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Vortex solvent bar microextraction for phthalate esters from aqueous matrices

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ABSTRACT

An improved hollow fiber solvent bar microextraction method termed as vortex solvent bar microextraction (VSBME) was developed. A short hollow fiber immobilized with organic extraction solvent was served as the solvent bar for microextraction of phthalate esters from aqueous matrices. The hydrophobic analytes were pre-focused at the bottom of the vortex under the vigorous magnetic stirring before extraction, which facilitated the mass transfer of analytes from aqueous matrix to organic extraction phase in the subsequent solvent bar microextraction. With the extraction solvent lost gradually from the hollow fiber under the stirring, the efficient extraction was maintained by the absorption of analytes in the porous membrane. After extraction, the analytes were desorbed from the hollow fiber membrane using 50 μL organic solvent. The phthalate esters with 1-octanol/water partition coefficients ranging from 1.69 to 8.83 were used as model compounds to investigate the extraction performance. Extraction conditions such as type and volume of extraction solvents, stirring intensity, extraction time, sample concentration and volume were investigated and optimized. Analysis was carried out with gas chromatography–mass spectrometry (GC–MS). Under the optimum conditions, this new method gave super high enrichment factors (over 1500), good reproducibility ($<7.1\%$, $n=6$) in a rapid extraction within 5 min. It allowed the determination of phthalate esters at ng L^{-1} level. Compared with the other microextraction methods, the proposed VSBME was simpler, more robust and had higher enrichment efficiency. The matrix effects on the extraction performance were also investigated with bottled ice red tea, red wine and human urine.

1. Introduction

Microextraction techniques, generally represented by solid-phase microextraction (SPME) and liquid-phase microextraction (LPME), have the most important advantages that they can integrate sampling, extraction, concentration and sample introduction into one step [1,2]. Compared with SPME, the fairly recently developed LPME is more simple and inexpensive as a result of without needing special coating material and reducing the extracting solvents to microliters level. Since the drop-in-drop system was firstly reported by Liu and Dasgupta [3] in 1996, three main modes of LPME including single-drop microextraction (SDME), hollow fiber liquid-phase microextraction (HF-LPME) and dispersive liquid–liquid microextraction (DLLME), have been developed. There are different modifications and improvements for each mode in recent years. LPME is now becoming a popular microextraction method, particularly for organic chemicals in aqueous matrices.

SDME is the solvent microextraction technique developed by Cantwell and Jeannot [4] to extract analytes into a single drop. In this technique, the acceptor phase is an organic solvent microdrop and normally uses a syringe as holder. With the advantages of using the simplest implementation, the high enrichment factors and the matching with the afterwards injection of chromatography, SDME aroused great interest from its beginning. It can be performed in different modes, including headspace-SDME (HS-SDME) [5], direct immersion-SDME (DI-SDME) [3], static SDME, dynamic SDME [6], continuous-flow (CF-SDME) [7], two-phase and three-phase SDME [8,9]. A key concern is that the solvent drop is easily dislodged and instable when it is immersed directly in complex matrix for extraction [10].

DLLME was developed by Rezaee et al. [11], the extraction solvent insoluble in water is firstly dissolved in a water miscible organic solvent such as methanol or acetone, and the mixed solution is rapidly introduced into the aqueous sample to form a cloudy solution. Extraction equilibrium could be achieved in a few seconds due to the droplets' large extraction surface [12]. The centrifugation operation separated the extractant phase from aqueous solution. An alternative phase separation method based on solidification of floating organic drop was developed by Zanjani et al. [13] to avoid using centrifugation.

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Pedersen-Bjergaard and Rasmussen [14] proposed HF-LPME technique. LPME based on porous hollow fiber membrane possesses obvious benefits: (1) the dislodgement of the solvent drop in SDME can be avoided in HF-LPME by protecting the solvent with a porous membrane; (2) the requirement for phase separation in DLLME is eliminated; (3) faster mass transfer could be obtained because of the extensive specific surface contact area and toleration to higher agitation speed; (4) it is simple to set up the two-phase or three-phase extraction; and (5) it is easy for automation. Similar with SDME, static [15], dynamic [16], direct immersion, headspace [17], two-phase and three-phase modes [18] also could be applied in HF-LPME. Various configurations of HF-LPME have been developed. The basic HF-LPME system uses microsyringes for introduction and collection of the acceptor phase. Solvent bar microextraction (SBME) without using microsyringe was proposed by Jiang and Lee [19]. In this method, a solvent bar was formed by flame-sealing the organic phase in a short length of hollow fiber membrane (2 cm) and then moved freely in the aqueous sample under magnetic stirring. After extraction, one end of the hollow fiber was trimmed off and then the extractant was withdrawn into a syringe for analysis. The extraction efficiency of SBME mode was increased by the free movement of solvent bar.

