Hollow fiber supported liquid-phase microextraction using ionic liquid as extractant for preconcentration of benzene, toluene, ethylbenzene and xylenes from water sample with gas chromatography-hydrogen flame ionization detection

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ABSTRACT

A novel method has been developed for the analysis of benzene, toluene, ethyl-benzene, and *o*-, *m*- and *p*-xylenes (BTEXs) in water using hollow fiber supported liquid-phase microextraction (HF-LPME) followed by gas chromatography-hydrogen flame ionization detection. Ionic liquid 1-butyl-3-methy-limidazolium hexafluorophosphate ([BMIM][PF$_6$]) was acted as the extractant for extraction and preconcentration of BTEXs from aqueous samples, and a porous-walled polypropylene hollow fiber was utilized to stabilize and protect [BMIM][PF$_6$] during the extraction process. Various parameters that affect extraction efficiency were investigated in detail, and the optimized experimental conditions were as follows: 8 μL of [BMIM][PF$_6$] as extraction solvent for the target analytes in 20 mL of sample solution, 30 min of extraction time, a stirring rate of 1400 rpm and 15% NaCl (w/v) in aqueous sample at 25 °C (ambient temperature). The recovery was found to be 90.0–111.5% with RSD (*n* = 5) of 1.3–5.4%, and the detection limits (S/N = 3) were in the range of 2.7–4.0 μg/L. The proposed method was simple, cheap, rapid, sensitive and environmentally benign, and could act as an alternative to techniques for BTEXs analysis with expensive instrumentations.

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1. Introduction

Volatile organic compounds (VOCs) such as benzene, toluene, ethyl-benzene, and *o*-, *m*- and *p*-xylenes (BTEXs) have aroused increasing concern for their hazards on both human health and the ecological environment. Due to the discharge of waste water containing BTEXs from chemical factories into water environment, BTEXs has become one of the important factors affecting water quality, as heavy metals and other organic pollutants [1–3]. A serious problem encountered in the determination of BTEXs is that they usually present in water at very low concentrations, resulting in poor analytical accuracy and precision. Therefore, it is of vital importance to develop sensitive and reliable extraction and preconcentration approaches for BTEXs prior to their instrumental determination.

In the analysis of organic pollutants in environmental samples, the most difficult step is to extract the analytes from various matrices effectively and rapidly. Although classical liquid–liquid extraction (LLE) is still a widely used sample preparation technique,

it is considered to be a time-consuming and tedious operation. In addition, the use of large amounts of toxic organic solvents deteriorates the accuracy of trace analysis, causes an adverse health effect on laboratory workers and produces harmful laboratory waste to the environment.

Solid-phase microextraction (SPME), developed by Arthur and Pawliszyn [4], has been demonstrated to be a fast, simple, sensitive, solvent-free sampling and analysis technique [5,6]. However, SPME also suffers from some disadvantages such as sample carry-over, fiber fragility and relatively high cost.

Based on the miniaturization of traditional LLE, a new solvent-minimized extraction method termed liquid-phase microextraction (LPME) [7] has attracted increasing attention from the analysts for its effectiveness, cheapness, simplicity, and cleanup ability [8–13]. LPME combines extraction, concentration and sample introduction into one step. Single-drop liquid-phase microextraction gives comparable sensitivity and much better enrichment for analytes compared with LLE and SPE [12,14]. However, it was observed that the organic solvent drop is easily lost from the needle tip of syringe during extraction, especially when samples are subjected to vigorous agitation [15]. This is a consequence of the need for solvents with low vapor pressure so as to minimize the evaporation of the drop during extraction. Furthermore, drop-based

LPME suffered from a relatively small drop volume and thus a low sensitivity. Similar to SPME, there are two basic modes for LPME sampling: direct LPME and headspace LPME (HS-LPME). In 1999, Pedersen–Bjergaard and Rasmussen developed a hollow fiber-based LPME technique (HF-LPME) [16]. HF-LPME uses a porous-walled polypropylene hollow fiber to stabilize and protect the organic phase, to enhance the mechanical robustness and the extraction efficiency [17,18]. This technique can provide a high analytes preconcentration and excellent sample cleanup, with the advantage that the fiber is disposable after use because of its low price. However, there is still a loss of the organic solvent with a lower boiling point while samples are stirred vigorously.

Room temperature ionic liquids (RTILs) have shown several advantages over conventional organic solvents, including very low vapor pressure, good dissolving capacity for numerous compounds, and excellent thermal stability. Therefore, RTILs, regarded as a novel type of green solvents, have recently been used as alternatives to common organic solvents in many fields [19,20] including separation and enrichment in analytical chemistry [21–23].

