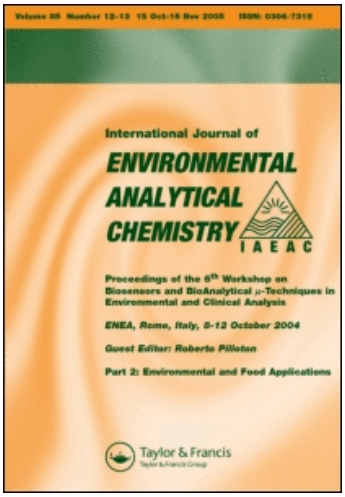

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Development of dispersive liquid-phase microextraction based on new ionic liquid 1,3-diisooctylimidazolium hexafluorophosphate as solvent for the extraction and determination of dicofol and its degradation products in water samples

Zaijun Li[ab]; Yinjun Fang[b]; Peipei Chen[a]; Zhongyun Wang[a]; Liping Wang[c]; Guoxiao Ren[b]; Yaru Huang[b]
[a] School of Chemical and Materials Engineering, Jiangnan University (formerly known as Wuxi University of Light Industry and Southern Yangtze University), Wuxi 214122, China [b] Zhejiang Zanyu Technology Limited Corporation, Hangzhou 311215, China [c] State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi 214122, China

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Development of dispersive liquid-phase microextraction based on new ionic liquid 1,3-diisooctylimidazolium hexafluorophosphate as solvent for the extraction and determination of dicofol and its degradation products in water samples

Zaijun Li[ab]*, Yinjun Fang[b], Peipei Chen[a], Zhongyun Wang[a], Liping Wang[c], Guoxiao Ren[b] and Yaru Huang[b]

[a]*School of Chemical and Materials Engineering, Jiangnan University (formerly known as Wuxi University of Light Industry and Southern Yangtze University), Wuxi 214122, China;* [b]*Zhejiang Zanyu Technology Limited Corporation, Hangzhou 311215, China;* [c]*State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi 214122, China*

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In the current paper we describe a novel sample preparation technique termed dispersive liquid-phase microextraction for the preconcentration and determination of 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (dicofol) and its degradation products in water samples that includes 2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1-dichloroethene(2,4′-DDE), 1,1-dichloro-2,2-bis(4-chloro phenyl)ethane(4,4′-DDE) and 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (2,4′-DDT) coupled with gas chromatography mass spectrometry (GC-MS), in which a new ionic liquid 1,3-diisooctylimidazolium hexafluorophosphate abbreviated as [D(*i*-C_8)IM][PF_6] was used as extraction solvent. For each one extraction, 1.00 mL of the methanol solution containing 40 μL of the ionic liquid was sprayed into 25.00 mL of water sample. In the meantime the ionic liquid was finely dispersed into the aqueous phase and analytes were rapidly migrated into the ionic liquid. After the solution was centrifuged for 2 min at 5000 rpm, the droplets of the ionic liquid are subsided in the bottom of the conical test tube (30.0 ± 0.2 μL). Moreover, the factors relevant to extraction efficiencies were investigated and optimised including the volume of the ionic liquid, disperser solvent, extraction time, sample pH and ionic strength. Under optimal conditions, the enrichment factors of the extraction were between 550 and 725 with an extraction efficiency ranging from 66% to 87% for each different analyte. Finally, 1.0 μL of the ionic liquid collected from above extraction was injected into the injector block of GC-MS instrument for analysis. The detection limit (S/N = 3), the relative standard deviations for 2.0 μg L^{-1} of the standard analyte ($n = 5$) and linearity in a calibration range were found to be 3–8 ng L^{-1}, 1.0–2.7% and 10–3000 ng L^{-1}, respectively. Good spiked recoveries over the range of 92.0–13.5% were obtained. The proposed method offers the advantages of simplicity of operation, rapidity, good extraction efficiency and enrichment factor; it has been successfully applied to determination of dicofol and its degradation products in environmental water samples.

Keywords: 1,3-diisooctylimidazolium hexafluorophosphate; ionic liquid; dispersive liquid-phase microextraction; dicofol; gas chromatography-mass spectrometry

*Corresponding author. Email: zaijunli@263.net

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1. Introduction

The use of chlorinated hydrocarbon insecticides has been sharply curtailed or banned, but they are still the active ingredients of some pest control products. In recent years, 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (dicofol) has become the main product of organochlorine pesticides (OCPs) in China. Dicofol is used worldwide as a pre-harvest miticide on cotton, citrus, vegetable, nuts, date palm and other crops. Dicofol is classified as a slightly toxic compound, having acute oral LD_{50} for rat of $587\,mg\,kg^{-1}$ and environmental endocrine-disrupting chemical. However, dicofol product always contains high impurity of 1,1,1-trichloro-2,2-dichlorophenylethane (DDT) and related compounds because DDT was often used as raw materials for synthesis of dicofol, and therefore becomes an important source of DDT. Moreover, dicofol is unstable under environmental conditions, its degradation may produce many high hazardous materials mainly including 2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1-dichloroethene (2,4′-DDE), 1,1-dichloro-2,s2-bis(4-chlorophenyl)ethane (4,4′-DDE) and 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (2,4′-DDT) [1]. Therefore, the analysis of dicofol and these compounds in environmental water samples is of importance.