In this work, we improved a vortex solvent bar microextraction (VSBME) method based on an unsealed hollow fiber. The short hollow fiber immobilized with organic phase serving as the solvent bar for microextraction. A quick and high efficient extraction was achieved by forming a strong vortex before extraction together with desorbing the analytes out of the microporous hollow fiber membrane for analysis. The mechanism of the extraction procedure was explained in detail. In order to investigate the extraction performance of VSBME, phthalate esters (PAEs) with 1-octanol/water partition coefficients (LogP) ranging from 1.69 to 8.83 were used as model compounds and analyzed by gas chromatography–mass spectrometry (GC–MS). Application of VSBME for the determination of phthalate esters in bottled mineral water, bottled ice red tea, red wine and human urine were compared to evaluate the matrix effects.

2. Experimental

2.1. Reagents and materials

Dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), dibutyl phthalate (DBP), diamyl phthalate (DAP), dihexyl phthalate (DHXP), diheptyl phthalate (DHP), di-2-ethylhexyl phthalate (DEHP) and dioctyl phthalate (DNOP) were purchased from AccuStandard, Inc.(USA). HPLC grade methanol and acetone were bought from J.T. Baker (USA). The phthalate esters were prepared in methanol as stock solutions. The working solutions were prepared from the stock solutions by diluting with methanol or water. The other organic solvents were analytical grade.

The Q3/2 Accurel polypropylene hollow fiber (600 μm i.d., 200 μm wall thickness and 0.2 μm pore size) was purchased from Membrana (Wuppertal, Germany). It was cut into 2 cm length segments which were then ultrasonically cleaned in acetone and dried before use.

2.2. Vortex solvent bar microextraction

The detailed operation and mass transfer procedure of VSBME was illustrated in Fig. 1. In a beaker, one vortex was formed in the center of the aqueous solution by controlling the speed of the magnetic stirrer. A 2 cm length of Q3/2 hollow fiber was immersed in xylene for a few seconds until the fiber membrane turned from white to transparent. The solvent bar was formed when the wall and lumen of the fiber were full of xylene. Then this solvent bar was thrown into the stirring aqueous solution and stirred around the bottom of the vortex during extraction. At the end of extraction, the fiber was taken out from the solution and put into a 100 μL of glass-insert. Then the fiber was vortex eluted with 50 μL acetone for 1 min. At last, the membrane was removed and 2 μL aliquot of the eluent was injected for GC–MS analysis.

2.3. Instruments and analytical conditions

Analysis was performed on a Shimadzu GCMS-QP2010 system (Kyoto, Japan). A 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 MS fused-silica capillary column (J&W Scientific, Folsom, CA, USA) was used for separation. Helium was used as the carrier gas at 1.2 mL min^{-1}. The GC conditions were as follows: injection temperature, 290 °C; injection mode, splitless; initial temperature, 150 °C held for 2 min, programmed to 290 °C at 20 °C min^{-1}, and then maintained at 290 °C for 3 min. The EI ion source temperature and the interface temperature were set at 250 °C and 290 °C respectively. The MS was operated on the total ion current (TIC) mode scanning from m/z 50 to 500 for identification purposes. Subsequently, selected ion monitoring (SIM) mode was applied for quantification.

A digital magnetic stirrer H01-1B (Shanghai Meiyingpu Instrument Manufacturing Co., Ltd., Shanghai, China) and a PTFE coated stirring bar (3 cm × 0.5 cm i.d.) were used for extraction. A vortex

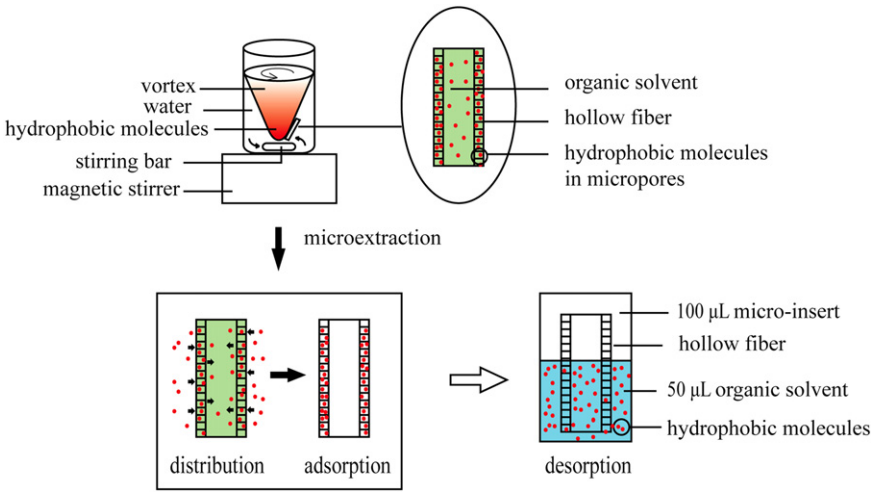

Fig. 1. Schematic diagram of the proposed VSBME. Four stages exist in the VSBME procedure: vortex focusing→distribution→adsorption→desorption.

mixer QL-901 (Kylin-Bell Lab Instruments Co., Ltd., Jiangsu, China) was used for eluting the analytes from the hollow fiber membrane.

