

# Trace Determination of Dichlorvos in Environmental Samples by Room Temperature Ionic Liquid-Based Dispersive Liquid-Phase Microextraction Combined with HPLC

Songhui Wang, Bingren Xiang\* and Qianqian Tang

Center for Instrumental Analysis, Key Laboratory of Drug Quality Control and Pharmacovigilance, Ministry of Education, China Pharmaceutical University, 210009 Nanjing, People's Republic of China

\*Author to whom correspondence should be addressed. Email: wangsonghui198604@163.com; cpuxiang@yahoo.com

Received 10 July 2011; revised 24 October 2011

**Using 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) room temperature ionic liquid (RTIL) as extraction solvent, tetrahydrofuran (THF) as disperser solvent, the organophosphorus pesticide dichlorvos in water was determined by dispersive liquid–liquid microextraction (DLLME) combined with high-performance liquid chromatography. Factors affecting RTIL–DLLME (type of disperser solvent, amount of RTIL, volume of disperser solvent, percentage of NaCl and volume and pH of water sample) were optimized by the single-factor method, obtaining the most favorable results when using 65  $\mu\text{L}$  of [BMIM][PF6] and 260  $\mu\text{L}$  of THF to extract the compound from an 8-mL water sample at pH 5.0 containing 25% (w/v) of NaCl. Under these optimum conditions, an enrichment factor of 215-fold was obtained. The calibration curves were linear in the concentration range of 2–1,000  $\mu\text{g/L}$ . The limit of detection calculated at a signal-to-noise ratio of 3 was 0.2  $\mu\text{g/L}$ . The relative standard deviations (RSD) for six replicate experiments at 20, 100 and 200  $\mu\text{g/L}$  concentration levels were 1.8%, 1.3% and 1.3 %, respectively. Then the proposed method was applied to the analysis of three different water sample sources (tap, farm and rain water) and the relative recoveries and RSD of spiked water samples were 95.6–102.4% and 0.6–3.1%, respectively, at three different concentration levels of 20, 100 and 200  $\mu\text{g/L}$ .**

## Introduction

Organophosphorus pesticides (OPPs), which can be released into the environment from manufacturing, transportation and agriculture applications, are widely found in water resources. In most cases, these compounds display high acute toxicity and do great harm to humans and the environment (1).

Generally, OPP residues in environmental water are often present at trace concentrations, so they are not directly analyzed with conventional chromatographic methods such as high-performance liquid chromatography (HPLC) and gas chromatography (GC). In most studies, the compounds of interest have to be concentrated to reach the minimum level required for each particular detector.

Two of the most common methods for sample pretreatment are liquid–liquid extraction (LLE) (2, 3) and solid-phase extraction (SPE) (4, 5). However, LLE consumes large amounts of time and organic solvents, which are potentially toxic. SPE requires a specific device loaded with a certain adsorption material, and it often suffers from the plugging of cartridges and consumption of appreciable amounts of toxic solvents at the elution step. Most importantly, the enrichment factors of both these methods are low. To overcome these limitations,

microextraction-based techniques such as liquid-phase microextraction (LPME) (6, 7) and solid-phase microextraction (SPME) (8, 9) have developed quickly. Among these techniques, liquid–liquid microextraction (LLME) is a single-step extraction with a high enrichment factor of analytes due to the high sample-to-solvent ratio. As a result, conventional LLME has been proposed as an efficient alternative to LLE (10, 11).

In recent years, a novel LPME technique termed dispersive liquid–liquid microextraction (DLLME) (12–15) has emerged as an attractive alternative for sample preparation due to its primary advantages: simplicity of operation, low time and cost, low consumption of organic solvents and high enrichment factors. The DLLME procedure is based on a ternary component solvent system similar to homogeneous LLE (12, 15–17). In this method, a mixture of extraction and disperser solvent is rapidly injected into the aqueous sample, which leads to the formation of a cloudy suspension consisting of fine droplets composed of extraction solvent–disperser solvent–water.

For the DLLME procedure, the selection of a suitable extraction solvent is of high importance. In general, extraction solvent should satisfy the following requirements: first, immiscibility with water; second, higher density than water; third, high extraction capability of compounds of interest, and finally, good chromatographic behavior (18, 19). During the last years, carbon tetrachloride, chlorobenzene and dichloromethane have been widely used as extraction solvents in DLLME. However, most of those extraction solvents are highly toxic.

