http://dx.doi.org/10.5935/0103-5053.20130133
J. Braz. Chem. Soc., Vol. 24, No. 6, 1034-1040, 2013.
Printed in Brazil - ©2013 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

An *in situ* Ionic Liquid Dispersive Liquid-Liquid Microextraction Method for the Detection of Pyrethroids by LC-UV in Environmental Water Samples

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Um método *in situ* de microextração líquido-líquido dispersiva com líquidos iônicos (IL-DLLME) foi desenvolvido como uma nova abordagem para a detecção de quatro pesticidas piretróides em amostras de água do ambiente. O método é simples, rápido, preciso e ambientalmente amigável. O líquido iônico hidrofóbico, $[C_8MIM]$-NTf_2, formado pelo líquido iônico solúvel em água $[C_8MIM]Cl$ e o reagente de troca iônica $LiNTf_2$ foi usado como solvente de extração. Os parâmetros experimentais que influenciam a eficiência de extração, incluindo a quantidade de líquido iônico (IL), a extração e tempos de centrifugação e a concentração de sal foram investigados e otimizados utilizando um design com matriz ortogonal (OAD). A razão molar adequada do $LiNTf_2$ para $[C_8MIM]Cl$ nas recuperações de analitos foi determinada após otimização do OAD. O método mostrou uma boa resposta linear no intervalo de 0,5 a 500 μg L^{-1} com coeficientes de correlação (R^2) acima de 0,9998. O desvio padrão relativo (RSD) variou de 0,6 a 1,9%. O fator de enriquecimento, o limite de detecção e recuperação variaram de 134 a 153, 0,02 a 0,18 μg L^{-1} e de 89,7 a 95,6%, respectivamente. Para as amostras de água, o RSD variou entre 0,02 e 2,34% e a recuperação variou de 91,4 a 99,9%.

An *in situ* ionic liquid dispersive liquid-liquid microextraction (IL-DLLME) method was developed as a new approach for the detection of four pyrethroid pesticides in environmental water samples. The method is fast, simple, accurate and environmentally friendly. The hydrophobic ionic liquid, $[C_8MIM]$-NTf_2, formed by the water-soluble ionic liquid $[C_8MIM]Cl$ and the ion exchange reagent $LiNTf_2$ was used as the extraction solvent. The experimental parameters affecting the extraction efficiency, including the amount of the IL, the extraction and the centrifugation times and the salt concentration were investigated and optimized using an orthogonal array design (OAD). A suitable molar ratio of $LiNTf_2$ to $[C_8MIM]Cl$ on the recoveries of analytes was determined after OAD optimization. The method showed a good linear response in the range of 0.5 to 500 μg L^{-1} with correlation coefficients (R^2) above 0.9998. The relative standard deviation (RSD) varied from 0.6 to 1.9%. The enrichment factor, the limit of detection and recovery ranged from 134 to 153, 0.02 to 0.18 μg L^{-1} and 89.7 to 95.6%, respectively. For water samples, the RSD ranged from 0.02 to 2.34% and the recovery ranges from 91.4 to 99.9%.

Keywords: *in situ* IL-DLLME, pyrethroid pesticides, orthogonal array design, HPLC-UV, environmental samples

Introduction

Pyrethroids are pesticides based on the chemical structures of natural pyrethrins but have better biological performance and lower mammalian toxicity.[1,2] Pyrethroids are used worldwide for crop pest control and environmental health. The use of pyrethroids has brought many benefits to people. However, in recent years, studies have shown that pyrethroids have estrogenic activity, can interfere with the endocrine system and cause cumulative toxicity.[3,4] Therefore, it is important to develop an efficient, economical and convenient method for the detection of pyrethroids.

In recent years, the negative effects of pesticides present in food and in the environment on humans have gained more attention. A more efficient sample preconcentration and pretreatment method is needed for the determination of the concentrations of trace analytes in complex matrices.

