to emulsify the organic solvent. Next, 50.0-μL Hamilton syringes (Bonaduz, Switzerland) were used to inject the organic solvent and surfactant solution into aqueous samples. Then, 5-mL centrifuge glass vials were used for the extraction and collection procedure (Fig. 1). The centrifuge process was produced on an 80-2 centrifuge (Changzhou Guohua Electric Appliance Co., Ltd., Jiangsu, China). A 50.0-μL Hamilton gas-tight syringe was applied for the collection of floated organic solvent and injection into the HPLC. Separation and detection of PAHs were performed using an Agilent 1200 high performance liquid chromatography system (Agilent Technologies, Palo Alto, CA, USA) and fluorescence detector (FLD). An Agilent Eclipse PAH column (250 mm × 4.6 mm, i.d.: 5 μm) was applied to separate PAHs. The column temperature was set at 30 °C. Acetonitrile and water were employed as the mobile phase. The gradient elution started with 60% water and 40% acetonitrile, after which the acetonitrile content was increased to 60% (0–26 min), 90% (26–31 min) and 100% (31–40 min). The flow rate was 0.8 mL min^{-1} at 0–22 min, which was then raised to 1.0 mL min^{-1} at 22–40 min. Finally, 5 min were necessary to re-establish the initial conditions. The detection wavelengths were chosen as follows: 0–13 min (λ_{ex} = 221, λ_{em} = 337), 13–19 min (λ_{ex} = 227, λ_{em} = 315), 19–23 min (λ_{ex} = 252,

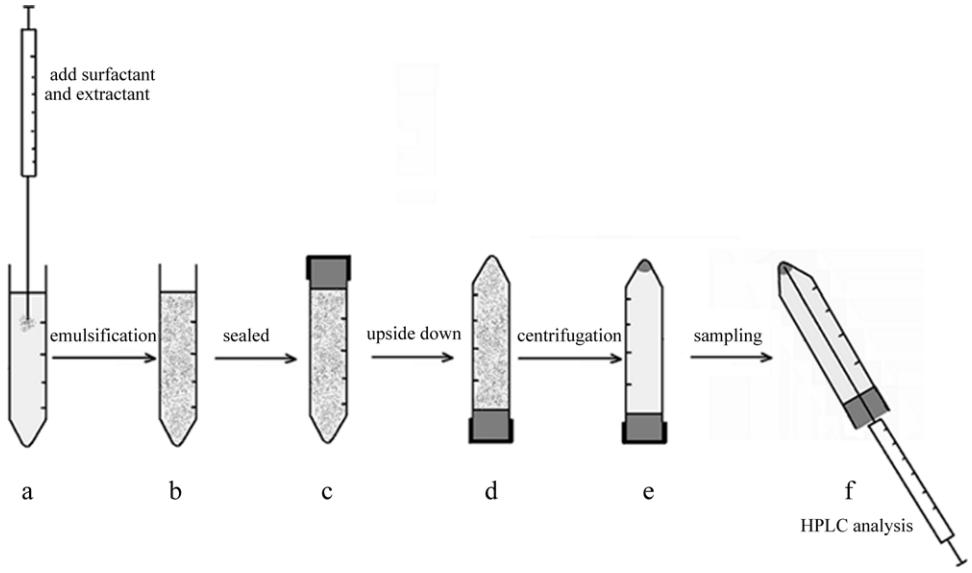

Fig. 1. Schematic representation of USAEME (a) 20 μL of cyclohexane solvent and 10 μL of Tween 80 solution were injected rapidly into a 5-mL glass test tube with a conical bottom containing 5.00 mL of double-distilled water. (b) A cloudy solution (water/Tween 80/cyclohexane) was formed in a test tube using sonication. (c) A rubber plug was inserted into the test tube to seal it. (d) It was turned upside down. (e) After centrifuging (3500 rpm) for 3 min, the fine, dispersed droplets of cyclohexane were collected at the conical bottom of test tube. (f) 10 μL of cyclohexane, which was collected at the conical bottom, was removed using a 50-μL microsyringe and was injected into the HPLC for analysis.

