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Optimization of temperature-controlled ionic liquid dispersive liquid phase microextraction combined with high performance liquid chromatography for analysis of chlorobenzenes in water samples

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ABSTRACT

Temperature-controlled ionic liquid dispersive liquid phase microextraction (TCIL-DLPME) combined with high performance liquid chromatography-diode array detection (HPLC-DAD) was applied for preconcentration and determination of chlorobenzenes in well water samples. The proposed method used 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) as the extraction solvent. The effect of different variables on extraction efficiency was studied simultaneously using an experimental design. The variables of interest in the TCIL-DLPME were extraction solvent volume, salt effect, solution temperature, extraction time, centrifugation time, and heating time. The Plackett–Burman design was employed for screening to determine the variables significantly affecting the extraction efficiency. Then, the significant factors were optimized by using a central composite design (CCD) and the response surface equations were developed. The optimal experimental conditions obtained from this statistical evaluation included: extraction solvent volume, 75 μL; extraction time, 20 min; centrifugation time, 25 min; heating time, 4 min; solution temperature, 50 °C; and no addition of salt. Under optimal conditions, the preconcentration factors were between 187 and 298. The limit of detections (LODs) ranged from 0.05 μg L^{-1} (for 1,2-dichlorobenzene) to 0.1 μg L^{-1} (for 1,2,3-trichlorobenzene). Linear dynamic ranges (LDRs) of 0.5–300 and 0.5–500 μg L^{-1} were obtained for dichloro- and trichlorobenzenes, respectively. The performance of the method was evaluated for extraction and determination of chlorobenzenes in well water samples in micrograms per liter and satisfactory results were obtained (RSDs < 9.2%).

1. Introduction

Chlorobenzenes (CBs) are released into the aquatic environment mainly from chemical industries. CBs are used for industrial and domestic purposes such as being used as solvents, degreasers, pesticides and chemical intermediates in production of other chemical compounds [1,2]. CBs are hazardous to health and have been ranked as priority pollutants by the US Environmental Protection Agency (EPA) [3]. The most common ways to extract CBs are liquid–liquid extraction (LLE) [4,5], solid-phase extraction (SPE) [6–8], solid-phase microextraction (SPME) [9–14], liquid phase microextraction (LPME) [15,16], headspace liquid phase microextraction (HS-LPME) [17–19], and dispersive liquid–liquid microextraction (DLLME) [20]. Applications of the conventional LLE and SPE methods were limited [21,22] with respect to their disadvantages such as solvent losses, large secondary wastes, having a long procedure, and complex equipment. The solvent microextraction technique effectively overcomes these problems by reducing the amount of the organic solvent. Further, extraction, preconcentration and sample introduction are performed in one step [23]. DLLME is an effective technique among the microextraction methods, proposed by Assadi et al. in 2006 [24]. The classical DLLME has many merits, but it still has some drawbacks such as using toxic solvents as the extraction solvent and using a third component (disperser solvent) that usually decreases the partition coefficient of the analytes into the extraction solvent. Recently, TCIL-DLPME method has overcome these problems by using ionic liquid as a solvent [25]. Ionic liquids (ILs) have been considered as green solvents. These liquids constitute a class of non-molecular ionic solvents with low melting points (<100 °C) resulting from combinations of organic cations and various anions. They have unique properties such as low volatility, chemical and thermal stability, and good solubility for both organic and inorganic molecules. ILs exhibit high solubility for many different classes of analytes allowing for the selectivity to be easily controlled by simply changing the combination of cations and anions. Furthermore, ILs typically exhibit short reten-

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tion times in reversed-phase separations and elute near the column dead volume, thereby having little effect on the separation of the analytes.

In recent years, ILs have attracted much interest and are being applied increasingly as the extraction solvent replacing the volatile solvents in sample preparation [26–30]. TCIL-DLPME is based on temperature changes making ILs completely disperse in the aqueous phase and increasing the chance of mass transfer into the IL phase. Consequently, the IL is condensed into one drop by cooling and centrifugation [31].

