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Magnetic stirring-assisted dispersive liquid–liquid microextraction followed by high performance liquid chromatography for determination of phthalate esters in drinking and environmental water samples

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ABSTRACT

A simple, fast and efficient method for the preconcentration of phthalate esters (PEs) in water samples was developed using magnetic stirring-assisted dispersive liquid–liquid microextraction (MSA-DLLME) followed by high performance liquid chromatography coupled with ultraviolet detection (HPLC–UV). This novel microextraction method is based on the fast injection of extracting solvent into the aqueous solution, which is being stirred by a magnetic stirrer, to form a cloudy binary component solvent (aqueous solution:extracting solvent) system. The extraction parameters such as type and volume of extracting solvent, pH of sample, salt addition, extraction time and stirring rate were optimized. Under the optimal conditions (extracting solvent: 200 μL dodecane; pH of sample: 6.5; extraction time: 5 min; stirring rate: 1000 rpm), linearity was observed in the range of 2–1000 μg L^{-1} for dimethyl phthalate (DMP) and 1–1000 μg L^{-1} for diethyl phthalate (DEP), benzyl butyl phthalate (BBP) and di-n-butyl phthalate (DBP) with correlation determination values above 0.99 for them. The limits of detection and quantification were ranged from 0.13 to 0.38 μg mL^{-1} and 0.43 to 1.27 μg mL^{-1}, respectively. The ranges of intra-day and inter-day precisions ($n=5$) at 100 μg L^{-1} of PEs were 1.50–2.65% and 2.31–3.35%, respectively. Finally, the MSA-DLLME method was successfully applied for preconcentration of PEs in drinking and environmental water samples.

1. Introduction

Phthalate ester is a common name for dialkyl or alkyl aryl esters of phthalic acid, which is used as plasticizers in household consumption and industrial polymeric materials. In fact, PEs are incorporated into the polymeric material of sealants, adhesives, paints, coatings, packaging, children's toys, waxes, pharmaceuticals, food products, textiles, printing inks, and the like [1] to improve their flexibility, durability, and workability [2].

PEs are famous as pollutants due to their potential risks to environment and human health. Due to the fact that there is no covalent bond between the PEs and polymer chains, the compounds are easily released from polymeric products into the environment, especially water resources [3] during the process of production, manufacture, usage and disposal. With respect to health effects, PEs are often classified as endocrine disruptors or hormonally active agents (HAAs) whose exposure may result in disruption of hormone activity in the male reproductive tract and some carcinogenic effects [4,5]; therefore, making efforts to develop analytical methods for the survey of PEs residue in water samples is the main challenge and very important step for evaluating water safety and possible risks to human health.

The most commonly used techniques for analyzing PEs in water samples consist of: gas chromatography (GC) coupled with electron capture (EC) [6,7], flame ionization (FI) [8,9], mass spectrometry (MS) [10–15] detection and high performance liquid chromatography (HPLC) coupled with ultraviolet (UV) [16–20] and MS [21] detection.

However, due to the very low concentration levels of PEs in environmental water samples and the complexity of the different matrices, the direct use of chromatographic methods is limited by their sensitivity and selectivity; that is why a sample preparation step prior to these analytical methods is necessary. The traditional preconcentration techniques which were widely used to monitor PEs in water samples were liquid–liquid extraction (LLE) [22,23] and solid-phase extraction (SPE) [24,25]. Unfortunately, these methods suffer from the disadvantages of being time-consuming, labor-intensive and requiring large volumes of samples and toxic organic solvents. To overcome LLE and SPE disadvantages, miniaturized sample preparation techniques were developed in recent years and applied for monitoring of PEs including: single drop microextraction (SDME) [8], hollow fiber–liquid phase

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microextraction (HF–LPME) [26], solid phase microextraction (SPME) [10], stir-bar sorptive extraction (SBSE) [15], cloud point extraction (CPE) [17], homogeneous liquid–liquid extraction (HLLE) [27] and dispersive liquid–liquid microextraction (DLLME) [28,29].