Compared with the conventional extraction solvents mentioned previously, room temperature ionic liquids (RTIL) have unique advantages: they are less toxic, less contaminating and less volatile, and provide better solubility for most organic and inorganic compounds, higher thermal stability and a wider temperature range as a liquid phase (20–22). Referring to those advantages, RTILs have been applied widely in DLLME and some other extraction techniques. 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6] is one of the RTILs that have been employed in DLLME. It has been used as extraction solvent for the determination of biogenic amines in beer (23).

In this work, [BMIM][PF6]–DLLME has been combined with HPLC–ultraviolet (UV) detection and applied for the extraction of dichlorvos in water samples. [BMIM][PF6] was demonstrated to be a suitable extraction solvent for DLLME. To achieve the best extraction efficiency, some parameters related to DLLME were optimized and the proposed procedure was applied in the analysis by HPLC of water samples from three different sources.

## Experimental

### Chemicals and solvents

Pesticide analytical standard of dichlorvos was from Jiangsu Academy of Agricultural Sciences (Jiangsu, China). [BMIM][PF6] was purchased from Shanghai Crystal Pure Reagent Co. (Shanghai, China), with a purity of 97% and used as obtained. HPLC-grade methanol was obtained from Hanbon Science and Technologies Co. (Jiangsu, China). HPLC-grade THF was obtained from Shanghai Ling Feng Chemical Reagent Co. (Shanghai, China). HPLC-grade acetonitrile was obtained from Jiangsu Yonghua Fine Chemical Co. (Jiangsu, China). Ethanol of analytical reagent grade was obtained from Nanjing Chemical Reagent Co. (Nanjing, China). NaCl and HCl of analytical reagent grade were from Nanjing Chemical Reagent Co. Stock solution of dichlorvos at 100 mg/L was prepared in double distilled water. Working solutions were prepared by diluting the standard stock solution with water.

The samples of tap water were collected from our laboratory (Nanjing, China). The samples of farm and rain water were collected from the local area of Nanjing. All of these samples were twice filtered through a 0.45- $\mu$ m membrane and stored at 4°C before being used.

### Instrumentation

The chromatographic system was the Shimadzu LC LC-10ATVP series (Tokyo, Japan) equipped with an LC-10 ATVP pump, a 7725 manual injector, an SPD-10 AVP detector and an N2000 workstation (Zhejiang University). Separation was carried out at room temperature on a reversed-phase Alltima C18 (150  $\times$  4.6 mm i.d., 5  $\mu$ m) column. An 80–2 centrifuge (Jintan Hengfeng Instruments Co.; China) was used for centrifuging. The UV spectra were obtained from an UV-2401 PC UV-vis recording spectrophotometer.

### DLLME procedure

Eight millilitres of doubly-distilled water spiked with analyte was put into a 10-mL centrifugal tube and the pH of the water sample was adjusted to 5.0 with 37% HCl. NaCl was added until a concentration of 25% (w/v) was reached. Subsequently, a mixture of 65  $\mu$ L of [BMIM][PF6] and 260  $\mu$ L of tetrahydrofuran (THF) as extraction and dispersion solvents, respectively, was rapidly injected into the aqueous phase and many small drops were formed. The sample was softly shaken, a cloudy suspension consisting of water, THF and [BMIM][PF6] was quickly formed and the analyte in a water sample was extracted into the fine droplets of [BMIM][PF6]. The mixture was then centrifuged at 4,000 rpm for 10 min and the dispersed fine droplets of [BMIM][PF6] settled to the bottom of the centrifugal tube. The upper aqueous phase was removed by a syringe and 10.0  $\mu$ L of the settled phase was withdrawn using a 25- $\mu$ L microsyringe and then injected into HPLC for quantification.

### Calculation of enrichment factor and relative recovery

Enrichment factor (EF) and relative recovery (RR) were used during the optimization and validation of the extraction conditions. Eqs. (1) and (2) were used for calculation of enrichment factor and relative recovery:

$$EF = \frac{C_{\text{sed}}}{C_0} \quad (1)$$

where  $C_{\text{sed}}$  and  $C_0$  are analyte concentration in the sedimented phase and the initial concentration of analyte within the sample, respectively. Calculation of  $C_{\text{sed}}$  was done by direct injection of dichlorvos standard solutions in water (the solubility of dichlorvos in water is 10000 mg/L):

$$RR = \frac{C_{\text{founded}} - C_{\text{real}}}{C_{\text{added}}} \times 100 \quad (2)$$

where  $C_{\text{founded}}$ ,  $C_{\text{real}}$ , and  $C_{\text{added}}$  are the concentrations of analyte after the addition of a known amount of standard to the real sample, the concentration of the analyte in the real sample and the concentration of a known amount of standard that was spiked to the real sample, respectively.