λ_{em} = 372), 23–28.7 min (λ_{ex} = 237, λ_{em} = 460), 28.7–34 min (λ_{ex} = 270, λ_{em} = 360), and 34–40 min (λ_{ex} = 270, λ_{em} = 390).

2.3. UASEME procedure

Fig. 1 shows the schematic procedure of the UASEME. A 5.00-mL aliquot of water containing 6% (w/v) NaCl was placed in a 5-mL glass test tube with a conical bottom. Next, 20 μL of cyclohexane as an extraction solvent, and 10 μL of 0.5 g L^{-1} Tween 80 as an emulsifier (the concentration of Tween 80 in sample solution was 1.0×10^{-3} g L^{-1}) were injected into the sample solution. The resulting mixture was then immersed into an ultrasonic bath at 25 ± 2 °C for 1 min of sonication. Then, a rubber plug was inserted into the test tube to seal it. Next, it was turned upside down and centrifuged at 3500 rpm for 3 min. After this process, the finely dispersed droplets of cyclohexane were collected at the conical bottom of the test tube; 10 μL of cyclohexane, which had collected at the conical bottom, was removed using a 50.0-μL microsyringe and was injected into the HPLC for analysis.

3. Results and discussion

3.1. Effect of type and volume of extraction solvent

For the UASEME procedure, the extraction solvent should meet the following requirements: (a) it should be less dense than water; (b) it should have low solubility in water and (c) it should form a stable emulsion system in the presence of an emulsifier after sonication. 1-Octanol, 1-dodecanol, n-tetradecane and cyclohexane were tested in the experiment. As shown in Fig. 2, the highest extraction efficiency was obtained when using cyclohexane as an extraction solvent. Therefore, cyclohexane was selected.

To optimise the volume of the extraction solvent, different volumes of cyclohexcane (15, 20, 30, 40, and 60 μL) were evaluated. The results indicated that the peak areas of all analytes reached maximum while using 20 μL of cyclohexane. The peak areas of all analytes decreased gradually with the increase of the cyclohexane volume because the concentration of the target analytes in the extraction solvent was diluted to some degree while using higher volumes of extractant. Therefore, 20 μL of cyclohexane was used for further experimentation.

3.2. Effect of type and concentration of surfactant

Choosing a surfactant is of great importance for obtaining a satisfactory initial concentration and extraction effect for analytes. Surfactant, which serves as an emulsifier, could accelerate the emulsification of the water-immiscible extraction solvent into the aqueous solution under ultrasound radiation. After emulsification, the extraction solvent is dispersed as fine droplets in the sample solution, which is favourable for the mass transfer of the analytes from aqueous to the organic phases. The effect of different surfactants (SDS, CATB, Triton X-10 and Tween 80) on the extraction

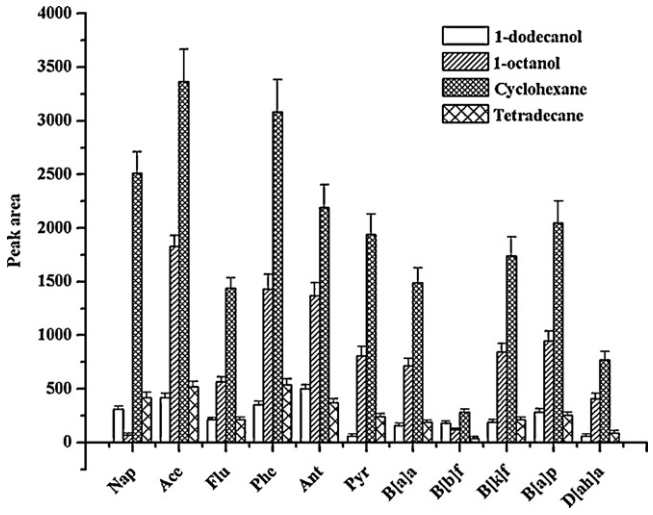

Fig. 2. Selection of the extraction solvent. Concentration of the standard mixed solution: 10 ng mL^{-1}; volume of the sample: 5 mL; extractant: 1-dodecanol, 1-octanol, cyclohexane and *n*-tetradecane; volume of extractant: 20 μL; surfactant (Tween 80) concentration: 1.0×10^{-3} g L^{-1}; extraction time: 1 min; salt addition: 6% (w/v), room temperature; error bars represent the standard deviation of the mean enrichment factors for *n* = 3 replications.

