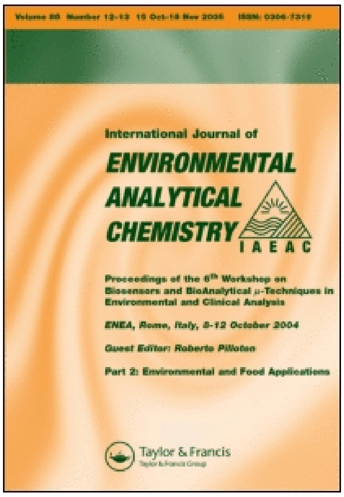

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Dispersive liquid-liquid microextraction based on ionic liquid in combination with high-performance liquid chromatography for the determination of bisphenol A in water

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Dispersive liquid–liquid microextraction based on ionic liquid in combination with high-performance liquid chromatography for the determination of bisphenol A in water

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A method termed dispersive liquid–liquid microextraction (DLLME) coupled with high-performance liquid chromatography-variable wavelength detection (HPLC-VWD) was developed. DLLME-HPLC-VWD is a method for determination of bisphenol A (BPA) in water samples. In this microextraction method, several parameters such as extraction solvent volume, sample volume, disperser solvent, ionic strength, pH, and disperser volume were optimised with the aid of interactive orthogonal array and a mixed level experiment design. First, an orthogonal array design was used to screen the significant variables for the optimisation. Second, the significant factors were optimised by using a mixed level experiment. Under the optimised extraction conditions (extraction solvent: ionic liquid [C_6MIM][PF_6], 60 µL; dispersive solvent: methanol, 0.4 mL; and $pH = 4.0$), the performance of the established method was evaluated. The response linearity of the method was observed in a range of 0.002–1.0 mg L^{-1} (three orders of magnitude) with correlation coefficient (R^2) of 0.9999. The repeatability of this method was 4.2–5.3% for three different BPA levels and the enrichment factors were above 180. The extraction recovery was about 50% for the three different concentrations with 3.4–6.4% of RSD. Limit of detection of the method was 0.40 µg L^{-1} at a signal-to-noise ratio of 3. In addition, the relative recovery of sample of Songhua River, tap water and barrel-drain water at different spiked concentration levels was ranged 95.8–103.0%, 92.6–98.6% and 87.2–95.3%, respectively. Compared with other extraction technologies, there have been the following advantages of quick, easy operation, and time-saving for the present method.

Keywords: dispersive liquid–liquid microextraction; bisphenol A; high-performance liquid chromatography; 1-hexyl-3-methylimidazolium hexafluorophosphate; interactive orthogonal array

1. Introduction

Bisphenol A (BPA) is widely used as an intermediate to synthesise epoxy resins and polycarbonate plastics, which are commonly employed in the production of lining for metal cans, food and beverage containers, with the result that BPA can be easily leached into food and routinely enter the human body [1,2]. BPA has been detected in a number of

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matrices such as water, drinking water, air, dust and so on. Because of its wide availability in the environment, there are possible adverse effects of BPA exposure on human health and wild animals [3]. BPA can represent mimic oestrogenic effects when absorbed by human and wild animals, even at trace levels. Thus, BPA becomes one of the most widely studied topics [4]. In order to evaluate the risk and the possible prevention of danger to humans and animals, the level of BPA in the surrounding environmental matrix should be measured. As the amount of BPA in environmental samples is lower than that of the detection limit of the involved instruments, extraction/pre-concentration of relevant compounds is required.