## Results and Discussion

### HPLC–UV method

As shown in Figure 1, the maximal absorbing wavelength of dichlorvos is 210 nm. However, 210 nm was not chosen as the detection wavelength of dichlorvos in this experiment. This was because a smooth baseline at 210 nm was not obtained during the HPLC procedure. According to preliminary experiments, we found that the appropriate wavelength of dichlorvos was 230 nm. However, Figure 2 clearly shows that the RTIL also had very strong absorption at 230 nm, which might submerge the peak of dichlorvos. To solve this problem mentioned, we chose 360 nm as the detection wavelength of RTIL and 230 nm for dichlorvos, respectively. Therefore, in this study, the wavelength setting was as follows: 0–9 min performed at 360 nm and 9–12 min performed at 230 nm. The mobile phase consisted of methanol and distilled water (48:52, v/v). The flow rate was 1.0 mL/min, and the injection volume was 10  $\mu$ L.

### DLLME optimization

In the [BMIM][PF6]–DLLME procedure, various extraction parameters could influence the EF and thus were investigated to obtain optimum values. In this experiment, triplicate extractions were performed for all experiments and the average of the results was used in preparation of all the curves.

### Selection of disperser solvent

In the DLLME procedure, the extraction solvent is dispersed entirely into the aqueous phase with the help of disperser solvent, which can decrease the interfacial tension. Therefore, the choice of a disperser solvent with appropriate miscibility in both extraction phase and aqueous phase plays an important role in the DLLME procedure. In the present work, four possible solvents, including methanol, THF, acetonitrile and ethanol, were selected as disperser solvents, and the results are shown in Figure 3. When methanol was employed as disperser solvent, a very low volume of sedimented phase was obtained, which was not enough for sample injection, and therefore the EF value of methanol could not be obtained. As shown in Figure 3, the EFs of acetonitrile and ethanol were only a bit lower than THF. THF gave the highest EF and an appropriate

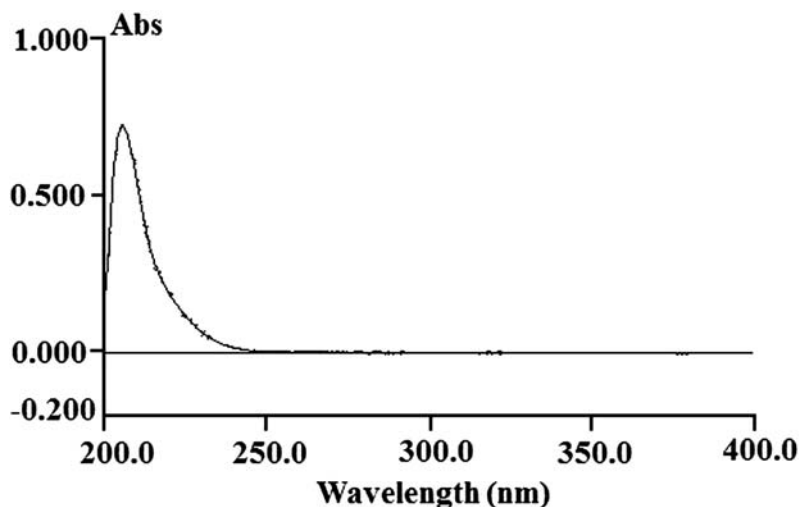


Figure 1. UV spectrum of dichlorvos at a concentration of 0.02 mg/mL.

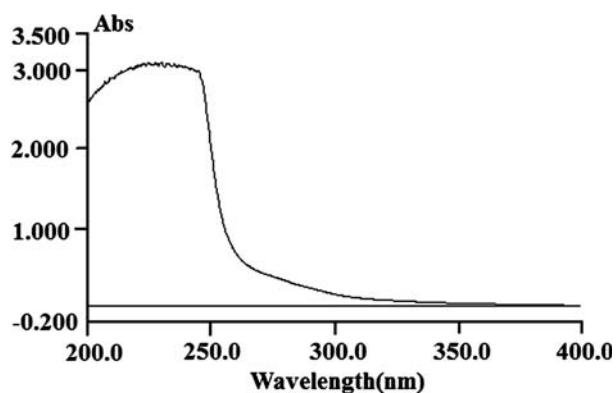


Figure 2. UV spectrum of [BMIM][PF6].

volume of settled phase. Therefore, the experiments were subsequently accomplished using THF as disperser solvent.

#### Effect of [BMIM][PF6] amount

In the DLLME procedure, the amount of extraction solvent was a crucial parameter that would have an important effect on the extraction efficiency.