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However, traditional liquid-liquid extraction (LLE) procedures are often considered to be labor intensive, time consuming, and environmentally unfriendly due to the use of large quantities of volatile and potentially toxic organic solvents. In the past few years, many research efforts have been focused on the development of efficient, miniaturized, and environmentally benign sample extraction methods, such as solid-phase microextraction (SPME)[5-11] and liquid-phase microextraction (LPME).[12-15]

Rezaee *et al.*[16] developed a dispersive liquid-liquid microextraction (DLLME) method, which has been used for the analysis of a variety of pesticides residues. DLLME is typically based on a ternary solvent system in which the extraction solvent (hydrophobic) and the dispersion solvent (hydrophilic) are rapidly injected into the aqueous sample, resulting in a turbid solution. The obtained turbid solution has a large contact area between the fine extraction solvent droplets and the aqueous analyte solution, remarkably decreasing the extraction time and increasing the extraction efficiency. This technique has many advantages over other microextraction methods because it is more convenient and simpler and requires less-expensive devices. This method has been successfully applied to the preconcentration and sensitive analysis of many pesticides.[17-19] However, DLLME involves the use of extraction solvents with densities greater than that of water, such as chloroform, chlorobenzene, carbon tetrachloride, and tetrachloroethane, and these solvents are toxic and pollute the environment. Consequently, the development of new DLLME methods aims to minimize the organic solvent consumption.[20]

Ionic liquids (ILs) are a class of non-molecular solvents with low melting points (< 100 °C) that combine organic cations and various anions. They have many advantageous properties, such as a negligible vapor pressure, chemical and thermal stability, and good solubility in both organic and inorganic solvents and solutions. ILs, novel green solvents, have been widely used in microextraction instead of traditional organic solvents.[21,22] This technique has been used for the sensitive analysis of organophosphorus insecticides,[23] heterocyclic insecticides,[24] pyrethroids,[25,26] phthalate esters,[27] polycyclic aromatic hydrocarbons,[28-30] and other analytes. In addition to the typical IL-DLLME method, temperature-controlled IL-dispersive LPME[31-35] has been used to extract different types of pesticides and has become an important subtype of DLLME. To improve the extraction efficiency of DLLME, ultrasound is applied to help disperse the IL extraction solvent. Ultrasound-assisted ionic liquid-dispersive LPME (USA-IL-DLPME) has been used for the detection of aromatic amines.[36] However, an organic dispersion solvent is required, not only in typical DLLME but also in modified DLLME, to promote the formation of fine droplets of the extraction solvents (ILs) within the aqueous solution.

The *in situ* halide exchange reaction is conducted using an ion exchange reagent to replace the chloride ions in the original ionic liquid to form a new hydrophobic ionic liquid. Due to the water solubility of the hydrophilic ionic liquid, after the ion-exchange reaction, the hydrophobic ionic liquid can disperse into fine droplets in water. This approach was first applied to the detection of metals.[37-39] Later a similar *in situ* IL-DLLME approach was utilized by Yao *et al.* for the detection of organic compounds.[40, 41] The *in situ* halide exchange reaction and the extraction process can be completed within a very short time with a high extraction efficiency. There is no need for an organic dispersive agent or heating steps in the extraction process, effectively shortening the extraction time and increasing the enrichment factor.

To the best of our knowledge, no previously published study has used the *in situ* DLLME process to extract pyrethroid compounds from water samples. Consequently, the main aim of this work was to expand the applications of the *in situ* DLLME method to the detection of a group of four pyrethroids (meperfluthrin, cyhalothrin, fenvalerate, and permethrin) in complex aqueous samples. In the extraction procedure, a hydrophilic IL (1-octyl-3-methylimidazolium chloride, [C_8MIM]Cl) and an ion-exchange reagent (lithium bis[(trifluoromethane)sulfonyl]imide, $LiNTf_2$) were added to the aqueous solution in sequence and a hydrophobic IL (1-octyl-3-methylimidazolium bis[(trifluoromethane) sulfonyl]imide, [C_8MIM]-NTf_2) was formed *in situ* as extraction solvent (Figure 1). Several factors, including the amount of the IL, the addition of sodium chloride, the extraction time and the centrifugation time, were studied using orthogonal array optimization to achieve the highest extraction efficiency. A suitable molar ratio of $LiNTf_2$ to [C_8MIM]Cl on the recoveries of analytes was determined after OAD optimization by comparing the