A number of approaches have been applied in sample preparation for chromatographic analysis of BTEXs compounds, including LLE [24], HS-SPME [25,26] and HS-LPME [27,28]. 1-Octanol, with a boiling point of 195 °C, was a typical organic solvent for LPME. Unfortunately, 1-octanol still contained a minor amount of impurities, which interfered with the determination of very low concentrations of BTEXs (below a 100 μg/L level) when using a flame ionization detector [27].

Gas chromatography (GC) is well known a comparatively inexpensive, robust and easy to operate analytical instrumentation that is widely used in most laboratories. In our previous work [29], room temperature ionic liquid was applied to HS-LPME of BTEXs in water samples followed by GC determination. The main advantage of RTILs as extractant for HS-LPME is the applicability of long-time headspace extraction even at high temperature [29,30]. However, the sensitivity obtained by HS-LPME coupled with GC was relatively low due to the small organic phase volume.

In the present study, we first developed a HF-LPME procedure using ionic liquid [BMIM][PF$_6$] as solvent for extraction, cleanup and enrichment of BTEXs from aqueous sample, prior to gas chromatography-hydrogen flame ionization detection (GC-FID), and thus provided an alternative to methods for BTEXs analysis with expensive instrumentations. Several factors that affect the extraction efficiency such as ionic liquid type, extractant volume, sampling temperature, extraction time, stirring rate, and salt content, were optimized. The proposed method was successfully applied to the determination of trace levels of BTEXs in river water.

2. Experimental

2.1. Chemicals

Benzene, toluene, ethyl-benzene, and o-, m- and p-xylenes were chromatographic grade (Kemio Chemical Reagent Center, Tianjin, China). [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$] were purchased from Shanghai Chengjie Chemical Co., Ltd. All other chemicals used were of analytical grade. Ultrapure water (15.7 MΩ cm^2 was used throughout.

Stock solutions of BTEXs (5000 mg/L) were prepared in methanol. Working standard solutions were prepared by diluting the standard solutions with ultrapure water just before use.

2.2. Synthesis of [BMIM][PF$_6$]

The rapid synthesis and characterization of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]) was described in our previous work [31].

2.3. Apparatus

A Shimadzu GC-2014 system equipped with a flame ionization detector (FID) was used for determinations. Separation was carried out on a 25 m × 0.25 mm, 0.25 μm capillary column (SPB^{TM}-1, Shimadzu, Japan). The injector and detector temperatures were 200 and 250 °C, respectively. The inlet was operated in split mode with a split ratio of 10:1. The flow-rate of carrier gas (nitrogen) was 1.0 mL/min. The following temperature program was employed: 45 °C for 2 min, 5 °C/min to 70 °C, held for 3 min. Then 35 °C/min to 140 °C, held for 1 min.

2.4. Extraction procedures

All the HF-LPME experiments were performed using polypropylene hollow fiber membrane (1-mm I.D., 200-μm wall thickness, 0.45-μm pore size) from Faculty of Chemical Engineering, Tianjin University, China. The fiber was cut into small segments with length of 10 cm. A 25-μL syringe was employed to introduce 8 μL of [BMIM][PF$_6$] into the lumen of each segment, and both ends of the hollow fiber were heat-sealed by sintering. Sample solution (20 mL) was transferred into a 50 mL of glass beaker containing a magnetic stirring bar, and 3 g of NaCl was added to the solution. Then the hollow fiber was submerged into the sample solution. The aqueous sample was stirred at 1400 rpm at room temperature (25 °C). After 30 min of extraction, the hollow fiber was removed from the solution, and one of its closed ends was cut and then the receiving phase was carefully withdrawn into the syringe; and finally 4 μL of the analyte-enriched solvent was injected directly into the GC-FID without further manipulation. Each segment of hollow fiber was used only for a single extraction to avoid contamination.

3. Results and discussion

HF-LPME technique has demonstrated several advantages over other extraction methods. Because of the small volume of extraction solvent used, no further concentration of the extract is required. In order to minimize the evaporation of extractant used in HF-LPME during extraction and therefore to enhance the extraction efficiency for target analytes, it is necessary to choose a proper organic solvent with a high boiling point.

RTILs, resulting from the combination of organic cations and various anions, exhibit negligible vapor pressures at room temperature and good extractability for various organic compounds.

