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Low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction combined with gas chromatography–mass spectrometry for the fast determination of phthalate esters in bottled water

Yufeng Zhang, Hian Kee Lee*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

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ABSTRACT

For the first time, a novel low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (LDS–VSLLME) was developed for the fast, simple and efficient determination of six phthalate esters (PEs) in bottled water samples followed by gas chromatography–mass spectrometry (GC–MS). In the extraction procedure, the aqueous sample solution was injected into a mixture of extraction solvent (toluene) and surfactant (cetyltrimethyl ammonium bromide), which were placed in a glass tube with conical bottom, to form an emulsion by the assistance of vortex agitation. After extraction and phase separation by centrifugation, and removal of the spent sample, the toluene extract was collected and analyzed by GC–MS. The addition of surfactant enhanced the dispersion of extraction solvent in aqueous sample and was also favorable for the mass transfer of the analytes from the aqueous sample to the extraction solvent. Moreover, using a relatively less toxic surfactant as the emulsifier agent overcame the disadvantages of traditional organic dispersive solvents that are usually highly toxic and expensive and might conceivably decrease extraction efficiency to some extent since they are not as effective as surfactants themselves in generating an emulsion. With the aid of surfactant and vortex agitation to achieve good organic extraction solvent dispersion, extraction equilibrium was achieved within 1 min, indicating it was a fast sample preparation technique. Another prominent feature of the method was the simple procedure to collect a less dense than water solvent by a microsyringe. After extraction and phase separation, the aqueous sample was removed using a 5-mL syringe, thus leaving behind the extract, which was retrieved easily. This novel method simplifies the use of low-density solvents in DLLME. Under the optimized conditions, the proposed method provided good linearity in the range of 0.05–25 μg/L, low limits of detection (8–25 ng/L) and good enrichment factors up to 290. The proposed method was successfully applied to the extraction of PEs in bottled water samples as a fast, efficient, and convenient method.

1. Introduction

Phthalate esters (PEs) are used primarily as plasticizers in polymeric materials to increase their flexibility and workability through weak secondary molecular interactions with polymer chains. Since they are physically bound to the polymer chains, they can be released easily from products and migrate into the water or food that comes into direct contact with them [1,2]. Certain PEs, as well as their degradation products and metabolites, can cause adverse effects on human health, especially on the kidney, liver and testicles [3]. Recently, the potential endocrine disrupting properties of PEs were also reported [4]. These compounds are therefore considered to be hazardous to the environment and human health. Some PEs (e.g. dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-*n*-butyl phthalate (DnBP)) are on the priority list released by the US Clean Water Act [5]. Food products contaminated with PEs have been reported [4], due to the use of plastics as food containers and packaging. Particularly, penetration of PEs from plastic packaging into water is common and has become a matter of public concern in recent years. Therefore, the development of sensitive and reliable analytical methods to evaluate and monitor trace amounts of PEs in different water samples are desirable for human health protection and environmental control.

Sample preparation of PEs is usually necessary before instrumental analysis to obtain sensitive and accurate results since environmental samples are complex, and PEs are present at extremely low concentrations. Typically, this would require an extraction step such as liquid–liquid extraction (LLE) or solid-phase extraction (SPE). However, conventional LLE consumes large amounts of toxic and expensive high purity organic solvents.

* Corresponding author. Tel.: +65 6516 2995; fax: +65 6779 1691.
E-mail address: chmleehk@nus.edu.sg (H.K. Lee).

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Although SPE requires much less solvent and is less time consuming than LLE, it is expensive and column conditioning, drying, etc. are necessary steps which add to the processing time. To address these shortcomings, much research has been directed toward the development of efficient, miniaturized and environmentally benign sample extraction methods, such as liquid-phase microextraction (LPME) [6] and solid-phase microextraction (SPME) [7]. There are numerous SPME [8–14] and LPME [15–19] methods that have been applied to PEs in various environmental samples [10,17,20–22].

In 2006, a rapid LPME method, dispersive liquid–liquid microextraction (DLLME), was introduced by Rezaee et al. [23]. In this procedure, a mixture of high-density organic solvent (extraction solvent) and water miscible solvent (dispersive solvent) was rapidly injected into an aqueous sample to form an emulsion. Due to the extraction solvent being highly dispersed in the aqueous phase, the surface area between extraction solvent and sample solution was essentially infinitely large, thus speeding up the extraction. After extraction, the extract can be sedimented to the bottom of the extraction vial by centrifugation. The advantages of DLLME include rapidity, low cost, ease of operation and high enrichment factor. However, the use of water-miscible organic dispersive solvent could decrease the partition coefficient of analytes with respect to the extraction solvent, which potentially reduces the extraction efficiency.

Recently, Regueiro et al. [24] developed ultrasound-assisted emulsification microextraction (USAEME). In USAEME, ultrasound radiation instead of organic dispersive solvent as used in DLLME was applied to assist the dispersion of the extraction solvent into aqueous samples; due to the elimination of dispersive solvent, high extraction efficiency could be achieved. Moreover, USAEME simplified the instrumentation required during the extraction process. However, with a longer sonication time (ca. 15 min), some analyte degradation might occur under some special conditions (e.g. large pressure, temperature gradients, high shear forces and free radical generation) [25].