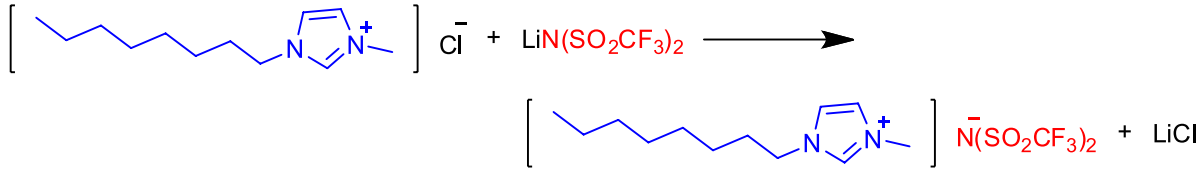

Figure 1. Formation of [C_8MIM]-NTf_2 by *in situ* reaction.

extraction efficiency using different molar ratio of $LiNTf_2$ to $[C_8MIM]Cl$. After the selection of the optimum sample pretreatment conditions, the performance of the *in situ* IL-DLLME-LC method was evaluated based on linearity, precision, and the detection and quantitation limits. Finally, this method was applied to real water samples, including tap water, bottled mineral water, reservoir water and river water.

Experimental

Reagents and Materials

All pesticide standards (meperfluthrin, cyhalothrin, fenvalerate, and permethrin) were obtained from Aladdin Reagent Corporation (Shanghai, China). $[C_8MIM]Cl$ was obtained from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). $LiNTf_2$ was purchased from Zhejiang Jiuzhou Pharmaceutical Co. (Zhejiang, China). The acetonitrile used for spectroscopy was purchased from Dikma Limited (Beijing, China), and the deionized water was purified using a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). Analytical-grade sodium chloride was obtained from the Beijing Chemical Factory (Beijing, China). The stock standard solutions of the individual insecticides (1 mg mL^{-1}) were prepared by dissolving each standard in HPLC-grade acetonitrile and were stored in a refrigerator, protected from light. Mixed standard solutions were prepared in acetonitrile. The aqueous working solutions were prepared daily by diluting the mixed standard solution to different concentrations in ultrapure water. Tap water, river water, and reservoir water samples from Beijing, China, were collected in glass bottles for method validation. The real water samples were stored in the refrigerator, protected from light, and filtered through a 0.22 μm mixed cellulose membrane (Agla, USA) before use.

Instrumentation

The chromatographic analysis was carried out on an Agilent 1200 HPLC system equipped with a variable wavelength detector (VWD) system (CA, USA). A high-pressure injection valve fitted with a 20 μL loop was used for sample injection. The separation of the analytes was carried out on an Agilent Eclipse Plus C18 column (250 mm × 4.6 mm, 5 μm). Acetonitrile/water (80:20, v/v) was used as the mobile phase at a flow rate of 1 mL min^{-1}. The injection mode was partial-loop injection, the injection volume was 10 μL, and the detection wavelength was 230 nm. The IL was weighed with a Mettler-Toledo AL104 electronic balance (Shanghai, China). Centrifugation was performed in a 52a centrifuge from the Baiyang Centrifuge Factory (Xi'an, China) at a rate of 3500 rpm. Filtration was performed with a 0.22 μm mixed cellulose membrane (Agla).

Extraction procedure

Approximately 0.02 g of $[C_8MIM]Cl$ was added to a glass test tube with a conical bottom. Then, 8770 μL of a spiked water sample was placed into the tube. The IL was completely dissolved into the aqueous phase after shaking. A $LiNTf_2$ aqueous solution (830 μL, 0.03 g mL^{-1}) was added to the tube. Subsequently, a turbid solution was formed. After gentle shaking, the tube was cooled in an ice-water bath for 1 min to enhance the extraction. Then, the turbid mixture was centrifuged at 3500 rpm for 5 min. The upper aqueous phase was removed with a syringe. Approximately 25 μL of $[C_8MIM]$-NTf_2 was deposited at the bottom and was then removed with an HPLC microsyringe. Of this amount, 10 μL was directly injected into the HPLC system for analysis.