However, each of the above-mentioned procedures has its own disadvantages; for instance, the main drawback of SDME is the instability of the drop at high stirring rates or temperatures [30]; HF–LPME procedure suffers from the manipulation of hollow fiber at the time of placing it at the tip of the needle of the microsyringe before the microextraction process, because manipulation could be a source of contamination [30]. Drawbacks of SPME and SBSE are mainly related to the polymeric extractant phase nature and the desorption process; in fact, the use of a polymer as extractant phase includes disadvantages such as batch-to-batch variation, artefact formation and low repeatability [30]. Using nonionic surfactants in CPE presents some important drawbacks: (1) a high background absorbance in the ultraviolet region and high fluorescence signals, when excitation wavelengths higher than 300 nm are used, due to the presence of an aromatic moiety in their structure and (2) large retention times, owing to the non-polar character of surfactant molecules [31]. In HLLE based on the addition of salt for phase separation, the presence of salts in samples like sea water sample reduces the extraction recovery [27].

DLLME is based on the fast injection of a mixture of extracting and disperser solvents into the aqueous solution to form a cloudy ternary component solvent (aqueous solution:extracting solvent:-disperser solvent) system; after centrifugation, the enriched analyte in the sedimented phase is withdrawn and determined by chromatography or spectrometry methods [32,33]. In recent years, several modes of DLLME such as ionic liquid cold-induced aggregation DLLME (IL-CIA-DLLME) [34] and ultrasound-assisted DLLME (UA-DLLME) [35] were applied for extraction of PEs. In conventional DLLME i.e. DLLME by extracting solvent with higher density than water such as dichloromethane, chloroform and carbon tetrachloride, the centrifugation of real samples causes problems for gathering the extraction products, especially in the case of sea water sample due to the presence of the interfering materials in the bottom of the conical test tube.

To overcome this problem, we applied inverted dispersive liquid–liquid microextraction (IDLLME) (according to our previous work [36]) for the extraction of PEs. In spite of the DLLME, IDLLME employs an extracting solvent with lower density than water and after centrifugation the extraction product is settled at the top of the sample. But our primary investigations indicated that using disperser solvent for the extraction of PEs, the extraction recoveries decreased; therefore, we used magnetic stirring-assisted dispersive liquid–liquid microextraction (MSA-DLLME) which had been developed by Zhang et al. [37] in 2009. MSA-DLLME is based on a binary system composed of the extracting solvent and the aqueous solution (without disperser solvent). Primarily, fast injection of the extracting solvent makes a cloudy solution which can help the acceleration of the mass transfer from the aqueous solution to the extracting solvent; then, magnetic stirring helps the permanence of the cloudy solution. This procedure showed sufficient specificity and simplicity of operation for the measurement of trace amounts of PEs in drinking and sea water samples.

2. Experimental

2.1. Chemical and standards

All standards of PEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) (purity range 98–99%) were from Alfa Aesar (Karlsruhe, Germany). Methanol and acetonitrile (HPLC-grade), acetone (99%), n-hexane, xylene, toluene and dodecane were purchased from Merck (Darmstadt, Germany). The water used for the mobile phase was double distilled deionized. Individual stock solutions of each PE compound were prepared in methanol and a standard mixture solution of all target compounds was prepared in methanol at a final concentration of 100 mg L^{-1}. The working solution was prepared by appropriate dilution of the stock solution with distilled water. All of the standard solutions were stored at 4 °C and brought to ambient temperature just prior to use.

2.2. Real samples

River and sea water samples were taken from the Babolrood River and the Caspian Sea (Babolsar) in the north of Iran. Tap water was taken from our laboratory and mineral water was purchased from Polur mineral water company, Amol, Iran. Also well water was collected from the local area (Babolsar, Iran). All water samples were collected into pre-cleaned, light-preserved glass bottles and each sample was filtered through 0.45 mm membrane filters (Millipore, Bedford, MA) immediately

