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Extraction and determination of polycyclic aromatic hydrocarbons in water samples using Stir bar sorptive extraction (SBSE) combined with dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO) followed by HPLC-UV

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Abstract

Stir bar sorptive extraction (SBSE) combined with dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO) was developed for the extraction and determination of some polycyclic aromatic hydrocarbons (PAHs) in different aqueous samples. The extracted PAHs were separated and determined using high performance liquid chromatography–ultraviolet detection (HPLC-UV). Some important extraction parameters were studied and optimized. The new SBSE-DLLME-SFO method provided high enrichment factors in the range of 1630-2637. The calibration graphs were linear in the range of 0.02-400 μg L^{-1} and the limits of detection (LODs) were in the range of 0.0067-0.010 μg L^{-1} for this technique. The optimized method exhibited a good precision level with relative standard deviations (RSDs%) values between 2.17% and 6.92%. The proposed method was successfully applied to the extraction of three PAHs in different spiked water samples.

Keywords: Dispersive liquid–liquid microextraction, Solidification of floating organic drop, Stir bar sorptive extraction, Polycyclic aromatic hydrocarbons

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic compounds, which are formed during the incomplete burning of organic matters by natural processes such as carbonisation. These compounds, which can be found in the environment (atmosphere, soil and water), possess significant toxicity potency of carcinogenic and mutagenic effects and can cause endocrine disruption.[1-3] PAHs are listed as priority pollutants by the US Environmental Protection Agency (EPA).[1-5] Hence, determination of PAHs in environment is very important and essential for human health.

Several samples pretreatment techniques such as liquid–liquid extraction (LLE)[6], solid-phase extraction (SPE),[7,8] cloud-point extraction (CPE),[9] hollow fiber liquid-phase microextraction (HF-LPME),[10,11] miniaturized homogeneous liquid–liquid extraction (MHLLE)[12] and solid-phase microextraction (SPME) based on TiO_2 nanotube array[13-16] and multiwall carbon nanotubes[17-19] have already been developed for the extraction of PAHs.

In recent years, Assadi and co-workers demonstrated a novel microextraction method called dispersive liquid–liquid microextraction (DLLME).[20-23] DLLME is based on a ternary solvent system in which a mixture of extracting and dispersive solvent is rapidly injected into an aqueous sample containing the analytes of interest, which caused formation of a cloudy solution. The main advantages of this technique are simplicity, rapidity of operation, high enrichment factor and low consumption of extraction solvent. Moreover, not only DLLME is a suitable sample preparation technique for a wide range of analytical instruments, but also it can be easily combined with most other sample preparation methods. A novel dispersive liquid–liquid microextraction method based on the solidification of floating organic drop (DLLME–SFO) was introduced by Leong et al.[24] It is based on DLLME and the solidification of floating organic drop.[20,25] In this method solvents with the densities lower than water are used and the floated extractant is solidified to be easily collected for analysis.

Recently, stir bar sorptive extraction (SBSE) has been proposed as a novel sample preparation method for the enrichment of priority organic compounds from food, environmental and biomedicinal aqueous matrices at trace level.[26-30] In SBSE, the sorbent (a layer of polydimethylsiloxane, PDMS) is coated on a magnetic stir bar and the liquid sample is stirred with this bar. After extraction, the trapped analytes on the bar can be desorbed, either thermally

for gas chromatography or into a solvent for liquid chromatography.[28] The extraction mechanism and the advantages of SPME and SBSE are identical, whereas the enrichment factor of SBSE is ~100 times higher than that of SPME.

The aim of this work was the combination of stir bar sorptive extraction (SBSE) with dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO) for highly efficient extraction and determination of some polycyclic aromatic hydrocarbons (PAHs) using HPLC-UV. The influence of different experimental parameters on the performance of both steps were thoroughly investigated and discussed. Finally, the applicability of the proposed method was tested by the determination of PAHs in water samples.

2 Experimental

2.1 Chemicals

PAHs (fluorene, fluoranthene, benz[a]anthracene, pyrene and benzo[a]pyrene) were purchased from Sigma- Aldrich. HPLC grade solvents acetonitrile, acetone, methanol, 1-undecanol and 1-decanol were obtained from Merck. Stock solutions of PAHs (1000 mg L^{-1}) were prepared in acetonitrile and stored in freezer at -10 ^{o}C. The working standards were prepared by subsequent dilution of stocks. Water samples were collected from Kermanshah (Iran) in glass bottles and stored in the dark at 4 ^{o}C before analysis.