Results and Discussion

DLLME optimization

Orthogonal array design (OAD) has been applied to optimize a variety of sample preparation processes including LPME, MAE (microwave-assisted extraction), UA-DLLME (ultrasound-assisted dispersive liquid-liquid microextraction), and USAEME (ultrasound-assisted emulsification-microextraction).[42-45] OAD is a straightforward and cost-effective approach that can obtain the optimal conditions of each parameter in limited numbers of experimental trials. First, we tested ranges of various experimental parameters, such as the amount of IL, NaCl concentration, extraction time and centrifugation time. The amount of IL was firstly optimized using the one-factor-at-a-time approach to determine the optimum range of the OAD. The optimum ranges of the other parameters (NaCl concentration, extraction time and centrifugation time) were determined according to the references.[46-48] A wide range of NaCl concentrations (0-15%) was set for OAD optimization. The range of the extraction time was 1 to 20 min and the centrifugation time ranged from 5 to 20 min.

In the IL-DLLME procedure, the amount of IL is an essential factor affecting the EF and the extraction recovery. The effect was examined using different amounts of IL (i.e., 0.01, 0.02, 0.03, 0.04 and 0.05 g) in a 10 mL water sample at a spiked level of 50 μg L^{-1}. The curves for the final recovery against the IL amount are shown in Figure 2. The recovery

increased greatly when the amount of [C_8MIM]Cl increased from 0.01 to 0.02 g. By increasing the amount from 0.02 to 0.05 g, the extraction recoveries for the four pyrethroids reached a constant level. Mass transfer of pyrethroids might reach the equilibrium state as the IL amount was higher than 0.02 g. However, enrichment factors decreased from 120-163 to 66-86 in the 0.03 to 0.05 g range as the volume of the sediment phase increased. Consequently, 0.02 g was used as the optimum quantity for the extraction in the further studies since the highest EFs were obtained and the recoveries were acceptable.

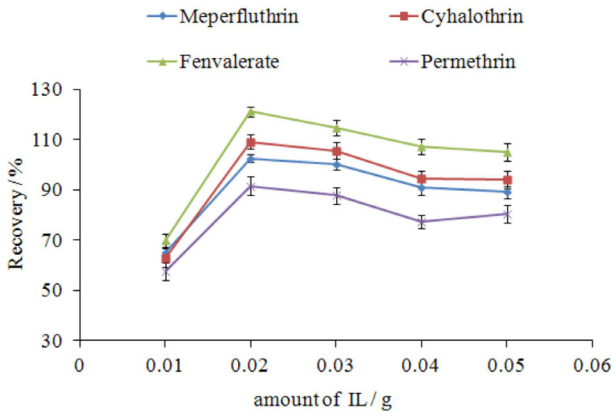

Figure 2. Effects of the IL amount on the recoveries of analytes. The extraction conditions were as follows: water sample volume, 10.00 mL; molar ratio of $LiNTf_2$ to [C_8MIM]Cl, 1:1; no NaCl addition; extraction time, 1 min; centrifugation time, 5 min; concentration, 50 μg L^{-1}.

The four relevant parameters (the amount of [C_8MIM]Cl, the NaCl concentration, the extraction time, and the centrifugation time) were studied using an orthogonal model to identify the factors that significantly affect the extraction efficiency.

Orthogonal screening

Instead of the traditional one-factor-at-a-time approach, an orthogonal experiment [L16 (4^4)] was conducted to determine the relative contribution of each factor. This experiment was carried out in a 10 mL water sample spiked with standard perithriods solution at 50 μg L^{-1} level. All analytes showed similar tendencies. The effects of the amount of [C_8MIM]Cl / g (A) (A1, 0.01; A2, 0.02; A3, 0.03; and A4, 0.04), the NaCl concentration (B) (B1, 0%; B2, 5%; B3, 10%; and B4, 15%), the extraction time / min (C) (C1, 1; C2, 5; C3, 10; and C4, 20), and the centrifugation time / min (D) (D1, 5; D2, 10; D3, 15; and D4, 20) on the recovery are summarized in Table 1. *Kn* is the mean effect of each parameter at different levels. R is the *Kn* range, and its value represents the extent to which the extraction efficiency was affected as the level of each parameter was varied.