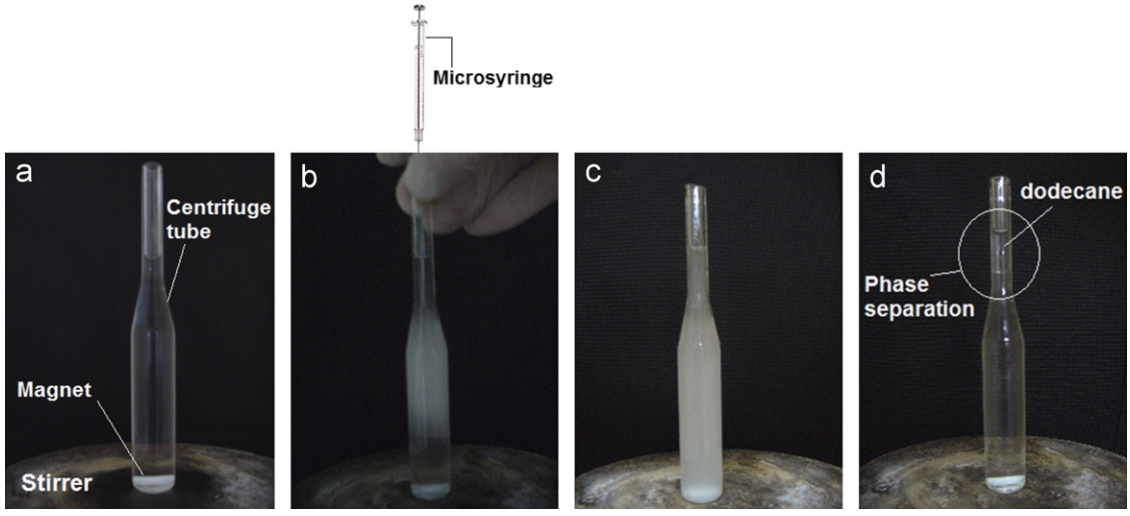

Fig. 1. Photography of different steps in MSA-DLLME: (a) before injection of extracting solvent (dodecane) into the sample solution; (b) beginning of injection; (c) completion of injection, speedy agitation by magnetic stirrer and formation of cloudy solution and (d) after centrifugation and phase separation.