Many extraction methods have been summarised in the literature [5–7]. Currently, several methods are in use to prepare samples prior to analysis, such as liquid–liquid extraction (LLE) [8], solid-phase extraction (SPE) [9], cloud point extraction (CPE) [10], single drop microextraction (SDME) [11,12], liquid-phase microextraction (LPME) [13,14], solid-phase microextraction (SPME) [15,16], and dispersive liquid–liquid microextraction (DLLME) [17–19]. It can be concluded that the focus of analysis is oriented towards development of environmentally friendly, time saving, inexpensive, and miniaturised apparatus. The conventional method of LLE consumes large amounts of sample and organic solvent, while SPE needs a long time for extraction and there is a high cost of the column [20]. The technologies of SDME and LPME use only a few microlitres of organic solvent, and SPME is free of solvent and easy to operate, but its fibre has limited lifetime and is fragile and expensive [11]. DLLME, the most popular miniaturised sample pre-treatment technique, has the advantages of both LPME and SPME, such as simplicity of operation, rapidity, low cost, and high efficiency [21]. In addition, the extraction process is independent of time because of an infinitely large surface area between extraction solvent and aqueous phase [22]. The performance of DLLME has been illustrated based on the successful determination of polycyclic aromatic hydrocarbons (PAHs), organophosphorus pesticides (OPPs), chlorobenzenes (CBs), BPA in water [21–24], and volatile phenols in red wines [25].

Ionic liquids (ILs) are salts, which are liquid at room temperature and are considered as 'green solvents' for various separation processes [26]. ILs are alternative to traditional organic solvents in analytical chemistry due to their unique properties such as negligible vapour pressure, good thermal stability, tunable viscosity, miscibility with water and organic solvents, as well as environmental friendliness and extractability for various organic compounds and metal ions [27,28].

Ionic liquid based dispersive liquid–liquid microextraction has been successfully applied to the determination of aromatic amines and four heterocyclic insecticides in water, mercury ion in water, and some lanthanoids in uranium dioxide powder [18,29–31]. So far, there have been many methods for the determination of BPA in water [24,32]. However, ionic liquid based dispersive liquid–liquid microextraction method for determination of BPA in water is still unreported.

The purpose of the present work is to investigate the possibility of [C_6MIM][PF_6] (an IL, 1-hexyl-3-methylimidazolium hexafluorophosphate) in sample pre-concentration using DLLME combined with high-performance liquid chromatography-varied wavelength detection (HPLC-VWD) for the routine measurement of trace level of BPA in water. The different experimental parameters influencing the yield of the sample preparation were optimised by the interactive orthogonal array and a mixed level experiment, and the established method was evaluated in detail, subsequently. Finally, several real water samples were analysed using this recommended method.

2. Experimental

2.1 *Chemicals and reagents*

Bisphenol A (99%+, Aldrich, USA); $[C_6MIM][PF_6]$ (99%, J&K Chemical, China); sodium chloride (GR, Tianjin, China); acetone and methanol (HPLC-grade, J&K Baker, USA); hydrochloride acid (AR, Tianjin, China) and deionised water was prepared by using Direct-Q3UV (Millipore, France).

Stock solution: an appropriate amount of BPA was weighed with high-precision electronic analytic balance (FA1004, Shanghai, China) and dissolved in methanol. Two hundred $mg\,L^{-1}$ of the stock solution was prepared and stored at 4°C. This solution was stored for a week and further diluted to the required concentrations before use including the standard solution.

Real water samples were used for evaluation of the method. Tap water was obtained from the laboratory (North China Electric Power University, Beijing, China), river water was collected from Songhua River (Jilin, Jilin Province, China), and wastewater was sampled from a barrel-drain near Beijing University of Agriculture (Beijing, China). After being filtered through a 0.45 µm PTFE syringe filter (Osmonics), the water samples were stored at 4°C in glass bottles and analysed within 24 h after collection.

2.2 *Sample preparation*

In a preliminary experiment, the interactive orthogonal array design, used as factor screening experiment, was employed. The levels of factors considered were IL volume (60 µL, 90 µL), sample volume (3 mL, 5 mL); dispersant type (methanol, acetone); pH (4.0, 7.0); ionic strength ($0\,mol\,kg^{-1}$, $0.4\,mol\,kg^{-1}$); and dispersant volume (0.4 mL, 0.6 mL). According to the interactive orthogonal array design, water samples were prepared.

In the optimisation experiment, a mixed level experiment used to optimise significant factors was designed. The levels of the significant factors considered were sample volume (5, 6, and 7 mL) and IL volume (50 and 60 µL); and the level of other factors were fixed: $pH = 4.0$, dispersant volume set at 0.4 mL, and no NaCl was added for the ion strength adjustment.