Methods for determination of OCPs have mainly gas chromatography [2], liquid chromatography–mass spectrometry (LC-MS) [3] and gas chromatography–mass spectrometry (GC-MS) [4,5]. Specifically, they have widely accepted/adopted GC-MS owing to its accuracy and sensitivity [6]. However, present GC-MS is not sensitive enough to directly determine ultra trace OCPs in environmental water samples; thus a suitable sample preparation was required to improve sensitivity. In many analytical procedures, sample preparation is the most time-consuming and cost-determining step. At present, liquid–liquid extraction (LLE) [7] and solid-phase extraction (SPE) [8] were widely applied to sample preparation for pesticide analysis in routine analysis. The main drawbacks of LLE include being labour-intensive and the use of large volumes of solvent, which often leads to the formation of emulsions. In addition, a large volume of sample is often required due to a very low concentration of the analytes in real water samples. SPE is less time-consuming than LLE but requires column conditioning and elution with organic solvents.

Recent research activities are oriented towards the development of efficient, economical, and miniaturised sample preparation methods. As a result, solid phase microextraction (SPME) [9–13] and liquid-phase microextraction (LPME) [14–16] have been developed rapidly. Among these, SPME is a solvent-free process developed by Arthur and Pawliszyn [17] that includes simultaneous extraction and preconcentration of the analytes from aqueous samples or the headspace of the samples. However, SPME is also expensive, its fibre is fragile and has limited life-time and sample carry-over can be a problem [18]. LPME requires very little solvents and minimal exposure to toxic organic solvents, and it has attracted increasing attention [19–24]. However, LPME is time-consuming and equilibrium could not be attained after a long time in most cases [25]. To overcome these problems, some improved LPME methods such as homogenous liquid phase microextraction (HLPME) and dispersive liquid-phase microextraction (DLPME) have been developed [26–29]. Among these, HLPME utilises the phase separation phenomenon from a homogeneous solution, and the target solutes are extracted into a separated phase. In HLPME, the initial condition is homogeneous solution; namely, there is no interface between the water phase and organic solvent. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple and requires only the

addition of a reagent. The ternary component solvent system and the perfluorinated surfactant system are the two usual modes of homogeneous liquid-phase extraction [26]. However, HLPME has also some problems. For instance, sometimes it is not compatible with some instrumental analysis and it also requires the addition of reagent such as acid, base, salt, etc. As a result of that, probably some interested compounds are destroyed. Moreover, the addition of reagent causes the release of heat during extraction. DLPME is based on a ternary component solvent system. In this method, the appropriate mixture of extraction solvent and disperser solvent is injected into aqueous sample by syringe, rapidly. Thereby, a cloudy solution is formed. The method offers simplicity of operation, rapidity, low-cost, high recovery and enrichment factor [27].

Ionic liquid is an ionic medium resulting from combinations of organic cation and inorganic anion and show liquid state at room temperature. They have been widely applied as green solvent in LLE [30], LPME [31,32] and SPME [33]. Recently, two classical ionic liquids, the $[C_6mim][PF_6]$ [34,35] and $[C_4mim][PF_6]$ [36], have been investigated as novel extraction solvents for DLPME. In these methods, ionic liquid was dispersed completely into the aqueous solution, and the analytes will more easily migrate into the ionic liquid phase because of the much larger contact area than that of conventional LPME and SPME. However, these also suffer from some drawbacks. On the one hand, the ionic liquid is difficult to be dispersed into the aqueous phase due to very high interfacial tension; a long heating process or mechanical agitation was required strongly to obtain a fine dispersed liquid. On the other hand, classical ionic liquids used in the above research have relatively high water-solubility. In present extraction systems, their aqueous phases often contain relatively high concentration of imidazolium and hexafluorophosphate. The fact results in serious salting-out effect in the presence of high ionic strength, which would effect the extraction performance and following analysis, and the emulsification phenomenon because of high surface activity of the imidazolium in the aqueous phase, which will prolong phase separation process. To resolve the above problem, a new ionic liquid, 1,3-diisooctylimidazolium hexafluorophosphate abbreviated as $[D(i\text{-}C_8)IM][PF_6]$ (see Figure 1), was designed, synthesised and developed as a novel extraction solvent

