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Dispersive liquid-liquid microextraction followed by high performance liquid chromatography for determination of phthalic esters in environmental water samples

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Abstract: A new method was developed for the simultaneous determination of six phthalic acid esters (PAEs) in different environmental water samples using salt-assisted dispersive liquid-liquid microextraction with carbon tetrachloride as an extraction solvent and acetonitrile as a dispersive solvent coupled to high-performance liquid chromatography with UV detection. The influence of the added NaCl to enrichment factor (EF) in DLLME was investigated. Salting-out effect causes the hydrophobicity of organic analytes to be increased and high EFs to be more pronounced than those in salt-free water. Greater EF, wider linearity, better recovery, smaller relative standard deviation (RSDs) and lower limit of detection were obtained at higher concentration of NaCl. Under the optimized extraction conditions, good linearity was observed for all analytes in a range of 1.00-100 $\mu g\cdot L^{-1}$ with the correlation coefficient (r^2)⩾0.9992. The limits of detection based on signal to noise of 3 were 0.01-0.03$\mu g\cdot L^{-1}$. The recoveries of PAEs were 97.5%-105.5% for spiked with 20 $\mu g\cdot L^{-1}$ of PAEs, The repeatability of the proposed method expressed as RSDs ranged from 3.13 to 5.32% (n=3). EFs are in the range of 78 to 262 fold. The method was applied to the determination of PAEs in water samples from local river, rain and

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urban wastewater treatment plant with the standard addition, the recoveries of PAEs were 86.2%-105.0%, 93.8%-107.0% and 92.4%-106.3%, the RSDs were below 6.79%. The current procedure afforded a convenient, inexpensive and reliable sample preparation with high extraction efficiency for trace PAEs in environmental water samples.

Keywords: Salting-out effect, Dispersive liquid-liquid microextraction, Phthalic acid esters, High performance liquid chromatography, Sample preparation

1. Introduction

Phthalic acid esters (PAEs) have a wide variety of industrial, agricultural and domestic applications. PAEs are used industrially as plasticizers in polymeric materials to increase their flexibility and transparency through weak secondary molecular interactions with polymer chains. Di (2-ethylhexyl) phthalate (DEHP) is widely used to soften polyvinylchloride plastics and non-polymers,[1] these compounds are also used as key additives in paper and paperboard manufacturing as defoaming agents, in capacitors as dielectrics, in food as preservatives, in construction adhesives, paper food wrapping, nail polish, dyes, insect repellents, plastic pipes, lubricants, detergents, perfumes, shampoos and bath soap.[2] Since they are not chemically bound to the products above mentioned, they can be released easily and migrate into the ecosystem or in water effluents during production and use.[3-5] PAEs are considered as ubiquitous environmental pollutants because of large and widespread use. PAEs as well as their metabolites can cause adverse effects on human health, especially on liver, kidney and testicles.[6-9] Dimethyl phthalate, diethyl phthalate, dibutyl phthalate,

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butylbenzyl phthalate, di-n-octyl phthalate and DEHP have been listed as priority contaminants and endocrine disrupting compounds by the US Environmental Protection Agency and other governmental agencies,[10,11] which are able to cause hormone disrupting activities for invertebrate, fish, avian, reptilian, and mammalian species.[12] Therefore, there are increasing demand for reliable and sensitive analytical methods for monitoring and determination of trace levels of these compounds in environmental matrices.

Until now, various pretreatment techniques have been developed to extract PAEs from different samples, such as liquid-liquid extraction,[13,14] solid-phase extraction,[15,16] which are considered expensive, time-consuming, labour-intensive and harmful for human health and environment. Thereafter, many researchers have been oriented towards the development of efficient, economical, and miniaturized sample preparation methods. As a result, solid phase microextraction,[17-20] liquid phase microextraction,[21,22] stir bar sorptive extraction[23,24] and hollow fiber liquid phase microextraction[25,26] have been developed. However, most of these methods require considerable extraction time to obtain satisfactory extraction efficiency.