The optimal conditions of sample preparation were obtained: an aliquot of 7 mL water sample (spiked at the level of 20 µg/L of BPA) after adjusting pH with DELTA320 pH meter (Mettler-Toledo Instruments, Shanghai, China) was placed in a 10 mL screw cap glass centrifuge tube with a conical bottom. Sixty µL of $[C_6MIM][PF_6]$ was added in 0.4 mL of methanol used as the dispersive solvent. Then, the mixed solution was transferred to the centrifuge tube rapidly. The mixture was gently shaken by hand for several seconds. After centrifugation for 8.0 min at 5000 rpm (Refrigerated Centrifuge 2–16PK, Sigma, Germany), about 20 ± 1 µL of IL phase was sedimented at the bottom of the centrifuge tube. Five µL of sedimented phase was removed using a 50 µL microsyringe (Agilent, USA) and injected into the HPLC system and analysed.

2.3 *Chromatographic conditions*

The employed HPLC system is Agilent 1200 HPLC (Agilent, USA) equipped with a rheodyne six-port valve with 20 µL loop manual injector, a vacuum degasser (G1322A), a double pump (G1312A) and a variable wavelength detector (G1314B, Agilent, USA) set at 280 nm. Data collection, integration and analysis were accomplished using Agilent Chem

Station software. The analytical chromatographic columns were TC-C18 (150 mm × 4.6 mm, 5 μm, Agilent) and ZORBAX SB-C18 (250 mm × 4.6 mm, 5 μm, Agilent).

Gradient elution was employed to separate the target compound from other compounds. Chromatographic condition A: 0–5 min methanol: deionised water = 70%: 30% (v v^{-1}), 5–10 min the percentage of methanol increased slowly from 70% to 85%, the following 8 min was used as post time with TC-C18 column (150 mm × 4.6 mm, 5 μm), and the retention time of BPA was found to be 3.9 min; Chromatographic condition B: 0–6 min the methanol increased from 60% to 80%, held for 9 min with ZORBAX SB-C18 column (250 mm × 4.6 mm, 5 μm). The retention time of BPA was found to be 7.1 min. The column temperature was kept at 30°C with a flow rate of 1.0 mL min^{-1}.

2.4 *Calculation of enrichment factor and extraction recovery*

The enrichment factor (EF) is defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) in the water sample:

$$\text{EF} = \frac{C_{\text{sed}}}{C_0} \tag{1}$$

First, the calibration graph between peak area and BPA concentration was obtained by direct injection of 5 μL standard solution of BPA in the range of 0.1–100 mg/L. Then 5 μL of sedimented phase was also injected into HPLC for analysis, and the value of peak area was recorded. Finally, calculation of C_{sed} was carried out, based on the obtained calibration graph. The extraction recovery (ER) is defined as the percentage of the total amount (M_0), which was extracted into the sedimented phase (M_{sed}).

$$\text{ER} = \frac{M_{\text{sed}}}{M_0} \times 100 = \frac{C_{\text{sed}} \times V_{\text{sed}}}{C_0 \times V_0} \times 100 = \left(\frac{V_{\text{sed}}}{V_0}\right)\text{EF} \times 100 \tag{2}$$

where V_{sed} and V_0 are the volumes of sedimented phase and water sample, respectively.

3. Results and discussion

3.1 *Preliminary experiment*

Effects of six variables with low and high levels were described as follows: IL volume (A), sample volume (B), type of disperser (C), pH (D), ionic strength (E) and dispersant volume (F), on DLLME of BPA in water samples were investigated. In order to estimate the optimal extraction conditions, the variables were examined by L_{16} (2^{15}) interactive orthogonal array design with 16 experimental trials. The positions of the variables and their interactions in columns are assigned and shown in Table 1. No level values of the two-variable interactions (e.g. A × B) were decided as they depended on the main variable value settings. The results of DLLME experiments are given in Table 1. In addition, the sum of response at both levels and the sum of squares of deviations for every parameter are shown in Table 1. It is worth noting that each of the experimental trials was conducted in duplicate with a blank test. The difference between the mean value of the duplicate extraction yield and value of blank test was calculated for analysis.