3.1. Selection of ionic liquid

Three commonly used ionic liquids, including [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$], were tested as extractants for BTEXs. It was found that the peak areas of BTEXs obtained using [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$] were comparable. For example, the peak area of toluene were 60852, 61843 and 59678, respectively, when [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$] were utilized. Therefore each of the ionic liquids could be used as an effective extraction solvent for BTEXs from water samples. However, the viscosity of [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$] were 450, 585, to 685 cP, respectively [32]. Because a high viscosity of extractant could reduce mass diffusion rates of BTEXs into the ionic liquid phase during extraction, and was also not compatible with the gas chromatography employed, [C$_4$MIM][PF$_6$] (i.e. [BMIM][PF$_6$]) was chosen as the extraction solvent due to its good extraction performance and low viscosity.
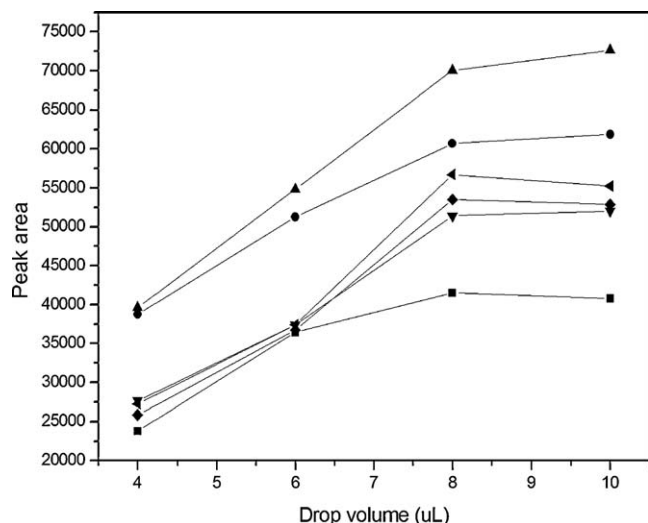
Fig. 1. Effect of [BMIM][PF$_6$] volume on the chromatogram peak areas of BTEXs: (■) benzene; (●) toluene; (▲) ethyl-benzene; (▼) o-xylene; (◆) m-xylene; (◀) p-xylene. X-axis: temperature (); Y-axis: peak area.

3.2. Effect of volume of [BMIM][PF$_6$]

Since the amount of analyte extracted depends on the extractant volume used, an experiment was conducted to study the effect of extractant volume on analytical signals. The volume of [BMIM][PF$_6$] was varied from 4.0 μL to 10.0 μL by an increment of 2.0 μL. 20 mL of 400 μg/L BTEXs aqueous solution was used to test the dependence of peak areas of BTEXs on [BMIM][PF$_6$] volume for an extraction time of 30 min in a 50-mL beaker. The results showed in Fig. 1 indicate that the peak areas enhanced with the increase of [BMIM][PF$_6$] volume, and when the volume was in the range of 8.0–10.0 μL, the curves become almost flat. An obvious drop in the peak area of each analyte was observed when the [BMIM][PF$_6$] volume was up to 12.0 μL, which could be attributed to the increase in extraction phase volume. Thus, 8.0 μL of [BMIM][PF$_6$] was used in our experiment.

3.3. Effect of temperature

The influence of temperature on extraction efficiency was investigated, in which the sampling temperature spanned from 25 to 55 °C. It can be seen from Fig. 2 that the analytical signals decreased with the increase of sampling temperature. For example, the amounts of BTEXs extracted at 55 °C were only about 40–60% of those extracted at 25 °C. Two causes accounted for these results. One is the exothermic effect during the analyte absorption in the ionic liquid within hollow fiber, which resulted in the drop of amount of analytes absorbed by [BMIM][PF$_6$] when the extraction temperature increased. The other is the reduction of BTEXs concentrations in aqueous phase due to the increase of vapor pressure of the analytes in the headspace at a higher temperature. Therefore, if a lower temperature is maintained during sampling, a higher sensitivity can be achieved. All the following experiments were then carried out at 25 °C.

3.4. Effect of extraction time

One of the important parameters affecting LPME was extraction time. As in SPME, it is not necessary for LPME to come to an exhaustive extraction. Since LPME is a solutes partitioning between the organic and aqueous phases, an appropriate extraction time during which equilibrium between the two phases is reached should
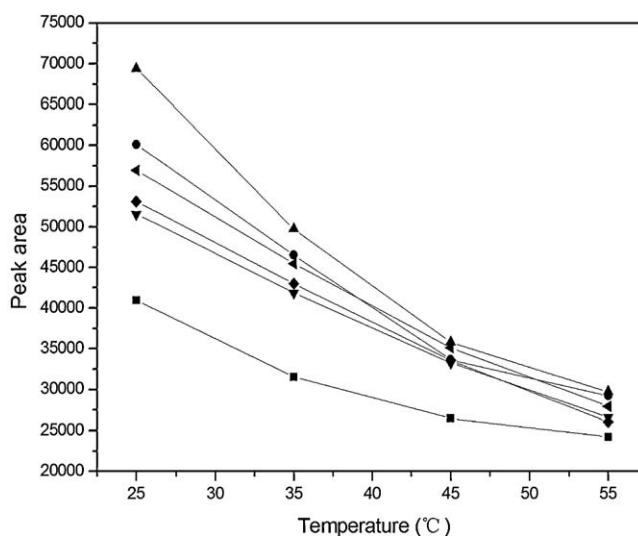

