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Research Article

Determination of insecticides in water using *in situ* halide exchange reaction-assisted ionic liquid dispersive liquid–liquid microextraction followed by high-performance liquid chromatography

A dispersive liquid–liquid microextraction (DLLME) method using *in situ* halide exchange reaction to form ionic liquid (IL) extraction phase was developed to determine four insecticides (i.e. methoxyfenozide, tetrachlorvinphos, thiamethoxam, and diafenthiuron) in water samples. The preconcentration procedure, followed by high-performance liquid chromatography and variable wavelength detectors (VWD), enabled the formation of the immiscible IL extraction phase; the insecticides were transferred into the IL phase simultaneously, which enhanced the efficiency and sufficiency, greatly shortening the operation time. The experimental parameters affecting the extraction efficiency including volume of extraction IL, extraction and centrifugation times, volume of the sample solution and exchanging reagent, and addition of organic solvent and salt were investigated and optimized. Under optimized conditions, the extractions yielded recoveries of the target analytes from 82 to 102%. The calibration curves were linear, and the correlation coefficient ranged from 0.9990 to 0.9999 under the concentration levels of 5–200 µg/L. The relative standard deviation ($n = 6$) was 2.9–4.6%. The limits of detection (LODs) for the four insecticides were between 0.98 and 2.54 µg/L.

Keywords: Dispersive liquid–liquid microextraction / Insecticides / *In situ* halide exchange reaction / Ionic liquid
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1 Introduction

Methoxyfenozide, tetrachlorvinphos, thiamethoxam, and diafenthiuron are insecticides widely used in agricultural

activities because of their effective ability to control pests and acarid. Insecticides can enter soil and water systems in different ways. They can be traced in the surface water, in the soil, and among organisms. It is a threat to aquatic organisms when these four insecticides enter the water system. However, few studies have focused on the pretreatment and analysis of the insecticides in aqueous systems. For that reason developing methods that apply to the residue analysis of the insecticides in water samples is necessary.

Owing to the low concentration and complex environmental matrices, most of the detection of insecticides in environmental samples requires preconcentration prior to instrumental analysis, such as high-performance liquid chromatography (HPLC) or gas chromatography (GC). Therefore, many pretreatment methods have been developed for the enrichment of the analytes. Liquid–liquid extraction (LLE) is a classic sample preparation approach widely used in environmental sample pretreatments [1, 2]. Solid-phase extraction (SPE) is a common alternative method in sample preparation [3–6]. However, the extraction or elution procedure often requires a large amount of toxic organic solvent, which is

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Abbreviations: [C6MIM]Cl, 1-hexyl-3-methylimidazolium chloride; DLLME, dispersive liquid–liquid microextraction; EF, enrichment factor; HF-LPME, hollow-fiber liquid-phase microextraction; HMIM-NTf₂, 1-hexyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide; IL-DLLME, ionic liquid-based dispersive liquid–liquid microextraction; IL-LPME, ionic liquid-based dispersive liquid-phase microextraction; LiNTf₂, lithium bis[(trifluoromethane)sulfonyl]imide; LLE, liquid–liquid extraction; LPME, liquid-phase microextraction; RTILs, room temperature ionic liquids; USA-IL-DLPME, ultrasound-assisted ionic liquid dispersive liquid-phase microextraction

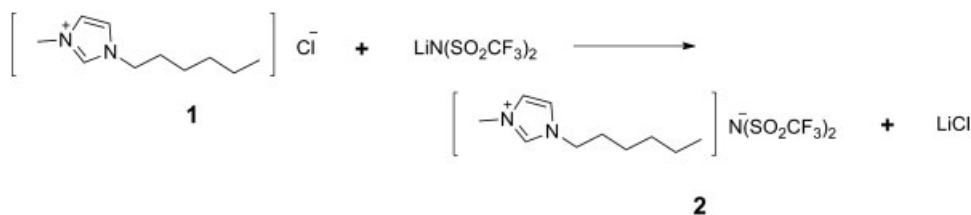
hazardous to the operators and to the environment. Recently, several microextraction (ME) approaches, which aim at miniaturizing the procedures, consuming less solvent and less time, and so on, have been established for the analysis of environmental samples. For example, different types of solid-phase microextraction (SPME) [7–10] and liquid-phase microextraction (LPME) have been developed as alternative techniques to the classical LLE and SPE.