Information about the relative merits of factors was obtained from the analysis of variance of the experimental results, which are demonstrated in Table 2. The parameters such as IL volume, sample volume, and type of disperser, show significant influence on the

Table 1. Assignment of factors and levels of the interactive orthogonal array design experiment along with the response.

Run	A	B	A × B	C	A × C		D × E	D			F		B × E		E	Y_i[a]
1	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	1.12
2	−	−	−	−	−	−	−	+	+	+	+	+	+	+	+	1.16
3	−	−	−	+	+	+	+	−	−	−	−	+	+	+	+	0.89
4	−	−	−	+	+	+	+	+	+	+	+	−	−	−	−	0.99
5	−	+	+	−	−	+	+	−	−	+	+	−	−	+	+	2.30
6	−	+	+	−	−	+	+	+	+	−	−	+	+	−	−	2.14
7	−	+	+	+	+	−	−	−	−	+	+	+	+	−	−	1.98
8	−	+	+	+	+	−	−	+	+	−	−	−	−	+	+	2.14
9	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	0.71
10	+	−	+	−	+	−	+	+	−	+	−	+	−	+	−	0.69
11	+	−	+	+	−	+	−	−	+	−	+	+	−	+	−	0.50
12	+	−	+	+	−	+	−	+	−	+	−	−	+	−	+	0.55
13	+	+	−	−	+	+	−	−	+	+	−	−	+	+	−	1.31
14	+	+	−	−	+	+	−	+	−	−	+	+	−	−	+	1.37
15	+	+	−	+	−	−	+	−	+	+	−	+	−	−	+	1.13
16	+	+	−	+	−	−	+	+	−	−	+	−	+	+	−	0.91
I[b]	12.72	6.61	8.88	10.8	9.81	9.84	10.13	9.94	9.81	9.78	9.97	10.03	10.24	9.99	9.64	$T^{d} = 19.89 S_T^{2\,f} = 5.25$
II[c]	7.17	13.28	11.01	9.09	10.08	10.05	9.76	9.95	10.08	10.11	9.92	9.86	9.65	9.90	10.25	
S_i^{2e}	1.93	2.78	0.28	0.18	0.005	0.003	0.009	–	0.005	–	0.0002	–	0.022	–	0.023	

[a] Y_i response representing the mean concentration of BPA in sedimented phase after DLLME, mg L^{-1}.
[b] sum of response at low level (−).
[c] sum of response at high level (+).
[d] total of response of the 16 trial runs.
[e] sum of squares of deviations for *i* parameter.
[f] sum of squares of deviations for all parameters.
A, B, C, D, E and F are the symbols of IL volume, sample volume, type of dispersant, pH, ionic strength and dispersant volume, respectively. '×' means interaction between the two factors.

Table 2. Analysis of variance based on interactive orthogonal array design for BPA.

Source of variance	Sum of squares	Degree of freedom	Mean square	F-ratio	Critical value 0.01	Critical value 0.005	Significance
A	1.93	1	1.93	742.3	16.26	22.78	**
B	2.78	1	2.78	1069.3	16.26	22.78	**
C	0.18	1	0.18	69.2	16.26	22.78	**
D	0.00006	1	–	–	16.26	22.78	
E	0.023	1	0.023	8.85	16.26	22.78	
F	0.0002	1	–	–	16.26	22.78	
A × B	0.28	1	0.28	107.7	16.26	22.78	**
B × E	0.022	1	0.022	8.46	16.26	22.78	
A × C	0.005	1	0.005	1.92	16.26	22.78	
D × E	0.009	1	0.009	3.46	16.26	22.78	
e^a	0.013	5	0.0026				
T^b	5.25	15					

[a] error.

[b] total of deviations.