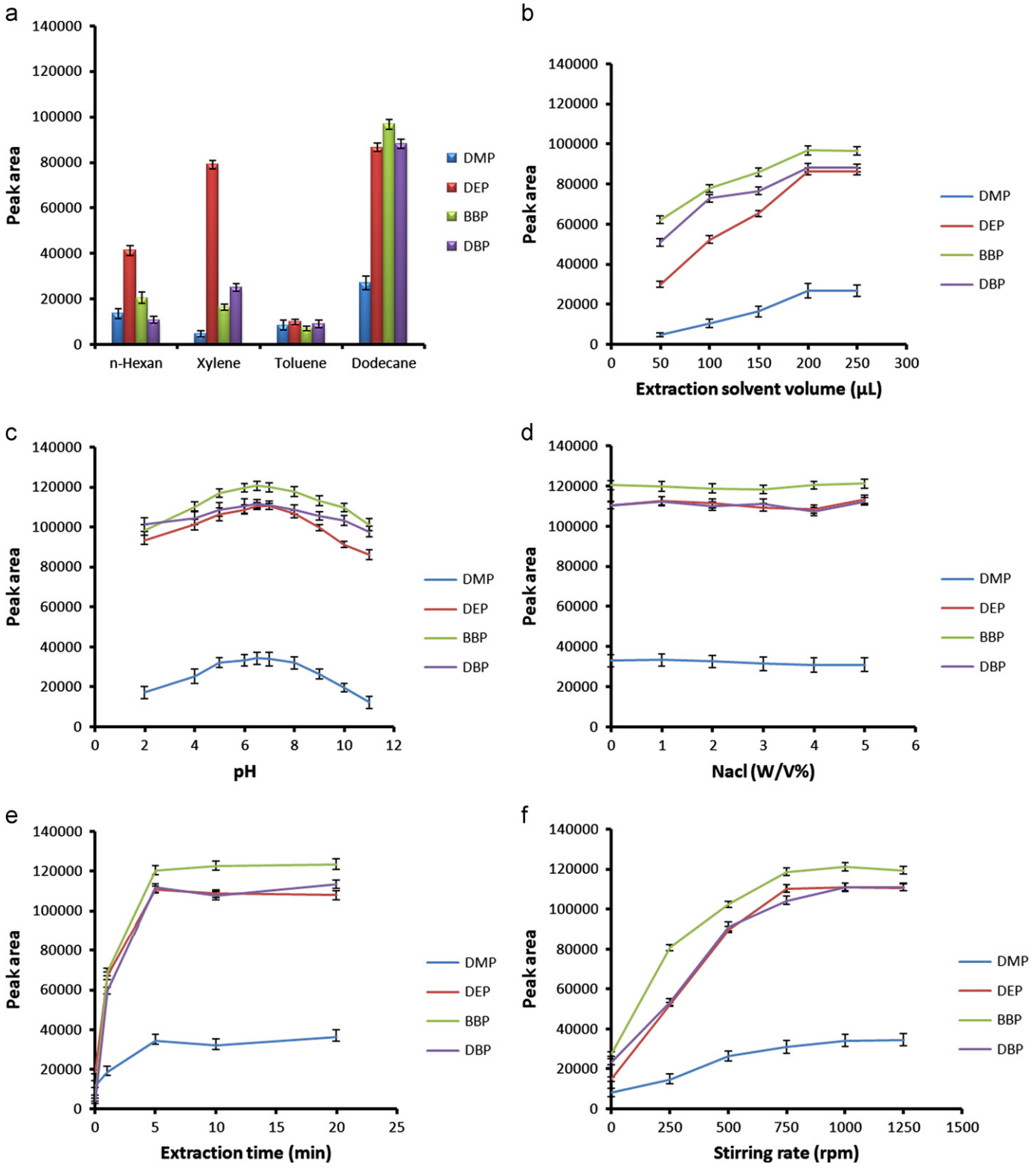

Fig. 2. Effect of different parameters on the extraction of PEs using MSA-DLLME; (a) effect of the type of extracting solvent (extraction conditions: aqueous sample volume, 10 mL; extracting solvent volume, 200 μL; pH of sample solution, 6.0; without salt addition; extraction time, 5 min; stirring rate 1000 rpm.); (b) effect of the volume of extracting solvent (extraction conditions: aqueous sample volume, 10 mL; extracting solvent, dodecane; pH of sample solution, 6.0; without salt addition; extraction time, 5 min; stirring rate 1000 rpm.); (c) effect of pH of sample solution (extraction conditions: aqueous sample volume, 10 mL; extracting solvent (dodecane) volume, 200 μL; without salt addition; extraction time, 5 min; stirring rate 1000 rpm.); (d) effect of salt addition (extraction conditions: aqueous sample volume, 10 mL; extracting solvent (dodecane) volume, 200 μL; pH of sample solution, 6.5; stirring rate 1000 rpm.); (e) effect of extraction time (extraction conditions: aqueous sample volume, 10 mL; extracting solvent (dodecane) volume, 200 μL; pH of sample solution, 6.5; without salt addition; stirring rate 1000 rpm.); (f) effect of stirring rate (extraction conditions: aqueous sample volume, 10 mL; extracting solvent (dodecane) volume, 200 μL; pH of sample solution, 6.5; without salt addition; extraction time, 5 min.).

after sampling in order to remove suspended solids. Then, all of them were stored under dark conditions in refrigerator (at 4 °C) until analysis.

2.3. Instrumentation and operating condition

The chromatographic analysis was performed on an HPLC system equipped with a series 10 LC pumps, UV detector model LC-95 set at 225 nm, and model 7125i manual injector with a 20 μL sample loop all from Perkin–Elmer (Norwalk, CT, USA). Separation was done by an isocratic elution on a C_{18} (250 × 4.6 mm, 10 μm) column from Dr. Maisch GmbH (Beim Brueckle, Germany). Mobile phase was a mixture of acetonitrile and water (65:35, v/v) with flow rate of 1.0 mL min^{-1}. Adjustment of pH was done by model 3030 Jenway pH meter (Leeds, UK). A Denley bench centrifuge model BS400 (Denley Instruments Ltd., Billingshurst, UK) was used to accelerate the phase separation.

2.4. Magnetic stirring-assisted dispersive liquid–liquid microextraction

A 10 mL of sample solution containing 100 μg L^{-1} of a mixture of DMP, DEP, BBP and DBP was placed in the handmade centrifuge tube (Fig. 1) with narrow neck (~5 mm i.d.) which was specially designed for the ease of withdrawing supernatant phase. A 200 μL portion of dodecane (as extracting solvent) was injected into the sample solution using 250 μL syringe rapidly and accompanied by vortex mixing at 1000 rpm stirring rate for 5 min until a cloudy solution was formed. To obtain appropriate phase separation, the cloudy solution was centrifuged for 3 min at 3000 rpm. Accordingly, after centrifugation the extraction product was settled at the top of the sample and in the neck of the handmade centrifuge tube (about 196 ± 2 μL) as supernatant phase. Finally, this product was injected to the HPLC using 20 μL sample loop.