Chemometric tools have been frequently applied to analytical method optimization. Among the advantages of such approaches is the reduction in the number of required experiments, resulting in lower reagent consumption and considerably less laboratory work. Thus, they are faster to implement and more cost-effective than traditional univariate approaches. These methods enable the simultaneous study of several control factors and the development of mathematical models that permit assessment of the relevance and statistical significance of the factors being studied. They also facilitate the evaluation of interaction effects among factors. In these methods, factors can be firstly screened by full factorial or fractional factorial designs to get knowledge of those with significant effects on the analytical response. After determining these significant factors, the optimum operation conditions are attained by using quadratic response surface experimental designs [32].

In this study, TCIL-DLPME combined with high performance liquid chromatography with diode array detection was applied for determination of CBs in well water samples. The effects of the following experimental variables on the extraction efficiency of the analytes were investigated and optimized by a multivariate strategy: extraction solvent volume, salt effect, solution temperature, extraction time, centrifugation time, and heating time. The investigation was based on an experimental design using the Plackett–Burman design for screening and central composite design for optimization of significant factors. Finally, the optimized procedure was employed to determine CBs in well water samples.

2. Experiment

2.1. Chemicals and reagents

1,2-Dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), sodium chloride and 1-butyl-3-methyl-imidazolium hexafluorophosphate of the highest purity available from Merck (Darmstadt, Germany) were used in this study. HPLC grade acetonitrile was purchased from Caledon (Georgetown, Ont., Canada). Ultrapure water was prepared using a Milli-Q system from Millipore (Bedford, MA, USA).

The water samples were taken from wells in Chemi Darou Industrial and Pharmaceutical Company (Tehran, Iran) and Shahid Beheshti University (Tehran, Iran) and kept in polyethylene bottles at ambient temperature. The extraction was performed without any dilution of the samples.

2.2. Preparation of standard solutions

A stock standard solution of CBs (1000 $\mu g\,mL^{-1}$) was prepared in acetonitrile. Working standard solutions were prepared in doubly distilled water. All the standard solutions were stored in a fridge at 4 °C and brought to ambient temperature just prior to use.

2.3. Instrumentation

Separation and quantification of CBs were carried out using Shimadzu LC-10AD VP HPLC system from Shimadzu Company (Kyoto, Japan) equipped with a diode array detector. An injection valve with a 5-μL loop was employed in the study. Class-VP software was used for the acquisition and processing of the data. Chromatographic separations were carried out using a Capital HPLC column (Scotland, UK) ODS-H C18 (250 mm × 4.6 mm I.D., 5 μm). A mixture of water and acetonitrile (24:76) at the flow rate of l mL min^{-1} was used as the mobile phase in isocratic elution mode. The injection volume was 5 μL for all samples. The detection was performed at the wavelength of 210 nm.

2.4. TCIL-DLPME procedure

A 5 mL aqueous sample solution containing 200 $\mu g\,L^{-1}$ of each chlorobenzene was placed in a 12 mL screw cap glass test tube with conical bottom and 75 μL of [C_4mim][PF_6] was added to the solution. Then, the conical tubes were heated in a water bath at 50 °C for 4 min. The IL completely dissolved in the solution under these conditions. The tube was thereafter cooled on an ice bath for 20 min and the solution became turbid. Then, the solution was centrifuged for 25 min at 3000 rpm. Fine droplets of the IL sedimented at the bottom of the test tube. The volume of the sedimented phase, determined by a 25 μL microsyringe, was about 15 μL. 5 μL of the sedimented phase was withdrawn and injected into the HPLC system for analysis.

2.5. Optimization strategy

There are several factors, such as extraction solvent volume, salt effect, solution temperature, extraction time, centrifugation time, and heating time that affect the extraction process. In order to obtain optimal conditions of TCIL-DLPME for extraction of CBs from well water samples, the Plackett–Burman design was used for screening the variables. After determining the variables that significantly affect the extraction process, and in order to investigate the interaction among these variables, a central composite design (CCD) was employed to develop the corresponding response surface equation. The experimental design matrix and data analysis were carried out by the StatGraphics Plus Package, version 5.1.