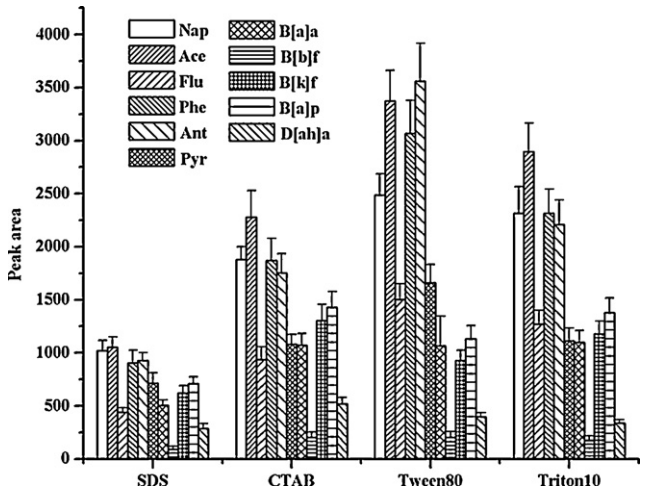

Fig. 3. Selection of surfactant. Concentration of the mixture standard solution: 10 ng mL^{-1}; volume of the sample: 5 mL; extractant (cyclohexane) volume: 20 μL; surfactant: SDS, CTAB, Tween 80, Triton X-10; extraction time: 2 min; salt addition: 6% (w/v), room temperature; error bars represent the standard deviation of the mean enrichment factors for $n = 3$ replicates.

recovery is given in Fig. 3. As a result, among the surfactants investigated, SDS and CTAB gave a lower extraction recovery for the analytes than did Tween 80 and Triton X-10. Tween 80 and Triton X-10 gave a comparable result for the extraction of the analytes. SDS and CTAB are ionic-type surfactants with higher hydrophilicity. Tween 80 and Triton X-10 are polyoxyethylene-type, non-ionic surfactants. Maybe the nonpolar analyte PAHs were easily emulsified by the non-ionic surfactant. So the extraction efficiency of PAHs in the presence of ionic surfactants is less efficient in comparison with non-ionic surfactants. Based on the experimental result, selecting either Tween 80 or Triton X-10 as the surfactant is reasonable. Considering that Tween 80 is more commonly used and is cheaper than Triton X-10 in China, Tween 80 was selected as an appropriate surfactant for subsequent studies.

Surfactant concentration is another important parameter for effective extraction. The influence of the Tween 80 concentration was investigated by changing its concentration from 0, 0.4, 0.6 1.0, 5.0, 10.0, 20.0, 50.0×10^{-3} g L^{-1} (Fig. 4). The surfactant molecules can be associated in an aqueous solution to form molecular aggregates called micelle. The minimum concentration of the surfactant required for this phenomenon to occur is called critical micelle concentration (CMC). The results indicated that when the concentration of Tween 80 in the sample solution was higher than its CMC (1.4×10^{-2} g L^{-1}) [32], the extraction efficiency began to decrease. The reason for this could be that a fraction of the analytes could incorporate into the micelles when the surfactant concentration was higher than the CMC, thus resulting in an increased solubility of the analytes in the sample solution. Based on the experimental results, the concentration of Tween 80 was chosen at 1.0×10^{-3} g L^{-1}.

3.3. Effect of ionic strength

In our salting out effect, salt addition decreases the solubility of the analytes in the aqueous phase and improves the extraction efficiencies. Therefore, the effect of NaCl amount on the extraction efficiency was tested in the range of 0–18% (w/v). The result demonstrated an improvement for all analytes when 6% NaCl was added. Furthermore, salt addition enhanced the phase separation after centrifugation, and the extraction solvent was easily collected at the conical end of the vial. As a result, 6% NaCl (w/v) was used in further experiments.

3.4. Effect of extraction time and temperature

Ultrasound extraction time is defined as the interval from the beginning of the emulsification to the moment before centrifugation. The effect of time on the extraction efficiency was examined in the range of 0–3 min. As a result, the extraction equilibrium could be achieved within 1 min. It revealed that the contact surface between extraction solvent and aqueous sample was infinitely larger and the equilibrium state was achieved within 1 min. As a result, 1 min was chosen for future experiments.