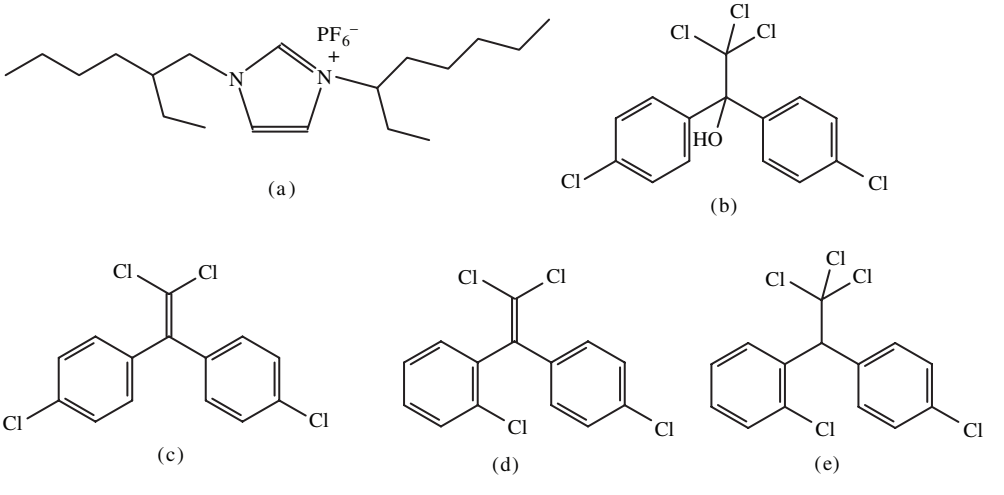

Figure 1. Chemical structures of the $[D(i\text{-}C_8)IM][PF_6]$ (a), dicofol (b), 4,4′-DDE (c), 2,4′-DDE (d) and 2,4′-DDT (e).

for DLPME. In this study, dicofol and its three degradation products were selected as model compounds to optimise the factors relevant to the extraction efficiency and evaluate the applicability of the method. The experiment showed the proposed method offers the advantage of simplicity of operation, rapidity, high extraction efficiency and enrichment factor.

2. Experimental

2.1 *Reagents*

Ionic liquid 1,3-diisooctylimidazolium hexafluorophosphate used in this study was synthesised and purified in the lab. Dicofol and 2,4′-DDE, 4,4′-DDE and 2,4′-DDT were purchased from Institute of Agro-Environmental Protection, Ministry of Agriculture of China (Tianjin, China). Proper amounts of each standard OCPs were dissolved in methanol to obtain a stock standard solution with a concentration of $20\,mg\,L^{-1}$. A fresh standard solution containing each OCP with a concentration of $200\,\mu g\,L^{-1}$ was prepared in methanol every week and stored at 4°C. HPLC-grade methanol, acetone and acetonitrile were purchased from Sigma-Aldrich. The double-distilled water was prepared in the lab using quartz-glass vaporisation purchased from Yarong (Shanghai, China) and all the other solvents were of analytical reagent grade unless stated and were purchased from Shanghai Chemical Company (Shanghai, China). All glassware were decontaminated overnight in $6.0\,mol\,L^{-1}$ nitric acid and thoroughly washed with double-distilled water before use. One percent (w/v) sodium hydroxide and $1.0\,mol\,L^{-1}$ diluted hydrochloric acid were used for adjusting the pH value of the water samples.

2.2 *Preparation of the ionic liquid*

One mol of 1-bromoisooctane and 0.5 mol of 1-trimethylsilylimidazole (distilled freshly) was transfered to a 500 mL round bottom flask which was fitted with a reflux condenser and nitrogen protecting facilities. Fifty mL of toluene was added to the flask as solvent. After the mixture was stirred at 70°C for 18 h, a transparent viscous product, 1,3-diisooctylimidazolium bromide, was formed. The liquid was cooled and then transferred into a 2000 mL beaker. Then 500 mL of potassium hexafluorophosphate (0.5 mol) was added to the well stirred mixture. After the addition of the reagent, the mixture was continuously stirred for 4 h. The water phase was then discarded and the formed 1,3-diisooctylimidazolium hexafluorophosphate was washed with water until bromide ion was wiped off using a silver nitrate test. The collected ionic liquid [D(*i*-C_8)IM][PF_6] was heated to 110°C under vacuum to remove water, the solvent and raw materials, total yield of the ionic liquid was about 78%.

A DRX-500 nuclear magnetic resonance spectrometer (Bruker, Russ, Germany) and a FALA2000104 model infrared photometer (Boman, Canada) were used to measure the nuclear magnetic resonance spectrometry (NMR) and infrared spectrometry (IR) of the product, respectively. The results are listed in the following: ^{1}H NMR (500 MHz, CD_3OCD_3), 0.58 (t, 6H), 0.75 (t, 6H), 0.65 ~ 0.72 (m, 4H), 0.82 ~ 0.94 (m, 4H), 1.25 ~ 1.32 (m, 4H), 1.34 ~ 1.42 (m, 4H), 1.82 ~ 2.00 (m, 2H), 4.38 (d, 4H), 7.85 (d, 1H), 7.85 (d, 1H), 9.12 (s, 1H). IR (neat): ν_{max}/cm^{-1} 3160 (CH), 2961 and 2869 (CH), 1564 and 1462 (conj. CC), 1382 (CH), 1163 (CH), 840 (PF). Moreover, the density, thermal decomposition temperature, water-solubility and apparent viscosity of the

product were measured at $25 \pm 0.02^{\circ}C$ by using the bottle method, thermogravimetry on HTG-1 thermogravimetric analysis (Beijing Heng Jiu Science Instrument Co., Beijing, China), ultraviolet spectrophotometry on Beckman DU-7HS spectrophotometer (Beckman company, America) and RVDV-3 model manual viscosity measurement system (Brook-Field Company, USA), respectively. The results were $1.13\,g\,L^{-1}$, $399.15^{\circ}C$ and $0.39\,g\,L^{-1}$ and 785.10 cP, respectively.