3. Results and discussion

In this study, TCIL-DLPME combined with HPLC-DAD was developed for the extraction and determination of CBs in well water samples.

3.1. Screening design

Screening design is includes examining different factors for the main effects to reduce the number of factors. A particular type of such designs is Plackett–Burman design [33], which assumes that the interactions can be completely ignored. So, the main effects are calculated with a reduced number of experiments.

Based on the preliminary experiments, at least six factors might have affected the experimental response in the present work. Therefore, six factors (extraction solvent volume, salt effect, solution temperature, extraction time, centrifugation time, and heating time) at two levels were selected. The low and high values for each factor were selected from the results of previous experiments (Table 1).

The Plackett–Burman design was used to determine the main effects. The overall design matrix showed 12 runs to be carried out

Table 1
Experimental variables and levels of the Plackett–Burman design.

Variable	Key	Level	
		Low	High
Temperature (°C)	A	50	80
Extraction solvent volume (μL)	B	50	100
Extraction time (min)	C	10	50
Centrifugation time (min)	D	5	25
Ionic strength (%, w/v)	E	0	10
Heating time (min)	F	1	4

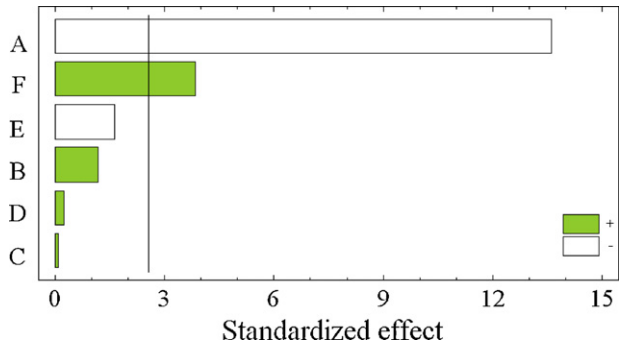

Fig. 1. Pareto charts of the main effects obtained from the Plackett–Burman design for CBs.

randomly in order to eliminate the effects of extraneous or nuisance variables. The ANOVA results were evaluated for determining the main effects. The normalized results of the experimental design were evaluated at a 5% of significance and analyzed by standardized Pareto chart (Fig. 1). Since all analytes showed similar results, only one chart was chosen as a representative example of the analytes. The standard effect was estimated for computing the *t* statistic for each effect. The vertical line on the plot judges statistically significant effects. The bar extracting beyond the line corresponds to the effects that are statistically significant at the 95% confidence level [34]. Furthermore, the positive or negative sign (corresponding to a colored or colorless response) can be enhanced or reduced, respectively, when passing from the lowest to the highest level set for the specific factor.

According to Fig. 1, temperature was the most significant factor having a negative effect on the extraction efficiency in this study. Heating time was the next most important positive significant factor. Also, as shown in Fig. 1, ionic strength appeared to have a negative effect on the extraction efficiency. In fact, by increasing NaCl concentration, the sedimented phase volume increased owing to the decreased solubility of the extraction solvent [35]. Extraction solvent volume was shown to have a positive effect on the extraction efficiency. Both extraction and centrifugation time had non-significant positive effects on the extraction efficiency. The extraction time was considered from the moment that the solution containing completely dissolved IL was put into the ice bath for the set interval. Generally, the longer the extraction time, the easier it is to reach extraction balance [36].

As shown in Fig. 2, the peak areas for analytes increased along with the centrifugation time increase. In fact, centrifugation controls the complete and fast phase separation. With short centrifugation times, total phase separation was not achieved and very small drops of the IL were still observed in the suspension. To continue the optimization process, three variables were fixed at appropriate values (extraction time: 20 min; centrifugation time: 25 min, and no addition of salt), considering the results of the first screening study.