To study the effect of extraction solvent amount on the EF, a series of experiments was performed by changing the amount of [BMIM][PF6] within a certain range (55, 60, 65, 70 and 75  $\mu\text{L}$ ) with other conditions kept unchanged. Figure 4 shows the variation of EF of analyte versus the amount of [BMIM][PF6]. At first, by increasing the amount of [BMIM][PF6] from 55 to 65  $\mu\text{L}$ , the EF increased markedly; then, as the amount of [BMIM][PF6] increased from 65 to 75  $\mu\text{L}$ , the EF decreased.

The reason was as follows: if the amount of extraction solvent was low, the extraction capability of extraction solvent was also low. As a result, the EF was low. With the increase of the amount of extraction solvent, the extraction capability increased, and the EF increased as a result. However, when the amount of extraction solvent was increased, the volume of the

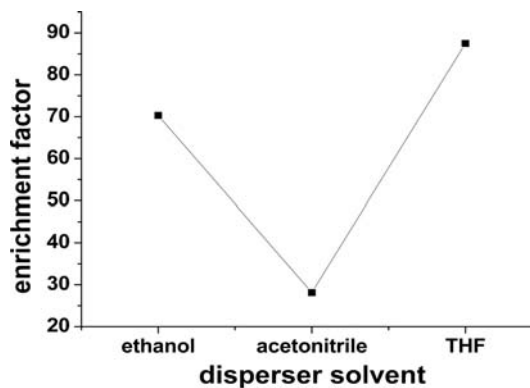
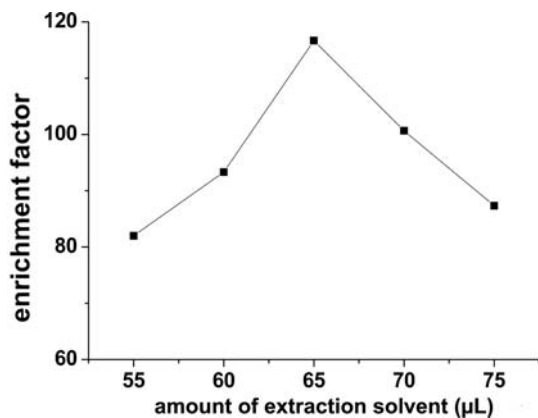


Figure 3. Effect of disperser solvent on enrichment factor. Extraction conditions: amount of [BMIM][PF6], 60  $\mu\text{L}$ ; disperser solvent volume, 180  $\mu\text{L}$ ; NaCl (w/v), 20%; aqueous sample volume, 8 mL; pH of the aqueous sample, 7; centrifugal time, 10 min.

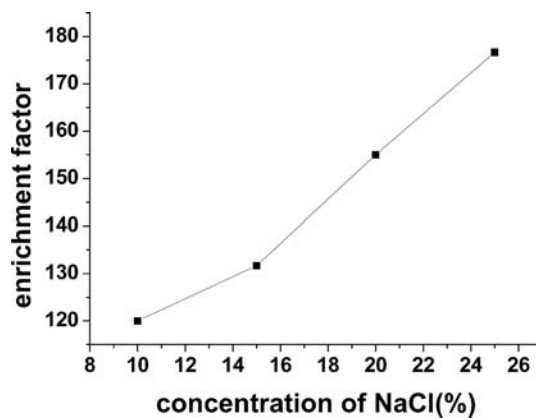
sedimented phase also increased, which resulted in the reduction of EF of the analyte. Therefore, there was a point, and when the amount of extraction solvent reached this point, the EF peak value was reached. In this paper, the volume of 65  $\mu\text{L}$  was chosen as the optimum extraction solvent amount.

#### Optimization of the volume of THF

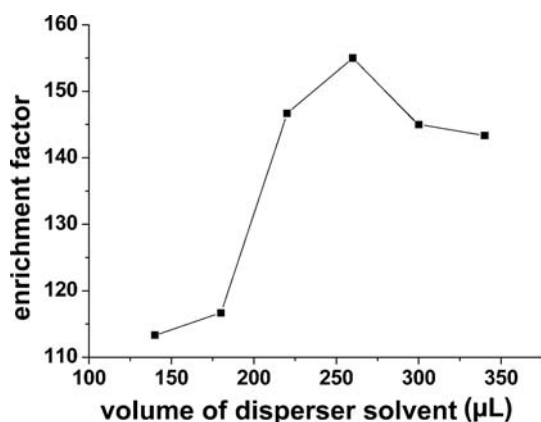
The volume of disperser solvent affects the formation of the cloudy suspension and the solubility of extraction solvent in the water sample, which influence the extraction efficiency. To investigate the effect of the disperser solvent volume on the extraction efficiency, various volumes of THF (140, 180, 220, 260, 300 and 340  $\mu\text{L}$ ) containing 65  $\mu\text{L}$  [BMIM][PF6] were tested. As shown in Figure 5, the EF of the analyte first increased and then decreased by increasing the volume of THF. At low volumes of THF, the cloudy suspension was not formed completely, so the EF of analyte was low; however, at high-volume THF, the solubility of [BMIM][PF6] in aqueous phase