2.5. Calculation of preconcentration factor, extraction recovery and relative recovery

The preconcentration factor (*PF*) was defined as the ratio between the analyte concentration in the supernatant phase (C_{sup}) and the initial concentration of analyte (C_0) in the aqueous sample, as follows:

$$PF = \frac{C_{sup}}{C_0} \quad (1)$$

To investigate the influence of various experimental parameters on the extraction efficiency of PEs from the standard samples, we used extraction recovery percent (*ER%*), which is defined as the percentage of the total analyte (n_0) in the standard samples extracted into the supernatant phase (n_{sup}).

$$ER\% = \frac{n_{sup}}{n_0} \times 100 = \frac{C_{sup} \times v_{sup}}{C_0 \times v_0} \times 100 \quad (2)$$

where V_{sup} and V_0 are the volume of the supernatant phase and the volume of the aqueous sample, respectively.

On the other hand, to compare the extraction efficiency in the different matrices of the real samples, relative recovery (*RR*) was obtained from the following equation:

$$RR\% = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \quad (3)$$

where C_{found}, C_{real} and C_{added} represent the concentration of the analyte after adding a known amount of standard to the real sample, the concentration of the analyte in the real sample and the concentration of a known amount of standard spiked in the real sample, respectively.

3. Results and discussion

3.1. Optimization of MSA-DLLME

To obtain good sensitivity, precision and selectivity for extraction and determination of PEs, the effects of various experimental parameters on MSA-DLLME of PEs such as type of the extracting solvent as well as its volume, pH of the solution, salt addition, extraction time and stirring rate were optimized using one-variable-at-a-time optimization method. All the experiments were performed in triplicates and the average of the results was reported. To evaluate the extraction efficiency in different conditions, the peak area was used. For the ease of calculations, all the

Table 2
Determination of PEs in water samples.

Water sample	Compound	Found (μg L^{-1})	Added (μg L^{-1})	*RR%*	*R.S.D.%* (*n*=3)
Mineral	DMP	nd	1.00	26.54	2.61
	DEP	nd	1.00	82.67	1.44
	BBP	nd	1.00	98.92	1.85
	DBP	nd	1.00	93.63	1.84
Tap	DMP	nd	1.00	25.82	2.77
	DEP	nd	1.00	84.80	1.65
	BBP	nd	1.00	97.08	2.13
	DBP	nd	1.00	95.52	1.89
Well	DMP	nd	1.00	26.06	2.75
	DEP	nd	1.00	81.92	1.56
	BBP	nd	1.00	96.25	1.95
	DBP	nd	1.00	90.47	2.52
River	DMP	0.58	1.00	27.76	3.82
	DEP	1.23	1.00	80.41	2.06
	BBP	nd	1.00	102.71	3.52
	DBP	nd	1.00	93.11	3.43
Sea	DMP	0.61	1.00	28.13	3.92
	DEP	0.69	1.00	85.68	2.70
	BBP	nd	1.00	94.38	3.15
	DBP	nd	1.00	89.84	3.01

Table 1
Analytical performance of MSA-DLLME for determination of PEs.

Compounds	LOD (μg L^{-1})	LOQ (μg L^{-1})	LR (μg L^{-1})	R^2	Intra-day assay[a] (*n*=5)			Inter-day assay[a] (*n*=5)		
					PF	*ER%*	*R.S.D.%*	*PF*	*ER%*	*R.S.D.%*
DMP	0.38	1.27	2–1000	0.9992	13.67	27.34	2.65	13.78	27.50	3.35
DEP	0.19	0.63	1–1000	0.9976	41.66	83.32	1.50	42.24	84.48	2.31
BBP	0.13	0.43	1–1000	0.9932	49.38	98.76	1.83	48.68	97.35	2.43
DBP	0.21	0.70	1–1000	0.9983	47.34	94.68	1.76	46.80	93.59	2.41

[a] At 100 μg L^{-1} concentration.

supernatant phases were diluted to a constant volume (300 μL) through adding dodecane.