More recently, a novel LPME method, vortex-assisted liquid–liquid microextraction (VALLME) was developed by Yiantzi et al. [25]. In this procedure, the extraction solvent was dispersed into aqueous samples by vortex mixing, which is a powerful but mild emulsification procedure. VALLME overcomes the main disadvantages of DLLME (need for dispersive solvent) and USAEME (potential analyte degradation) as mentioned above. Since its introduction, it has been successfully applied to the determination of organochlorine pesticides [26], perfluorooctane sulfonate [27], polychlorinated biphenyls [28] and organophosphorus pesticides [29] from different sample matrices due to its simplicity and high efficiency in the extraction process.

Surfactants are amphiphilic organic compounds which contain both hydrophilic heads and hydrophobic tails [30]. A surfactant can reduce both the surface tension of water by adsorbing at the liquid–gas interface, and the interfacial tension between oil and water by adsorbing at the liquid–liquid interface [31], thus serving 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 LPME was developed by Wu et al. [30] and proved to be efficient, simple, rapid and cost-effective. The application of a surfactant as an emulsifier in VALLME combines the advantages of both VALLME and DLLME. To date, only one application of vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (VSLLME) has been reported [29]. In this work, the addition of surfactant Triton X-114 as emulsifier greatly enhanced extraction efficiency and reduced extraction time. VALLME is usually carried out for 2 min [25–28], while for this work only 30 s was enough for the extraction. After extraction, the two phases could be separated by centrifugation and the sediment phase could be easily collected for further analysis. However, high-density solvent chlorobenzene was used, which is undesirable since it is potentially toxic. In addition, the use of a high-density solvent limits the wider applicability of the method due to a more limited choice of solvents.

In the present study, low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (LDS–VSLLME) with gas chromatography–mass spectrometry (GC–MS) was for the first time applied to the fast determination of six PEs in bottled water samples. In the proposed procedure, a solvent of lower density than water, toluene, was employed as extraction solvent, and cetyltrimethyl ammonium bromide (CTAB) was used as emulsifier to facilitate the dispersion of organic solvent in the aqueous sample. After a 30 s extraction assisted by vortex agitation, phase separation was achieved by centrifugation. The supernatant (extraction solvent) was collected at the conical bottom of the tube after removing the aqueous sample by a syringe. This method avoids the necessity of a special homemade device for the collection of low-density organic solvents [32], which is tedious and troublesome to fabricate. In order to evaluate the proposed method, conventional DLLME, LDS-DLLME and USAEME were carried out for comparison with the performance of LDS–VSLLME. Under the optimized microextraction conditions, the developed method was applied to analyze bottled water samples.

2. Experimental

2.1. Reagents and materials

The PE standards (DMP, DEP, DnBP, benzyl butyl phthalate (BzBP), di-2-ethyl hexyl phthalate (DEHP) and di-*n*-octyl phthalate (DnOP)) were bought from Supelco (Bellefonte, PA, USA) in the form of a methanolic stock solution containing 2000 mg/L of each compound. Their structures are shown in Table 1. HPLC–grade methanol (purity 99.9%), acetone (purity 99.9%) and toluene (purity 99.9%) were purchased from Tedia Company (Fairfield, OH, USA). 1-Octanol (purity >99%), toluene (purity 99.9%), CTAB (purity >99%), polyoxyethylene octyl phenyl ether, Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) (n = 9–10) (purity >99%) and polyethylene glycol tert-octylphenyl ether, Triton X-114 ($C_{14}H_{22}O(C_2H_4O)_n$) (n = 7–8) (purity >99%) were bought from Sigma–Aldrich (St. Louis, MO, USA), while chlorobenzene (purity 99.9%), cyclohexane (purity 99.9%) and isooctane (purity 99.9%) were from Fisher (Loughborough, UK). Sodium chloride (NaCl) was obtained from Goodrich Chemical Enterprise (Singapore). Sodium dodecyl sulfate (SDS) (purity 99%) was purchased from BDH Laboratory Supplies (Poole, England). Ultrapure water was produced on a Nanopure (Barnstead, Dubuque, IA, USA) water purification system.