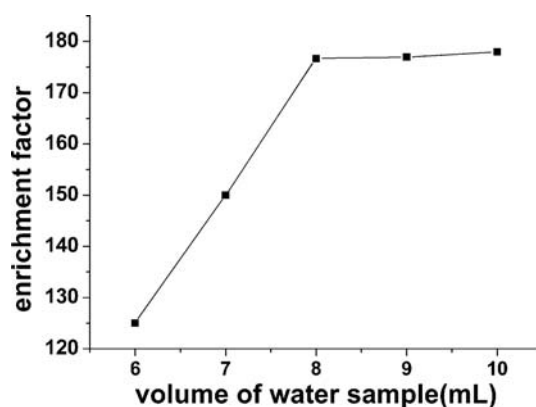
**Figure 4.** Effect of the volume of [BMIM][PF6] on the enrichment factor. Extraction conditions: disperser solvent, THF; disperser solvent volume, 180 µL; NaCl (w/v), 20%; aqueous sample volume, 8 mL; pH of the aqueous sample, 7; centrifugal time, 10 min.



**Figure 6.** Effect of the addition of NaCl on the enrichment factor. Extraction conditions: disperser solvent, THF; amount of [BMIM][PF6], 65 µL; disperser solvent volume, 260 µL; aqueous sample volume, 8 mL; pH of the aqueous sample, 7; centrifugal time, 10 min.



**Figure 5.** Effect of the volume of THF on the enrichment factor. Extraction conditions: disperser solvent, THF; amount of [BMIM][PF6], 65 µL; NaCl (w/v), 20%; aqueous sample volume, 8 mL; pH of the aqueous sample, 7; centrifugal time, 10 min.



**Figure 7.** Effect of the volume of aqueous sample on the enrichment factor. Extraction conditions: disperser solvent, THF; amount of [BMIM][PF6], 65 µL; disperser solvent volume, 260 µL; NaCl (w/v), 25%; pH of the aqueous sample, 7; centrifugal time, 10 min.

increased, and therefore the EF decreased. According to the results, 260 µL THF was chosen to obtain a high EF.

#### Selection of the content of NaCl

The addition of salt has an important effect on the extraction efficiency in the RTIL–DMLLE technique. Salt can decrease the solubility of the extraction solvent in the aqueous phase and thus improves the extraction performance by increasing the ionic strength of sample solution.

In this experiment, the salt concentration was investigated in a certain range [0, 5, 10, 15, 20, 25, 30% (w/v)]. The volume of the settled phase was not enough for HPLC injection when the concentration of NaCl was lower than 10% (w/v), at which the obtained [BMIM][PF6] phase floated on the sample solution, and could not be acquired when the concentration of NaCl was 30% (w/v). Results are shown in Figure 6. As shown in the figure, the EF of the analyte increased along with the increase of salt concentration from 10 to 25%. According to the results, 25% was chosen as the optimum concentration of salt.

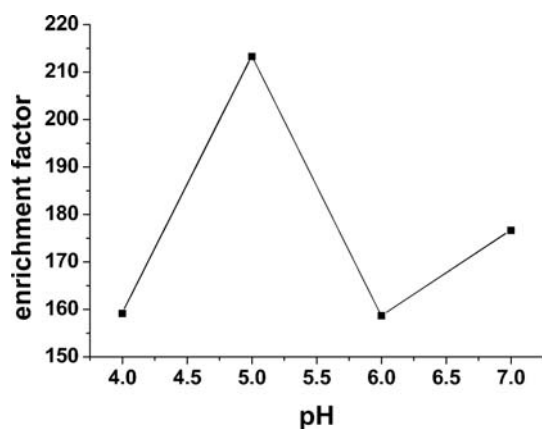
#### Effect of volume of water sample

During the DLLME process, the volume of water sample can influence the sample-to-sedimented phase ratio. Generally speaking, the larger the ratio between the water sample and the settled phase, the higher the EF obtained. To examine the effect of water sample volume, a series of volumes of 6, 7, 8, 9 and 10 mL were evaluated. The enrichment factors are given in Figure 7. With an increase of the volume of the aqueous sample from 6 to 8 mL, the EFs of the analyte increased gradually. No distinct changes were observed in the EF for higher water sample volume. At a low water sample volume, the sample-to-sedimented phase ratio was small, which led to a low EF of extraction. As the volume of water sample increased, the EF also increased. However, when the volume of the water sample reached 8 mL, the growth of EF was not obvious. Therefore, to conserve resources, 8 mL was adopted for further use.