2.4. Calculations

The enrichment factor and recovery are often used to evaluate the extraction performance. In this study, enrichment factor (E_f) was defined as the ratio of the concentration of analytes in 50 μL acetone eluent after extraction (C_o) to the concentration in water sample before extraction (C_w^i), i.e. $E_f = C_o/C_w^i$. Recovery (R) was calculated as $R = E_f(V_o/V_w)$. V_o and V_w were the volumes of acetone eluent and the aqueous sample respectively.

3. Results and discussion

3.1. Vortex solvent bar microextraction

3.1.1. Phenomena in VSBME

The extraction procedure of VSBME was clearly demonstrated by a process of color change phenomena (see Supporting Information 1). An aqueous solution of Sudan IV at 10 ng mL^{-1} was prepared, which looked like colorless and transparent before stirring. When a vortex formed in the center of the solution under magnetic stirring, red color appeared at the bottom of vortex due to the hydrophobic property of Sudan IV. The solvent bar immersed with xylene changed from transparent to red as soon as it was thrown into the vortex due to the rapid transfer of Sudan IV molecules from aqueous phase to xylene phase. With the VSBME continuing, the red color of solvent bar faded. At the end of extraction, the centrifugal force of vortex led to the loss of xylene from fiber which turned back to white color with red spots. The adsorption of Sudan IV on fiber membrane was proved by the red color of eluent after eluting the fiber membrane with acetone. In contrast, no focusing phenomenon of vortex was observed for the water soluble rhodamine in the same extraction procedure (see Supporting Information 2).

The above phenomena revealed that there were four stages in the extraction procedure of VSBME: focusing→distribution→adsorption→desorption. The operation and mechanism are illustrated in Fig. 1. Two extraction processes, liquid-phase extraction and solid-phase extraction occurred sequentially.

3.1.2. Mass transfer model in the liquid-phase extraction process of VSBME

In thermodynamic aspect, VSBME is based on the same phase distribution theory as traditional liquid–liquid extraction (LLE). The analyte molecules distribute between the aqueous sample phase and the organic extraction phase and the equilibrium concentration in the organic phase, C_o, is expressed as [20]

$$C_o = \frac{KC_w^i}{1+KV_o/V_w} \tag{1}$$

where C_w^i is the initial concentration of analyte in aqueous sample; V_o and V_w are the volumes of organic phase and water phase; K is the equilibrium distribution coefficient of analyte between the water phase and organic phase.

The difference of VSBME from LLE is that it increases the mass transfer markedly in kinetic aspect. To describe the detailed mechanism of VSBME, a mass transfer model of two-phase solvent microextraction proposed by Jeannot and Cantwell [4,21] was employed. Three basic postulates of mass transfer theory of solvent microextraction were summarized [20]: (1) the rate of mass transfer is proportional to the concentration difference between the interface and bulk solution; (2) no adsorption of analyte molecules at the interface itself; (3) distribution equilibrium will prevail at all times in the two solvent layers adjacent to the interface.

The above three postulates have been expressed with mathematical equations. The rate constant (k) for the two-phase extraction process is finally expressed as [20]

$$k = A_i\overline{\beta}\left(K\frac{1}{V_w}+\frac{1}{V_o}\right) \tag{2}$$

where A_i is water-organic interfacial area; $\overline{\beta}$ is the overall mass transfer coefficient:

$$\frac{1}{\overline{\beta}} = \frac{K}{\beta_w}+\frac{1}{\beta_o} \tag{3}$$

where β_w and β_o are the mass transfer coefficients of water phase and organic phase.

The actual moles of analytes extracted into the organic phase n_o at equilibrium is calculated as [20]

$$n_o = \frac{KC_w^i}{1/V_o+K/V_w} = \frac{KC_w^iV_w}{V_w/V_o+K} \tag{4}$$

According to Eqs. (1)–(4), the mass transfer in VSBME liquid-phase extraction procedure was facilitated in several ways: (i) in the first focusing step, the initial concentration of water phase (C_w^i) was increased by focusing the hydrophobic molecules on the bottom of vortex; (ii) in the second distribution step, by holding the organic solvent with a 2 cm porous hollow fiber membrane, the interfacial area (A_i) was enlarged and the volume of organic phase (V_o) was kept as small as to several microliters; (iii) the overall mass transfer coefficient ($\overline{\beta}$) was enhanced simultaneously through vigorous stirring the water sample in which β_w was enhanced; (iv) the rate and the amount of analytes extracted were increased by selecting the hydrophobic analytes with higher K. The other practical consideration from the above equations is that the opposing effects of volumes on the rate of extractions and the amount extracted (n_o). The rate of extraction will be enhanced by reducing both V_o and V_w as small as possible, while the extracted amount of analytes (n_o) obviously increases with both V_o and V_w.