Compared with other MEs, the LPME technique is better due to its advantages: fast and simple operation, low cost, low consumption of sample and solvent, and swiftness. Novel sample preconcentration methods have been established based on LPME. Single-drop microextraction (SDME) [11, 12] and hollow-fiber LPME (HF-LPME) [13] are two techniques that were developed earlier. Although these two techniques have been applied successfully to determine different kinds of pesticide analytes [14–18], their disadvantages, such as the instability of the organic drop or long extraction time, low sensitivity, and low repeatability, should not be ignored. After single-drop microextraction and HF-LPME, dispersive liquid–liquid microextraction (DLLME) was introduced by Rezaee et al. in 2006 [19]. This technique was based on a ternary component solvent system. In DLLME, a mixture of an extraction solvent (hydrophobic) and a disperser solvent (hydrophilic) is quickly injected into an aqueous solution, forming a turbid cloudy solution. Infinite amounts of fine droplets guarantee the huge contact area between the aqueous and hydrophobic phases. The analytes are easily transferred into the extraction solvent. DLLME exhibits a relatively high extraction efficiency, improved stability, and possible enhanced sensitivity and simplification of the extraction procedure compared with the conventional LPME. It has been successfully applied to the enrichment and sensitive determination of pesticides [20–22].

Room temperature ionic liquids (RTILs), which are composed of organic cations and various anions, are a class of non-molecular ionic solvents with low melting points ($<100^{\circ}\text{C}$). They can be regarded as green solvents [23, 24] because of their negligible vapor pressure, chemical and thermal stability, and good solubility in both organic and inorganic molecules. RTILs have been utilized in the field of analysis. A number of extraction methods are beginning to exploit alternative solvent systems containing ILs. Pretreatment procedures that use ILs combined with ME technique,

such as ionic liquid (IL)-based headspace microextraction [22, 25] and IL-based hollow-fiber LPME (IL-HF-LPME) [26, 27], have been introduced and developed in the recent years. The DLLME technique based on ILs has become increasingly popular as a successful model of LPME. This technique has been applied for the residue analysis of organophosphorus insecticides [28], heterocyclic insecticides [29], phthalate esters [30], polycyclic aromatic hydrocarbons [31–33], and other analytes. Aside from the typical IL-DLLME method, some modified methods have also been introduced and performed. The temperature-controlled IL dispersive LPME [34–38] has been used in determining different types of pesticides and has become an important branch of DLLME. To improve the extraction efficiency of DLLME, ultrasound is applied to help disperse the IL extraction solvent. The ultrasound-assisted ionic liquid dispersive LPME (USA-IL-DLPME) was established for the sensitive determination of aromatic amines [39]. However, an organic dispersive solvent is required, not only in typical DLLME but also in modified DLLME, to assist the extraction of solvents (ILs) to form fine droplets within the aqueous solution.

In the current study, *in situ* halide exchange reaction IL-DLLME and HPLC were applied to determine four insecticides in several water samples. *In situ* halide exchange reaction is based on ion exchange reagent (usually metal salts) to exchange the halide anion of the original IL to form a water immiscible IL (Scheme 1). A hydrophilic IL [C6MIM]Cl was added and dissolved first into the aqueous solution. By adding an ion-exchange reagent lithium bis-[(trifluoromethane)sulfonyl]imide (LiNTf₂) aqueous solution, an *in situ* halide exchange reaction proceeded to form a hydrophobic IL [C6MIM]-NTf₂. Ice-bath is used to enhance the extraction. Miscibility of the hydrophilic IL with the water enabled the formation of fine microdroplets of hydrophobic IL during the exchange process in water. Unlike in the temperature-controlled IL-DLLME, and USA-IL-DLPME, no organic dispersive solvent was used in this extraction procedure. The operation time was shorter, but the analyte enrichment factors were of high level. The halide exchange reaction and extraction were accomplished in a lesser time and with improved efficiency. Similar method without ice-bath has been evaluated for the determination of aromatic compounds [40]. The current research investigated on the application of the proposed method in insecticide analysis. The effects of



Scheme 1. Formation of hexyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide by *in situ* halide exchange reaction.

the volume of the extraction IL, the volume of the sample solution and exchanging reagent, the extraction and centrifugation times, and the addition of organic solvent and salt were investigated and optimized.