3.1.1. Selection of extracting solvent

Choosing the suitable extracting solvent was of great importance for the enrichment of PEs. Extracting solvent must have some properties such as (a) good chromatographic behavior, (b) lower density than water, (c) extraction capability of interested compounds and (d) low solubility in water. Hence 1-octanol (density, 0.82 g mL^{-1}), n-hexane (density, 0.65 g mL^{-1}), xylene (density, 0.86 g mL^{-1}), toluene (density, 0.87 g mL^{-1}) and dodecane (density, 0.75 g mL^{-1}) were studied for finding the most suitable extracting solvent for PEs.

In order to select the appropriate extracting solvent a series of experiments were performed using 200 μL of the mentioned extracting solvents. Our primary studies indicated that 1-octanol, as an extracting solvent for extraction of PEs has a poor chromatographic behavior (peak tailing) and covers some analytes peaks. However, the results shown in Fig. 2(a), indicate that dodecane provides the best analytical response among the other solvents; therefore, dodecane was selected as the suitable extracting solvent for subsequent experiments.

3.1.2. Volume of extracting solvent

To consider the effect of the extracting solvent volume on extraction efficiency of PEs, different volumes of dodecane were tested (50–250 μL). In accordance with Fig. 2(b), peak areas increased by the enhancement of dodecane's volume up to 200 μL but after this volume, the peak areas were almost constant; hence, 200 μL of dodecane was selected as the volume of extracting solvent.

3.1.3. pH of sample solution

The pH of the sample solution plays an important role in the extraction of organic compounds that possess an acidic or basic moiety; however, in the case of under-studying PEs, there are not any functional groups with acidic or basic property, but it is clear that esteric bonds are not stable in both violent acidic and violent alkaline aqueous solutions which leads to the formation of the bond constitutive materials i.e. carboxylic acid and alcohol. The effect of pH on MSA-DLLME of PEs from water samples were studied in the range of 2–11. In line with Fig. 2(c), the best pH for extraction of PEs is 6.5. The stability of the main structure of PEs decreases in both very low and very high pH values of the aqueous sample. Thus, for the subsequent experiments the pH of the working solutions was adjusted at 6.5.

3.1.4. Salt addition

To study the effect of salt addition on extraction recoveries, various experiments were performed by adding different amounts of NaCl in the range of 0–10% (w/w). Results showed that the addition of NaCl has no remarkable effect on the MSA-DLLME of PEs (Fig. 2(d)). Therefore, all the extraction experiments were carried out without the addition of salt.

3.1.5. Extraction time

In MSA-DLLME, extraction time was defined as the time interval between the injection of extracting solvent to the sample solution and before starting to centrifuge; in fact, extraction time was defined as the stirring time. The effect of extraction time was monitored by varying the stirring time from 0 to 20 min (Fig. 2(e)). The obtained results showed that peak areas for PEs were increased by prolonging the extraction time up to 5 min and were remained almost constant from 5 to 20 min. Therefore, 5 min was selected as the optimum extraction time.

3.1.6. Stirring rate

Stirring the aqueous solution during the injection of extracting solvent makes a stable cloudy solution and accelerates the mass transfer of analytes from the aqueous solution to the extracting phase which is the most important goal of the analyzer to obtain a good extraction recovery. The effect of stirring rate on the extraction of PEs was studied in the range of 0–1250 rpm. As can be seen in Fig. 2(f), peak areas were increased up to 1000 rpm and at the higher rate, the variations of peak areas versus the stirring rate are not significant. Thus, all the extraction experiments were performed at 1000 rpm stirring rate.

3.2. Analytical performance of the MSA-DLLME-HPLC

Under optimum condition, figures of the merits of the proposed method, consisting of linear ranges (LRs), determination coefficient (R^2), limits of detection (LODs), limits of quantification (LOQs), extraction recoveries (ERs) and preconcentration factors (*PFs*) for determination of PEs were obtained (Table 1). Calibration curves for PEs were obtained by spiking the standards directly

Table 3
Comparison of MSA-DLLME with conventional DLLME methods for determination of PEs in water samples.