Fig. 2. Effect of extraction temperature on the chromatogram peak areas of BTEXs: (■) benzene; (●) toluene; (▲) ethyl-benzene; (▼) o-xylene; (◆) m-xylene; (◀) p-xylene.

be chosen. The amount of analytes transferred into the ionic liquid will reach its maximum value when this equilibrium is established. Fig. 3 illustrates the time dependence of the peak areas of BTEXs. It is apparent that the amount of BTEX components extracted into [BMIM][PF$_6$] increased with the extraction time. When the extraction time was longer than 30 min, the analytical signals remained practically constant, indicating that equilibrium was achieved for BTEXs. Thus, an extraction time of 30 min was chosen to allow a sensitive determination of BTEX compounds.

3.5. Effect of stirring rate

In extraction methods, agitation of sample solution is routinely applied to accelerate the extraction kinetics. Increasing agitation rate of the donor solution enhances extraction, because the diffusion of analytes from aqueous solution to acceptor phase is facilitated. Therefore, equilibrium between the two phases can be achieved more rapidly. Agitation can also improve the repeatability of the extraction method [33].
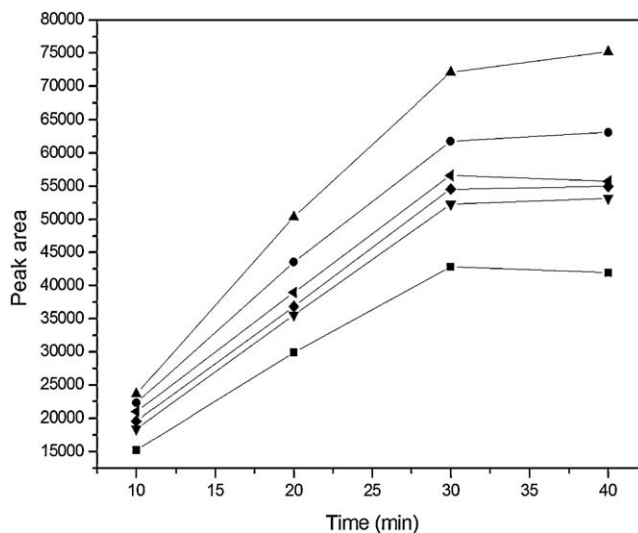

Fig. 3. Effect of extraction time on the chromatogram peak areas of BTEXs: (■) benzene; (●) toluene; (▲) ethyl-benzene; (▼) o-xylene; (◆) m-xylene; (◀) p-xylene.
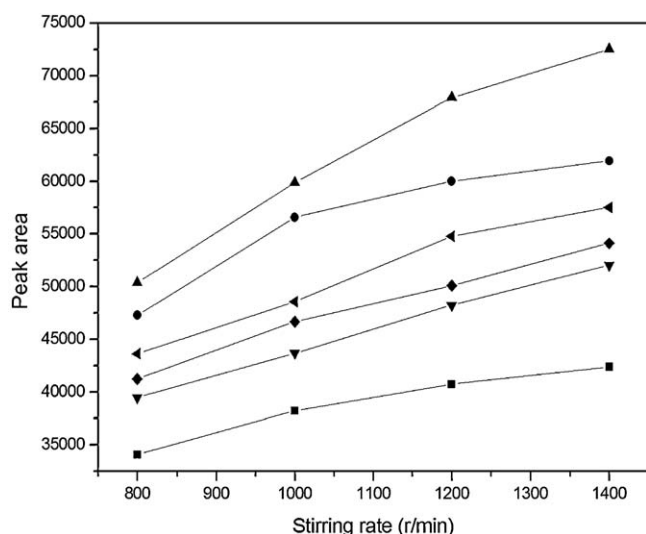
Fig. 4. Effect of stirring rate on the chromatogram peak areas of BTEXs: (■) benzene; (●) toluene; (▲) ethyl-benzene; (▼) o-xylene; (♦) m-xylene; (◄) p-xylene.

The effect of sample solution agitation was evaluated using a stirring speed of from 800 to 1400 rpm. Fig. 4 displays the influence of stirring speed on the peak areas of BTEXs. It can be seen from Fig. 4 that the extraction process was accelerated when increasing stirring speed from 800 rpm up to 1400 rpm. However, it was also observed that air bubbles would generate on the surface of hollow fiber when stirring rate was set at 1600 rpm. In our experiments, 1400 rpm was selected as the optimum stirring rate.