Dispersive liquid-liquid microextraction (DLLME) was developed by Assadi and co-workers for the preconcentration and determination of target analytes.[27] This technique is based on the formation of tiny organic droplets in the sample solution using a water-immiscible organic solvent dissolved in a water-miscible organic dispersive solvent.[28,29] DLLME offers several distinctive traits such as rapidity, high enrichment factor, easy operation, and no need of large amount of extraction solvent,

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low cost and easy linkage to most of analytical instrument. Thus, DLLME has been frequently used for the determination of organic and inorganic contaminants in different samples.[30-35] However, the main drawback is that DLLME is somewhat matrix-dependent in complex matrices addressed.[36] Matrix effect such as highly saline solutions is a major problem in DLLME.[36,37] Salt addition is frequently used to adjust the ionic strength, improve the extraction efficiency and reduce the limit of detection as a result of the so-called salting-out effect, salting-out effect causes the aqueous solubility and activity of organic chemicals altered and the hydrophobicity to be increased.

In this study, a novel and fast salt-assisted dispersive liquid-liquid microextraction (SA-DLLME) followed by high performance liquid chromatography (HPLC) with UV detection has been applied for concentration and determination of six PAEs in environmental water samples. The influence of various experimental parameters, such as the kind and volume of extraction solvent and dispersive solvent, ultrasonic time, pH and salt concentration were studied and optimized. Under the optimized extraction conditions, the proposed method was applied to determine PAEs in the Lanzhou section of the Yellow River and related environmental water samples for the first time.

2. Experimental

2.1 Reagents and standards

All chemical reagents were of analytical grade, otherwise stated. Certified individual standards of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl

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phthalate (DnBP), butylbenzyl phthalate (BBP), di-n-octyl phthalate (DnOP) and di(2-ethylhexyl) phthalate (DEHP) were purchased from AccuStandard (New Haven, CT, USA). Their relevant physicochemical properties are given in Table 1. Individual standard stock solutions were prepared in methanol at a concentration of 500 mg·L^{-1} and stored at 4 ^{o}C in refrigerator. Mixtures of the standard solutions were prepared daily using doubly distilled with the stock solution.

Chloroform, carbon tetrachloride and chlorobenzene (Beijing Chemical Works, China) served as the extraction solvents. HPLC-grade methanol was purchased from Shandong Yuwang Industry Co., Ltd. (Yucheng, China). HPLC-grade acetonitrile, acetone and ethanol were from Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium chloride was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 0.45 μm micropore membrane was supplied by Automatic Science Instrument Co., Ltd. (Tianjin, China).

Table 1 Physical properties of PAEs[4]

PAEs	Abbreviation	Alkyl chain length	Molecular weight	Solubility in water (mg·L^{-1})	logK_{ow} [b]
Dimethyl phthalate	DMP	1	194.19	4000	1.60
Diethyl phthalate	DEP	2	222.24	1080	2.42
Di-*n*-butyl phthalate	DnBP	4	278.35	11.2	4.50
Butylbenzyl phthalate	BBP	4,6 [a]	312.39	2.69	4.73
Di-(2-ethylhexyl) phthalate	DEHP	8	390.56	0.09	8.39
Di-*n*-octyl phthalate	DnOP	8	390.56	0.022	8.06

[a] Aromatic ring

[b] The log of octanol-water partition coefficients

2.2 Instrumentation

All separations were performed on Waters 600E multi-solvent delivery system

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(Milford, MA, USA) consisting of a Rheodyne 7725i injector equipped with a 5-μL sample loop, Waters 2487 dual λ absorbance detector and a Waters Sunfire C_{18} chromatographic column (150mm×4.6mm, 5μm) at a flow rate of 1.0 $mL·min^{-1}$. A N2000 workstation (Zhejiang University, China) was used for the acquisition of data. The mobile phase consisted of methanol and water, and was applied in gradient mode. The separation gradient was started with 75% methanol and held for 6 min, followed by a linear increase to 85% in 5 min at a flow rate of 1.0 $mL·min^{-1}$, then changed to 100% in 7 min. After 5 min at 100%, the gradient was reversed to the initial condition in 5 min and equilibrated for an additional 5 min before the next sample was injected. All of PAEs were detected at 280 nm.

The centrifugation of the cloudy solutions was performed to on a TD_6 centrifuge (Changsha, China). The pH values were measured with a Sartorius PB-10 acidimeter (Beijing, China). Doubly distilled water, used in all experiments, was produced on SZ-93 automatic doubly distilled water device (Shanghai, China).