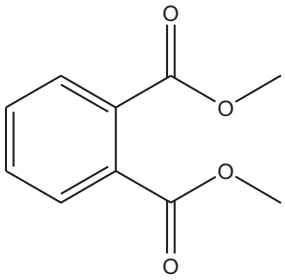
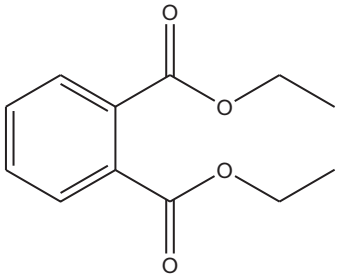
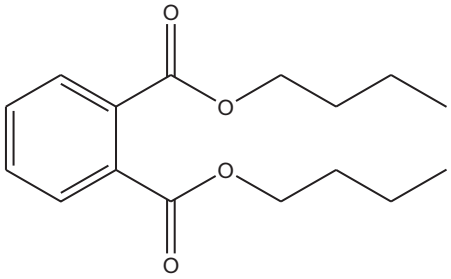
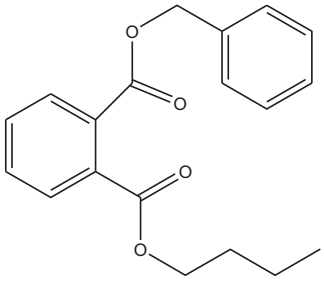
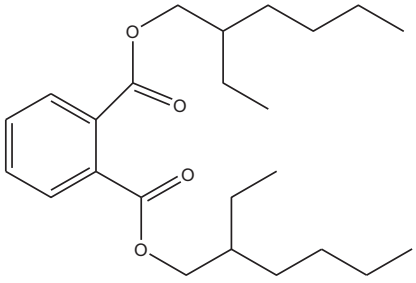
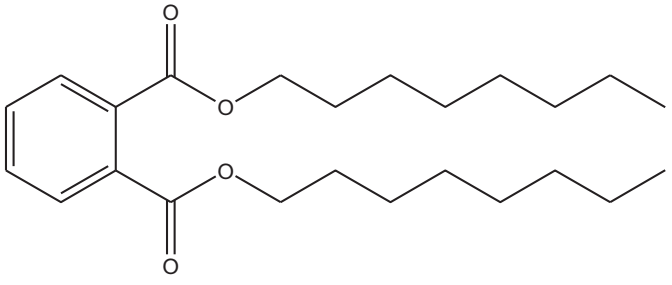
Both of the 100-μL HPLC microsyringe used for the addition of extraction solvent and surfactant, and the 10-μL microsyringe used for GC–MS injection were purchased from SGE (Sydney, Australia). The 5-mL plastic syringe was bought from HSW (Tuttlingen, Germany).

A stock solution containing all analytes (at 10 mg/L of each) was prepared in methanol and stored at 4 °C. Water samples were prepared by spiking ultrapure water with analytes at known concentrations (5 μg/L) daily to study extraction performance under different conditions. Bottled water samples were bought from a local market and were stored in the dark at 4 °C and then analyzed without filtration.

2.2. Instrumentation

Analysis was carried out on a Shimadzu QP2010 (Kyoto, Japan) GC–MS system with a DB-5 MS fused silica capillary column (30 mm × 0.25 mm I.D., film thickness 0.25 μm) (J&W Scientific, Folsom, CA, USA). Helium was employed as carrier gas at a flow rate

Table 1
Chemical structures of PEs considered in this work.

Analyte	CAS number	Structure
DMP	131-11-3	
DEP	84-66-2	
DnBP	84-74-2	
BzBP	85-68-7	
DEHP	117-81-7	
DnOP	117-84-0	