3.6. Effect of salt

The addition of salt to sample solution can decrease the solubility of analytes in water and consequently improve their extraction because of salting-out effect [34]. In this study, the effect of salt concentration on extraction efficiency of BTEXs from water was tested by adding sodium chloride (NaCl) to 20 mL of water samples at concentrations of 5, 10, 15, and 20% (w/v), respectively. Based on the results shown in Fig. 5, it can be concluded that the extraction efficiency increased with NaCl concentration up to 15% and then decreased with further addition of the salt, except the peak areas of m-xylene and o-xylene almost kept unchanged. This phenomenon
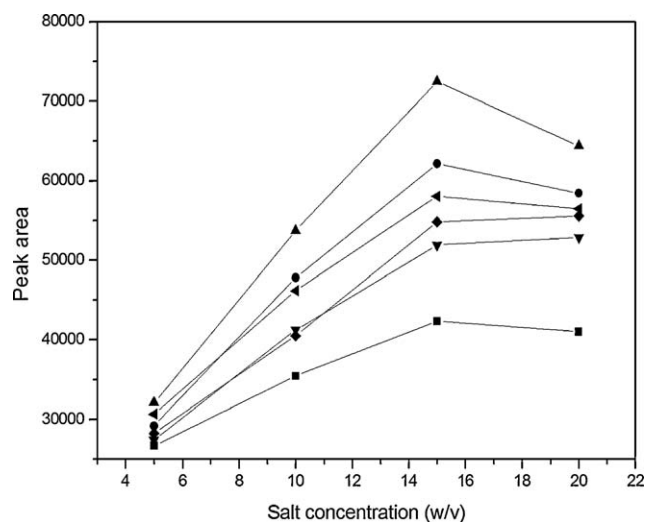

Fig. 5. Effect of salt concentration on the chromatogram peak areas of BTEXs: (■) benzene; (●) toluene; (▲) ethyl-benzene; (▼) o-xylene; (♦) m-xylene; (◄) p-xylene.

Table 1
Figures of merit of the proposed method.

Analytes	Linear range (μg/L)	r^2	LODs (μg/L)	RSDs (n = 5) (%)[a]
Benzene	10–500	0.9948	3.0	3.1
Toluene	5–500	0.9976	2.2	1.3
Ethyl-benzene	5–500	0.9936	2.7	2.8
o-Xylene	10–500	0.9988	3.5	5.4
m-Xylene	10–500	0.9963	4.0	1.5
p-Xylene	10–500	0.9986	3.2	5.1

[a] Water samples spiked at 0.2 mg/L for each compound.

can be explained as follows: at the beginning of extraction, salting out effect played a predominant role, resulting in a decrease of dissolubility of BTEXs in aqueous phase and therefore an improvement of extraction. With the increasing of NaCl concentration, another effect caused by the presence of salt changed the physical properties of the extraction film, due to the interaction of salt molecules with ionic liquid molecules, reducing the mass diffusion rates of the analytes from bulk solution into the organic phase. Although the ionic liquid located in the pores of hollow fiber became more easily dissolved in the aqueous phase at a higher salt concentration [35], it was not observed a significant change in the volume of organic phase in the presence of 20% salt, because the bulk of ionic liquid was within the lumen of hollow fiber and protected by the polypropylene wall. In the subsequent experiment, 15% NaCl was selected as the optimum addition of salt.

3.7. Evaluation of the method performance

To validate the applicability of the proposed HF-LPME procedure, calibration curves were plotted using 6 spiking levels of water in the concentration range 5–1000 μg/L for BTEXs. For each level, five replicate extractions were performed under the optimal conditions. The linear dynamic range, correlation coefficient (r^2), the limits of detection (LODs) and the related standard deviations (RSDs) were calculated and are summarized in Table 1. Detection limit is a very important criterion to evaluate an analytical method. In this work, The LODs were calculated at a signal-to-noise ratio of 3.

3.8. Comparison of the HF-LPME with other extraction techniques

Table 2 compares the LODs, RSDs and extraction time for headspace liquid-phase microextraction (HS-LPME) [29], headspace solid phase microextraction (HS-SPME) [25], headspace solvent microextraction (HSE) [28], liquid–liquid extraction (LLE) [24], directly suspended droplet microextraction (DSDME) [36], headspace using a needle trap device (HS-NT) [37], direct immersion single drop microextraction (DI-SDME) [38] and the proposed HF-LPME method for the extraction of BTEXs from water samples coupled with gas chromatography-hydrogen flame ionization detection. As can be seen from Table 2, the LODs and RSDs of HF-LPME–GC-FID for BTEXs are better than or comparable with those of other methods, except LLE–HS–GC–MS. However, compared with LLE–HS–GC–MS, the proposed approach is simpler and cheaper. Although HSM–GC-FID takes a much shorter extraction time than the developed method and the other techniques, its selected extraction solvent still have some impurities that could interfere with the analysis.