Temperature is another important parameter that can affect the emulsification process. To investigate the effect of temperature, different temperatures ranging from 25 to 45 °C were tested. The results indicated that the temperature had no remarkable effect on extraction. The occurrence of this phenomenon may be because the surfactant enhanced the contact area between the extraction solvent and the aqueous solution. Therefore, the extraction process was carried out at 25 °C.

3.5. Validation of the method

Under the optimum conditions, some parameters of the proposed UASEME–HPLC-FLD method such as linearity (LR), limits of detection (LODs), enrichment factors (EFs) and reproducibility

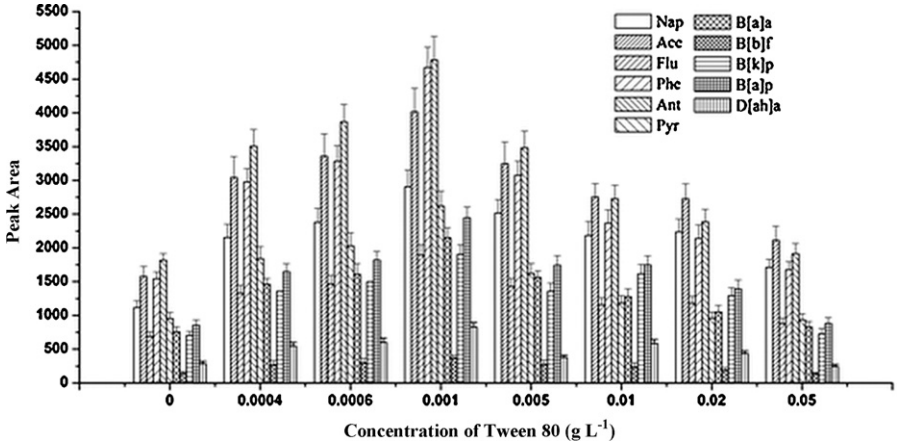

Fig. 4. Selection of surfactant concentration. Concentration of mixture standard solution: 10 ng mL^{-1}; volume of the sample: 5 mL; extractant (cyclohexane) volume: 20 μL; surfactant: Tween 80; extraction time: 1 min; salt addition: 6% (w/v), room temperature; Error bars represent the standard deviation of the mean enrichment factors for $n = 3$ replicates.

Table 1
Analytical performance data for the PAHs by the UASEME technique.

Analytes	LR[a] (ng L^{-1})	r	LOD (ng L^{-1})	EF[a]	RSD[b] (%) (n = 6)
Nap	2–20000	0.9991	0.6	213	4.4
Ace	10–20000	0.9992	3.1	247	5.5
Flu	10–20000	0.9995	4.2	119	7.9
Phe	2–10000	0.9986	0.7	166	9.4
Ant	1–10000	0.9984	3.2	213	10.8
Pyr	50–20000	0.9968	16.1	187	5.4
B[a]a	10–20000	0.9925	3.6	246	10.7
B[b]f	50–20000	0.9921	62.5	179	2.3
B[k]f	10–10000	0.9986	3.7	137	1.9
B[a]p	1.0–20000	0.9949	3.3	154	1.8
D[ah]a	10–20000	0.9933	4.1	90	8.1

[a] Extraction conditions: sample volume, 5 mL; surfactant (Tween 80) concentration: 4.0×10^{-4} mol L^{-1} Tween 80, extraction solvent (cyclohexcan) volume: 20 μL; salt addition: 6% (w/v); room temperature; extraction time: 1 min.
[b] Relative standard deviation.

were investigated. As shown in Table 1, calibration curves were drawn in the concentration range of 10–2000 ng L^{-1} with respect to Ace, Flu, B[a]A, B[a]P and D[ah]A, 10–1000 ng L^{-1} for Ant and B[k]F, 50–2000 ng L^{-1} for Pyr and B[b]F, 2–2000 ng L^{-1} for Nap and 2–1000 ng L^{-1} for Phe, respectively. Good LR were obtained for all PAHs, with correlation coefficients (r) ranging from 0.9921 to 0.9995 and with LODs in the range of 0.6–62.5 ng L^{-1} for PAHs. The EFs of the 5-mL aqueous sample ranged between 90 and 247. The precision of the proposed method was evaluated in terms of reproducibility (RSD% <10.8, n = 6) at 500 ng L^{-1} of each PAHs.