According to the R values, the effects on the mean extraction yields of the target analytes increased in the order C < D < B < A. These results indicated that the amount of [C_8MIM]Cl was the most important factor affecting the extraction efficiency. The extraction efficiency against the amount of [C_8MIM]Cl showed a similar trend to the one-factor-at-a-time approach in Figure 2. The NaCl concentration was another critical parameter for the extraction efficiency. Based on the orthogonal screening results, the amount of [C_8MIM]Cl, extraction time, centrifugation time and concentration of NaCl were selected as 0.02 g, 1 min, 5 min and 0%, respectively.

Table 1. Orthogonal screening results

No.	A	B	C	D	Recovery / %
1	A1	B1	C1	D1	81.4
2	A1	B2	C2	D2	64.6
3	A1	B3	C3	D3	49.2
4	A1	B4	C4	D4	53.8
5	A2	B1	C2	D4	91.1
6	A2	B2	C1	D3	92.2
7	A2	B3	C4	D2	86.8
8	A2	B4	C3	D1	77.8
9	A3	B1	C3	D2	98.7
10	A3	B2	C4	D1	83.0
11	A3	B3	C1	D4	86.8
12	A3	B4	C2	D3	84.6
13	A4	B1	C4	D3	92.5
14	A4	B2	C3	D4	87.1
15	A4	B3	C2	D1	87.9
16	A4	B4	C1	D2	83.0
K1	62.3	90.9	85.9	85.0	–
K2	87.0	81.7	82.0	80.4	–
K3	88.3	78.2	78.2	76.6	–
K4	87.6	74.8	79.0	83.2	–
R	26.0	16.1	7.6	8.4	–

Optimization of the molar ratio of $LiNTf_2$ to [C_8MIM]Cl

The amount of the ion-exchange reagent is an important factor affecting the extraction efficiency. The effect was investigated by varying the molar ratio of $LiNTf_2$ to [C_8MIM]Cl from 1:1 to 3:1 (830, 1250, 1660, 2490 μL of 0.03 g mL^{-1} $LiNTf_2$ solution). As shown in Figure 3, the recovery decreased and basically reached a constant level when excess $LiNTf_2$ was added to the extraction mixture. This result may be attributed to the fact that the addition of $LiNTf_2$ greatly increased the viscosity of the solution, which may have made it difficult for molecules to diffuse into the IL extraction phase. Although the addition of

$LiNTf_2$ may result in a higher volume of sedimented IL, it may prevent the analytes from transferring into the IL phase, leading to the obvious decrease in the peak area. When excess $LiNTf_2$ aqueous solution was added, the EF also tended to decrease. Thus, the molar ratio was fixed to 1:1 in the subsequent investigations.

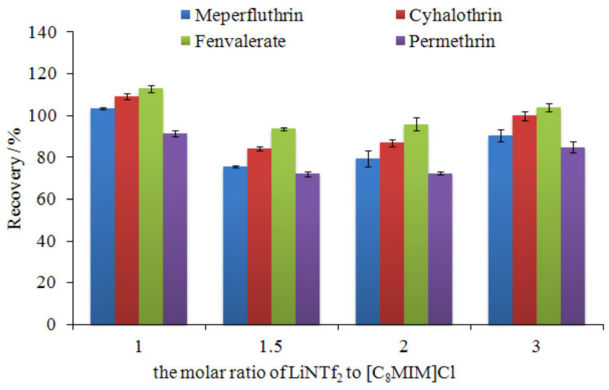

Figure 3. Effect of the molar ratio of $LiNTf_2$ to $[C_8MIM]Cl$ on the recoveries of analytes. The extraction conditions were as follows: water sample volume, 10.00 mL; amount of $[C_8MIM]Cl$, 0.02 g; no NaCl addition; extraction time, 1 min; centrifugation time, 5 min; concentration, 50 μg L^{-1}.