3.1.3. Mechanism in the solid-phase extraction process of VSBME

As the extraction continued, the organic solvent lost gradually under the vigorous agitation and the extraction of VSBME went into the solid-phase extraction process. In this process, the adsorption mechanism was more favorable to explain the extraction of hydrophobic compounds with the hydrophobic microporous membrane. Those non-polar analyte molecules were "imprisoned" in the hydrophobic micropores of hollow fiber membrane until they were "liberated" by a strong-elution solvent in the last desorption step.

The proofs of the adsorption of hydrophobic small organic chemicals on hollow fiber membrane depending on diffusion and surface reaction limitation have been presented previously [22,23]. Dry microporous membrane has been applied for SPE [24–26], which can provide limits of quantification (LOQ) at ng L^{-1} levels. Therefore, the adsorption kinetics on fiber membrane in VSBME can be explained similarly.

3.2. Optimization of VSBME

According to Eqs. (1)–(4), in our study, several critical factors were optimized with PAEs of different octanol–water partition coefficients. The factors included extraction solvent (related to K), stirring intensity (related to $\overline{\beta}$), organic solvent volume (related to V_o), extraction time (related to k), sample concentration (related to C_w^i) and sample volume (related to V_w).

3.2.1. Extraction solvent selection

Three main physical properties of extraction solvent relating to its stability in the process of HF-LPME are water solubility, vapor pressure and viscosity. 19 organic solvents with different physical properties were selected, including two alkanes, four haloalkanes, two aromatic hydrocarbons, two halogenated aromatics, two alcohols, two ethers, one nitrile and three ionic liquids as indicated in Fig. 2. 20 pieces of 2 cm length of hollow fiber were held with stainless needles. 19 of hollow fibers were immersed into the 19 organic solvents respectively for HF-LPME except for a dry fiber for blank contrast. These 20 fibers were then inserted into a 600 mL of aqueous sample containing DMP, DEP, DPP, and DBP at the same concentration of 100 ng mL^{-1}. A static extraction was carried out at 600 rpm stirring speed for 30 min. At the end of extraction, these fibers were eluted with 50 μL of acetone separately. A blank test of the same operation with blank water was performed firstly and tested for background correction.

The extraction efficiencies of different solvents in static HF-LPME for four phthalate esters are shown in Fig. 2. The dry hollow fiber displaying the lowest extraction efficiency illustrated that liquid-phase extraction is the main mechanism for VSBME. In hollow-fiber based LPME, the mass transfer through the solvent layer in the pores of membrane is the diffusion-controlled rate-determining step and the solvent is desired to have low viscosity to accept the analytes [20]. The color of the hollow fiber changed from white to transparent when it was immersed into 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, tetrachloromethane, toluene, xylene and bromobenzene. It meant that the polarity of these solvents was matched well to that of the fiber and the micropores were wet effectively. Unlike these solvents, ionic liquids were hard to permeate the micropores of hollow fiber membrane because of their super high viscosity over 390 cP [20]. Therefore, although ionic liquids were the most stable on the hollow fiber, they did not show the highest extraction response among the selected solvents. As shown in Fig. 2, xylene presents the highest extraction efficiency for four phthalate esters. Although chlorobenzene and bromobenzene also present good extraction ability for targets, their toxicity is higher than that of xylene. Thus, xylene was selected as the extraction solvent.

3.2.2. Stirring intensity

The agitation rate must be controlled in the solvent microextraction techniques that used sample agitation. This ensures a balance between a rapid mass transfer and the stability of the solvent [27]. Although the hollow fiber can protect the solvent in traditional SBME and make it withstand a higher stirring speed, solvent loss and air bubbles produced at higher stirring speed still should be considered [19]. In our experiments, it was found that the stirring speed was affected by the viscosity of sample solution, sample volume, the shape of vessel, the depth of sample solution and the size and shape of the stirring bar. Only the stirring speed cannot indicate the real agitation intensity. The ratio of the depth of vortex to the height of the sample solution (HV/HS) is a more representative parameter to illustrate the agitation intensity. Three values of HV/HS were compared for the enrichment efficiencies. These three values were about 1/4, 1/2 and 1, corresponding to the stirring speeds of ~300 rpm, ~600 rpm and ~900 rpm for 100 mL of water in a 100 mL glass beaker with a magnetic cylindrical stirring bar (3 cm × 0.5 cm i.d.). As shown in Fig. 3, ultra-high peak area response was found when the bottom of vortex contacted to the stirring bar, i.e. HV/HS ≈ 1. So the stirring speed in VSBME was controlled to make the maximal vortex.