2 Materials and methods

2.1 Reagents

Methoxyfenozide, tetrachlorvinphos, thiamethoxam, and diafenthiuron were obtained from the Agricultural Environmental Protection Institution (Tianjin, China). Their structures are listed in Supporting Information Fig. S1. 1-Hexyl-3-methylimidazolium chloride [C6MIM]Cl was obtained from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). LiNTf₂ was purchased from Zhejiang Jiuzhou Pharmaceutical (Zhejiang, China). HPLC-grade methanol and acetonitrile were purchased from Dikma Technologies (CA, USA). Analytical-grade sodium chloride, potassium dihydrogen phosphate, and potassium hydroxide were obtained from the Beijing Chemical Factory (Beijing, China).

The stock standard solutions of the individual insecticides (2 mg/mL) were prepared by dissolving each standard in HPLC-grade methanol and stored in a refrigerator, protected from light. Mixed standard solutions were prepared in methanol. The working standard aqueous solutions were prepared daily by diluting the mixed standard solution in different concentrations using ultrapure water. Tap water, river water, and reservoir water 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 (Agl, USA) before use. The four insecticides are stable in neutral environment according to their chemical properties; acid or base could make some of them hydrolyze or degrade. Therefore, the pHs of all aqueous samples were adjusted at 7 using phosphate buffer.

2.2 Instrumentation

The chromatographic analysis was carried out on an Agilent 1200 HPLC system equipped with a variable wavelength detector (VWD) detector system (CA, USA). A high-pressure injection valve fitted with a 20-μL loop was used for the sample injection. The separation of the analytes was carried out on an Agilent Eclipse Plus C18 column (5 μm, 4.6 mm × 250 mm). Methanol/water (77:23, v/v) system was used as the mobile phase at a flow rate of 1 mL/min. The injection mode was partial-loop injection, injection volume was 10 μL, and the detection wavelength was 240 nm. ILs were weighed with a Mettler-Toledo AL104 electronic balance (Shanghai, China). Centrifugation was performed in a 52a centrifuge from the Baiyang Centrifuge Factory (Xin'an, China) at a rate of 3500 rpm. The filtration used 0.22-μm mixed cellulose membrane (Agl).

2.3 Extraction procedure

About 0.027 g of [C6MIM]Cl was added into a glass test tube with a conical bottom. Then, 8 mL of spiked water sample was placed into the tube. The IL completely dissolved into the water sample after shaking. A LiNTf₂ aqueous solution (1280 μL, 0.03 g/mL) was added into the tube. Subsequently, a turbid cloudy solution was formed. After gently 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 10 min. The upper aqueous phase was removed with a syringe. About 25 μL of RTIL was deposited at the bottom and was then taken out with an HPLC microsyringe. Of this amount, 10 μL was directly injected into the HPLC system for analysis.

3 Results and discussion

In the current study, some significant parameters in the extraction procedure were investigated in detail to obtain an optimum extraction procedure. Optimization includes the volume of the extract solvent, volume of the sample, amount of the ion-exchange reagent, salting-out effect, addition of organic dispersive solvent, centrifugation time, and extraction time. Enrichment factor (EF) and extraction recovery were taken as the parameters to evaluate performance. EF is defined as the analyte concentration ratio between the sedimented phase (IL phase) and the initial water sample. The equations of the two parameters are shown in Eqs. (1) and (2)

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

where EF, C_{sed} , and C_0 are the enrichment factor, analyte concentration in the sediment, and the initial analyte concentration in the aqueous sample before adding the LiNTf₂ aqueous solution, respectively. The C_{sed} was obtained from calibration graph of direct injection of insecticides standard solution in methanol.