A, B, C, D, E and F are the symbols of IL volume, sample volume, type of disperser, pH, ionic strength and disperser volume, respectively. '×' means interaction between the two factors.

extraction as evidenced by F values ($> F_{0.005}$) which implies that more attention should be paid to the three parameters for a maximum response in the further optimisation experiments. However, the parameter C, the type of disperser, can be identified as methanol, and other parameters can be determined on the measure index as the influence of the two different levels is relatively small (F value $< F_{0.01}$). Other insignificant parameters, sample pH and disperser volume, were selected as 4.0 and 0.4 mL in the following experiments, respectively, and without addition of NaCl for the ion strength adjustment.

In addition, the significant difference was observed for the interaction of A × B, but it was less important than that of individual factor based on F ratio. Hence, the interaction of A × B was not considered in the following experiments together with insignificant interactions of the other two variables.

3.2 *Optimisation experiments*

Parameters A and B were chosen as significant factors for further experiments to obtain the optimal extraction conditions. BPA concentration in sedimented phase (C_{sed}) as a function of sample volume (V_0) or IL volume (V) is illustrated in Figure 1. It was indicated that effects of both factors on C_{sed} are opposite: positive for the sample volume and negative for the IL volume, which can explain that the interaction of A × B is less significant than that of individual factor. However, less than 2 µL of sedimented phase was recovered after centrifugation when 50 µL of IL was added in 9 mL of water sample, indicating that the solubility of IL was non-negligible, which is consistent with the previous work [33]. The loss of IL is probably because of the water solubility of IL, and about 0.75 g of IL can be dissolved in 100 mL of water [33]. Therefore, a mixed level $2^1 \times 3^1$ experiments was designed. In order to obtain the maximum C_{sed}, volume levels of IL were selected as

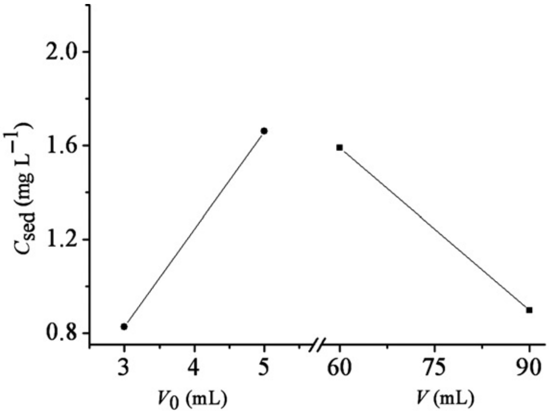

Figure 1. Effects of the sample volume and IL volume on the BPA concentration in sedimented phase. Notes: C_{sed} is the average of eight measurements (the parameter of interest is kept constant, and the other parameters are changed). Each of the measurements was corresponding to an individual extraction condition. A set of extraction conditions was corresponding to a trial in the interactive orthogonal array design.

50 μL and 60 μL, and levels of sample volume were set as 5, 6, and 7 mL. Subsequently, six trial runs of the design array were carried out.

The data of the mixed level $2^1 \times 3^1$ experiments are shown in Figure 2. The water sample volume is between 5 and 7 mL at a constant extraction solvent of 50 and 60 μL, increment of C_{sed} is observed, and a maximum C_{sed} appears when water sample volume is 7 mL. As seen from Figure 2, the optimal extraction conditions can be obtained as follows: IL = 60 μL, sample volume = 7 mL as denoted by λ_1 or IL = 50 μL, and sample volume = 7 mL as denoted by λ_2. The sedimented phase is more easily withdrawn with a microsyringe when 60 μL of IL was used. Additionally, because there is a little increment in the volume of the sedimented phase when the volume of IL increased from 50 to 60 μL and the extraction recoveries are about 20% and 50% under conditions λ_2 and λ_1, respectively. Hence, the optimised DLLME conditions are selected as IL = 60 μL, $V_0 = 7$ mL.