In the comparison of the proposed method with other techniques, the proposed method showed its advantages over SPE, SPME, DLLME, DLLME-SFO and UAME in terms of LODs and extraction time (Table 3). Furthermore, the proposed method provided higher EFs than that of DLLME-SFO–HPLC-VWD.

3.6. Application of the method

The optimised UASEME method was applied to the extraction of PAHs in tap, rain and wastewater samples. As can be seen in Fig. 5 and Table 2, the tap water suffered from contamination of 162 ng L^{-1} Nap, 56 ng L^{-1} Ace and 207 ng L^{-1} Flu, whereas rainwater and wastewater were contaminated by different levels of Nap, Ace, Flu, Phe, Ant and B[k]F. It was revealed that this method provided low LODs for PAHs analysis. The recovery was evaluated by a sample solution spiked with tested analytes at concentrations of

Table 2
Relative recoveries obtained in the determination of PAHs in spiked tap, rain and waste water samples.

Compounds	Spiked (ng L^{-1})	Tap water (n = 6)			Rain water (n = 6)			Waste water (n = 6)		
		Found (ng L^{-1})	RR (%)	RSD (%)	Found (ng L^{-1})	RR (%)	RSD (%)	Found (ng L^{-1})	RR (%)	RSD (%)
Nap	0	19			162			268		
	50	73	108	4.5	202	80	7.2	327.5	119	5.9
	500	544	105	5.7	677	103	5.3	798	106	4.1
Ace	0	nd			56			74		
	50	55.5	111	6.1	96	80	6.8	134	120	6.2
	500	520	104	4.2	576	104	4.1	604	106	3.6
Flu	0	nd			207			205		
	50	54.5	109	5.6	252	90	6.3	261.5	113	5.8
	500	510	102	3.8	556	100	5.9	515	103	3.9
Phe	0	30.0			267			309		
	50	84.5	109	7.6	315.5	97	7.2	367	116	6.2
	500	545	103	5.8	772	101	4.6	809	100	4.3
Ant	0	nd			55			54		
	50	53.5	107	6.4	93.5	77	5.8	114	120	6.7
	500	455	91	3.7	480	85	3.9	609	111	4.5
Pyr	0	nd			nd			nd		
	50	46.5	93		36.5	73	7.8	58	116	5.8
	500	570	114		495	99	6.2	500	100	3.2
B[a]A	0	nd			nd			nd		
	50	55.5	111		59.5	119	5.4	51	102	6.5
	500	535	107		570	114	3.2	465	93	3.8
B[a]F	0	nd			nd			nd		
	50	55.5	111		52.5	105	4.8	42.5	85	5.3
	500	480	96		565	113	2.9	400	80	3.7
B[k]F	0	nd			27			15		
	50	58.5	117		79.5	105	6.1	70	110	4.8
	500	460	92		532	101	5.3	520	90	3.6
B[a]P	0	nd			nd			nd		
	50	58.5	117		41.5	83	5.7	46.5	93	5.3
	500	530	106		565	113	3.9	415	83	3.1
D[ah]A	0	nd			nd			nd		
	50	58	116		41.5	83	6.4	44	88	5.7
	500	385	77		400	80	3.4	430	86	3.4

Table 3
Comparision of UASEME method with other published methods for determination of PAHs.