Extraction recovery R% is computed as follows:

$$R\% = \frac{C_{sed} \cdot V_{sed}}{C_0 \cdot V_0} \times 100 = EF \times \frac{V_{sed}}{V_0} \times 100 \quad (2)$$

where V_{sed} is the volume of the sediment phase, and V_0 is the initial volume of the aqueous sample before adding the ion-exchange reagent. The recovery was used to represent the extraction recovery (ER) in figures for convenience.

Optimization was carried out using working solutions containing 20 μg/L of each insecticide. The injection volume was 10 μL in all cases.

3.1 Effect of the IL amount

In the IL-DLLME procedure, the amount of IL is an essential factor affecting EF and the extraction recovery. The effect was examined using different amounts of IL (i.e. 0.02,

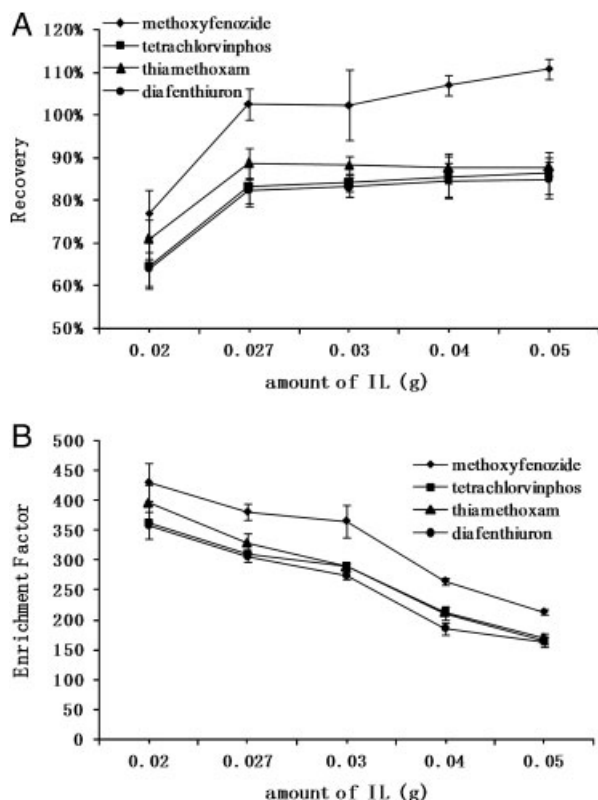


Figure 1. Effects of the IL amount on (A) recoveries and (B) enrichment factors of the four studied insecticides at a spiked concentration of 20 $\mu\text{g/L}$, sample volume of 8 mL, LiNTf₂ solution volume of 1280 μL (0.03 g/mL), injection volume of 10 μL , extraction time of 1 min, and centrifugation time of 10 min at 3500 rpm.

0.027, 0.03, 0.04, and 0.05 g) in an 8-mL water sample at a spiked level of 20 $\mu\text{g/L}$. Volumes of the sedimented phase ranged from 19 to 54 μL with the increase in initial [C6MIM]Cl. The curves of the final EF and recovery against the IL volume are shown in Fig. 1. Recovery increased intensively when the volume increased from 0.02 to 0.027 g. A slight difference was observed when the IL amount was added again. In contrast, EF showed a monotone decreasing trend. According to Eqs. (1) and (2) and previous studies [41], the amount of insecticides would increase with more IL were used, but the concentration of insecticides in sedimented IL would decrease. Consequently, 0.027 g of [C6MIM]Cl that gave the best compromise between recovery and EF was indicated for the extraction in further investigations.

3.2 Effect of the water sample volume

The volume of the water sample is another important factor affecting extraction efficiency. Although this factor and the IL volume overlap, it still has value for study. The volume of the water sample seriously affected the volume of sedimen-