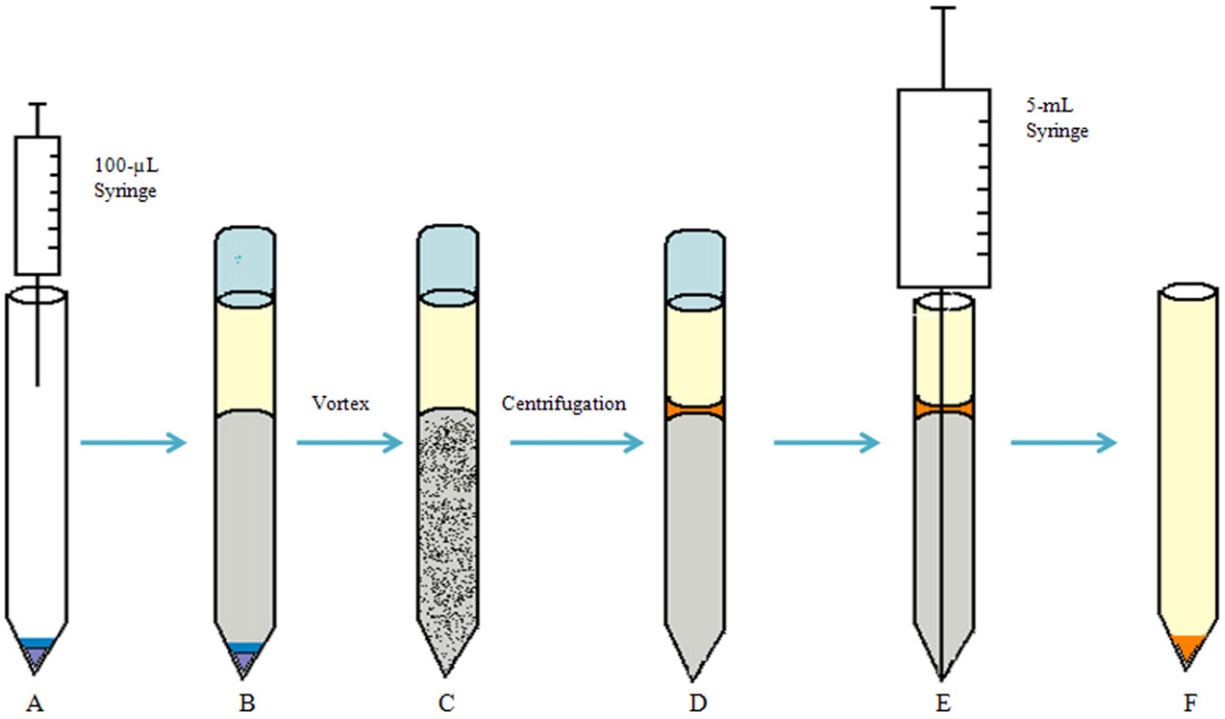


Fig. 1. The LDS–VSLLME procedure (A) introduction of extraction solvent and surfactant solution, (B) addition of sample solution, (C) vortex agitation for 1 min, (D) phase separation after centrifugation, (E) removal of the aqueous phase, and (F) extraction solvent remaining at the bottom of the extraction tube.

of 1.65 mL/min. The injector temperature was set at 250 °C. The GC oven temperature was initially set at 100 °C and then programmed to 280 °C at 10 °C/min and then held for 4 min. The GC–MS interface was maintained at 270 °C. All injections were in splitless mode. Selective ion monitoring (SIM) mode was adopted for quantitative determination of the analytes. The masses monitored by the detector were set as follows: 6–7 min, *m*/*z* 135, 163, 164, 194 (DMP); 8–8.5 min, *m*/*z* 149, 150, 176, 177 (DEP); 12–12.5 min, *m*/*z* 149, 150, 205, 223 (DnBP); 15.5–16 min, *m*/*z* 91, 149, 150, 206 (BzBP); 17–17.5 min, *m*/*z* 149, 150, 167, 279 (DEHP); 18.5–20 min, *m*/*z* 149, 150, 167, 279 (DnOP).

2.3. LDS–VSLLME procedure

Fig. 1 shows the LDS–VSLLME procedure. Briefly, 30 μL toluene and 50 μL 2.0×10^{-2} mol/L aqueous solution of detergent CTAB were first injected into a 10 mL glass tube with a conical bottom, using a 100-μL HPLC microsyringe. A 5 mL water sample was added in the tube subsequently. The resulting mixture was then vigorously shaken on a vortex agitator (Scientific Industries, Bohemia, NY, USA) at 3200 rpm for 1 min. As a result, an emulsion containing fine droplets was formed facilitating mass transfer of the target analytes into the extraction solvent. The emulsion was disrupted by centrifugation at 4000 rpm for 5 min, the organic phase formed a layer at the top of the aqueous sample. The aqueous phase was then completely removed using a 5.0 mL syringe, leaving behind the organic solvent (~15 μL) at the bottom of the conical tube. One microliter of the extract could be easily withdrawn using a 10-μL GC syringe and injected into the GC–MS system for analysis.

2.4. Comparative studies

The performance of LDS–VSLLME was compared with conventional DLLME, LDS-DLLME and USAEME. Spiked ultrapure water samples (3 μg/L of each PE) were used for the comparative extractions.

2.4.1. Conventional DLLME

For DLLME, a 5 mL water sample was placed in a 10 mL glass tube with a conical bottom. A mixture of 500 μL acetone (dispersive solvent) and 30 μL chlorobenzene (extraction solvent) was rapidly injected into the aqueous solution. Immediately, an emulsion was formed. After centrifugation at 4000 rpm for 5 min, the organic extract (~11 μL) settled at the bottom of the centrifuge tube. One microliter of extract was injected into the GC–MS system for analysis. The conditions used here were most favorable for extraction.

2.4.2. LDS-DLLME

For LDS-DLLME, the procedure was similar to that for DLLME as described above, except that the extractant solvent was toluene (30 μL). The extract was left at the top of the water sample, which was removed as described above (Section 2.3), leaving behind ca. 7 μL of the extract. One microliter of the extract was injected into the GC–MS system for analysis.

2.4.3. USAEME

Thirty microliters of toluene were rapidly injected into a 5 mL water sample in a 10 mL glass tube with a conical bottom. After injection, the tube was immersed in an ultrasonic water bath. Upon application of 35 kHz of ultrasound frequency, an emulsion formed in the tube. After 1 min of ultrasonication/extraction, the emulsion was separated into two phases by centrifugation at 4000 rpm for 5 min. The upper layer (organic extract, ~23 μL) was collected as described above (Section 2.3) and 1 μL of the extract was analyzed by GC–MS.