2.3 Environmental water samples

In this experiment, environment water samples including 4 river water (pH, ~7.55), 1 rainwater (pH, 7.49) and 2 wastewater samples (pH, 7.84 and 7.62) were collected in amber glass containers in May of 2013. The water samples of the Yellow River were freshly collected from different sites in Lanzhou section of the Yellow River. Rain water sample was taken from inside school. Wastewater samples were collected from local wastewater treatment plants. All environmental water samples were filtered through 0.45 μm micropore membranes, then stored in the dark at 4 ℃, the pH value

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of water samples was adjusted to 7.0 prior to analysis.

2.4 DLLME procedure

A 10-mL aliquot of the aqueous solution was transferred in a 15-mL screw cap glass conical test tube. Thereafter a mixture of extraction solvent (carbon tetrachloride 40 μL) and disperser solvent (acetonitrile 750 μL) was injected rapidly into the aqueous samples with 150 $g \cdot L^{-1}$ NaCl. The cloudy solution was formed and immersed into an ultrasonic water bath for 2 min. After centrifugation at 4000 rpm for 5 min, the dispersed droplets of extraction solvent were sedimented at the bottom of conical test tube. The upper aqueous phase was removed with a syringe, and the sedimented phase was directly injected for HPLC analysis.

3. Results and discussion

3.1 Optimization of salt-assisted dispersive liquid-liquid microextraction

To determine the optimized extraction conditions, the EF and extraction recovery (ER) were used to evaluate the extraction efficiency under different conditions. EF was defined as the ratio between the analyte concentration in the sedimented phase (c_{sed}) and the initial concentration of analyte (c_0) within the sample:

$$EF = \frac{c_{sed}}{c_0} \qquad (1)$$

ER was defined as the percentage of the total analyte amount which was extracted to the sedimented phase (n_{sed}).

$$ER\% = \frac{n_{sed}}{n_0} \times 100 = EF \times \frac{V_{sed}}{V_{aq}} \times 100 \qquad (2)$$

where c_{sed} and c_0 are the concentration of analyte in the sedimented phase and the

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initial analyte concentration in the aqueous phase, respectively, V_{sed} and V_{aq} are the volumes of sedimented phase and aqueous phase, respectively.

3.1.1 Effect of the kind and volume of extraction solvent

Some characteristics, such as low solubility in water, extraction capability of interested compounds and good chromatographic behavior, put extra limitations on the selection of extraction solvent in DLLME method. Halogenated hydrocarbons such as dichloroethane (1.32 $g{\cdot}mL^{-1}$), chloroform (1.47 $g{\cdot}mL^{-1}$), carbon tetrachloride (1.59 $g{\cdot}mL^{-1}$) and chlorobenzene (1.11 $g{\cdot}mL^{-1}$) as extraction solvents were examined in order to find the most suitable solvent for SA-DLLME. For this purpose, using 1000 μL acetone and 40 μL extraction solvent, series of sample solutions were studied. The results show that $CHCl_3$ as the extraction solvent can not form the emulsion with acetone, CCl_4 and C_6H_5Cl can form cloudy solutions which are easily centrifuged, and EFs is higher when CCl_4 as the extraction solvent compared with C_6H_5Cl. CCl_4 was employed as an extraction solvent in the following experiment.

To investigate the effect of extraction solvent volume on enrichment factor, additional experiments were performed by using 1000 μL acetonitrile containing different volumes of CCl_4. Figs. 1 shows curves of EF versus volume of extraction solvent, as can be seen, by increasing the volume of CCl_4 from 20.0 to 100.0 μL, EF increased first then decreased gradually, the maximum extraction efficiency was obtained when the volume of CCl_4 is 40 μL, therefore, 40 μL of CCl_4 was selected for further experiments.