#### pH of water sample

The pH of the water sample is expected to induce a significant impact on the extraction efficiency. This is because the pH of





**Figure 8.** Effect of the pH of aqueous sample on the enrichment factor. Extraction conditions: disperser solvent, THF; amount of [BMIM][PF<sub>6</sub>], 65  $\mu$ L; disperser solvent volume, 260  $\mu$ L; NaCl (w/v), 25%; volume of the aqueous sample, 8 mL; centrifugal time, 10 min.

**Table I**  
Performances of the Proposed Method

Compound	LR ( $\mu$ g/L)	$R^2$	Spiked levels ( $\mu$ g/L)			LOD ( $\mu$ g/L)	EF
			20	100	200		
Dichlorvos	2–1,000	0.9999	97.8 $\pm$ 1.8*	96.5 $\pm$ 1.3	96.9 $\pm$ 1.3	0.2	215

\*Relative recovery, mean  $\pm$  standard deviation (%) ( $n = 6$ ).

the water sample affects the existing station (charge, solubility and ionization degree) of both dichlorvos and [BMIM][PF<sub>6</sub>], which has an effect on the extraction capacity of the [BMIM][PF<sub>6</sub>]. To examine this parameter, experiments were carried out with the pH of the original aqueous samples varying from 4.0 to 7.0. Because OPPs may degrade under alkaline conditions, a pH value above 7.0 was not tested. The results displayed that the sample pH had a notable effect on the EF and the best extraction efficiency was obtained at pH 5.0.

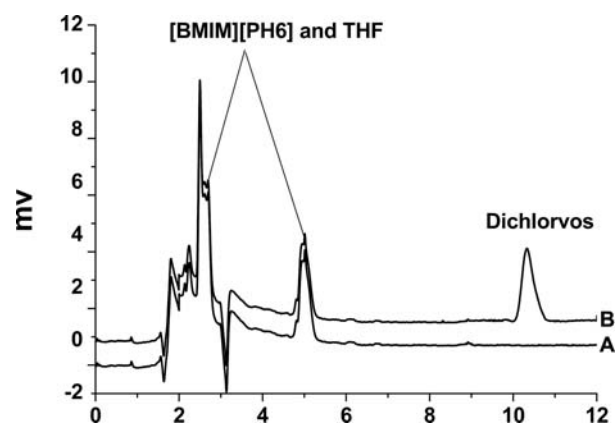
#### Other factors

**Extraction time:** in the DLLME procedure, the rate of extraction is extremely fast (only a few seconds). According to the preliminary experiments, after the injection of RTIL and shaking softly a few times, the aqueous sample could be centrifuged directly.

**Centrifugation time:** in this paper, the maximum rate of 4,000 rpm was used to gain the largest separation extent in a shorter time. We found that when the centrifugation time reached 10 min, the EF became constant, so the centrifugation time was set at 10 min.

#### Optimized extraction conditions

**Disperser solvent:** THF; amount of [BMIM][PF<sub>6</sub>]: 65  $\mu$ L; volume of disperser solvent: 260  $\mu$ L; NaCl: 25% (w/v); volume of aqueous sample: 8 mL; pH of aqueous sample: 5; centrifugation time: 10 min.



**Figure 9.** Chromatograms of blank water sample (A) and water sample spiked with dichlorvos at 100  $\mu$ g/L (B).

**Table II**  
Relative Recovery and RSD Values of Dichlorvos in Three Real Water Samples

Compound	Spiked levels ( $\mu$ g/L)	Tap water	Rain water	Farm water
Dichlorvos	0	—	—	—
	20	102.1 $\pm$ 1.2*	98.7 $\pm$ 2.0	101.9 $\pm$ 2.8
	100	97.6 $\pm$ 0.6	95.9 $\pm$ 1.2	95.6 $\pm$ 0.8
	200	98.4 $\pm$ 0.4	102.4 $\pm$ 2.9	99.5 $\pm$ 3.1

\*Relative recovery, mean  $\pm$  standard deviation (%) ( $n = 3$ ).