3.2.3. Organic solvent volume

Since autosampler was used for sample injection in the GC–MS analysis, 50 μL of acetone in a 100 μL glass micro-insert was used for elution. A 2-cm length of Q3/2 hollow fiber was selected to match with the depth of the glass micro-insert. About 10 μL of xylene could be immobilized in the fiber wall. The largest volume held by the whole hollow fiber including lumen and wall was ~15 μL. The peak area response was best at the solvent volume of 15 μL. Besides that, the operation of immersing the hollow fiber with solvent was very convenient without needing to measure the solvent volume. Therefore, operation of immersing the hollow fiber with solvent was used in this work.

3.2.4. Extraction time

Various extraction time was investigated by extracting 100 mL of aqueous solution containing 1 ng mL^{-1} of each PAE at HV/HS

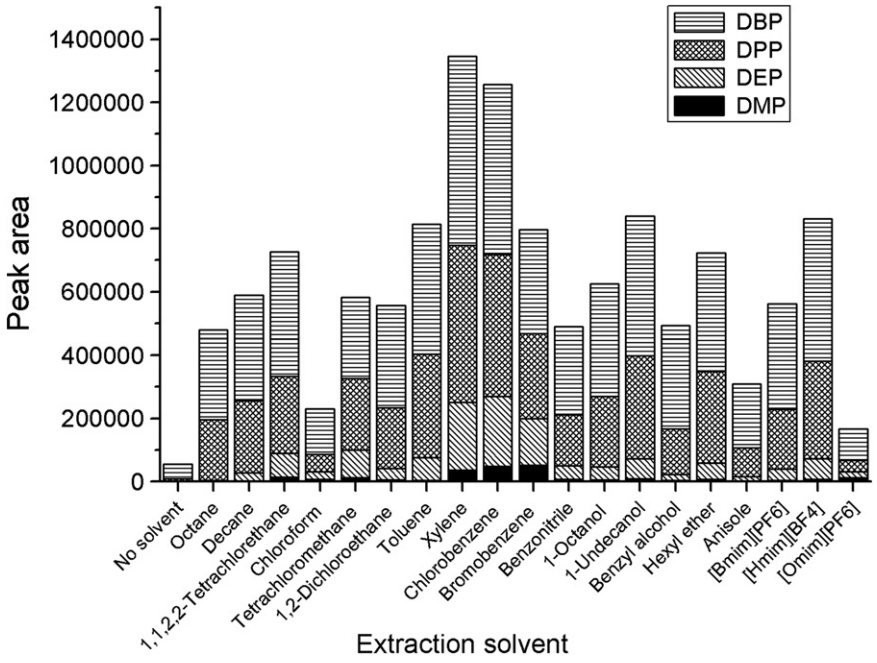

Fig. 2. Effect of extraction solvent on extraction efficiency of four phthalate esters.

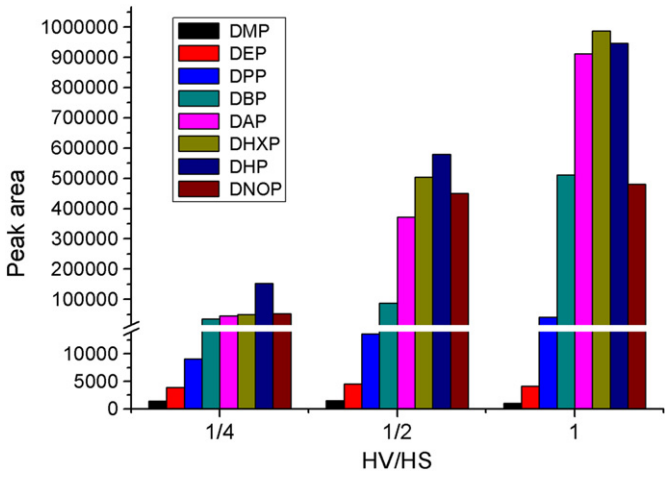

Fig. 3. Effect of stirring intensity on extraction efficiency. Stirring intensity: HV/HS ≈ 1/4, 1/2 and 1; sample concentration: 1 ng mL^{-1}; sample volume: 100 mL; stirring time: 10 min.