Extraction method	Detection system	LR (ng L^{-1})	LOD (ng L^{-1})	RSD (%)	EF	Time (min)	Refs.
MWCNTs-SPE[a]	GC–MS[h]	20–5000	2.0–8.5	1.2–12.1	–	30	[12]
PDMS/DVB-SPME[b]	GC–MS	10–5000	0.07–0.76	6.1–11.8	–	84	[14]
SBME[c]	GC–MS	0–200	0.1–7.3	2.7–14.7	–	720	[15]
DLLME[d]	GC–FID[i]	20–200000	7–30.0	1.4–10.2	603–1113	1.5	[20]
DLLME-SFO[e]	HPLC-VWD[j]	100–50000	45–1100	1.3–4.4	88–118	5	[24]
UAME[f]	GC–FID	50–100000	20–50	≤7.9	1776–2714	7	[28]
UASEME[g]	HPLC-FLD[k]	2–20000	0.6–62.5	1.8–10.8	90–247	1	This work

[a] Multi-walled carbon nanotubes-solid phase extraction.
[b] Polydimethylsiloxane–divinylbenzene fiber-solid phase microextraction.
[c] Stir bar sorptive extraction.
[d] Dispersive liquid–liquid microextraction.
[e] Dispersive liquid–liquid microextraction based on the solidification of floating organic droplet.
[f] Ultrasound-assisted emulsification microextraction.
[g] Ultrasound-assisted surfactant enhanced emulsification microextraction.
[h] Gas chromatography–mass spectrometry.
[i] Gas chromatography–flame ionization detector.
[j] High performance liquid chromatography with UV detector.
[k] High performance liquid chromatography with FLD detector.

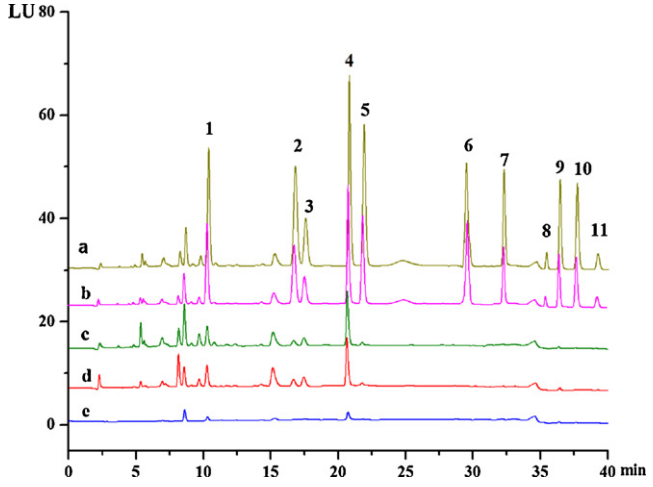

Fig. 5. Chromatograms of blank tap water (e), blank rainwater (d), blank wastewater (c), wastewater samples spiked with 10 ng mL^{-1} of PAHs treated without Tween 80 (b), and wastewater samples spiked with 10 ng mL^{-1} of PAHs treated with Tween 80 (a). The samples were analysed via the proposed UASEME and HPLC-FLD method. Peak identification: (1) naphthalene, (2) acenaphthene, (3) fluorene, (4) phenanthrene, (5) anthracene, (6) pyrene, (7) B[a]A, (8) B[b]F, (9) B[k]F, (10) B[a]P, and (11) D[a,h]A.

50 ng L^{-1} and 500 ng L^{-1}, and the results are listed in Table 2. Satisfactory relative recoveries in the range of 73–120% and 77–114% were obtained, respectively.

4. Conclusion

In the present study, low density organic solvents were used in the UASEME method for extraction and determination of PAHs in tap, rain and wastewater samples. The proposed method avoids using chlorinated solvents that are commonly used as extraction solvents in UASEME and DLLME. The conical bottom glass centrifuge vials were used for emulsification, centrifugation and easy collection of the floating organic solvents on the surface of the aqueous samples. These vials can be utilised in other dispersive or emulsification-based microextraction techniques. The results of optimization showed that the emulsification temperature and the equilibrium time have no significant effect on the extraction efficiency of the PAHs using this method. The higher independence of extraction efficiency to the above parameters leads to a more precise and robust method that can be suitable for analysis of the PAHs in complex matrices. Under optimised working conditions, EFs of up to 247 were obtained from the targeted analytes, allowing us to reach LODs in the level of ng L^{-1} of the PAHs with an acceptable precision. Also, the extraction time for the proposed method only takes a few seconds and is comparable with the DLLME method. The proposed method is, therefore, an efficient, rapid, simple and cheap microextraction method that can serve as a complementary technique for DLLME and USAEME methods, which have been used with organic solvents that are more dense than water samples.

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