2.3 *General extraction procedure*

Twenty-five mL of double-distilled water was placed in a 45 mL screw cap glass test tube with conic bottom and spiked at the level of $2\,\mu g\,L^{-1}$ of OCP. 1.00 mL of methanol containing 40 μL of the [D(*i*-C_8)IM][PF_6] was injected into the water sample by using a 1.00 mL syringe rapidly, then the mixture was manually shaken well for 2 sec. A cloudy solution was formed in the test tube, the mixture was then centrifuged for 2 min at 5000 rpm. Accordingly, the droplet of extraction phase was sedimented in the bottom of the conical test tube. Finally, 1.00 μL of sedimented phase was removed using a 1.00 μL of microsyringe (zero dead volume, Hamilton) and injected into GC-MS for analysis.

2.4 *Chromatographic conditions for analysis*

Trace Ms gas chromatography-mass spectrometer (Finnigan, USA) with a DB-5 MS capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific, USA) was used for separation and analysis. Helium (99.9999%) was used as the carrier gas at a flow rate of $1.0\,mL\,min^{-1}$. The injector temperature was kept at $250^{\circ}C$ and all injections were made in the splitless mode. The temperature programme was arranged with an initial temperature of $120^{\circ}C$, and then increased at $15^{\circ}C\,min^{-1}$ to $260^{\circ}C$, and then held at $260^{\circ}C$ for 5 min. The MS was operated in electron impact mode with an ion source temperature of $200^{\circ}C$. The target compounds were quantified in the selected ion monitor mode, using characteristic fragment ions for each compound: 139, 250 (dicofol), 246, 318 (2, 4′-DDE), 246, 318 (4, 4′-DDE), 165, 235 (2, 4′-DDT). The mass spectrometer was operated in the selected ion monitor mode for chromatographic runs. The data process was performed with Xcalibur software. For the qualitative analysis, volatile compounds were identified by comparing the mass spectra of the analytes obtained with those of the authentic standards from the NIST 98 and WILEY 6.0 libraries with a resemblance percentage of above 80%. For sample analysis, 1.0 μL of the droplet of extraction solvent was directly injected into the injector block of the GC-MS instrument, in which a small glass tube is placed in the injection block to avoid ionic liquid leaking into the chromatographic column [37].

2.5 *Calculation of enrichment factor, extraction efficiency and recovery*

The enrichment factor (*EF*) was defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) within the sample.

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

The C_{sed} was obtained from calibration graph of direct injection of DCFs standard solution in the ionic liquid at the range of 10–2500 $ng\,L^{-1}$. The extraction efficiency (*EE*)

was defined as the percentage of the total analyte amount (n_0) which was extracted to the sedimented phase (n_{sed}).

$$EE = \frac{n_{sed}}{n_0} \times 100 = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 \quad (2)$$

$$EE = \left(\frac{V_{sed}}{V_{aq}}\right) EF \times 100 \quad (3)$$

where V_{sed} and V_{aq} are the volume of sedimented phase and sample solution, respectively. The recovery (R) was obtained as the following equation:

$$R = \frac{C_{founded} - C_{real}}{C_{added}} \times 100 \quad (4)$$

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

2.6 *Preparation of samples*

The river water sample was collected from Beijing-Hangzhou Grand Canal in Wuxi city. Two lake water samples were taken from Taihu Lake in Wuxi city. The well water and rain water samples were collected from Jiangnan University. All water samples were filtered through a 0.45 μm pore-size cellulose acetate filter (Shanghai Sunyear, Shanghai, China) immediately and collected in amber-glass bottles without headspace. In order to avoid the degradation of dicofol during the storing and the analysis, 1.0 mL of acetate acid was added to each litre water sample [36]. The samples were stored in the dark at 4°C until their analysis.

3. Results and discussion

Although the proposed DLPME method, based on new ionic liquid [D(*i*-C_8)IM][PF_6] as extraction solvent and an appropriate organic solvent as disperser solvent, is a new process, it has some similarities with conventional LLE. In order to obtain optimal extraction performance, some important factors that would influence the extraction performance should be investigated in detail. A series of experiments were designed for such a goal. In this procedure, the extraction efficiencies of four target analytes were used to optimise extraction conditions, and evaluate extraction performance and its application of the proposed method.