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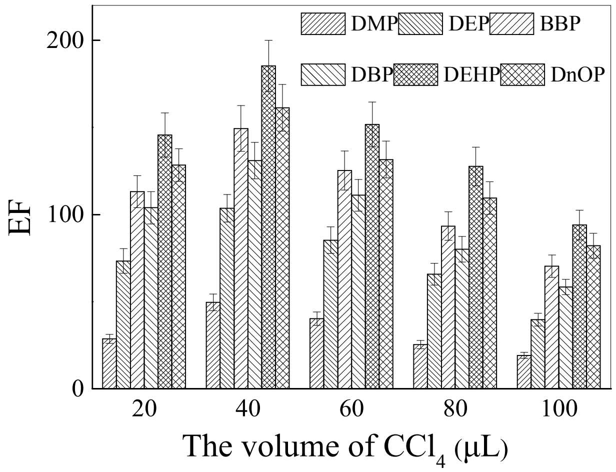

Fig. 1 Effect of volume of CCl_4 on EF. Extraction conditions: Extraction solvents, CCl_4; Disperser solvent, 1000 μL CH_3CN; pH, 7.0; Ultrasonic time, 2 min; Centrifugation time, 5 min; No addition of salt.

3.1.2 Effect of the kind and volume of disperser solvent

The addition of disperser solvent decreases the interfacial tension between the two phases and facilitates the formation of fine droplets in aqueous phase. As a result, this phenomenon speeds up the mass-transfer process of analytes from aqueous phase to organic phase and thereby overcomes the problem of the time taken.[27] The miscibility of the disperser solvent in the organic phase (extraction solvent) and the aqueous phase (sample solution) is essential for the selection of a disperser solvent. For this purpose, methanol, ethanol, acetonitrile and acetone were selected for use in the extraction procedure. The result was shown in Fig. 2. acetonitrile contributes to the highest EFs in the presence of 40 μL CCl_4, acetonitrile was chosen as disperser solvent.

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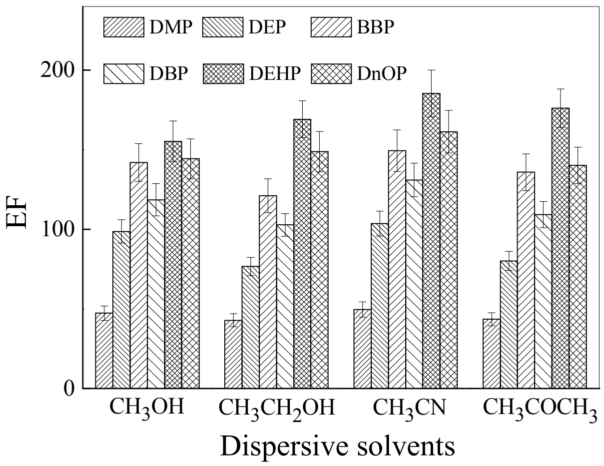

Fig. 2 Effect of different disperser solvents on EF. Extraction conditions: Extraction solvents, 40 μL CCl_4; Disperser solvent, 1000 μL; pH, 7.0; Ultrasonic time, 2 min; Centrifugation time, 5 min; No addition of salt.

The volume of disperser solvent directly affects the formation of the cloudy solution (water/disperser solvent/extraction solvent), and the degree of dispersion of extraction solvent in the aqueous phase, thus affecting the extraction efficiency.[6] Therefore, different volumes of acetonitrile were investigated to obtain the best results in terms of extraction efficiency. As can be seen in Fig. 3, the results indicated that the EFs increased first then decreased gradually with the increasing volume of methanol from 200 μL to 1250 μL for the reason mentioned above. Therefore, 750 μL acetonitrile was employed for the following work.

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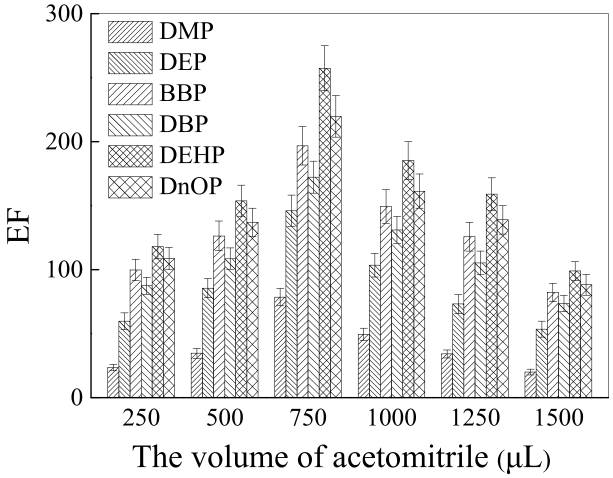

Fig. 3 Effect of volume of acetonitrile on EF. Extraction conditions: Extraction solvents, 40 μL CCl_4; Disperser solvent, CH_3CN; pH, 7.0; Ultrasonic time, 2 min; Centrifugation time, 5 min; No addition of salt.