#### Analytical features of the method

The parameters such as linear range (LR), reproducibility, limits of detection (LODs) and extraction efficiencies were investigated under the optimized conditions to evaluate the proposed method performance. The results are summarized in Table I. Linearity was observed in the range of 2–1,000  $\mu$ g/L with correlation coefficient ( $r^2$ ) at 0.9999. The reproducibility, or relative standard deviation (RSD), was studied from six replicate extractions of spiked water samples at three different concentration levels of 20, 100 and 200  $\mu$ g/L. The average extraction recoveries for the analyte were 97.8%, 96.5% and 96.9%, respectively. The corresponding RSDs were 1.8%, 1.3% and 1.3%. The sensitivity of this proposed method was determined by LODs, based on a signal-to-noise ratio of 3. The obtained value was lower than the value given by Japan, which allows a maximum concentration of 10  $\mu$ g/L of dichlorvos for tap water and environmental water (24).

#### Real water sample analysis

The practical applicability of the developed method was evaluated by extracting dichlorvos from different sources water samples, including tap water, farm water and rain water. Each sample was spiked with the target analyte at three different concentration levels of 20, 100 and 200  $\mu$ g/L and analyzed in triplicate using the DLLME procedure. Figure 9 shows the typical chromatogram of dichlorvos after DLLME in blank water and spiked water. The results showed that the analyzed water samples were free of dichlorvos contamination. The relative recoveries of the analyte in three water samples are listed in

**Table III**

Comparison Between the Developed Method and Two Available Methods

Methods	LR ( $\mu\text{g/L}$ )	LOD ( $\mu\text{g/L}$ )	Characteristics
DLLME-HPLC-UV	2–1,000	0.2	Equipment is common and economic.
MAE-HS-SPME*	5–75	1.0	Equipment is expensive.
CL-FIA <sup>†</sup>	20–3100	0.8	CL detector is not common and the CL reaction procedure is easily affected.

\*MAE-HS-SPME: microwave-assisted extraction coupled to headspace solid-phase microextraction.

<sup>†</sup>CL-FIA: chemiluminescence flow-injection.

Table II. The data display that the relative recoveries are in the range of 95.6–102.4% and RSD is in the range of 0.6–3.1% at different spiking concentration levels of 20, 100 and 200  $\mu\text{g/L}$ .

## Conclusions

In this paper, a new RTIL-DLLME method combined with HPLC-UV was developed for the determination of dichlorvos in water samples. Employing [BMIM][PF<sub>6</sub>] as the extraction solvent in DLLME gained several advantages: it reduced the exposure danger of the toxic solvent used in the conventional extraction process, enhanced the sensitivity and shortened the operation time. To evaluate the developed method, we compared the developed method with two other available methods (25, 26) that have been used in the determination of dichlorvos. Results are shown in Table III. According to Table III, it is clear that the developed method has a wider linear range (the ratio between upper and lower limit of linear range is 500) and lower LOD, and the equipment used in the developed method are simpler and more economic. In addition, the performance of the method in the extraction and determination of dichlorvos from tap water, farm water and rain water was perfect, showing a relative recovery of 95.6–102.4% and RSD of 0.6–3.1%. All of these facts indicated that RTIL-DLLME can be employed as an appropriate method for the trace determination of dichlorvos.

## Acknowledgments

Financial support from the CEEUSRO combination projects of education ministry of Guangdong province (No. 2007A090302100) is gratefully acknowledged.