3. Results and discussion

It is well known that the most important problem concerning PE analysis is the risk of contamination, resulting in over-estimated concentrations. The sources of contamination can be present in

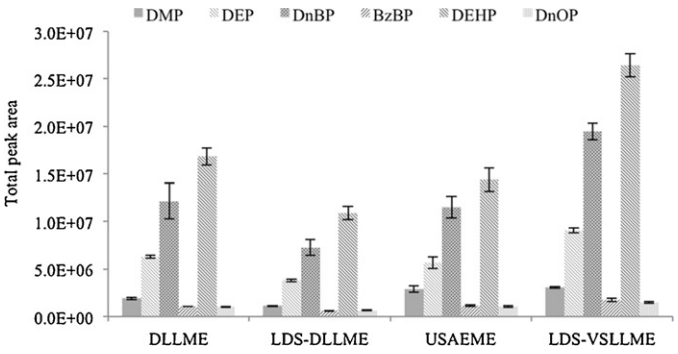


Fig. 2. Comparison of DLLME, LDS-DLLME, USAEME, and LDS–VSLLME.

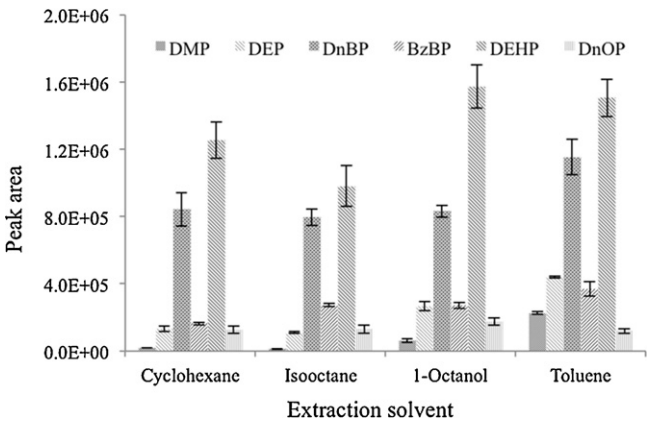


Fig. 3. Effect of extraction solvent on extraction. Extraction conditions: sample volume, 5.0 mL; extraction solvent volume, 40 μL; Triton X-100 concentration, 0.2 mmol/L; vortex time, 1 min.

any step of the analytical procedure. In this work, special care was taken to avoid the contact of reagents and solutions with plastic materials. Laboratory glassware was washed prior to use with ultrapure water, acetone and methanol, and then dried at 100 °C overnight. They were stored in heat-treated aluminum foil to minimize exposure. Despite these precautions, a problem with PE contamination was encountered. In a blank run (LDS–VSLLME of ultrapure water), DEP, DnBP and DEHP were detected. In isolating the problem, it was discovered that the toluene was the source of the contamination. Direct injection of the toluene used indicated that it was contaminated with DEP, DnBP and DEHP. The concentrations of these PEs were similar to those detected after the blank analysis (data not shown). This result indicated that the extraction procedure apparently did not introduce extraneous PEs, and all the contaminants were from the toluene. To address the problem, toluene from another supplier was evaluated. However, the contamination problem was even worse. As a result, we continued to use the first brand of toluene, but taking into account the PE contamination in the solvent in the subsequent optimization and validation experiments, and real-world sample analysis.

3.1. Comparison of LDS–VSLLME with conventional DLLME, LDS-DLLME and USAEME

It can be clearly seen from Fig. 2 for the six representative PEs that LDS–VSLLME gave the best extraction results (the total peak area is defined as the product of GC peak area of 1 μL extract multiplied by the volume of final extract for a particular extraction method), followed by DLLME, USAEME and LDS-DLLME. Moreover, the toluene, which is used as extraction solvent in the proposed method, LDS–VSLLME, is much less toxic in comparison with the chlorinated solvents widely used in conventional DLLME. The simple low-density solvent collection approach expands the applicability of DLLME. Compared with USAEME, much higher extraction efficiency was obtained; this may be due to that the combination of surfactant and vortex agitation was highly efficient for the dispersion of the organic extraction solvent, and thus extraction equilibrium could be achieved in a short time. Most importantly, the proposed technique employed a surfactant as a substitute for the large amount of dispersive solvent (up to several 100 μL) that is often applied in DLLME. This also addresses the issue of a reduced partition coefficient when a large volume of dispersive solvent is used in the latter method which inhibits the mass transfer of analytes to the extraction solvent. Moreover, a surfactant is relatively less toxic compared to an organic dispersive solvent, especially one that is as volatile as acetone.

3.2. Determination of the most favorable extraction conditions

To achieve the best LDS–VSLLME conditions, the effect of different extraction parameters including the type and volume of extraction solvent, the type and concentration of the surfactant, salt addition, and vortex time were studied in terms of the peak areas of analytes. All experiments were performed at least in triplicate. To achieve the best dispersion of the extraction solvent, the maximum speed setting of the vortex agitator (3200 rpm) was applied during all the experiments.

3.2.1. Effect of extraction solvent

The selection of an appropriate extraction solvent is of great importance in LDS–VSLLME. The organic extraction solvent determines the partition coefficient between the extraction phase and donor phase. In this method, a suitable solvent has to meet the following requirements: (1) having a good extraction affinity for the target analytes to ensure high enrichment; (2) being immiscible with water; (3) having a lighter density than water; and (4) having good chromatographic behavior. To select the most suitable one, four common low-density organic solvents were evaluated as extraction solvent including cyclohexane (density 0.78 g/mL), 1-octanol (density 0.82 g/mL), isooctane (density 0.69 g/mL) and toluene (density 0.87 g/mL). Peak areas were compared and the results for all the PE analyses are shown in Fig. 3. The figure shows that toluene and 1-octanol have comparable extraction efficiencies which were higher than those obtained with the other solvents; this may be accounted for by their better solvation capabilities toward the target analytes. However, considering the better GC–MS peak shapes (not shown) achieved when using toluene as solvent, it was preferred.