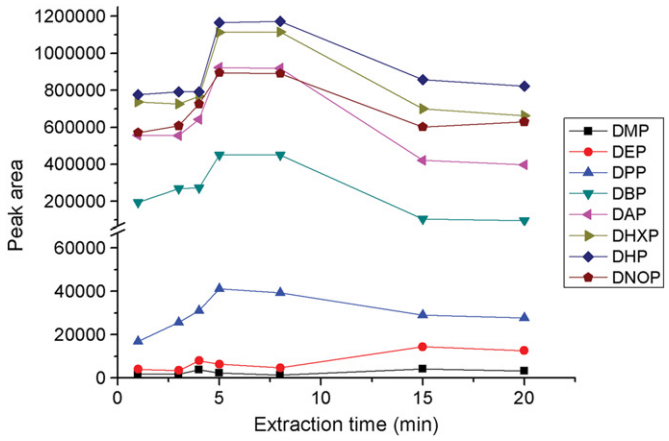

Fig. 4. Extraction time profile of phthalate esters in water solution. Stirring intensity: HV/HS ≈ 1; sample concentration: 1 ng mL^{-1}; sample volume: 100 mL.

value equal to 1. Fig. 4 shows that the analytical signals reached to relative high values at 1 min and reached to the highest values at 5 min. Longer extraction time would not always bring a higher enrichment. Thus, the extraction could reach to equilibrium very quickly in VSBME. Therefore, an extraction time of 5 min was used for the subsequent experiments.

3.2.5. Sample concentration and volume

According to the Eq. (1), the concentration of analytes in organic phase (C_o) will increase with the initial aqueous sample concentration (C_w^i). However, Eq. (4) indicates that for the sample at ultra low concentration, even total mass ($C_w^i V_w$) of analyte is increased to the same by enlarging the sample volume (V_w), the concentration in organic phase (C_o) obtained from the moles extracted (n_o) could not be as high as the sample at higher concentration but smaller sample volume. Therefore, the recovery will be lower for the larger sample volume. That is why two-phase LPME is not suitable for the ultra trace analysis.

VSBME, due to the vortex focusing, possible will bring some difference. Hence, with the same organic phase volume (V_o) by using the consistent hollow fiber size, three sample concentrations and volumes containing the same mass ($C_w^i V_w$) of each phthalate were compared. Considering longer time for mass transfer in the relative larger sample volume of 500 mL and 1000 mL, instead of the previous optimized 5 min for 100 mL, 10 min of extraction time was used for all these three samples in comparison. With the stirring bar of same size (3 cm × 0.5 cm i.d.), the vortex formed in the beaker of 1000 mL (15.5 cm × 11.2 cm i.d.) and 500 mL (12.2 cm × 9.0 cm i.d.) was long and slender under the stirring speed of 1300 and 1100 rpm respectively, while the vortex formed in the beaker of 100 mL (7.2 cm × 5.2 cm i.d.) was short and relative fat under the stirring speed of 900 rpm. This vortex flow generated by a magnetic stirrer could be explained with Rankine vortex model [28]. According to the Rankine vortex model [29,30], the tangential velocity is proportional to the radial distance within the forced vortex core (r), while it is inversely proportional to the radial distance in the free vortex zone. The maximum intensity of the flow is reached at the radius of the forced vortex core, r. As shown in Fig. 5, the intensity of the flow around the wall of beakers (distance was at the radius of

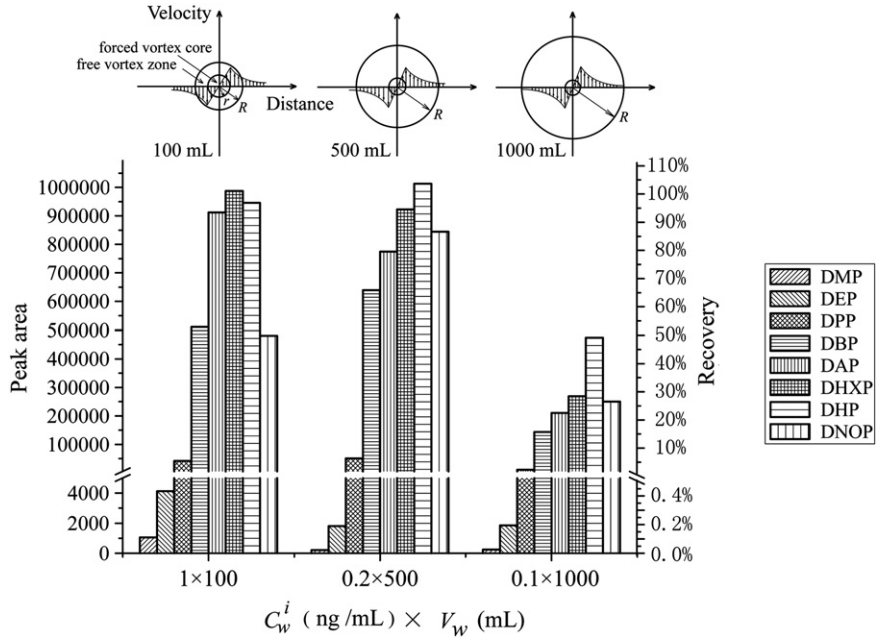

Fig. 5. Effects of the sample concentration and volume on VSBME and the Rankine vortex models. Stirring intensity: HV/HS ≈ 1; extraction time: 10 min.