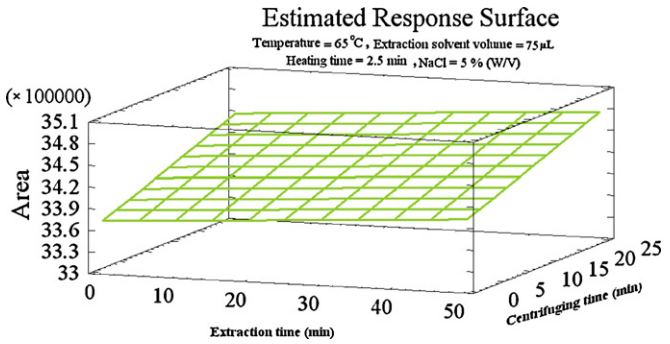

Fig. 2. Response surface for CBs using the Plackett–Burman design obtained by plotting of extraction time *vs.* centrifugation time.

3.2. Optimization design

In the next step, a central composite design was employed to optimize the three factors (temperature, extraction solvent volume, and heating time) that were chosen from the first screening design. The examined levels of the factors are given in Table 2.

This design permitted the response to be modeled by a second-order polynomial fit, which can be expressed as the following equation:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2$$

where x_1, x_2, and x_3 are the independent variables, β_0 is the intercept, β_1–β_{33} are the regression coefficients, and y is the response function (area). The number of experiments is defined by the expression: $(2^f + 2f + C)$, where f is the number of factors and C is the number of center points. This design consists of a factorial design (2^f) augmented with $(2f)$ star points and central points (C) [37]. The star points are located at $+\alpha$ and $-\alpha$ from the center of the experimental domain. An axial distance, α, was selected with a value of 1.682 in order to establish the rotatability condition of the central composite design.

In this study, f and C were both set at 3, indicating that 17 experiments had to be carried out. The experimental data showed good agreement with the second-order polynominal equations. The coefficients of determination, R^2, were higher than 0.97 for the areas, which were statistically acceptable at $p < 0.05$ levels. The data obtained were evaluated by ANOVA. The effects determined by this analysis are shown using Pareto chart in Fig. 3. Based on the central composite design, the three factors (temperature, extraction solvent volume, and heating time) were the most important variables for all the analytes. As Fig. 3 shows, temperature has the greatest

Table 2
Experimental variables, levels and star points of the central composite design (CCD).

Variable	Key	Level			Star points ($\alpha = 1.682$)	
		Lower	Central	Upper	$-\alpha$	$+\alpha$
Temperature (°C)	A	50	65	80	39.77	90.22
Extraction solvent volume (μL)	B	50	75	100	32.95	117.04
Heating time (min)	C	2	3	4	1.32	4.68

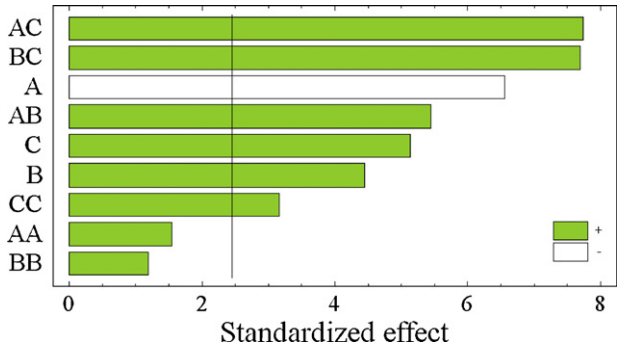

Fig. 3. Pareto charts of the main effects in the central composite design for CBs. AA, BB and CC are the quadratic effects of the temperature, extraction solvent volume and heating time, respectively. AB, AC and BC are the interaction effects between temperature and extraction solvent volume, temperature and heating time, and extraction solvent volume and heating time, respectively.

influence on the peak area and a negative effect upon the extraction. In fact, temperature plays the main role in this method to achieve good sensitivity of the target analytes detection [31]. Temperature was the driving force for the complete dispersion of the IL into the aqueous solution. The negative effect on the extraction recovery was probably due to loss of these compounds at higher temperatures. Further, heating time had a significant positive effect on the extraction recovery, due to the complete solubilization and dispersion of the IL in the aqueous solution at longer times in the hot bath. Fig. 3 shows that the extraction solvent volume had a significant positive effect upon the extraction recovery. In fact, the volume of the IL determined the occurrence of cloudy state of sample solution. But a portion of the amount of the IL added could be dissolved in the sample solution; therefore, the cloudy state increased along with larger volumes of the IL. The positive effect revealed that the