3.3 *Quantitative analysis*

In order to study the applicability of the proposed method to determination of BPA in a real water sample, several common performance parameters including limit of detection (LOD), repeatability and recovery were evaluated. Linearity of calibration curve was observed in the range of 0.002–1.0 mg L^{-1} (three order magnitude) for BPA, and the coefficient of correlation (R^2) obtained was 0.9999 without internal standard. The calculated LOD of DLLME based on signal-to-noise ratio of 3 was below 0.40 μg L^{-1}. The repeatability and accuracy were studied by extracting three different spiked water samples (high-concentration: 0.2 mg L^{-1}; middle-concentration: 0.01 mg L^{-1}; and low-concentration: 0.002 mg L^{-1}). The extraction concentrations were 35.74, 1.84 and 0.362 mg L^{-1}, respectively, and the relative standard deviation (RSD) was calculated to be lower than 5.3% ($n = 5$) for all samples. The extraction recovery and enrichment factors ranged from 48.5–55.3% and 181–190, respectively.

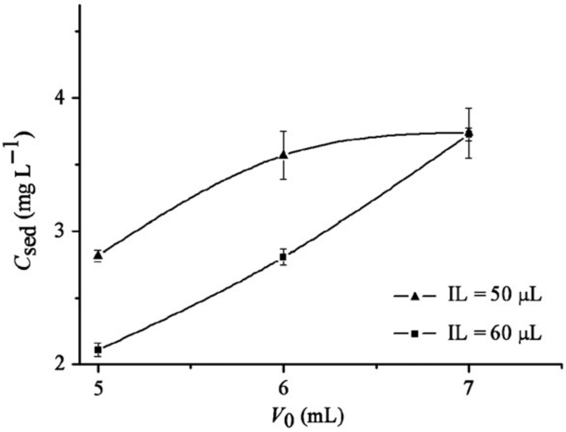

Figure 2. Effect of water sample volumes on BPA concentration in the sedimented phase after DLLME.
Notes: Extraction condition: sample volume, V_0, (5, 6 and 7 mL); extractant volume, IL, (50 and 60 μL); disperser solvent (methanol), 0.4 mL; BPA, 0.02 mg/L; pH = 4; without NaCl.

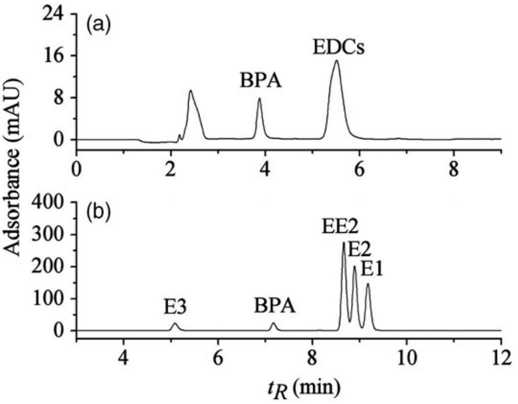

Figure 3. Chromatograms of BPA and other four EDCs under chromatographic condition A (a) and condition B (b).
Notes: Extraction condition: sample volume, 7 mL; extractant volume, 60 μL; disperser solvent (methanol), 0.4 mL; pH = 4; without NaCl. 0.01 mg/L of EDCs (a) and 0.10 mg/L of EDCs (b).

3.4 *Application to real water samples*

As shown in Figure 3(a), it is obvious that BPA is separated from some other endocrine disrupting chemicals (EDCs) such as 17-α-Ethynylestrdiol (EE2), Estrone (E1), Estradiol (E2), and Estriol (E3) under chromatographic condition A. The five EDCs mentioned above can be separated from each other under chromatographic condition B, as demonstrated in Figure 3(b), which implies that the selected EDCs in water samples can be determined simultaneously.

Several real water samples, tap water obtained from the laboratory, river water collected from Songhua River, and wastewater sampled from a barrel-drain near

Table 3. Relative recoveries and relative standard deviation of BPA from spiked real water samples.

Water samples	Concentration (μg L^{-1})	Added concentration (mg L^{-1})	Founded concentration (% RSD[b], $n = 5$) (mg L^{-1})	R^c(%)
Songhua River	nd[a]	0.2	0.1978 (4.7)	98.9
		0.02	0.01930 (8.1)	96.5
		0.002	0.001906 (10.8)	95.3
Tap water	nd[a]	0.2	0.2059 (3.0)	103.0
		0.02	0.01972 (4.8)	98.6
		0.002	0.001711 (5.6)	85.5
Barrel-drain water	8	0.2	0.1986 (9.1)	95.8
		0.02	0.02651 (4.5)	92.6
		0.002	0.009744 (9.2)	87.2

[a] not detected.
[b] % relative standard deviation, $n = 5$.
[c] % relative recovery.