Method	Extracting solvent	Consumption of organic solvent (μL)	Compounds	LOD (μg L^{-1})	LO (μg L^{-1})	LR (μg L^{-1})	R^2	Intra-day precision[a]
DLLME–HPLC–UV[31]	Carbon tetrachloride	791	DMP	1.80	6.00	5–5000	0.9992	5.9
			DEP	0.88	2.93	5–5000	0.9996	5.2
			BBP	–	–	–	–	–
			DBP	0.64	2.13	5–5000	0.9998	4.3
DLLME–GC–MS[32]	Chlorobenzene	509.5	DMP	0.008	0.027	0.05–100	0.9931	4.6
			DEP	–	–	–	–	–
			BBP	0.002	0.007	0.02–100	0.9901	6.1
			DBP	0.005	0.017	0.02–50	0.9940	5.9
IL-CIA-DLLME–HPLC–UV[34]	$[C_8MIM][PF_6]$	782	DMP	0.68	2.26	2–100	0.9968	3.5
			DEP	1.05	3.50	2–100	0.9994	3.7
			BBP	1.36	4.53	2–100	0.9974	2.2
			DBP	–	–	–	–	–
Present work	Dodecane	200	DMP	0.38	1.26	2–1000	0.9992	2.65
			DEP	0.19	0.62	1–1000	0.9976	1.50
			BBP	0.13	0.43	1–1000	0.9932	1.83
			DBP	0.21	0.71	1–1000	0.9983	1.76

[a] In the present work, intra-day precision is expressed as R.S.D. and it was assessed by five determinations in 1 day.