Based on the orthogonal screening and the optimization of the molar ratio of $LiNTf_2$ to $[C_8MIM]Cl$, the following optimal conditions were used in the proposed DLLME method: 0.02 g $[C_8MIM]Cl$ as the extraction solvent, 830 μL $LiNTf_2$ solution (0.03 g mL^{-1}), 1 min extraction time, 5 min centrifugation time, and no NaCl addition.

Martix effect

Compounds with a high molecular mass (such as humic acids that are commonly found in environmental matrices) can affect the ionization of lower mass molecules in complex matrices.[49] Humic acid is common high molecular weight compounds in the environment and organisms, and it was selected as interferences to study the matrix effect in this type of analysis. To study the influence of the matrix on the extraction procedures, standard solutions with humic acid were extracted under the optimized conditions. Figure 4 showed that the extraction recoveries were in the range of

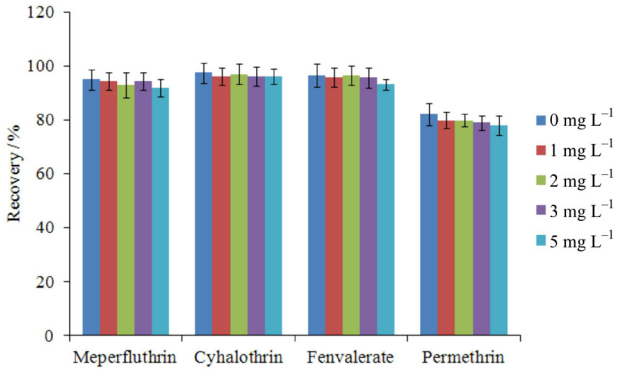

Figure 4. The matrix effect on the extraction recoveries.

80-97% for all the studied pyrethroids at different humic acid concentrations (0-5 mg/L). These results indicated that there was no significant matrix effect on the extraction efficiencies under in-situ metathesis reaction combined with ionic liquid dispersive liquid-liquid microextraction.

Extraction conditions are as follows: 10.0 mL sample solution with different humic acid concentrations (0-5 mg L^{-1}) and no salt addition, 0.02 g of $[C_8MIM]Cl$ and 830 μL $LiNTf_2$ solution (0.03 g mL^{-1}) for the extraction solvent, 1 min extraction time and 5 min centrifugation at 3500 rpm.

Method validation

The *in situ* IL-DLLME technique was evaluated based on linearity, the limit of detection (LOD), precision, the EF, and the recovery under the optimized condition. The results are listed in Table 2. This method exhibited high linearity for all analytes in the range from 0.5 to 500 μg L^{-1}, with correlation coefficients (R^2) above 0.9998. The LOD was calculated using three times the signal-to-noise ratio (S/N = 3). Limit of detection values between 0.02 and 0.18 μg L^{-1} were obtained. The limit of quantitation (LOQ) was calculated using 10 times the signal-to-noise ratio (S/N = 10), and these values were in the range of 0.05-0.60 μg L^{-1}. The relative standard deviations (RSDs) of the analytes ranged from 0.6 to 1.9%. The extraction recoveries and enrichment factors of the proposed method were acceptable, ranging from 89.7 to 95.6% and 134 to 153, respectively.

Table 2. Performance characteristics of the in-situ IL-DLLME method combined with HPLC

Compounds	Linear equation	Linearity / (μg L^{-1})	Correlation coefficient (R^2)	RSD / %	Enrichment factors	LOD / (μg L^{-1})	LOQ / (μg L^{-1})	Recovery / %
Meperfluthrin	y = 1.502x + 1.575	0.5-500	1	1.89	153	0.18	0.60	95.6
Cyhalothrin	y = 2.664x + 0.695	0.5-500	0.9999	0.93	142	0.02	0.05	92.2
Fenvalerate	y = 3.043x – 0.299	0.5-500	1	0.58	139	0.03	0.10	91.4
Permethrin	y = 3.066x – 4.213	0.5-500	0.9998	1.53	134	0.04	0.14	89.7