3.2.2. Effect of extraction solvent volume

In LDS–VSLLME, the volume of extraction solvent is also an important parameter, as it impacts on the enrichment factor. To study the effect of extraction solvent volume on extraction, the volume of toluene was varied over the range of 20–60 μL, and the results are shown in Fig. 4. According to Fig. 4, the extraction efficiencies decreased when the volume of toluene used was increased from 20 to 60 μL. This can be explained by the dilution effect. At smaller volumes of the extraction solvent, higher extraction efficiency was obtained as expected. However, when the volume of toluene was 20 μL, it was relatively difficult to retrieve it reproducibly after extraction. Thus, in consideration of the extraction efficiency, volume and reproducibility, 30 μL of

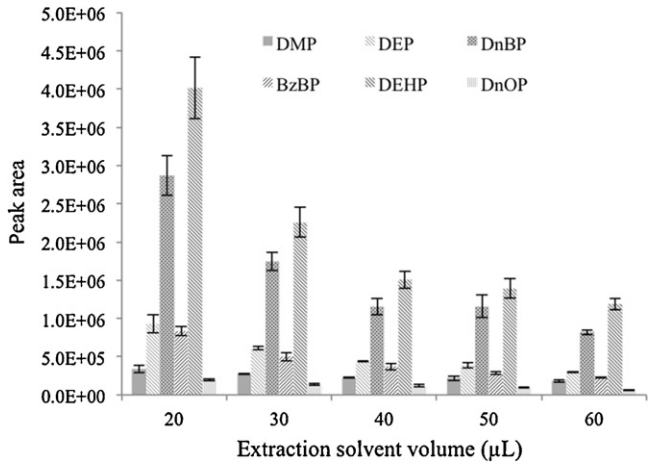


Fig. 4. Effect of the solvent volume on extraction. Extraction conditions: extraction solvent, toluene; sample volume, 5.0 mL; Triton X-100 concentration, 0.2 mmol/L; vortex time, 1 min.

toluene were selected as the most suitable volume for subsequent experiments.

3.2.3. Effect of the type and concentration of surfactant

The surfactant, which serves as an emulsifier, accelerates the emulsification of the water-immiscible organic extraction solvent in the aqueous solution under vortex mixing. Three different types of surfactants (anionic (SDS), cationic (CTAB) and non-ionic (Triton X-100 and Triton X-114)) were investigated. Their critical micellar concentrations (CMCs) are 7, 0.91, 0.24 and 0.21 mmol/L, and hydrophile–lipophile balance (HLB) values are 40, 15.8, 13.4 and 12.4, respectively. Fig. 5 shows the variation of the extraction efficiency with, and without the surfactants under consideration. According to Fig. 5, Triton X-100 and CTAB gave comparably good extraction efficiency for all the analytes. The effect of different surfactants on the extraction efficiency could be related to the hydrophobicity and polarity of the analytes and the HLB value of the surfactants. When the HLB value of a surfactant is between 8 and 18, it can be used as an emulsifier [30]. This suggests that SDS is not suitable for use as an emulsifier since its HLB value is much higher than 18. Triton X-100 and CTAB might have a suitable hydrophobicity for the PEs, thus resulting in better and comparative extraction efficiency. Based on the experimental results, selection of either Triton X-100 or CTAB as the surfactant was reasonable. However, after extraction, for some reason that we have yet to determine, the extract volume when CTAB was used (~15 μL) was relatively larger than that (~4 μL) when Triton X-100 was used. Thus, for this reason, and for more convenient handling (the preparation of a CTAB solution is much easier due to its solid state

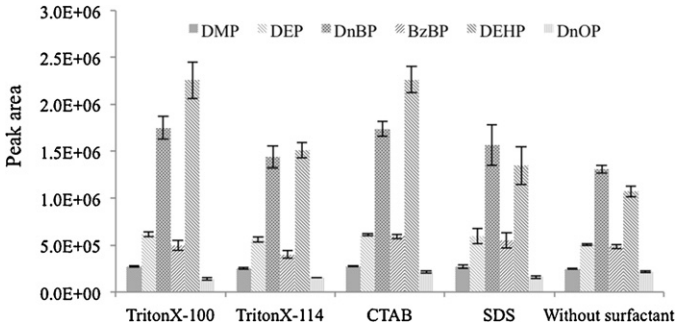


Fig. 5. Effect of different surfactants on extraction. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 30 μL toluene; surfactant concentration, 0.2 mmol/L; vortex time, 1 min.