3.1.3 Effect of pH

Sample pH is another important parameter that might affect the extraction efficiency, because the analytes will be present at different forms (as ions or neutral form) due to decomposition or dissociation at different pH. Extraction efficiency is related to the existing form of analytes. Therefore, series of experiments were performed to investigate the effect of pH on DLLME. The sample pH was adjusted in the range of pH 3-8. It can be seen from Fig. 4 that EFs of all PAEs had a slight increase when pH changed in the range of 3-7, but greatly deceased when pH was from 7 to 8, a maximum EFs was obtained at pH 7. Hence, pH 7 was selected in the following studies.

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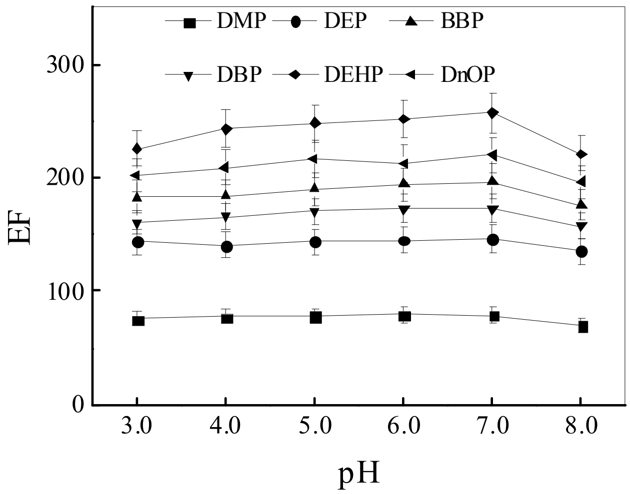

Fig. 4 Effect of pH on DLLME. Extraction conditions: Extraction solvents, 40 μL CCl_4; Disperser solvent, 750 μL CH_3CN; Ultrasonic time, 2 min; Centrifugation time, 5 min; No addition of salt.

3.1.4 Effect of ultrasonic time

In the SA-DLLME procedure, the interface between the extraction solvent and the bulk aqueous sample was enormously enlarged by forming a cloudy solution[24]. An ultrasound-assisted process can promote fine droplets of extraction solvent and accelerate the formation of cloudy solution. Hence, ultrasonic time plays an important role in this procedure. However, there are disadvantages in prolonging ultrasonic time, such as loss of extraction solvent and analytes. The effect of ultrasonic time was evaluated in the range of 1-5 min and it was seen from Fig. 5 that ultrasonic for 2 min was enough to form a complete cloudy solution. Hence, 2 min was chosen for the dispersive procedure.

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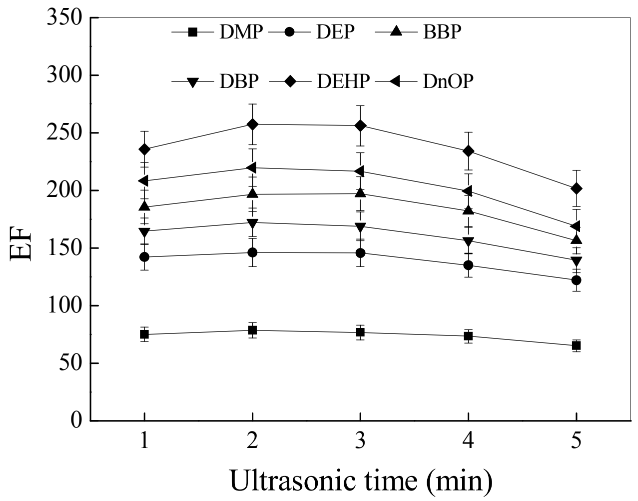

Fig. 5 Effect of ultrasonic time on DLLME. Extraction conditions: Extraction solvents, 40 μL CCl_4; Disperser solvent, 750 μL CH_3CN; pH, 7.0; Centrifugation time, 5 min; No addition of salt.