3.1 *Effect of the ionic liquid volume*

The volume of extraction solvent was a crucial parameter, which would have an important effect on the extraction efficiency. To investigate the effect of extraction solvent volume on the extraction, a series of methanol solutions containing a different volume of the ionic liquid were subjected to the same DLPME procedure. The experimental conditions were

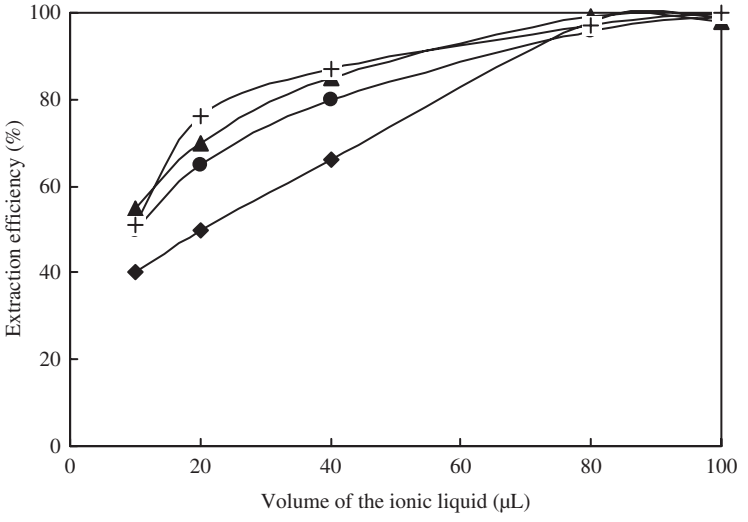

Figure 2. Effect of the volume of the ionic liquid on extraction efficiency of dicofol and its degradation products. Extraction conditions: water sample volume, 25 mL; disperser solvent, 1.00 mL of methanol; room temperature; (◆) dicofol, (●) 2,4′-DDT, (▲) 2,4′-DDE and (+) 4,4′-DDE, 2 μg L^{-1}; centrifugation time, 2 min.

fixed and included the use of 1.00 mL of methanol containing different volumes of the ionic liquid (10.0, 20.0, 40.0, 80.0 and 100 μL). Figures 2 and 3 show the curve of the extraction efficiency and enrichment factor versus volume of the ionic liquid, respectively. The results clearly indicated that by increasing the volume of the ionic liquid from 10 to 100 μL the volume of the sedimented phase increases from 1 to 89 μL. Figure 2 shows that with increasing the volume of the ionic liquid the extraction efficiency increased rapidly for all analytes. When the volume of the ionic liquid reached 80 μL, the extraction efficiency would reach a platform. As the volume of the sedimented phase increases, the enrichment factor decreases remarkably when increasing the volume of the ionic liquid as shown in Figure 3. Subsequently, at low volume of extraction solvent, a high enrichment factor is obtained. However, the reproducibility of the method is also an important parameter to routine pesticides analysis in environmental water samples. To examine the reproducibility of the method, for each different volume of the ionic liquid five replicate extractions were carried out and their relative standard deviations (RSDs) were calculated. The RSDs were 33.2–40.8% for 10 μL of the ionic liquid, 5.0–15.0% for 20 μL of the ionic liquid, 0.9–1.2% for 40 μL of the ionic liquid, 1.0–1.5% for 80 μL of the ionic liquid and 1.0–1.3% for 100 μL of the ionic liquid. The above data indicated that when the volume of the ionic liquid is bigger than 40 μL the reproducibility of the method is very good. Thereby, the gain in sensitivity and reproducibility were achieved by using 40 μL of the ionic liquid as extraction solvent which the volume of the settled ionic liquid phase is about 30.5 μL.

3.2 *Choice of the disperser solvent*

Hydrophobic ionic liquid is difficult to be dispersed into the water phase due to its low water-solubility and high viscosity. To improve the miscibility of the ionic liquid in water and form a fine dispersive phase for the extraction, a suitable disperser solvent was

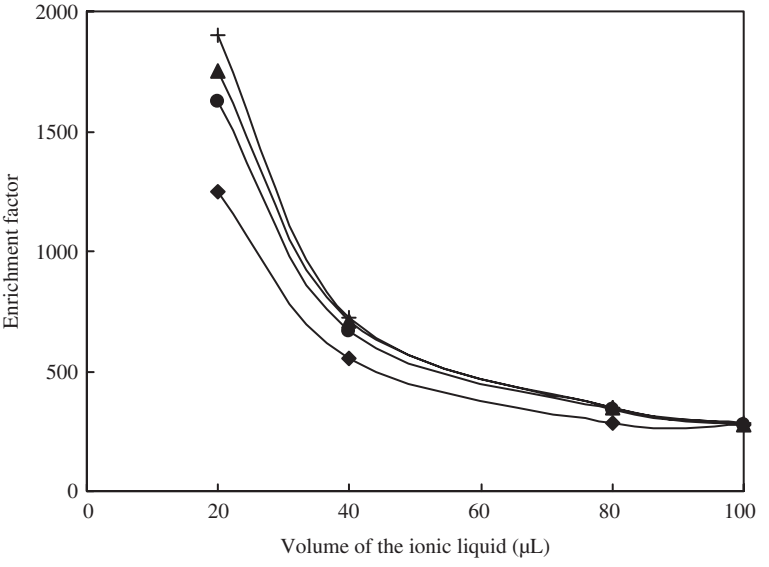

Figure 3. Effect of the volume of the ionic liquid on enrichment factor of dicofol and its degradation products. Extraction conditions: water sample volume, 25 mL; disperser solvent, 1.00 mL of methanol; room temperature; (◆) dicofol, (●) 2,4′-DDT, (▲) 2,4′-DDE and (+) 4,4′-DDE, 2 μg L^{-1}; centrifugation time, 2 min.