2.2 Apparatus

Chromatographic analysis was carried out by a Knauer HPLC with Chromgate software version 3.1 having Smartline 1000-1 and Smartline 1000-2 binary pumps, Smartline UV 2500 variable wavelength programmable detector (Berlin, Germany), on-line solvent vacuum degasser and manual sample injection with a 20µL injection loop (model 7725i, Rheodyne, Cotati, CA, USA). Separations were carried out on an H5-ODS C18 column (15 cm × 4.6 mm, with 5 µm particle size) from Anachem (Luton, UK). A mixture of water/acetonitrile (30:70 v/v) at a flow rate of 0.8 mL min^{-1} was used as a mobile phase in isocratic elution mode and the detection was

performed at the wavelength of 270 nm. A centrifuge (Hettich, EBA 20, Tuttlingen, Germany) was used for centrifugation.

2.3 Stir bar sorptive extraction device

Stir bars coated with a 0.5 mm film thickness layer (24 μL) of PDMS (Twister TM: the magnetic stirring rod is incorporated in a glass jacket and coated with PDMS) were obtained from Gerstel (Gerstel GmbH, Mulheiman der Ruhr, Germany). New stir bars were conditioned as follows: the stir bar was placed into a vial containing an acetonitrile:methanol solution (80:20, v/v) and conditioned for 24 h under agitation. Between successive extractions, the used stir bar was cleaned twice in methanol for 15 min at 35 ^{o}C, under magnetic stirring rate of 800 rpm, followed by a drying step using a lint-free tissue. The analysis of desorption solvent of two steps confirmed an insignificant carryover.

2.4 SBSE-DLLME-SFO procedure

Prior to use, new or used stir bars were conditioned as described in section 2.3. At the extraction step, 100 mL of water sample containing 15 μg L^{-1} of analytes was stirred with the stir bar for 40 min at 300 rpm. After extraction, the stir bar was removed using a clean tweezers and dried with lint free-tissue. Then the stir bar was placed into a 2 mL glass vial containing 0.5 mL of methanol (as disperser solvent). After 15 min, the stir bar was removed and 30 μL of 1-undecanol (as extraction solvent) was added to this solution and injected rapidly into the 5 mL of aqueous solution containing 1% (w/v) potassium chloride (for improvement of the formation of floated drop) which was placed in a screw cap glass test tube with conical bottomed. A cloudy solution, resulting from the dispersion of the fine 1-undecanol droplets in the aqueous solution was formed in the test tube. In this step, the PAHs in the methanol were extracted into the fine droplets of 1-undecanol within few seconds. Then the mixture was centrifuged for 5 min at 5000 rpm. After centrifugation, the glass tube was transferred into the ice bath and then the solidified organic solvent was transferred into the conical vial where it started to melt at room temperature. Finally 10 μL of acetonitrile was added to melt and 30 μL of the resulting solution was injected into the HPLC system for analysis.

3 Results and discussion

In the present study, a SBSE-DLLME-SFO method combined with HPLC-UV was developed and applied to simultaneous preconcentration and determination of the PAHs fluorene (Flu.), fluoranthene (Flut.), pyrene (Pyr.), benz[a]anthracene (BaA) and benzo[a]pyrene (BaP) from different water samples. To reach a high extraction recovery and enrichment factor, the SBSE and DLLME conditions were optimized. The enrichment factor (EF) was defined as the ratio of the analyte concentration in the floated phase (C_{flo}) to the initial concentration of analyte (C_0) within the sample (i.e., $EF = C_{flo}/C_0$), where the analyte concentration in the collected phase was calculated from the direct calibration graph (0.2-10 mg L^{-1}) of PAHs in acetonitrile.

3.1 Optimization of the DLLME parameters

3.1.1 Effect of type and volume of extraction solvent

The selection of an appropriate extraction solvent is very important in DLLME procedure, in order to obtain an efficient extraction. In the selection of extraction solvent some factors such as low solubility in water, extraction capability of interested compounds, having melting point near room temperature (in the range of 10-30 ^{o}C) and lower density than water should be considered. According to these considerations, 1-undecanol (d=0.83 g/ml, mp=19 ^{o}C) and 1-decanol (d=0.83 g/ml, mp=6.4 ^{o}C) were studied as extraction solvent. The results revealed that 1-undecanol has better extraction efficiency than 1-decanol. Therefore, 1-undecanol was selected as the extraction solvent for subsequent experiments.