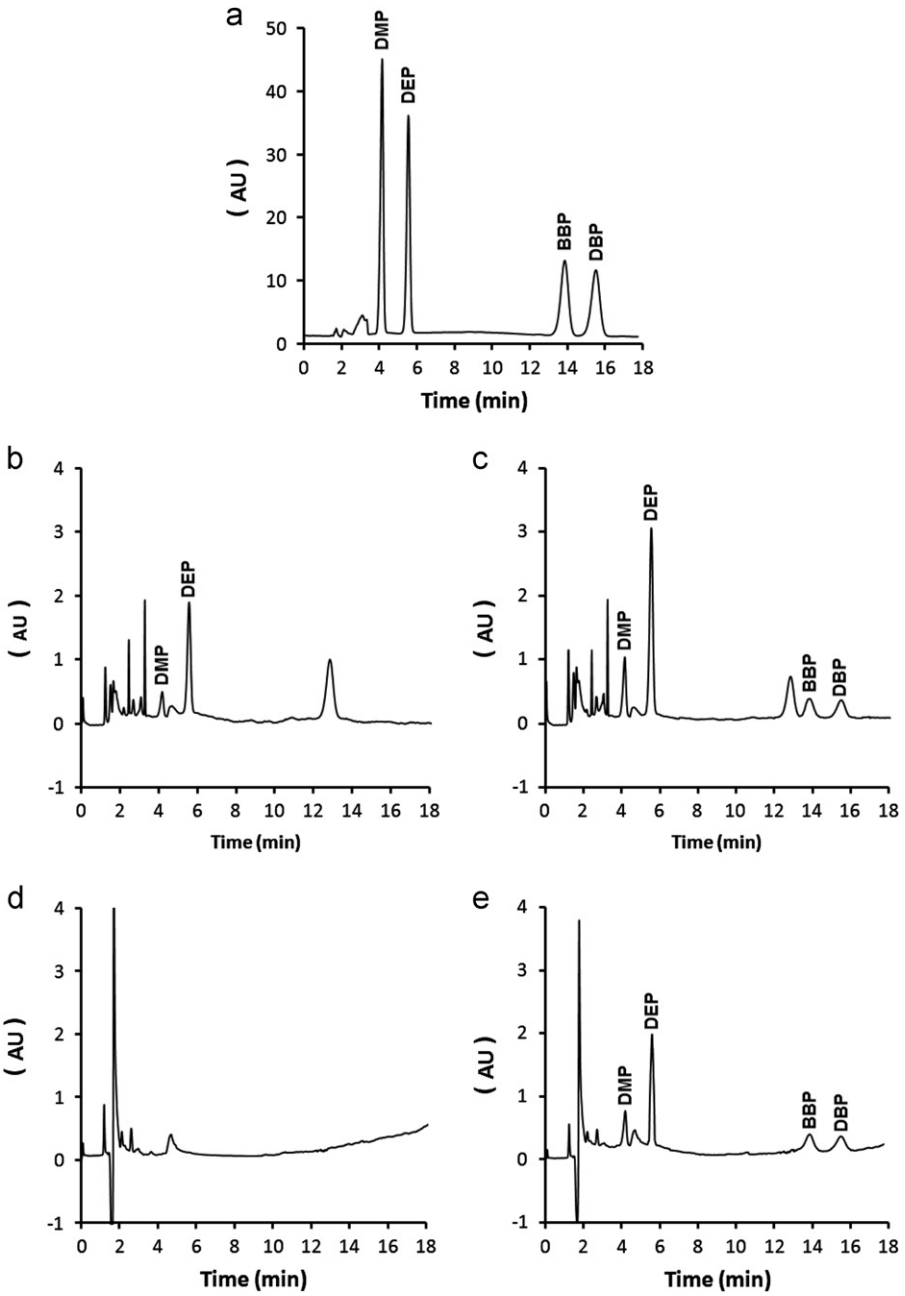

Fig. 3. Representative chromatograms of PEs standard solution and real samples; (a) chromatogram of standard solution of PEs after direct injection to the HPLC (HPLC conditions: water:acetonitrile (35:65 v/v); flow rate: 1.0 mL min^{-1}; column: C_{18} (250 × 4.6 mm^2, 10 mm); room temperature; λ=225 nm.); (b) chromatogram of river and (c) spiked river after MSA-DLLME; (d) chromatogram of mineral water and (e) spiked mineral water after MSA-DLLME; experimental details are described in the text.

into distilled water and extracting under optimum conditions. Linearity was observed over the range of 2–1000 μg L^{-1} for DMP and 1–1000 μg L^{-1} for DEP, BBP and DBP in the initial solution with determination coefficients in the range of 0.9932–0.9992.

Limits of detection (LODs) and limits of quantification (LOQs) for the proposed method were determined by spiking samples with PEs standards at low concentrations, extracted by the described MSA-DLLME method and calculated as the concentration giving peaks for which the signal-to-noise ratio was 3 and 10, were in the range of 0.13–0.38 μg L^{-1} and 0.43–1.27 μg L^{-1} respectively.

The intra- and inter-day precision of the method in water samples were determined as the relative standard deviation (R.S.D. %). Intra-day precision was assessed by five determinations in 1 day, while inter-day precision was evaluated by five determinations in different days. RSDs that were obtained for both of them presented acceptable precisions, i.e. they were obtained in the rage of 1.50–2.65 and 2.31–3.35 for intra- and inter-day assay, respectively.

3.3. Analysis of real water samples using MSA-DLLME–HPLC

To evaluate applicability of the proposed method in real samples, five different water samples were extracted using the MSA-DLLME. All the samples were spiked with PEs standards at five levels; subsequently, they were extracted using the MSA-DLLME technique and finally the extracts were analyzed by HPLC method. Table 2 shows that with respect to the complexity of the matrices studied, the average results of three replicate analysis of each water samples, obtained by the proposed method, are in

satisfactory agreement (relative recoveries between 80.41% and 102.71% for DEP, BBP and DBP) with the added amounts of PEs standards ($1\ \mu g\ L^{-1}$), with R.S.D. ($n=3$) less than 4.0%. This indicates that the method is feasible for the determination of PEs in water samples. Fig. 3 shows the chromatograms obtained from river and mineral water samples by MSA-DLLME–HPLC–UV.

4. Conclusion

MSA-DLLME followed by HPLC–UV has been developed for rapid and sensitive determination of PEs at trace levels in real water samples. The MSA-DLLME is based on a binary component solvent system of water sample and low-density extraction solvent (dodecane). No disperser solvent was employed. In a comparative study which is shown in Table 3, the precision of the represented method for extraction of PEs from water samples was higher than the other conventional methods. Although it has poor responses for DMP (because DMP is slightly polar in comparison with other PEs), dodecane as an extracting solvent is safer and it has a good chromatographic behavior compared with chlorinated solvents; as a result, the evaporation step in the proposed method is eliminated so that it leads to the excellent precision. Furthermore, consumption of organic solvent in this method is lower than the others. Overall, this study indicates that the MSA-DLLME method is suitable for conducting studies on referral infected of PEs in the environmental and drinking water samples with sufficient specificity, simplicity and sensitivity.

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