beaker, *R*) was in the same order of *r*: 100 mL > 500 mL > 1000 mL. The peak area response of those PAEs depended on the amount of hydrophobic molecules that were focused at the bottom of vortex for microextraction. Adsorption on the wall of beaker and dispersion in the larger water volume would decrease the extracted amount of molecules. Strong flow intensity was helpful to weaken the adsorption and improve the extraction. In both cases of 100 and 500 mL samples, the flow intensity on the wall of beaker was so strong as to resist the adsorption. Therefore, most of the molecules in these two samples were extracted and showed similar peak area response that was much larger than 1000 mL sample. It confirmed that the vortex focusing plays an important effect on the mass transfer of VSBME. Considering 100 mL was relative small sample volume and higher response of DMP and DEP in this volume, 100 mL was selected as the sample volume in the following experiments.

According to the above results, the optimum experimental condition of VSBME applied for the determination of phthalate esters in water were selected as following: 100 mL aqueous sample; HV/HS ≈ 1 stirring intensity; xylene as extraction solvent; 5 min extraction time; 2 cm length of Q3/2 hollow-fiber membrane immersed in extraction solvent; 50 μL desorption solvent.

Table 1
Analytical performance.

Chemical	LogP*	LR (μg L^{-1})	r^2	LOD (ng L^{-1})	E_f	RSD (%) (n=6)
DMP	1.69	0.5–10	0.9968	76.2	8	5.3
DEP	2.71	0.1–10	0.9986	35.7	57	6.4
DPP	3.73	0.1–10	0.9975	10.8	273	4.9
DBP	4.75	0.1–10	0.9999	0.4	1214	4.7
DAP	5.77	0.1–10	1.0000	0.6	1560	7.1
DHXP	6.79	0.1–10	0.9997	0.7	1506	6.9
DHP	7.81	0.1–10	0.9996	0.5	1271	6.8
DEHP	8.52	0.1–10	0.9960	1.0	874	6.5
DNOP	8.83	0.1–10	0.9957	1.2	718	4.6

* Data were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2011 ACD/Labs).

Table 2
Comparison of VSBME with other methods for determination of PAEs in water*.

Method	LOD (ng L^{-1})	LR (μg L^{-1})	RSD (%)	Extraction time (min)	V_w (mL)
HF-LPME-GC–MS [31]	5–100	0.5–10	4–19	20	5
DLLME-GC–MS [32]	2–8	0.02–100	4.6–6.8	≥3	5
SDME-GC–FID [33]	20–100	0.1–50	3.5–8	25	20
SPME-GC–MS [34]	3–85	0.1–20	1.3–21.7	60	10
SPME-GC–FID [35]	20–10,000	0.1–300	2.2–19	20	10
VSBME-GC–MS	0.4–76	0.1–10	3.0–7.1	5	100

* PAEs in these methods for comparison were different.

3.3. Analytical performance

Under the optimum conditions, the analytical performance of the proposed method was evaluated with a series of aqueous standard solutions containing various concentrations of PAEs. The enrichment factor and relative standard deviation (RSD) of each analyte were achieved in six replicate VSBME experiments for 100 mL of deionized water containing PAEs at 10 μg L^{-1}. The linearity of VSBME was investigated over a concentration range of 0.1 ~ 10 μg L^{-1} and expressed with linear range (LR) and correlation coefficients (r^2). Limits of detection (LODs) were calculated based on the signal to noise (S/N) of 3 by comparing with the signal to noise of values obtained with the sample at 0.1 μg L^{-1} after VSBME performing. These results were summarized in Table 1. Super high enrichment factors over 1000 were obtained for DBP, DAP, DHXP and DHP which LogP values are in the range of 4.75 ~ 7.81. The relative lower enrichment factors of DEHP and DNOP could be explained with the reason of adsorption on the beaker because of their very high hydrophobic property. On the other hand, DMP, DEP and DPP with lower LogP values presented weaker enrichment were due to their relatively good distributions in water phase.

3.4. Comparison of VSBME with other methods

Table 2 indicates the values of LOD, LR, RSD and the extraction time of other microextraction methods and VSBME for the determination of phthalate esters from water samples. Since the vigorous vortex made the hydrophobic chemicals focusing and the mass transfer was facilitated, VSBME provided lower LOD and very short extraction time as compared with other microextraction methods. The low RSD values were probably because of the operation of VSBME was simple and robust without considering the organic solvent lost during extraction.