To examine the effect of extraction solvent volume, a series of experiments were performed by using 0.5 mL of methanol containing different volumes of 1-undecanol (10, 20, 30, 40 and 50 µL). According to Fig.1, the extraction efficiency of analytes decreases with the increase of extractant volume, while the concentration of analytes in the floating phase decreases slightly due to the dilution effect. Subsequently, at an intermediate volume of extraction solvent, high enrichment factor and good recovery are obtained. Therefore, 30 µL of 1-undecanol was selected as the volume of extraction solvent.

(Fig. 1)

3.1.2 Effect of type and volume of disperser solvent

The miscibility of disperser solvent in the extraction solvent and aqueous phase is the most important factor for selection of disperser solvent. Several disperser solvents including methanol, acetonitrile, ethanol and acetone were examined and the effect of these solvents on the performance of DLLME was investigated. The results showed that methanol gives the best extraction efficiency and, thus, it was chosen as disperser solvent (Fig.2), and the effect of its volume was investigated in the range of 250-2000 μL. According to the results in Fig.3, the extraction efficiency increased by increasing the volume of methanol up to 0.5 mL and decreased thereafter. At low volume of methanol, the cloudy state could not be formed completely; therefore the extraction efficiency was low. On the other hand, increasing of the disperser solvent volume leads to decreased extraction efficiency due to the enhanced solubility of analytes in aqueous solution. As a result, 0.5 mL was used as the optimal volume of methanol for further studies.

(Fig. 2) and (Fig.3)

3.2 Optimization of the SBSE parameters

3.2.1 Effects of extraction and desorption time

The extraction time is a very important factor because it influences the partition of the solutes between the matrix and the polymer.[30] Fig.4 shows the extraction efficiency of PAHs during different times. As shown in Fig.4, the equilibrium time was achieved after 40 min. After this time, no substantial increase was obtained with additional extraction time. Therefore, based on these results, 40 min was chosen as the optimal adsorption time. The effect of desorption time was also evaluated for the target analytes by studying different times. The results indicated that a desorption time period of 15 min is sufficient for complete desorption (Fig.5).

Also, the effect of number of desorption steps on the extraction efficiency was studied by using three consecutive desorption procedures. The results revealed that the majority of the analytes are desorbed in the first step.

(Fig. 4) and (Fig. 5)

3.2.2 Effect of salt addition

The influence of salt concentration on the extraction of PAHs was studied by adding different amounts of KCl (0-5% w/v). Generally the increasing ionic strength of solution can improve the extraction efficiency through reducing the solubility of analytes in the aqueous sample. However, due to the non-polarity of the PAHs compounds used, salt addition resulted in reduced extraction efficiency. This fact was also reported by other authors.[31,32] This phenomenon could be explained by helping to move PAHs to the water surface (oil effect) by minimizing their interaction with the PDMS stir bar and, subsequently, minimizing the PAHs extraction. Therefore, no salt was added in further experiments.

3.3. Analytical characteristics

The method showed a good linearity over the calibration range 0.02–400 μg mL^{-1} with the square of correlation coefficients (r^2) of larger than 0.991. The limit of detections (LODs), based on signal- to- noise ratio (S/N) of 3 were in the range of 0.0067-0.01 μg mL^{-1} for the proposed method. The enrichment factors of PAHs were quite high from 1630 to 2637. The relative standard deviations (RSDs) for five replicates varied from 2.17 to 6.92%. The obtained results are summarized in Table 1.

(Table 1)

3.4. Real samples analysis

Since polycyclic aromatic hydrocarbons (PAHs) are mainly considered as common environmental pollutants, which are carried into rivers, lakes and other water sources, different water samples are mainly tested for their presence. Thus, in this work the applicability of the proposed extraction method was investigated in four different water samples (i.e., tap, well, ground and lake waters). The results showed that all samples were free from PAHs. Thus, they were spiked with PAHs standard solutions at different levels to assess matrix effects (Table 2). Fig.6 shows typical chromatograms for the tap water samples before and after spiking with standard concentration of PAHs.