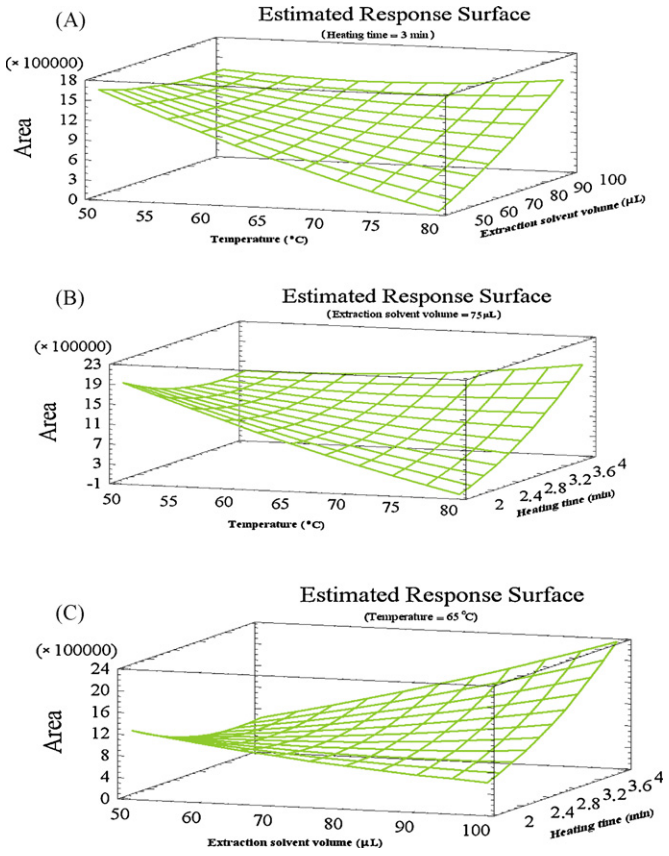

Fig. 4. Response surfaces for CBs using the central composite design obtained by plotting of: (A) the extraction solvent volume *vs.* temperature, (B) temperature *vs.* the heating time, and (C) the extraction solvent volume *vs.* the heating time.

Table 3
Limit of detections, regression equations, correlation of determinations, dynamic linear ranges and preconcentration factors for TCIL-DLPME.

Analyte	LOD ($\mu g\,L^{-1}$)	r^2	Regression equation	DLR ($\mu g\,L^{-1}$)	Preconcentration factor
1,2-Dichlorobenzene	0.05	0.994	$Y = 19874X + 13989$	0.5–300	267
1,3-Dichlorobenzene	0.05	0.992	$Y = 19192X + 14798$	0.5–300	218
1,4-Dichlorobenzene	0.05	0.995	$Y = 24061X + 12216$	0.5–300	298
1,2,3-Trichlorobenzene	0.1	0.997	$Y = 17020X + 11488$	0.5–500	206
1,2,4-Trichlorobenzene	0.1	0.992	$Y = 17042X + 11928$	0.5–500	187

Table 4
Determination of CBs in well water samples of Chemi Darou Industrial and Pharmaceutical Company (Tehran, Iran) and well water of Shahid Beheshti University (Tehran, Iran).

Sample	Analyte	C_{added} ($\mu g\,L^{-1}$)	C_{found} ($\mu g\,L^{-1}$)	RSD% ($n = 4$)	Relative recovery (%)
Well water	1,2-Dichlorobenzene	–	9.5	4.3	–
		50.0	60.5	4.8	102.0
	1,3-Dichlorobenzene	–	8.0	6.4	–
		50.0	60.5	6.8	105.0
	1,4-Dichlorobenzene	–	11.0	6.1	–
		50.0	58.0	5.8	94.0
	1,2,3-Trichlorobenzene	–	10.0	6.8	–
		50.0	61.3	5.7	102.6
	1,2,4-Trichlorobenzene	–	11.5	4.6	–
		50.0	63.8	4.2	104.6
Well water	1,2-Dichlorobenzene	–	–	–	–
		10.0	11.1	7.8	111.0
	1,3-Dichlorobenzene	–	–	–	–
		10.0	9.3	9.2	93.0
	1,4-Dichlorobenzene	–	–	–	–
		10.0	9.1	9.1	91.0
	1,2,3-Trichlorobenzene	–	–	–	–
		10.0	10.9	7.8	109.0
	1,2,4-Trichlorobenzene	–	–	–	–
		10.0	9.7	8.8	97.0