required. Acetone, acetonitrile and methanol are used for this purpose. A series of sample solution was investigated by using 1.00 mL of each disperser solvent containing 40 μL of the ionic liquid. The recoveries by using acetone, acetonitrile, and methanol as disperser solvents were ranged 65.0–82.2%, 52.5–80.6%, and 66.0–87.3% respectively. According to these results, variations of extraction efficiencies using different disperser solvents are not remarkable, thus, methanol is selected, because of less toxicity and low cost. Moreover, the effect of the volume of methanol (as disperser solvent) on the extraction efficiency of the analytes was investigated well. The experimental conditions were fixed and included the use of different volumes of methanol 0.50, 1.00, 1.50, and 2.00 mL which contains a constant volume of the ionic liquid (40 μL), respectively. The results are shown in Figure 4. According to the curve, the extraction efficiencies increases and then decreases by increasing the volume of methanol. It seems, at a low volume of methanol, cloudy state is not formed well, thereby, the extraction efficiencies decrease. At the high volume of methanol, the solubility of OCPs in water increases, therefore, the extraction efficiency decreases. As a result, 1.00 mL of methanol was chosen as optimum volume.

3.3 *Effect of extraction time*

The proposed extraction mainly includes the migration of the analytes and phase separation two processes. In the migration step, the analytes are migrated from aqueous phase to the organic phase (the ionic liquid) and finally reach the distribution equilibrium between two phases. Commonly, the migration time is one of the most important factors in most of the extraction procedures, especially in the microextraction such as SPME and LPME. In the proposed DLPME extraction, the migration time is defined as an interval time between injection of the mixture of disperser (methanol) and extraction solvent

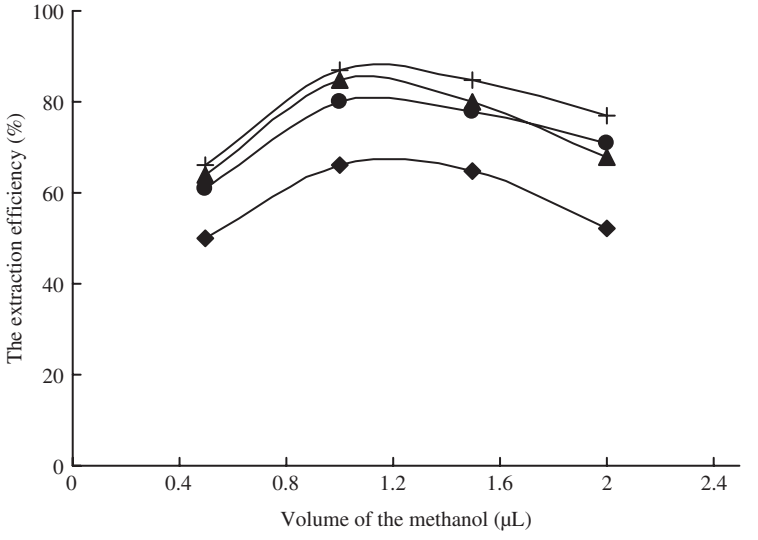

Figure 4. Effect of the volume of methanol on extraction efficiencies of dicofol and its degradation products. Extraction conditions: water sample volume, 25 mL; room temperature; volume of the ionic liquid, 40 μL; (◆) dicofol, (●) 2,4′-DDT, (▲) 2,4′-DDE and (+) 4,4′-DDE, 2 μg L^{-1}; centrifugation time, 2 min.

(the ionic liquid), and before starting to centrifuge. The effect of time was investigated in the range of 0–10 min with constant experimental conditions. The results showed clearly the migration time has no influence on extraction efficiency of the analytes. The fact revealed that the surface area between extraction solvent and aqueous phase is infinitely large, the migration of the analytes from aqueous phase to extraction phase is very fast. Subsequently, the equilibrium state is achieved quickly. To shorten extraction time, a centrifugation step was used to accelerate phase separation. In general, a higher rate of centrifugation led to a shorter time. So, the maximum rate of 5000 rpm was used in the experiments. In order to reach best enrichment, the centrifugation time was considered in the range of 0.5 min to 5 min. The results indicated the extraction efficiencies of OCPs gradually increased along with the prolongation of the centrifugation time. When the centrifugation time was over 1.0 min, the extraction efficiency of the analytes almost had no further increase. For the sake of saving time, 2.0 min was used as the optimal centrifugation time. So, whole extraction process can be completed within 3 min.