(Table 2) and (Fig. 6)

3.5. Comparison of SBSE-DLLME-SFO with other methods

Characteristics of the proposed method have been also compared with other methods which were used for the extraction and determination of PAHs in Table 3. As it can be seen, the proposed method shows limit of detections (LODs) comparable with those of most previously reported methods, while, the EF of this method is higher than those of previously published methods. The RSDs for the proposed method are lower than those of the mentioned methods. These results reveal that the presented method is sensitive and simple technique and can be used for the PAHs preconcentration and determination from aqueous samples.

(Table 3)

4 Conclusions

In this work SBSE combined with DLLME-SFO technique for highly efficient extraction and HPLC-UV determination of PAHs from different water samples. It should be noted that UV detection is the most usual and widespread detection technique in high performance chromatography and the instrument is the most available one. The results of this study revealed that the proposed technique gives high extraction efficiency and low LODs. Compared to the other methods, this technique uses small volume of organic solvents and has a good linearity over a wide range of

concentration. The most important advantage of this technique is that the use of large sample volumes and toxic organic solvents has been omitted.

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Figure Captions

Fig. 1 Effect of extraction solvent volume on the extraction efficiency. Conditions: sample volume, 5 mL; extraction solvent, 1-undecanol; disperser solvent, 0.5 mL methanol; centrifuging time and speed, 5min with 5000 rpm; concentration of analytes, 100 μg L^{-1}.

Fig. 2 Effect of disperser solvent kind on the extraction efficiency. Conditions: sample volume, 5 mL; extraction volume, 30 μL 1-undecanol; disperser solvent, 0.5 mL; centrifuging time and speed, 5min with 5000 rpm; concentration of analytes, 100 μg L^{-1}.

Fig. 3 Effect of disperser solvent volume on the extraction efficiency. Conditions: sample volume, 5 mL; extraction volume, 30 μL 1-undecanol; disperser solvent, methanol; centrifuging time and speed, 5 min with 5000 rpm; concentration of analytes, 100 μg L^{-1}.

Fig. 4 Effect of extraction time on the SBSE-DLLME-SFO efficiency. Condition: sample volume, 100 mL; stirring speed, 300 rpm; desorption time, 15 min; concentration of analytes, 15 μg L^{-1}, DLLME-SFO parameters are the same as in Figure 2.

Fig. 5 Effect of desorption time on the SBSE-DLLME-SFO efficiency. Condition: sample volume, 100 mL; stirring speed, 300 rpm; extraction time, 40 min; concentration of analytes, 15 μg L^{-1}. DLLME-SFO parameters are the same as in Figure 2.

Fig. 6 Chromatograms related to extraction of the target analytes of the non-spiked (A) and spiked (B) tap water at the concentration level of 25 μg L^{-1} of Flu., Flut., Pyr. and BaP and 20 μg L^{-1} of BaA.

391 **Table 1** Figures of merit in the SPE-DLLME-SFO

Analyte	LR[a] (μg L^{-1})	R^{2b}	LOD[c] (μg mL^{-1})	RSD[d] (%)	EF[e]
Flu.	0.05-400	0.9910	0.0098	2.17	2223
Flut.	0.02-400	0.9940	0.0067	3.94	1630
Pyr.	0.02-200	0.9990	0.0067	6.92	2637
BaA	0.06-250	0.9932	0.010	5.73	1708
BaP	0.04-200	0.9968	0.0095	6.03	1735

392 [a] Linear range. [b] Square of correlation coefficient. [c] Limit of detection (S/N=3). [d] Relative
393 standard deviation at concentration level of 20 μg L^{-1} for Flu., BaA and BaP, 15 μg L^{-1} for Flut.
394 and 30 μg L^{-1} for Pyr., respectively. [e] Enrichment factor
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412 **Table 2** Determination of PAHs in spiked water samples

Sample	Analytes	Added (μg L^{-1})	Found (μg L^{-1})	Relative recovery (%)
Tap water	Flu.	25	23.2±2.0[a]	92.8
	Flut.	25	22.9±1.3	91.6
	Pyr.	25	21.1±1.9	84.4
	BaA	20	19.0±1.6	95.0
	BaP	25	24.4±1.5	97.6
Lake water	Flu.	20	18.0±1.6	90.0
	Flut.	15	14.6±1.2	97.3
	Pyr.	25	24.0±2.0	96.0
	BaA	15	14.7±1.3	98.0
	BaP	20	18.9±1.1	94.5
Ground water	Flu.	20	17.1±1.5	85.5
	Flut.	10	9.5±0.80	95.5
	Pyr.	20	18.0±1.9	90.0
	BaA	20	17.6±1.7	88.0
	BaP	15	13.8±1.0	92.0
Well water	Flu.	20	17.9±1.8	89.5
	Flut.	10	9.6±0.50	96.0
	Pyr.	20	18.2±1.4	91.0
	BaA	20	17.4±1.6	87.0
	BaP	15	14.0±1.0	93.3

413 [a] Mean found amount ± standard deviation (n = 3).