3.1.5 Effect of salt on EF

Salt addition influences the partition coefficient of analyte. By adding salt into the sample solution, the ionic strength will increase and the aqueous solubility of analytes will decrease. This salting out effect causes the analytes more easily to pass from the sample into the organic phase, accordingly, the salt addition improves the extraction efficiency and sensitivity. Various experiments were performed by adding different amounts of NaCl and the results were shown in Fig. 6, EF of PAEs greatly increased with decreasing solubility or increasing $\log K_{O/W}$ values of PAEs in Table 1, Greater EF values were obtained in salt water. This result suggests that the addition of NaCl decrease the solubility of PAEs in water phase and thereby the distribution coefficients of PAEs increase. EFs are almost constant when the concentration of NaCl is in the range of 150-300 $g{\cdot}L^{-1}$, addition of excessive salt increased the density and viscosity of the aqueous phase, thereby not facilitating the phase separation of organic microdrop from aqueous phase. According to theses facts, the subsequent

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experiments were carried out with addition of 150 g·L^{-1} NaCl.

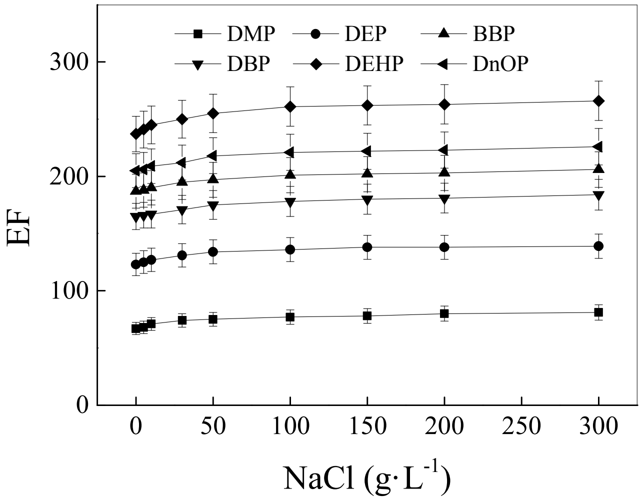

Fig. 6 Effect of salt on EF of PAEs. Extraction conditions: Extraction solvents, CCl_4; Disperser solvent, 750 μL CH_3CN; pH, 7.0; ultrasonic time, 2 min Centrifugation time, 5 min.

3.1.6 Effect of salt on extraction time

Salt addition has also a significant effect on the viscosity of aqueous phase besides greater EF as mentioned above. Due to very large surface area between extraction solvent and aqueous phase and rapid mass transfer of target analytes from aqueous phase to extraction solvent in DLLME, the equilibrium state is very quickly achieved although the viscosity of aqueous phase increases at high concentration of NaCl. As a result, the viscosity of aqueous phase has a negligible effect on extraction time of PAEs. However greater viscosity of aqueous phase is not favorable for the phase separation of CCl_4 microdrops.

3.1.7 Effect of salt on centrifugation time

The density of aqueous phase increased close to extractant due to salt addition, which is not favorable for the phase separation. Centrifugation was a crucial step in

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the DLLME method, because it can accelerate the phase-separation process, especially for especially for the solution containing much NaCl, centrifugation time could affect the volume of settled phase. For these reasons, the centrifugation time was optimized from 2 to 15 min at 4000 rpm. The experimental results show that the best performance is obtained at 5 min. Therefore, 5 min was chosen as optimum.

3.2 Analytical performance of SA-DLLME-HPLC-UV

The regression analysis was typically performed for DLLME-HPLC-UV of PAEs in salt-free water and in aqueous solutions of 10g·L^{-1} NaCl (near physiological saline), 30 g·L^{-1} NaCl (near seawater) and 150 g·L^{-1} NaCl under optimized conditions. Corresponding correlation coefficients (r^2) was calculated. Recovery (R), relative standard deviations (RSDs) and limits of detection (LODs) were evaluated for the spiked water with 20μg·L^{-1} each PAE and summarized in Table 2. These data demonstrate that higher concentration of NaCl affords wider linearity, better recovery, smaller RSDs and lower LODs of PAEs in aqueous phase.