peak areas of analytes increase when the volume of the IL increases. This can be explained by the fact that the IL had a certain degree of solubility in the water samples, and the dissolved portion of the IL did not sediment down when the temperature decreased and the solution was centrifuged at 3000 rpm. When larger volumes of the extraction solvent were used, a larger portion of the IL sedimented and higher extraction recovery was obtained.

According to Fig. 3, the quadratic term of heating time (CC) and interactions between temperature/heating time (AC), extraction solvent volume/heating time (BC), and temperature/extraction solvent volume (AB) showed a significant effect on the extraction efficiency. The regression models obtained were used to calculate the response surface for each variable separately. Fig. 4 shows response surface plots for the peak areas. Accordingly, the plots given in Fig. 4 were used for interpreting the variation of relative areas as a function of each pair of the independent variables graphically. Fig. 4A demonstrates a significant positive interaction between extraction solvent volume and temperature, indicating that lower temperature values are optimal for the extraction process. Lower extraction efficiencies were obtained at higher temperatures due to loss of analytes. In Fig. 4B, the interaction between temperature and heating time can be observed, suggesting that complete dispersion of the IL into the aqueous solution can occur by applying lower temperatures for longer times. As heating time increased, the surface plot of the peak area responses (Fig. 4C) increased significantly. According to the overall results of the optimization study, the following experimental conditions were chosen: extraction solvent volume, 75 μL; heating time, 4 min; and temperature, 50 °C.

3.3. Evaluation of performance of the method

Regression equations, correlation of determination (r^2), linear dynamic ranges (LDRs), limit of detections (LODs), and preconcentration factors (PFs) were calculated under optimal conditions and summarized in Table 3.

The LODs were calculated as the analyte concentrations equal to three times the standard deviation of the blank signal divided by the slope of the calibration curve. The LODs were obtained in the range of 0.05 μg L^{-1} (for 1,2-dichlorobenzene) to 0.1 μg L^{-1} (for 1,2,3-trichlorobenzene).

The PFs were calculated as the ratio of final concentration of the analyte in the organic phase to its concentration in the original solution (which is 50 μg L^{-1} of each analyte) under optimal conditions. The preconcenteration factor was obtained by the following equation:

$$\mathrm{PF} = \frac{C_{\mathrm{IL,\,final}}}{C_{\mathrm{aq,\,initial}}}$$

where $C_{\mathrm{IL,\,final}}$ and $C_{\mathrm{aq,\,initial}}$ are the final concentration and initial concentration of analyte in the IL and aqueous solution, respectively. $C_{\mathrm{IL,\,final}}$ of each extracted analyte was calculated using the calibration curve obtained from the direct injections of standard solutions of each analyte in the range of 3–80 mg L^{-1}. The PFs obtained were in the range of 187–298.

The water samples were collected from wells in Chemi Darou Industrial and Pharmaceutical Company (Tehran, Iran) and Shahid Beheshti University (Tehran, Iran) and analyzed by TCIL-DLPME combined with HPLC-DAD. Analysis of samples showed that they contained some of the target analytes. Therefore, all the real water samples were spiked with CB standards at different concentration levels (10 and 50 μg L^{-1}) to assess the matrix effects.

Fig. 5A shows the chromatogram obtained by TCIL-DLPME under optimal conditions for the standard solution containing 100 μg L^{-1} of the analytes. The chromatogram by TCIL-DLPME obtained for water samples taken from wells in Chemi Darou Industrial and Pharmaceutical Company (Tehran, Iran) is shown in Fig. 5B.