## References

- Barata, C., Solayan, A.; Role of B-esterases in assessing toxicity of organophosphorus (chlorpyrifos, malathion) and carbamate (carbofuran) pesticides to *Daphnia magna*. *Aquatic Toxicology*, (2004); 66: 125–139.
- Wang, J.H., Zhang, Y.B.; Determination of multiclass pesticide residues in apple juice by gas chromatography-mass spectrometry with large-volume injection. *Journal of Separation Science*, (2006); 29: 2330–2337.
- Sannino, A.; Determination of three natural pesticides in processed fruit and vegetables using high-performance liquid chromatography/tandem mass spectrometry. *Rapid Communication in Mass Spectrometry*, (2007); 21: 2079–2086.
- Topuz, S., Özhan, G.; Simultaneous determination of various pesticides in fruit juices by HPLC-DAD. *Food Control*, (2005); 16: 87–92.
- Albero, B., Sánchez-Brunete, C.; Multiresidue determination of pesticides in juice by solid-phase extraction and gas chromatography-mass spectrometry. *Talanta*, (2005); 66: 917–924.
- Zhang, J., Lee, H.K.; Application of liquid-phase microextraction and on-column derivatization combined with gas chromatography-mass spectrometry to the determination of carbamate pesticides. *Journal of Chromatography A*, (2006); 1117: 31–37.
- Xie, H.Y., He, Y.Z.; On-column liquid-liquid-liquid microextraction coupled with base stacking as a dual preconcentration method for capillary zone electrophoresis. *Journal of Chromatography A*, (2009); 1216: 3353–3359.
- Lachenmeier, D.W., Nerlich, U.; Automated determination of ethyl carbamate in stone-fruit spirits using headspace solid-phase microextraction and gas chromatography-tandem mass spectrometry. *Journal of Chromatography A*, (2006); 1108: 116–120.
- Li, X.J., Gan, P.S.; Determination of 23 organophosphorous pesticides in surface water using SPME followed by GC-MS. *Journal of Chromatographic Science*, (2010); 48: 183–187.
- USEPA Method 8011. American Society for Testing and Materials, Philadelphia, PA, [http://www.accustandard.com/asi/pdfs/epa\\_methods/8011.pdf](http://www.accustandard.com/asi/pdfs/epa_methods/8011.pdf) (accessed May 2011) (1992)
- USEPA Method 552.3. American Society for Testing and Materials, Philadelphia, PA, <http://www.caslab.com/EPA-Methods/PDF/EPA-Method-5523rev10.pdf> (accessed May 2011) (2003)
- Rezaee, M., Assadi, Y.; Determination of organic compounds in water using dispersive liquid-liquid microextraction. *Journal of Chromatography A*, (2006); 1116: 1–9.
- Farajzadeh, M.A., Bahram, M.; Dispersive liquid-liquid microextraction followed by high-performance liquid chromatography-diode array detection as an efficient and sensitive technique for determination of antioxidants. *Analytica Chimica Acta*, (2007); 591: 69–79.
- Rezaee, M., Yamini, Y.; Dispersive liquid-liquid microextraction combined with high-performance liquid chromatography-UV detection as a very simple, rapid and sensitive method for the determination of bisphenol A in water sample. *Journal of Chromatography A*, (2009); 1216: 1511–1514.
- Berijani, S., Assadi, Y.; Dispersive liquid-liquid microextraction combined with gas chromatography-flame photometric detection: Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. *Journal of Chromatography A*, (2006); 1123: 1–9.
- Jeannot, M.A., Przyjazny, A.; Single drop microextraction—Development, applications and future trends. *Journal of Chromatography A*, (2009); 1217: 2326–2336.
- Rezaee, M., Yamini, Y.; Evolution of dispersive liquid-liquid microextraction method. *Journal of Chromatography A*, (2009); 1217: 2342–2357.
- Zang, X.H., Wu, Q.H.; Developments of dispersive liquid-liquid microextraction technique. *Chinese Journal of Analytical Chemistry*, (2009); 37: 161–168.
- Xie, S.F., Xiang, B.R.; Determination of medroxyprogesterone in water samples using dispersive liquid-liquid microextraction with low solvent consumption. *Microchimica Acta*, (2010); 168: 253–258.
- Sun, P., Armstrong, D.W.; Ionic liquids in analytical chemistry. *Analytica Chimica Acta*, (2010); 661: 1–16.
- Liu, J.F., Jönsson, J.A.; Application of ionic liquids in analytical chemistry. *Trends in Analytical Chemistry*, (2005); 24: 20–27.
- Buszewski, B., Studzinska, S.; A review of ionic liquids in chromatographic and electromigration technique. *Chromatographia*, (2008); 68: 1–10.
- Huang, K.J., Jin, C.X.; Development of an ionic liquid-based ultrasonic-assisted liquid-liquid microextraction method for sensitive determination of biogenic amines: Application to the analysis of octopamine, tyramine and phenethylamine in beer samples. *Journal of Chromatography B*, (2011); 879: 579–584.

24. Ministry of Public Health and Welfare (Japan). Various standards for agricultural chemicals concerning water quality. (Information from Norio Kurihara) (1997).
25. Chen, Y.L., Su, Y.S.; Determination of dichlorvos by on-line microwave-assisted extraction coupled to headspace solid-phase microextraction and gas chromatography–electron-capture detection. *Journal of Chromatography A*, (2002); 976: 349–355.
26. Wang, J.N., Zhang, C.; Development of a luminol-based chemiluminescence flow-injection method for the determination of dichlorvos pesticide. *Talanta*, (2001); 54: 1185–1193.