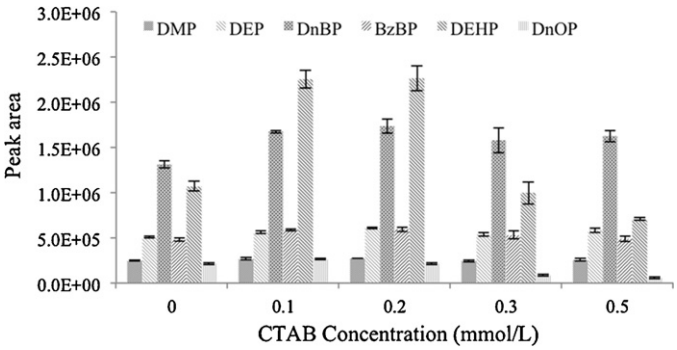


Fig. 6. Effect of CTAB concentration on the extraction. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 30 μL toluene; vortex time, 1 min.

compared with Triton X-100 which is a high viscosity liquid), CTAB was favored as the optimal surfactant (see also the following paragraph).

Surfactant concentration also plays an important role in the emulsification and mass transfer process, which affect the extraction efficiency. In order to study the influence of the concentration of CTAB, different concentrations ranging from 0 to 0.5 mmol/L were investigated. As shown in Fig. 6, the extraction efficiency increased when surfactant concentration was increased from 0 to 0.2 mmol/L. After that, the extraction efficiency began to decrease. A possible explanation is that when the surfactant concentration was increased from 0 to 0.2 mmol/L, the free surfactant monomer increased, resulting in an improved dispersion process. Eventually, however, aggregation of pre-micelles occurred as the level of surfactant reached the CMC, which caused a decrease in extraction efficiency, possibly as a result of stronger interaction between the analytes and the pre-micelles (i.e. there was competition between the pre-micelles and the extraction solvent for the analytes) [31]. In addition, there was formation of foam observed when the concentration of CTAB was further increased to 0.5 mmol/L. Concomitant with the increase in the amount of surfactant, the volume of the organic solvent phase decreased, making the retrieval of the extract problematical. In view of this, a concentration of 0.2 mmol/L of CTAB was found to be suitable.

3.2.4. Effect of salt

Salt addition to the water sample may have several different effects on extraction (salting-out, salting-in or no effect). Usually, depending on the solubility of the target analytes, adding salt to water sample normally enhances extraction of the relatively more polar analytes. For investigating the influence of the salt addition on the performance of LDS–VSLLME, different amounts of NaCl (in the range of 0–200 mg/mL) were added into water samples while the other conditions were kept constant. The results (not shown) indicated that with the increase of the salt content (from 0 to 200 g/L), the extraction efficiency decreased for most of the target analytes except in the case of the more polar DMP (whose extraction generally remained constant). An explanation for this is that with the increase of the salt content, the viscosity and density of the solution increased, leading to an inhibition of the mass transfer process, thus overcoming the salting-out effect. Thus as a compromise and for operational convenience, no salt was added in subsequent experiments.

3.2.5. Effect of vortex time

Vortex time (duration of the vortexing) is one of the main factors in LDS–VSLLME. It affects both the emulsification and mass transfer processes, and thus influences the extraction efficiency of the method. For the present study, the effect of the vortex time

Table 2
Quantitative results of the proposed LDS–VSLLME–GC–MS method.

Analyte	Linearity (μg/L)	r^2	RSD (%) (n = 5)	LOD (ng/L)	Enrichment factor
DMP	0.1–25	0.9823	10.7	20	260
DEP	0.05–25	0.9829	1.72	8	280
DnBP	0.05–25	0.9984	11.9	8	200
BzBP	0.05–25	0.9923	6.39	8	290
DEHP	0.1–25	0.9860	0.95	10	290
DnOP	0.1–25	0.9992	0.80	25	260

Table 3
PEs in bottled water samples determined by LDS–VSLLME and GC–MS.

Analyte	Concentration of PEs in bottle water (μg/L)	Spiked bottle water (1 μg/L)		Spiked bottle water (0.1 μg/L)	
		Relative recovery (%)	RSD (%)	Relative recovery (%)	RSD (%)
DMP	0.051	94.2	3.95	106.6	11.3
DEP	0.32	94.6	4.27	89.9	11.5
DnBP	0.40	88.5	7.35	98.4	10.9
BzBP	n.d.	73.5	8.44	77.4	4.77
DEHP	0.25	90.7	8.04	97.3	11.7
DnOP	0.12	92.4	3.67	93.5	3.39

n.d. = not detected.