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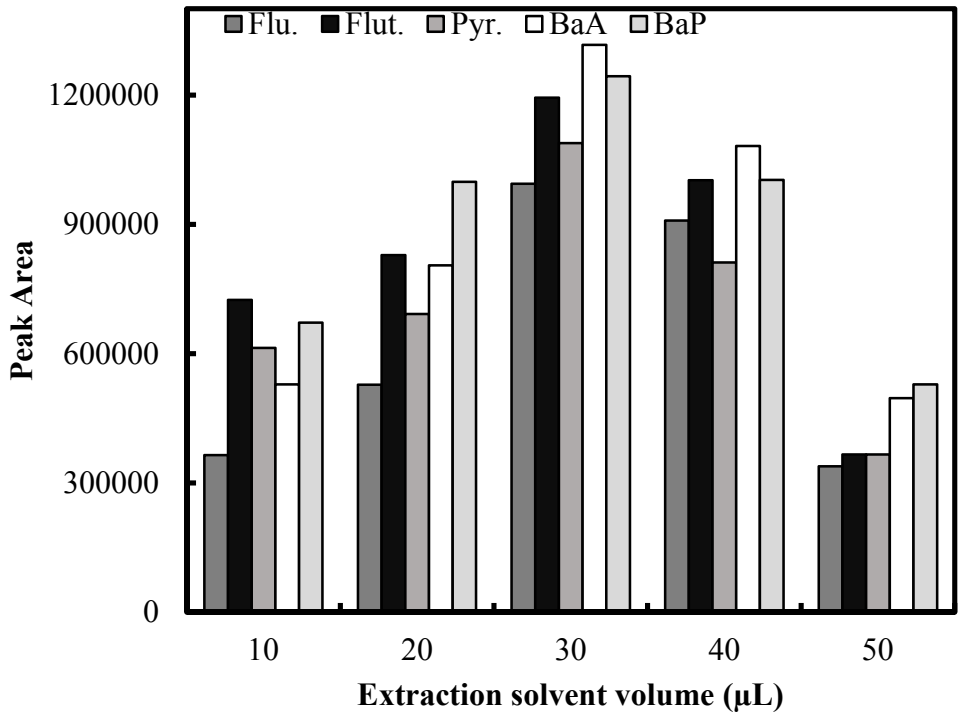
418 **Table 3** Comparison of the proposed method with other extraction methods for determination of
419 PAHs

Method	Analyte	LR ($\mu g\ L^{-1}$)	LOD ($ng\ mL^{-1}$)	RSD (%)	EF	Ref.
AA-DLLME[a]	Flut.	0.04-800	0.008	7.3	310-	33
	Pyr.	0.02-400	0.004	5.6	325	
DLLME-SFO[b]	Flut.	1-500	1.10	4.3	116	34
HLLE[c]	Flu.	0.1-400	0.071	4.2-10.3	232	35
	Flut.	0.2-400	0.067		226	
	Pyr.	0.4-400	0.031		245	
DLLME	Flu.	0.02-200	0.008	2.1	902	20
	Flut.	0.02-200	0.010	6.9	1016	
	Pyr.	0.02-200	0.010	5.3	1046	
	BaA	0.02-20	0.01	9.3	1047	
	BaP	0.05-20	0.02	7.7	971	
IL-DLLME[d]	Flu.	0.05-40	0.0002	4.5	317.4	36
	Flut.	0.05-40	0.0008	4.5	328.6	
	Pyr.	0.02-20	0.0001	4.4	336.6	
	BaA	0.02-20	0.00004	5.7	332.6	
	BaP	0.02-20	0.00004	2.5	338.2	
MSPE[e]	Flu.	0.2-100	0.10	6.9	242	37
	Flut.	0.1-100	0.05	8.3	413	
	Pyr.	0.05-100	0.02	5.6	600	
SBSE-LD-MEKC-	Flu.	25-125	10	<12	-	38
DAD[f]	Flut.	27-133	11		-	
	Pyr.	27-133	11		-	
SBSE-DLLME-SFO	Flu.	0.05-400	0.0098	2.17	2223	This
	Flut.	0.02-400	0.0067	3.94	1630	work
	Pyr.	0.02-200	0.0067	6.92	2637	
	BaA	0.06-250	0.010	5.73	1708	