Table 2

Analytical parameters of DLLME-HPLC-UV for PAEs in different salt water (n=3)

PAEs	NaCl (g·L^{-1})	Linearity (μg·L^{-1})	r^2	Spiked (μg·L^{-1})	Detected (μg·L^{-1})	R (%)	RSDs (%)	LODs (μg·L^{-1})
DMP	0	2.00-100	0.9991	20	18.5	92.5	5.62	0.08
DEP	0	2.00-100	0.9989	20	21.8	109	6.17	0.10
DnBP	0	2.00-100	0.9992	20	19.2	96.0	5.25	0.10
BBP	0	2.00-100	0.9985	20	21.4	107	5.84	0.10
DnOP	0	10.00-100	0.9992	20	21.0	105	5.12	0.20

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DEHP	0	10.00-100	0.9994	20	19.1	95.5	5.51	0.16
DMP	10	2.00-100	0.9998	20	19.3	96.5	5.27	0.04
DEP	10	2.00-100	0.9992	20	20.9	104.4	5.34	0.06
DnBP	10	2.00-100	0.9998	20	21.5	107.7	6.18	0.06
BBP	10	2.00-100	0.9980	20	21.2	106.2	5.96	0.06
DnOP	10	10.00-100	0.9994	20	19.1	95.6	5.57	0.16
DEHP	10	5.00-100	0.9992	20	19.4	97.1	4.96	0.12
DMP	30	2.00-100	0.9996	20	19.4	97.0	4.71	0.02
DEP	30	2.00-100	0.9994	20	19.3	96.5	4.59	0.03
DnBP	30	2.00-100	0.9979	20	21.4	106.9	5.77	0.03
BBP	30	2.00-100	0.9981	20	21.1	105.6	5.34	0.03
DnOP	30	5.00-100	0.9994	20	19.5	97.5	4.47	0.06
DEHP	30	5.00-100	0.9991	20	19.6	98.0	4.31	0.06
DMP	150	1.00-100	0.9992	20	20.8	104.0	4.12	0.01
DEP	150	1.00-100	0.9992	20	19.5	97.5	3.81	0.02
DnBP	150	1.00-100	0.9994	20	21.1	105.5	5.32	0.02
BBP	150	1.00-100	0.9996	20	20.8	104.0	4.75	0.02
DnOP	150	1.00-100	0.9996	20	20.7	103.5	3.86	0.03
DEHP	150	5.00-100	0.9994	20	19.7	98.5	3.13	0.03

Extraction conditions: Extraction solvents, CCl_4; Disperser solvent, 750 μL CH_3CN; pH, 7.0; ultrasonic time, 2 min Centrifugation time, 5 min.

3.3 Analysis of real water sample

The current method was applied to the determination of six PAEs in Yellow River water, rainwater and sewage water samples under the optimum conditions. The results were shown in Table 3, except river water 1, DnBP and DEHP were found in other water samples, this indicates DnBP and DEHP are the two most widely used PAEs. With the increase of population density, water was polluted by PAEs, only BBP was

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not detected, the remaining PAEs were found in river water 4, local plastic greenhouses, sewage treatment plant and large landfill may contributed to it. Higher concentrations of all PAEs were found in rainwater, these data demonstrate that local environment, including water environment, has been polluted by PAEs.

All the water samples were fortified with the target analytes at concentration of 5 $\mu g \cdot L^{-1}$ to study matrix effects on the extraction recovery, the recoveries of six PAEs were ranged from 86.2%-105.0% for river water, 93.8%-107.0% for rain water and 92.4%-106.3% for wastewater with RSD less than 6.79%. The results suggest that the proposed method could be an effective sample preparation method for the determination of PAEs in environmental water sample matrices.

Table 3 Analytical results of SA-DLLME in different environmental water samples (n=3)