3.9. Analytical application

The proposed method was applied to the determination of trace amounts of BTEXs in Zhujiang River (Guangzhou, China) water. Water samples were filtered through 0.45 μm of micropore

Table 2
Comparison of HF-LPME–GC-FID with other methods.

Analytes	Method	LOD (μg/L)	RSD (%)	Time (min)	Reference
Benzene	HF-LPME–GC-FID	3.0	3.1	30	This work
Toluene		2.2	1.3		
Ethyl-benzene		2.7	2.8		
o-Xylene		3.5	5.4		
m-Xylene		4.0	3.5		
p-Xylene		3.2	5.1		
Benzene	HS-LPME–GC-FID	3.5	6.3	20	[29]
Toluene		3.3	3.2		
Ethyl-benzene		6.2	6.0		
o-Xylene		8.6	2.5		
m-Xylene		10.6	9.3		
p-Xylene		12.9	5.5		
Benzene	HS-SPME–GC-FID	200	8.3	30	[25]
Toluene		100	6.9		
Ethyl-benzene		800	3.5		
Xylene		800	10		
Benzene	HSM–GC-FID	5.0	2.7	6	[28]
Toluene		1.9	3.5		
Ethyl-benzene		1.3	4.9		
o-Xylene		1.2	5.9		
m, p -Xylene		0.72	5.0		
Benzene	LLE–HS–GC–MS	0.43	4.0	15	[24]
Toluene		0.42	3.6		
Ethyl-benzene		0.25	2.4		
o-Xylene		0.32	2.5		
m, p-Xylene		0.26	2.2		
Benzene	DSDME–GC-FID	7	2.2	25	[36]
Toluene		3	2.5		
Ethyl-benzene		1	1.8		
o-Xylene		0.8	2.4		
Benzene	HS–NT–GC-FID	25	7	50	[37]
Toluene		10	1		
o-Xylene		10	8		
p-Xylene		10	8		
Benzene	DI–SDME–GC-FID	10	4.7	25	[38]
Toluene		5	6.5		
Ethyl-benzene		5	8.7		
o-Xylene		6	7.7		

Table 3
Analytical results of BTEXs in river water ($n = 4$).

Analytes	Found (μg/L)	Added (μg/L)	Sum (μg/L)	Recovery (%)
Benzene	ND	20.0	18.0 ± 1.5	90.0 ± 7.5
Toluene	18.2 ± 0.6	20.0	37.1 ± 2.0	94.5 ± 10.0
Ethyl-benzene	ND	20.0	22.3 ± 1.2	111.5 ± 6.0
o-Xylene	ND	20.0	18.7 ± 1.1	93.5 ± 5.5
m-Xylene	9.6 ± 0.7	20.0	30.0 ± 2.2	102.2 ± 11.0
p-Xylene	12.5 ± 0.3	20.0	30.9 ± 1.0	91.9 ± 5.0

membranes before use. The analysis was made in four replicates, and the recovery for spikes of BTEXs was also tested. The analytical results are tabulated in Table 3.

4. Conclusions

In the present work, a novel technique, RTILs-based HF-LPME, was developed for the extraction and enrichment of BTEXs at trace levels from water, followed by gas chromatography-hydrogen flame ionization detection. Ionic liquid [BMIM][PF$_6$] was a suitable solvent for extraction and preconcentration of the analytes, and the hollow fiber could effectively protect the ionic liquid and enhance the extraction efficiency for BTEXs, giving increased sensitivity of determinations and therefore lowering the limits of detection. The proposed approach has a number of advantages, such as simplicity, low cost, less consumption of solvent, short analysis time and environmentally benign. Because hollow fiber is cheap and therefore disposable, the possibility of carry-over interference can be easily avoided. The developed procedure was successfully applied to the analysis of trace BTEXs in water, and could be acted as an alternative to methods for BTEXs analysis with expensive instrumentations such as gas chromatography–mass spectrometry. However, due to its involatility, the ionic liquid used will keep staying in the injection port of GC, requiring daily replacement of quartz wool and cleaning the glass tube for GC. On the other hand, just because it is difficult to vaporize in GC injector, no ionic liquid went into the detector of GC. Consequently, its interference with the determination of very low concentrations of BTEX components was not observed.