BaP	0.04-200	0.0095	6.03	1735

[a]Alcoholic-assisted dispersive liquid–liquid microextraction. [b]Dispersive liquid–liquid microextraction based on solidification of floating organic drop. [c]Homogeneous liquid–liquid extraction. [d]Ionic liquid dispersive liquid–liquid microextraction. [e]Magnetic solid phase extraction. [f]Stir bar sorptive extraction and liquid desorption was combined with micellar electrokinetic capillary chromatography(MEKC) and diode-array detection.


Flu.
Flut.
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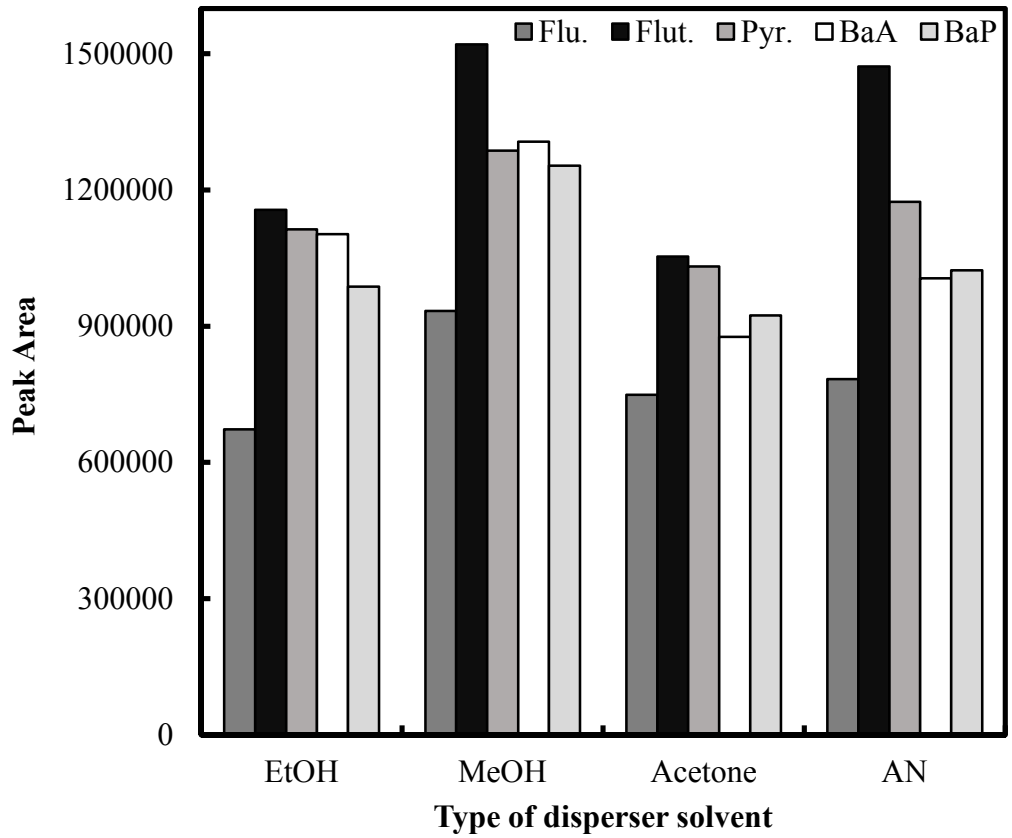
Extraction solvent volume (µL)