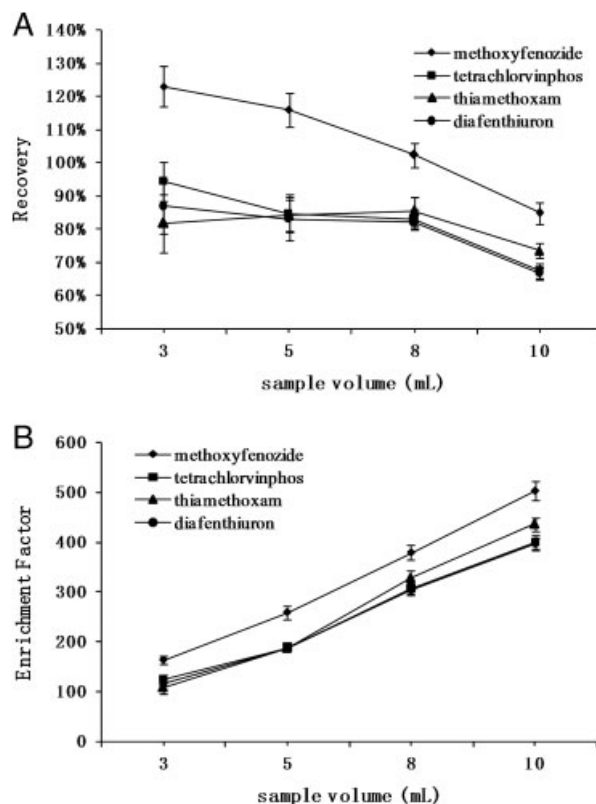


Figure 2. Effects of the sample volume on the (A) recoveries and (B) enrichment factors of the four studied insecticides with HMIM-Cl amount of 0.027 g, LiNTf₂ solution volume of 1280 μL (0.03 g/mL), spiked concentration of 20 $\mu\text{g/L}$, injection volume of 10 μL , extraction time of 1 min, and centrifugation time of 10 min at 3500 rpm.

ted IL phase and the complexity of the operation. Water samples of 3, 5, 8, and 10 mL were used to evaluate and optimize this factor. Other factors were at optimum level. After centrifugation, 32, 28, 25, and 19 μL of the sedimented HMIM-NTf₂ (1-hexyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide) phase were obtained. Curves of EF and recovery versus the sample volume are plotted in Fig. 2. When the volume of water sample increased, more HMIM-NTf₂ would be dissolved in the water and the volume of extract would decrease. The increase of water sample also means more insecticides require to be extracted. These two points made the amount of methoxyfenozide decrease in sedimented IL; the recovery decreased consequently. Recovery of the rest of the insecticides was maintained at an acceptable level except when the 10 mL sample was used. EF showed a monotone increasing trend against the sample volume. This finding can be attributed to the increase in the concentration of the insecticides when the IL phase decreases. However, there were too many ILs dissolved in water when the 10-mL sample was used. The absolute quantity was not acceptable. Thus, the water sample at 8 mL was proven optimal for the *in situ* DLLME procedure. It will be used for further investigation.

3.3 Effect of salting-out

In organic-based ME procedures, the salting-out effect can promote the separation of the aqueous solution and the organic phase by lowering the solubility of the organic solvent in water (commonly used in LLE, solid-phase microextraction, and LPME). However, the results may be different in IL-based ME procedures. To investigate the effect, a series of experiments was performed by adding various amounts of NaCl to the sample from 5 to 20% w/v. Supporting Information Fig. S2 shows that the adding of salt leads to the results on the selected insecticides that the concentration of thiamethoxam and diafenthiuron in the sedimented phase decreased intensively and concentration of methoxyfenozide and tetrachlorvinphos decreased slightly. Therefore, the addition of salt resulted that recovery of thiamethoxam and diafenthiuron decreased and recovery of methoxyfenozide and tetrachlorvinphos decreased slightly; the EFs showed a monotone decreasing trend in each insecticide. Considering that the adding of the salts will decrease the recovery of insecticides, we decided to not to add salt to the sample in all subsequent experiments.