References

[1] T. Ligor, B. Buszewski, Extraction of trace organic pollutants from aqueous samples by a single drop method, Chromatographia 51 (2000) S279–S282.
[2] X.G. Ma, Z.X. Zhang, Wavelt smoothing applied to the determination of trace arsenic, lead, antimony and selenium in environmental water by ICP-OES, J. Anal. At. Spectrom. 19 (2004) 738–742.

[3] B. Vrana, A. Paschke, P. Popp, Calibration and field performance of membrane-enclosed sorptive coating for integrative passive sampling of persistent organic pollutants in water, Environ. Pollut. 144 (2006) 296–307.

[4] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62 (1990) 2145–2148.

[5] A. Bouaid, L. Ramos, M.J. Gonzalez, P. Fernández, C. Cámara, Solid-phase microextraction method for the determination of atrazine and four organophosphorus pesticides in soil samples by gas chromatography, J. Chromatogr. A 939 (2001) 13–21.

[6] A.L. Dimitra, A.A. Triantafyllos, Determination of the fungicides vinclozolin and dicloran in soils using ultrasonic extraction coupled with solid-phase microextraction, Anal. Chim. Acta 514 (2004) 125–130.

[7] H. Liu, P.K. Dasgupta, Analytical chemistry in a drop. Solvent extraction in a microdrop, Anal. Chem. 68 (1996) 1817–1821.

[8] K.J. Huang, H. Wang, M. Ma, M.L. Sha, H.S. Zhang, Ultrasound-assisted liquid-phase microextraction and high-performance liquid chromatographic determination of nitric oxide produced in PC12 cells using 1,3,5,7-tetramethyl-2,6-dicarbethoxy-8-(3′,4′-diaminophenyl)-difluoroboradiaza-*s*-indacene, J. Chromatogr. A 1103 (2006) 193–201.

[9] E. Psillakis, N. Kalogerakis, Developments in liquid-phase microextraction, Trends Anal. Chem. 22 (2003) 565–574.

[10] S. Pedersen-Bjergaard, K.E. Rasmussen, Bioanalysis of drugs by liquid-phase microextraction coupled to separation techniques, J. Chromatogr. B 817 (2005) 3–12.

[11] S. Shariati-Feizabadi, Y. Yamini, N. Bahramifar, Headspace solvent microextraction and gas chromatographic determination of some polycyclic aromatic hydrocarbons in water samples, Anal. Chim. Acta 489 (2003) 21–31.

[12] J. Zhang, T. Su, H.K. Lee, Headspace water-based liquid-phase microextraction, Anal. Chem. 77 (2005) 1988–1992.

[13] Z.F. Fan, X.J. Liu, Determination of methylmercury and phenylmercury in water samples by liquid–liquid–liquid microextraction coupled with capillary electrophoresis, J. Chromatogr. A 1180 (2008) 187–192.

[14] H.F. Wu, C.H. Lin, Direct combination of immersed single-drop microextraction with atmospheric pressure matrix-assisted laser desorption/ionization tandem mass spectrometry for rapid analysis of a hydrophilic drug via hydrogen-bonding interaction and comparison with liquid–liquid extraction and liquid-phase microextraction using a dual gauge microsyringe with a hollow fiber, Rapid Commun. Mass Spectrom. 20 (2006) 2511–2515.

[15] E. Psillakis, N. Kalogerakis, Fast extraction, clean-up and detection methods for the rapid analysis and screening of seven indicator PCBs in food matrices, Trends Anal. Chem. 21 (2002) 40–53.

[16] S. Pedersen-Bjergaard, K.E. Rasmussen, Liquid–liquid–liquid microextraction for sample preparation of biological fluids prior to capillary electrophoresis, Anal. Chem. 71 (1999) 2650–2656.

[17] G. Shen, H.K. Lee, Hollow fiber-protected liquid-phase microextraction of triazine herbicides, Anal. Chem. 74 (2002) 648–654.

[18] T.S. Ho, T. Vasskog, T. Anderssen, E. Jensen, K.E. Rasmussen, S. Pedersen-Bjergaard, 25,000-fold pre-concentration in a single step with liquid-phase microextraction, Anal. Chim. Acta 592 (2007) 1–8.

[19] D.J. Bauer, K.W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, Phosphines with 2-imidazolium and *para*-phenyl-2-imidazolium moieties—synthesis and application in two-phase catalysis, J.Organomet. Chem. 630 (2001) 177–184.