Fig. 1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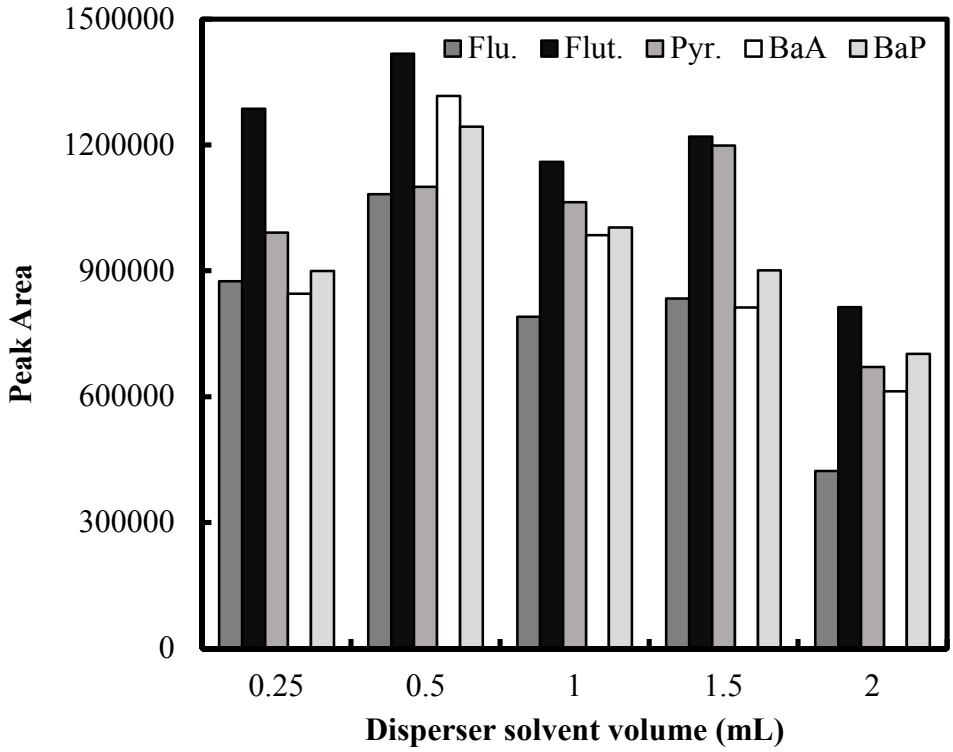
Type of disperser solvent

Fig. 2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0.25
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Disperser solvent volume (mL)

Fig. 3

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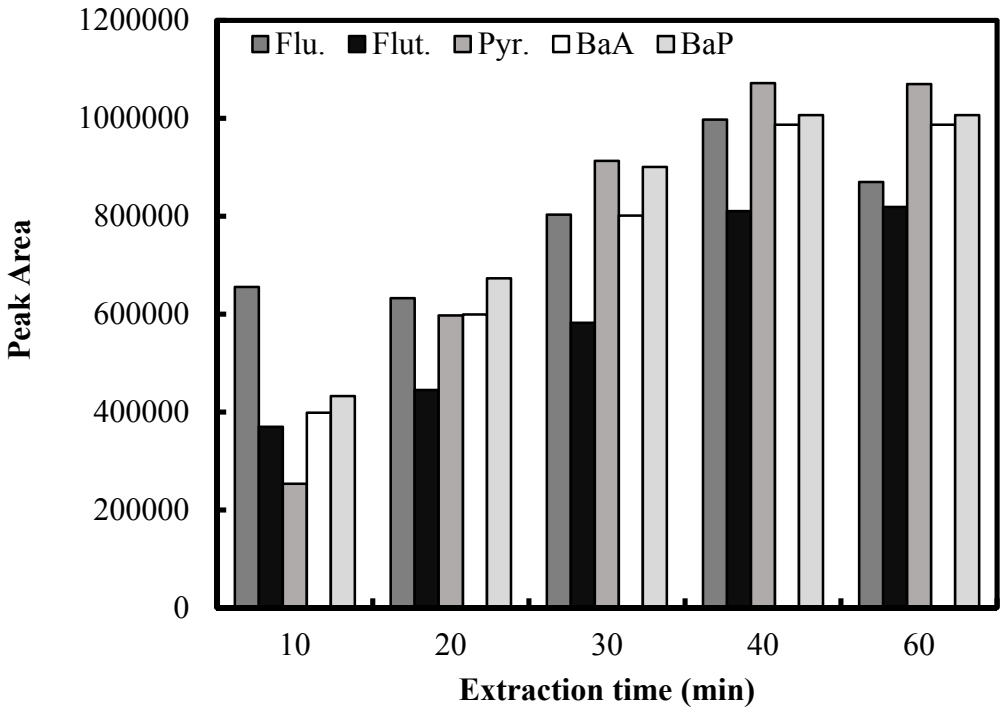