Beijing University of Agriculture, were analysed by HPLC-VWD after DLLME procedure. BPA was not detected in samples of Songhua River and tap water in the laboratory, both of which were likely to be not contaminated by BPA or perhaps the concentration was below the detection limit of the proposed method. The concentration of BPA in barrel-drain water was detected as 0.008 mg L^{-1}. In addition, in order to assess the matrix effects, three different BPA levels were spiked in real water and the relative recoveries are given in Table 3. The data show that the relative recoveries ranged 85.5–103.0% at the different spiked concentration levels. The results demonstrate that the three real water matrices have little effect on the extraction method, and the extraction method can be applied to the real water for the BPA determination.

3.5 *Comparison of DLLME with other methods*

The comparison of this method in terms of LOD, RSD, extraction time and sample volume needed with other methods was carried out (the results are shown in Table 4). Compared with the results of one report [24], LOD of the proposed method was a little higher. In comparison with others, the limit of detection of DLLME-HPLC-VWD was at the same order of magnitude as those of the methods such as SPE-HPLC-ESI-MS [4] and LLE-GC-MS-SIM [34], and better than that of SPE-HPLC-FLD [35], but higher than those of other methods such as SPE-GC-MS [36], SPME-HPLC-FLD [37], and HF-LPME-ESI-MS [38]. All of the organic solvents used in other methods were harmless to operator and environment, but the IL used as extraction solvent was an environmentally friendly solvent, which was non-toxic to the operator. In addition, IL used was much less than extraction/desorption solvent in other methods except the HF-LPME-MS. It is worthy to note that the derivatisation process takes more time when MS was employed, and SPE and SPME consumed chemical reagent that complicated the extraction process. Additionally, this method only needed several seconds for extraction procedure. All the results revealed that DLLME was a fast, reproducible microextraction method.

Table 4. Comparison of DLLME-HPLC-VWD with other extraction methods for determination of BPA.

Methods	LOD[a] (μg/L)	RSD[b] (%)	T^c (min)	Extractant (Volume) (mL)	Sample volume (mL)	References
SPE-HPLC-ESI-MS	0.7	17.6	>4	Methanol (8.5)	9	[4]
DLLME-HPLC-UV	0.07	6.0	3	Chloroform (0.142)	10	[24]
LLE-GC-MS-SIM	0.17	9.9	9	Dichloromethane (60)	200	[34]
SPE-HPLC-FLD	2.7	3.9	>30	Dichloromethane (8)	4	[35]
SPE-GC-MS	0.0053	10	>50	Ethyl acetate (10)	1000	[36]
SPME-HPLC-FLD	0.02	9.8	20	Acetonitrile (0.18)	4	[37]
HF-LPME-ESI-MS	0.02	6.7	15	Toluene (0.002)	1	[38]
DLLME-HPLC-VWD	0.40	5.3	Several seconds	$[C_6MIM]PF_6$ (0.06)	7	Proposed method

[a] limit of detection.
[b] relative standard deviation.
[c] extraction time.

4. Conclusions

The present paper describes a DLLME combined with HPLC-VWD method that can be applied to analysis of BPA in environmental water samples. The experimental results demonstrated that the proposed method was of repeatability, linearity over a wide range with three orders of magnitude and detection limit at the $\mu g\,L^{-1}$ level. The developed method could be successfully used to determine BPA in real water samples and the relative recovery was satisfying, although only 50% of the extraction recovery was obtained. Both sample preparation time and consumption of toxic organic solvent were minimised.

Compared with other extraction methods such as solid-phase extraction, liquid-phase microextraction and solid-phase microextraction, the proposed method employed a much shorter extraction time, and this method was also simple and inexpensive. However, more research work on increasing the extraction recovery is required.

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