3.5. Real sample analysis

Bottled mineral water, bottled ice red tea and red wine from supermarket and human urine were analyzed using VSBME combined with GC–MS. Mass chromatograms of the bottled mineral water spiked with phthalate esters were compared with blank bottled mineral water and the methanol standard solution of PAEs at the concentration of 1 μg L^{-1} in Fig. 6. It was seen that

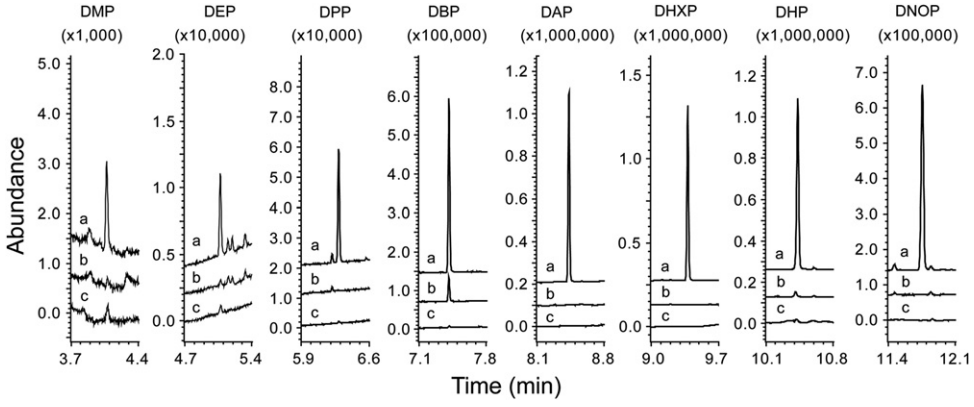

Fig. 6. Expanded mass chromatograms of the bottled mineral water spiked with eight phthalate esters at 1 μg L^{-1} after VSBME enrichment (a), the blank bottled mineral water after VSBME (b), and standards solution of eight phthalate esters at 1 μg L^{-1} (c).

Table 3
Evaluation of matrix effect on VSBME (relative response to mineral water).

Chemical	Relative response to mineral water (%)						
	Mineral water	100% ice red tea	20% ice red tea[a]	100% urine	20% urine[a]	100% red wine[b]	20% red wine[a]
DMP	100	171[c]	192[c]	123	101	230[c]	232[c]
DEP	100	94	113	123	108	71	113
DPP	100	32	29	34	35	17	35
DBP	100	13	86	50	45	730[c]	688[c]
DAP	100	20	25	7	6	3	15
DHXP	100	25	22	9	8	6	19
DHP	100	23	22	12	7	10	19
DNOP	100	18	10	6	6	7	16

[a] 20 mL original samples spiked with 100 ng of PAEs, then diluted with mineral water to 100 mL to get the concentration at 1 $\mu g\,L^{-1}$.
[b] Original red wine contained 13% alcohol.
[c] High background in the original sample without standard addition.

the peak of DBP appeared in the mass chromatogram of the blank bottle mineral water. Repeated experiments and blank test using GC–MS verified that there was trace DBP in analytical grade of xylene extraction reagent. While the standard solutions of phthalate esters were prepared in the HPLC grade methanol and DBP at the concentration of 1 $\mu g\,L^{-1}$ was under the limit of detection. It clearly indicated that the good enrichment effects of these PAEs, especially for the chemicals with higher LogP, were obtained by VSBME.

Other matrices of bottled ice red tea, red wine and human urine were evaluated the effects on VSBME by comparing with the mineral water in Table 3. 100 mL of bottled ice red tea, red wine and human urine without dilution and 20 mL of each sample diluted with water to 100 mL were compared to evaluate the dilution effects on VSBME. All the samples were spiked with PAEs at concentration level of 1 $\mu g\,L^{-1}$ in the end sample volume of 100 mL. The results illustrated that matrix effect was obvious on VSBME. The relative response of chemicals at lower LogP like DMP and DEP were high because of their relative free dispersion in these matrices. Dilution of red wine could increase the enrichment of chemicals at higher LogP such as DAP, DHXP, DHP and DNOP. However, no obvious effect of dilution was observed for ice red tea and human urine. The possible reason was that the original red wine contained 13% alcohol, dilution with water was helpful to facilitate the hydrophobic chemicals move from water phase to organic phase. The relative response of DAP, DHXP, DHP and DNOP in human urine was low because quite a large amount of the chemicals combined with the components in urine at the low spiking concentration of 1 $\mu g\,L^{-1}$. Being the high enrichment effect of VSBME, the determination of PAEs was achieved with VSBME even in original ice red tea, red wine and human urine without further dilution.

4. Conclusion

A simple and high efficient vortex solvent bar mircroextraction method has been developed. Vigorous stirring formed vortex to focus the hydrophobic analytes and simultaneously confined the solvent bar moving around the bottom of vortex to accelerate extraction. This VSBME method presented rapid and excellent enrichment for phthalate esters in aqueous samples. The investigation illustrated that the VSBME has a potential application for extraction of other high hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs), pyrethroids or sudan dyes in aqueous matrices without further pre-treatment.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.08.009.

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