Table 3. Relative recoveries of the four pyrethroids in four real water samples at spiked levels of 50 and 500 μg L^{-1}

Sample	1	2	3	4	1	2	3	4
Tap water	50 μg L^{-1}				500 μg L^{-1}			
RR / %	98.8	94.5	94.9	94.8	95.8	95.1	93.6	95.3
RSD / %	1.83	0.61	0.87	1.24	1.90	1.06	1.38	0.22
Mineral water	50 μg L^{-1}				500 μg L^{-1}			
RR / %	95.6	92.2	91.4	89.7	92.1	93.1	92.4	92.3
RSD / %	1.89	0.93	0.58	1.53	0.14	0.02	0.85	0.85
Reservoir water	50 μg L^{-1}				500 μg L^{-1}			
RR / %	98.4	99.9	98.2	95.6	93.4	96.8	96	96.8
RSD / %	2.34	1.62	1.31	2.34	2.13	1.17	0.99	0.12
River water	50 μg L^{-1}				500 μg L^{-1}			
RR / %	93.8	96.2	96.9	95.1	92.1	98.1	95.7	96.3
RSD / %	1.55	1.99	1.33	1.42	1.55	0.98	0.65	1.1

Analysis of real water samples

The applicability of the *in situ* IL-DLLME method was validated by extracting analytes from four real water samples, including tap water, reservoir water, river water, and bottled mineral water. The results are shown in Table 3. The results indicated that the analytes concentration in the samples was below the LOQ of the method. These samples were then spiked with pyrethroids at concentrations of 50 and 500 μg L^{-1} to investigate the effect of the sample matrix. As shown in Table 3, the spiked recoveries were in the range of 91.4-99.9%, with the precisions of 0.02-2.34% (RSD). These results indicate that the matrix complexity had little effect on the *in situ* IL-DLLME method. Hence, this method has a wide range of applicability in the preconcentration of insecticides in water samples. A typical chromatogram for the tap water samples is presented in Figure 5.

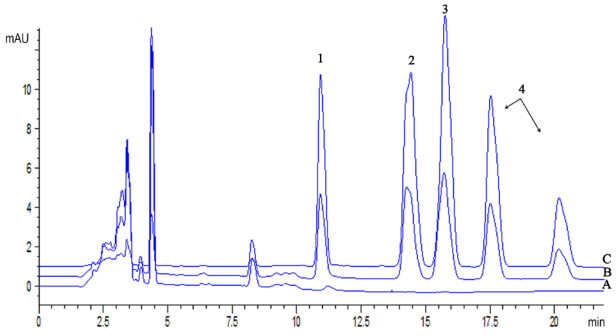

Figure 5. Chromatograms of the four studied insecticides in tap water samples preconcentrated using the proposed IL-DLLME method. (1) meperfluthrin; (2) cyhalothrin; (3) fenvalerate; (4) permethrin. Chromatogrames A-C: spiked levels were 0, 50 and 500 μg L^{-1}, respectively.

Conclusions

In situ IL-DLLME method was successfully applied for the determination of four pyrethroids in aqueous environmental samples, which including tap water, bottled mineral water, reservoir water and river water. In the developed method, the formation of immiscible IL and the subsequent transfer of the analytes take place in one step without the use of dispersive organic solvents, which are required in conventional DLLME. Optimization of the experimental variables was performed using OAD and the relative contributions of different parameters were determined. This method provides high recoveries, a wide linear range, good repeatability, and high enrichment factors within a very short time, covering the maximum limits permissible for pyrethroids in water samples set by international regulatory organizations. It is expected that this technique has the potential to be widely used in the preconcentration and extraction of analytes from aqueous samples in the future. The application of this in-situ IL-DLLME method to the study of more complex matrices is recommended to draw further conclusions.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Project No. 21277172, 20977112), Program for New Century Excellent Talents in University (NCET-10-0777) and New Teachers' Fund for Doctor Stations, Ministry of Education (Grant No. 20090008120015).

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Submitted: January 4, 2013
Published online: June 4, 2013