3.4 *Effect of sample pH*

Under the alkaline environment, dicofol was prone to decompose into 2,4′-DDE, 4,4′-DDE and 2,4′-DDT. For this reason, the effect of water sample acidity on the extraction and GC-MS analysis of dicofol was investigated well, the results showed dicofol is very stable in an acid environment (pH < 8) and its extraction efficiency kept at a maximum and unchanged, after that it dropped slowly. When the sample pH was higher than 9, the extraction efficiency decreased rapidly due to occurrence of the degradation of dicofol under alkaline conditions. Meanwhile an obvious increase in the peak area of its

metabolites was observed with increasing water sample pH. In order to avoid the degradation of dicofol in the water sample during the extraction and GC-MS analysis, 1.0 mL acetate acid was added to the water sample and therefore controlled acidity of the sample for each litre of water sample (about pH 6.6) [38].

3.5 *Effect of ionic strength*

Salt addition is frequently used to adjust ionic strength, improve the extraction efficiency and reduce the detection limit. The effect of the ionic strength on the extraction efficiencies by DLPME was examined across the concentration range of 0–10% (w/v) NaCl. The data from these experiments presented that the salt addition did not influence the extraction efficiency and enrichment factor significantly for any of the analytes in the presence of the salt in the concentration range of 0–3%. When salt concentration excess is over 3%, the extraction efficiencies will decrease slightly. This is due to the salting-out effect increasing the water-solubility of the ionic liquid in the presence of high concentration of the salt. As a consequence, all the extraction experiments were carried out without salt addition.

3.6 *Analytical performance*

The proposed DLPME procedure coupled with GC-MS was used for the quantitative analysis of dicofol and its three degradation products. The characteristic of calibration curves shown in Table 1 was obtained under optimised conditions. The linearity of the calibration curve was observed in the range of 10–3000 ng L^{-1} for most of the analytes. Coefficient of correlation (r^2) ranged from 0.9993 to 0.9998. The detection limit, based on signal-to-noise ratio (S/N) of 3 ranged from 3 to 8 ng L^{-1} using double-distilled water spiked with dicofol (or 2,4′-DDE, 4,4′-DDE, 2,4′-DDT) at very low level step by step. The relative standard deviations (RSDs) of the analytes were from 1.0 to 2.7% ($n = 5$) for 2.0 μg L^{-1} of each of the analytes in water samples. For using 40 μL of the ionic liquid as extraction solvent and 25 mL of water sample, the enrichment factors and extraction efficiency of the microextraction were in the range of 550–725 and 66–87% using double-distilled water spiked with the analyte1 at 1.000 μg L^{-1} concentration, respectively.

3.7 *Water sample analysis*

The results of the proposed extraction procedure applied to the determination of trace dicofol and its degradation products, are listed in Table 2. Results for the rain water sample showed that it was free of dicofol contamination. In other water samples, dicofol,

Table 1. Analytical characteristics of the proposed DLPME-GC-MS method.

Analytes	RSD (%), $n = 5$	EF	Linearity range (ng L^{-1})	Detection limit (ng L^{-1})	r^2	*EE* (%)
Dicofol	1.1	550	10–3000	6	0.9993	66
2,4′-DDE	2.4	708	10–3000	7	0.9997	85
4,4′-DDE	1.9	725	10–3000	8	0.9995	87
2,4′-DDT	2.7	667	8–3000	5	0.9998	80

Table 2. Analysis of OCPs in water samples.