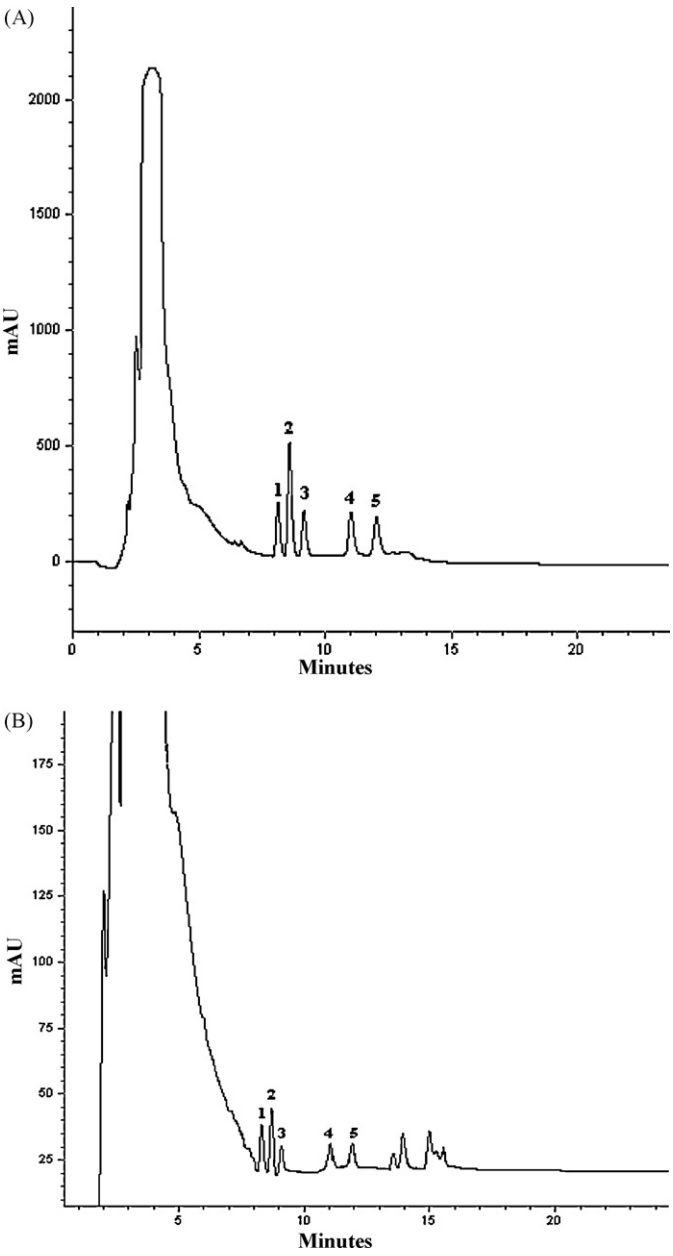

Fig. 5. (A) Chromatogram of the standard solution (100 μg L^{-1}) of CBs after TCIL-DLPME under optimal conditions: (1) 1,2-dichlorobenzene, (2) 1,4-dichlorobenzene, (3) 1,3-dichlorobenzene, (4) 1,2,3-trichlorobenzene and (5) 1,2,4-trichlorobenzene. (B) Chromatogram of TCIL-DLPME analysis of well water samples of Chemi Darou Industrial and Pharmaceutical Company under optimal conditions: (1) 1,2-dichlorobenzene, (2) 1,4-dichlorobenzene, (3) 1,3-dichlorobenzene, (4) 1,2,3-trichlorobenzene and (5) 1,2,4-trichlorobenzene.

Table 4 shows that the results of the four replicate analyses of each sample obtained by the TCIL-DLPME method is satisfactorily in agreement with the amounts of CBs added.

4. Conclusions

In the present study, a simple, environmentally friendly, rapid, easy-to-use microextraction technique based on ionic liquid was developed to extract CBs from aqueous samples. A multivariate optimization strategy was used to obtain optimal conditions for extraction of CBs by TCIL-DLPME. The optimization of TCIL-DLPME

variables was carried out using the response surface methodology and an experimental design. The resulting optimized procedure allowed quantification of trace levels of CBs in water samples using TCIL-DLPME combined with HPLC-DAD.

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