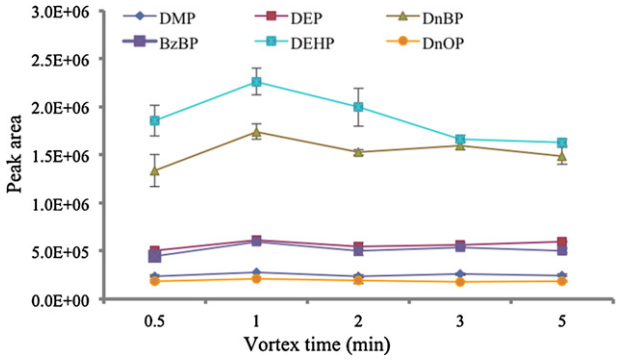


Fig. 7. Effect of vortex time. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 30 μL toluene; concentration of CTAB: 0.2 mmol/L.

was studied over the time range of 30 s to 5 min. Fig. 7 shows the extraction efficiency for PEs versus vortex time. It can be observed that the extraction efficiencies increased with the increase of vortex time from 30 s to 1 min; beyond 1 min, there was either a flattening out of the profile, or a slight decrease, depending on the analytes. This is due to the fact that the contact surface between extraction solvent and aqueous sample was greatly enhanced by the addition of surfactant and the vortex agitation, thus greatly increasing the mass transfer. As a result, the equilibrium state could be achieved within 1 min.

On the basis of the above discussion, the most suitable extraction conditions for LDS–VSLLME were as follows: 30 μL toluene as extraction solvent, 0.2 mmol/L of CTAB selected as the surfactant, vortex time of 1 min; and without salt addition. All the following experiments were carried out under these conditions. Fig. 8 shows a chromatogram of a spiked water sample (25 μg/L of each analyte) after extraction by the developed method under the described conditions.

3.3. Method validation

A series of experiments with regard to the linearity, repeatability, limits of detection (LODs) and enrichment factors (EFs) were performed to validate the proposed method at the developed working conditions. The results are listed in Table 2. The linearity of the method was explored at PE concentrations from 0.05 or 0.1, to 25 μg/L with good squared regression coefficients (r^2) of between 0.9823 and 0.9992. The LODs ranged between 8 and 25 ng/L. The results were comparable with those reported in previous microextraction studies, where SPME [12] or HF-LPME [15] was used for the extraction of PEs, but the present method was simpler to perform.

The repeatability of the method, expressed as relative standard deviation (RSD), was studied for five replicate experiments with spiked ultrapure water with PEs at concentrations of 5 μg/L. The RSDs for the PEs were below 11.9%, illustrating satisfactory repeatability was achieved by the proposed method. The EFs for the six PEs ranged from 200 (for DnBP) to 290 (for DEHP). These values highlight the good extraction performance of the new technique.

3.4. Analysis of real-world samples

The proposed method was applied for extraction of PEs from a 5 mL bottled water sample. To eliminate matrix effects, the standard addition method was adopted. The concentrations of PEs

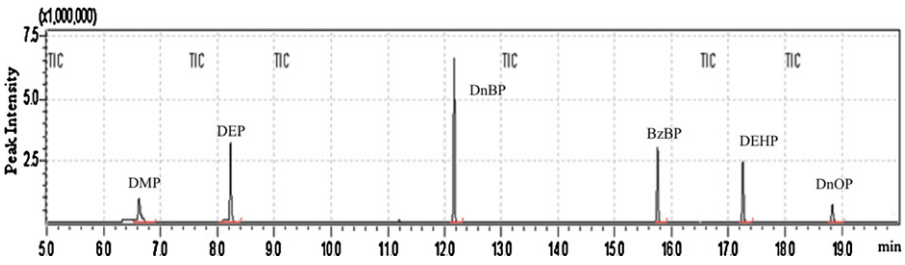


Fig. 8. Chromatogram of a spiked water sample extract under the most favorable extraction conditions: sample volume, 5.0 mL; extraction solvent, 30 μL toluene; concentration of CTAB, 0.2 mmol/L; vortex time, 1 min.

in the real-world samples were calculated using standard addition calibration after subtraction of the blank values. Three aliquots of the water sample were analyzed in parallel, with the results presented in Table 3. As expected, since PEs are ubiquitous in plastic packages, the water samples showed individual concentrations ranging from undetected to 0.4 μg/L. Relative recoveries, which indicate the effect of the sample matrix on extraction, were determined. Relative recoveries are defined as the ratios of analyte peak areas of spiked bottle water sample extracts and those of spiked ultrapure water extracts, with both types of samples spiked at the same concentrations of analytes (in this case, 0.1 μg/L and 1 μg/L). The relative recoveries varied between 73.5% and 106.6%, and RSDs ($n = 3$) were below 11.7%. The results indicated that the present method was suitable for the determination of PEs in environmental water samples, although matrix effects could arise when dealing with more complex samples.

4. Conclusion

In the present study, low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (LDS–VSLLME) was developed and for the first time applied for determining of PEs in bottled water samples. A low-density solvent, toluene, which is less toxic than chlorinated solvents widely used in conventional DLLME, was successfully used in conjunction with a simple method for its collection. The use of low-density solvents expands the applicability of DLLME. The important benefit of this approach was the elimination of a relatively large amount (several 100 μL) of organic dispersive solvent. With the aid of surfactant and vortex agitation, the organic extraction solvent was better dispersed and mass transfer was increased, resulting in extraction equilibrium being achieved in only 1 min, and high extraction efficiency. Overall, LDS–VSLLME was shown to be a fast, efficient, simple and cost-effective method for the determination of PEs in environmental water samples. Contamination of the toluene used in the procedure was addressed by using the standard addition method with background subtraction for quantitative measurements.

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