Sample	OCPs	OCPs added ($\mu g\,L^{-1}$)[a]	OCPs found ($\mu g\,L^{-1}$)	RSD (%)	Recovery (%)
River water	Dicofol	0.00	1.12 ± 0.03	1.5	
		2.00	3.10 ± 0.12	1.2	99.0
	2,4′-DDE	0.00	0.34 ± 0.03	1.7	
		2.00	2.35 ± 0.22	1.2	100.5
	4,4′-DDE	0.00	0.17 ± 0.05	1.2	
		2.00	2.23 ± 0.19	1.9	103.0
	2,4′-DDT	0.00	0.52 ± 0.03	2.0	
		2.00	2.44 ± 0.12	2.2	96.0
Lake water 1	Dicofol	0.00	1.36 ± 0.05	1.5	
		2.00	3.29 ± 0.33	1.1	96.5
	2,4′-DDE	0.00	0.22 ± 0.09	2.4	
		2.00	2.24 ± 0.11	1.4	101.0
	4,4′-DDE	0.00	0.33 ± 0.04	1.1	
		2.00	2.18 ± 0.12	1.3	92.5
	2,4′-DDT	0.00	0.53 ± 0.02	2.0	
		2.00	2.56 ± 0.45	1.6	101.5
Lake water 2	Dicofol	0.00	0.66 ± 0.05	1.2	
		2.00	2.60 ± 0.22	1.1	97.0
	2,4′-DDE	0.00	0.67 ± 0.12	1.8	
		2.00	2.58 ± 0.18	1.3	95.5
	4,4′-DDE	0.00	0.13 ± 0.04	1.2	
		2.00	2.18 ± 0.12	1.2	102.5
	2,4′-DDT	0.00	0.71 ± 0.07	2.2	
		2.00	2.55 ± 0.19	1.5	92.0
Well water	Dicofol	0.00	1.82 ± 0.13	1.4	
		2.00	3.77 ± 0.21	1.1	97.5
	2,4′-DDE	0.00	0.12 ± 0.02	2.2	
		2.00	2.19 ± 0.31	1.7	103.5
	4,4′-DDE	0.00	0.32 ± 0.04	1.9	
		2.00	2.30 ± 0.22	1.3	99.0
	2,4′-DDT	0.00	0.28 ± 0.05	2.1	
		2.00	2.19 ± 0.11	1.2	95.5
Rain water	Dicofol	0.00	0.00 ± 0.02	2.3	
		2.00	1.93 ± 0.32	1.6	96.5
	2,4′-DDE	0.00	0.00 ± 0.01	2.1	
		2.00	2.04 ± 0.27	1.3	102.0
	4,4′-DDE	0.00	0.00 ± 0.03	1.7	
		2.00	2.03 ± 0.42	1.6	101.5
	2,4′-DDT	0.00	0.00 ± 0.02	2.4	
		2.00	1.89 0.15	1.3	94.5

2,4′-DDE, 4,4′-DDE, 2,4′-DDT and were detected. The DLPME-GC-MS chromatograms are shown in Figure 5. The results of relative standard deviations (RSDs) for DLPME of the analytes from the water samples based on five replicate measurements are listed in Table 2. The data has shown that RSDs for the determination of dicofol and its degradation products were in the range from 1.1 to 2.4%. The results indicated the method has good accuracy. Since there is no certified reference material for environmental water samples, the percentage recovery was also employed for calculation of the

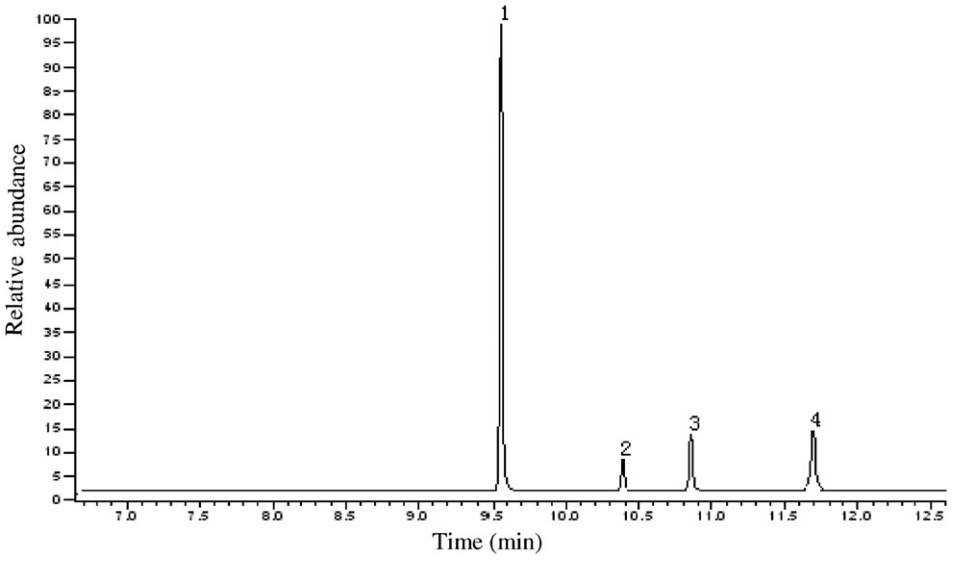

Figure 5. The GC-MS chromatogram of lake water samples, dicofol (1), 2,4′-DDE (2), 4,4′-DDE (3) and 2,4′-DDT (4).

method accuracy. Table 2 indicated the percentage recoveries are between 92.0% and 13.5%. These results demonstrated the applicability of the proposed method for determination of ultra trace dicofol and its degradation products in various water samples with various matrices.

4. Conclusion

This present paper reported a novel ionic liquid dispersive liquid-phase microextraction coupled with GC-MS for determination of dicofol and its three degradation products in several environmental water samples. The developed DLPME is very simple, fast, efficient and inexpensive for sample pretreatment, it reduces the exposure danger to the toxic solvent used in the conventional extraction, increases the stability of extraction without suspending related to single drop microextraction, largely decreases the salting-out and its effect on the following analysis due to low water-solubility of the ionic liquid [D(*i*-C_8)IM][PF_6] and easily avoids the degradation of the pesticide during the sample preparation step because of no long heating process. Therefore, the proposed method can be widely applied to the determination of trace pesticides in various complex samples such as water, soil and plant, etc.

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