Samples	PAEs	Original ($\mu g \cdot L^{-1}$)	RSD (%)	Spiked ($\mu g \cdot L^{-1}$)	Detected ($\mu g \cdot L^{-1}$)	Recovery (%)	RSD (%)
1	DMP	Nd	5.51	5.0	4.48	89.6	5.12
River water	DEP	Nd	5.89	5.0	4.31	86.2	5.38
	DnBP	Nd	6.13	5.0	4.68	93.6	5.29
	BBP	Nd	5.76	5.0	4.58	91.6	5.35
	DnOP	Nd	6.32	5.0	4.53	90.6	5.56
	DEHP	Nd	5.98	5.0	4.82	96.4	4.72
2	DMP	Nd	5.86	5.0	4.56	91.2	5.37
River water	DEP	Nd	5.74	5.0	4.45	89.0	5.11
	DnBP	1.18	6.85	5.0	5.96	96.4	5.75
	BBP	Nd	6.31	5.0	4.86	97.2	5.87
	DnOP	Nd	5.52	5.0	4.59	91.8	5.32
	DEHP	1.66	6.09	5.0	6.24	93.7	5.37
3	DMP	Nd	6.26	5.0	4.74	94.8	5.79
River water	DEP	Nd	6.38	5.0	4.77	95.4	5.85
	DnBP	1.57	7.16	5.0	6.31	96.0	6.71
	BBP	Nd	6.33	5.0	4.83	96.6	5.92
	DnOP	Nd	6.28	5.0	4.70	94.0	5.80

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	DEHP	2.15	5.96	5.0	7.37	103.1	5.34
4	DMP	1.25	6.35	5.0	5.96	95.4	5.77
River water	DEP	1.10	6.18	5.0	5.72	93.8	5.96
	DnBP	1.63	6.43	5.0	6.96	105.0	6.12
	BBP	Nd	6.29	5.0	5.18	103.6	5.94
	DnOP	0.96	5.84	5.0	5.62	94.3	5.15
	DEHP	2.46	5.06	5.0	7.83	105.0	4.77
5	DMP	2.58	7.36	5.0	7.31	96.4	6.43
Rainwater	DEP	1.52	6.52	5.0	6.26	96.0	5.94
	DnBP	5.41	6.79	5.0	10.9	104.7	6.35
	BBP	1.01	6.82	5.0	6.32	105.2	6.17
	DnOP	2.38	6.19	5.0	6.92	93.8	5.24
	DEHP	6.36	6.22	5.0	12.15	107.0	5.39
6	DMP	Nd	7.26	5.0	4.81	96.2	6.12
Wastewater	DEP	1.29	7.37	5.0	5.85	93.0	6.61
	DnBP	4.38	6.63	5.0	9.89	105.4	6.22
	BBP	1.17	6.89	5.0	6.46	104.7	6.37
	DnOP	2.15	5.72	5.0	6.82	95.4	5.25
	DEHP	4.91	6.96	5.0	10.39	104.8	6.71
7	DMP	Nd	6.11	5.0	4.69	93.8	5.92
Treated	DEP	Nd	6.25	5.0	4.82	96.4	5.77
wastewater	DnBP	1.93	7.24	5.0	7.37	106.3	6.86
	BBP	Nd	7.36	5.0	5.15	103.0	6.79
	DnOP	1.02	6.15	5.0	5.56	92.4	6.03
	DEHP	3.32	6.34	5.0	7.89	94.8	5.72

* Not detected or lower than LOD

4. Conclusions

In this study, SA-DLLME-HPLC-UV method for the determination of PAEs in water samples has been evaluated. The optimum conditions of extraction performance have been obtained. The established method can be applied to determine the concentration of PAEs in environmental water samples. The recoveries of those compounds studied in water are from 86.2% to 107.0%. Adequate repeatability, high recoveries and enrichment factors demonstrated that the method is feasible for quantitative analysis of PAEs in environmental water samples, and could be used in

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routine analysis.

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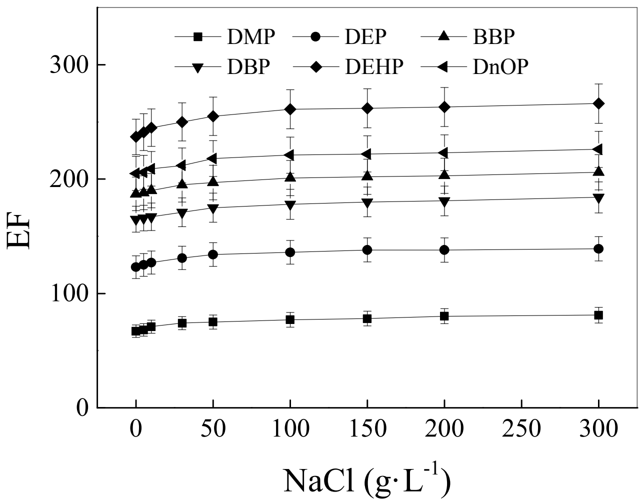

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