[20] M. Mori, R.G. Garcia, M.P. Belleville, D.P. Jeanjean, J. Sanchez, P. Lozano, M. Vaultier, G. Rios, A new way to conduct enzymatic synthesis in an active membrane using ionic liquids as catalyst support, Catal. Today 104 (2005) 313–317.

[21] G.T. Wei, Z. Yang, C.J. Chen, Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions, Anal. Chim. Acta 488 (2003) 183–192.

[22] C. Yao, J.L. Anderson, Dispersive liquid–liquid microextraction using an in situ metathesis reaction to form an ionic liquid extraction phase for the preconcentration of aromatic compounds from water, Anal. Bioanal. Chem. 395 (2009) 1491–1502.

[23] P. Sun, D.W. Armstrong, Ionic liquids in analytical chemistry, Anal. Chim. Acta 661 (2010) 1–16.

[24] C. Carrillo-Carrión, R. Lucena, S. Cárdenas, M. Valcárcel, Liquid–liquid extraction/headspace/gas chromatographic/mass spectrometric determination of benzene, toluene, ethylbenzene, (*o*-, *m*- and *p*-)xylene and styrene in olive oil using surfactant-coated carbon nanotubes as extractant, J. Chromatogr. A 1171 (2007) 1–7.

[25] F.J. Liu, N. Li, G.B. Jiang, J.M. Liu, J.A. Jönsson, M.J. Wen, Disposable ionic liquid coating for headspace solid-phase microextraction of benzene, toluene, ethylbenzene, and xylenes in paints followed by gas chromatography-flame ionization detection, J. Chromatogr. A 1066 (2005) 27–32.

[26] D.M. Chambers, D.O. McElprang, M.G. Waterhouse, B.C. Blount, An improved approach for accurate quantitation of benzene, toluene, ethylbenzene, xylene, and styrene in blood, Anal. Chem. 78 (2006) 5375–5383.

[27] A.L. Theis, A.J. Waldack, S.M. Hansen, M.A. Jeannot, Headspace solvent microextraction, Anal. Chem. 73 (2001) 5651–5654.

[28] A. Przyjazny, J.M. Kokosa, Analytical characteristics of the determination of benzene, toluene, ethylbenzene and xylenes in water by headspace solvent microextraction, J. Chromatogr. A 977 (2002) 143–153.

[29] H.M. Huang, X.G. Ma, Application of headspace liquid-phase microextraction using ionic liquid as extractant combined with gas chromatography-hydrogen flame ionization detector to the determination of BTEXs in water, in: Proceedings of International Conference on Energy and Environment Technology, 2, 2009, pp. 273–276.

[30] J.F. Peng, J.F. Liu, G.B. Jiang, C. Tai, M.J. Huang, Ionic liquid for high temperature headspace liquid-phase microextraction of chlorinated anilines in environmental water samples, J. Chromatogr. A 1072 (2005) 3–6.

[31] C.G. Pan, X.G. Ma, Microwave-assisted synthesis and characterization of 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid, J. Funct. Mater. 41 (2010) 153–155.

[32] S.Q. Li, S. Cai, W. Hu, H. Chen, H.L. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, Spectrochim. Acta B 64 (2009) 666–671.

[33] L. Zhao, H.K. Lee, Liquid-phase microextraction combined with hollow fiber as a sample preparation technique prior to gas chromatography/mass spectrometry, Anal. Chem. 74 (2002) 2486–2492.

[34] L. Zhao, L. Zhu, H.K. Lee, Analysis of aromatic amines in water samples by liquid–liquid–liquid microextraction with hollow fibers and high-performance liquid chromatography, J. Chromatogr. A 963 (2002) 239–248.

[35] M. Baghdadi, F. Shemirani, In situ solvent formation microextraction based on ionic liquids A novel sample preparation technique for determination of inorganic species in saline solutions, Anal. Chim. Acta 634 (2009) 186–191.

[36] A. Sarafraz-Yazdi, A.H. Amiri, Z.Z. Es'haghi, Separation and determination of benzene, toluene, ethylbenzene and o-xylene compounds in water using directly suspended droplet microextraction coupled with gas chromatography-flame ionization detector, Talanta 78 (2009) 936–941.

[37] J. De Crom, S. Claeys, A. Godayol, M. Alonso, E. Antico, J.M. Sanchez, Sorbent-packed needle microextraction trap for benzene toluene, ethylbenzene, and xylenes determination in aqueous samples, J. Sep. Sci. 33 (2010) 2833–2840.

[38] A. Sarafraz-Yazdi, Z. Seyed-Hadi Khaleghi-Miran, Es'haghi, Comparative study of direct immersion and headspace single drop microextraction techniques for BTEX determination in water samples using GC-FID, Int. J. Environ. Anal. Chem. 90 (2010) 1036–1047.