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501 **Fig. 4**

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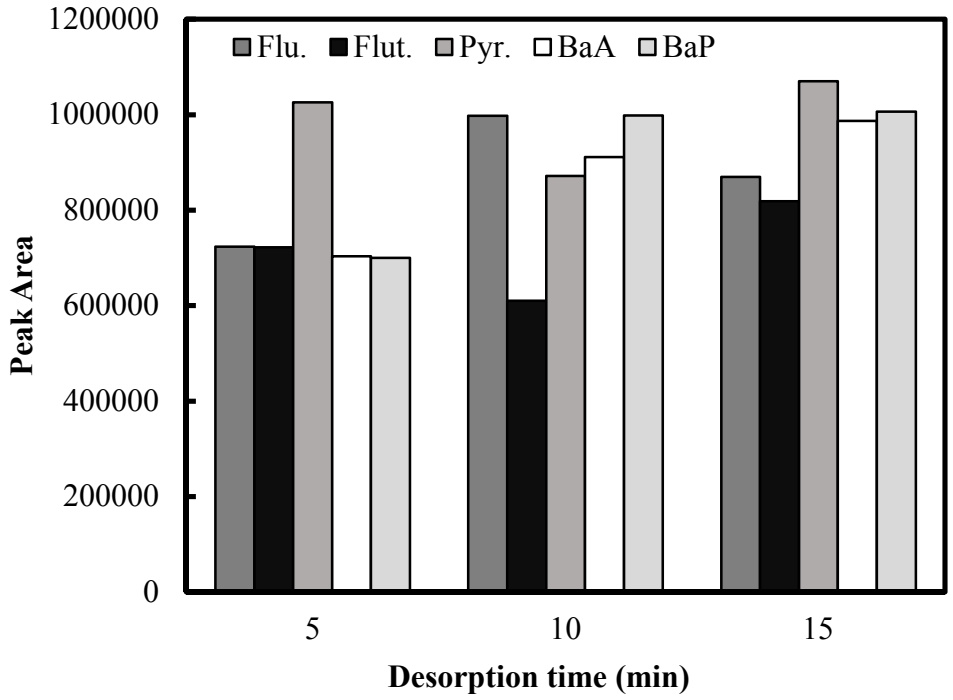
1200000
1000000
800000
600000
400000
200000
0
Peak Area
Flu.
Flut.
Pyr.
BaA
BaP
5
10
15
Desorption time (min)

Fig. 5

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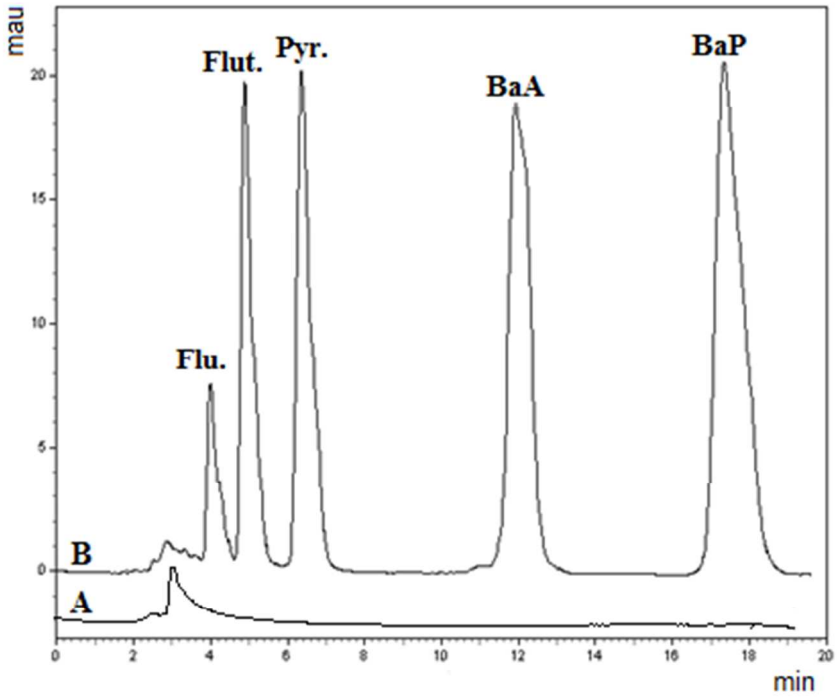

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532 **Fig. 6**

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Graphical Abstract

The proposed method offers advantages such as low consumption of organic solvents, high enrichment factors and good linearity over the investigated concentration range.