3.4 Effect of the amount of the ion-exchange reagent

The amount of ion-exchange reagent is another important factor affecting the extraction efficiency. The effect was investigated by varying the molar ratio of LiNTf₂ to [C6MIM]Cl from 1:1 to 3:1 (1280, 1920, 2560, 3840 μ L of 0.03 g/mL LiNTf₂ solution). As shown in Fig. 3, the recovery decreased and basically reached a constant level when excess LiNTf₂ was added for the extraction. This may be attributed to that the addition of LiNTf₂ increased the viscosity of the solution intensively, which may make it difficult for molecules to diffuse into the IL extraction phase. Although the addition of LiNTf₂ salt may result in a higher volume of

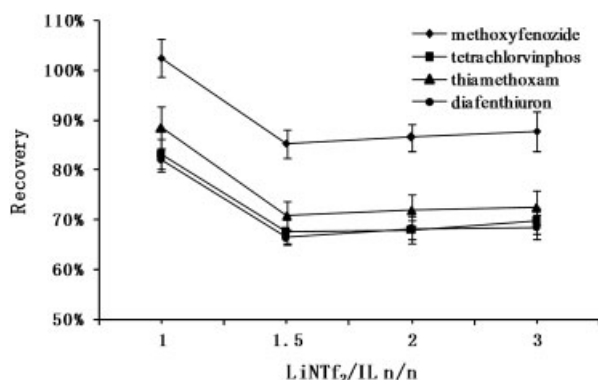


Figure 3. Effects of the amount of ion-exchange reagent on the recoveries of the four studied insecticides (1280, 1920, 2560, 3840 μ L of 0.03 g/mL LiNTf₂ solution) with HMIM-Cl amount of 0.027 g, spiked concentration of 20 μ g/L, sample volume of 8 mL, injection volume of 10 μ L, extraction time of 1 min, and centrifugation time of 10 min at 3500 rpm.

sedimented IL, it may prevent the analytes from transferring to the IL phase, leading to the obvious decrease in the peak area. Because adding excess LiNTf₂ aqueous solution increased the volume of the system, the EF did not display a normal trend valid for discussion. Based on these results, the molar ratio was fixed to 1:1 in succeeding investigations.

3.5 Effect of the addition of the dispersive solvent

In the DLLME procedure, the addition of the organic dispersive solvent was essential to obtain high extraction efficiency. Acetonitrile, methanol, and acetone were commonly used in recent studies [25, 27, 34, 36, 37]. Due to the similar function of methanol and acetonitrile, we took the latter to represent the organic disperser and discuss the dispersive effect. To investigate the effect, extractions that added 5–20% v/v of acetonitrile were performed. Acetonitrile were first added to the aqueous sample before injecting the LiNTf₂. As shown in Supporting Information Fig. S3, EF and the recovery of the insecticides tended to decrease with the increase in acetonitrile content. The decrease in the peak area of each analyte and the volume of sedimented IL phase led to this finding. Dispersive solvents are known to dissolve analytes and IL. Therefore, the addition of acetonitrile prevented the insecticides from transferring to the IL phase in the *in situ* DLLME procedure. Acetonitrile tends to compete with IL in extracting the analytes. Hence, extraction without adding organic dispersive solvents was appropriate for the subsequent experiments.

3.6 Effect of extraction and centrifugation time

Extraction time is defined as the interval between the formation of the turbid solution before ice-bath and the initiation of centrifugation. It is one of the essential factors in most IL-based ME procedures. In USA-DLPME and temperature-controlled DLPME, extraction time significantly affects the sufficiency and efficiency of the procedures [27, 32, 35]. In the present study, experiments were performed with extraction time from 1 to 30 min to obtain the optimum condition. According to the results (Supporting Information Fig. S4), recovery has little difference when more extraction time is consumed. *In situ* halide exchange reaction and the mass transfer of analytes can be concluded to concur simultaneously and very quickly. The [HMIM]⁺ cation and the NTf₂[−] anion reacted sufficiently and reached equilibrium rapidly. This reaction led to higher extraction efficiency and shorter operation time than in the classical IL-based DLLME procedures. Thus, only gently shaking and 1 min of ice-bath was required to obtain good performance in this procedure.

In the DLLME procedure, centrifugation was applied to separate the IL phase and the aqueous phase from the turbid mixed system. The parameter determined the amount of sedimented IL and absolute quantity of analytes

preconcentrated in IL (i.e. recovery). Extractions were performed with centrifugation at 3–10 min at a rate of 3500 rpm. Results indicate that when the centrifugation time was 3 min, IL was not completely precipitated at the bottom. The amount of IL could not support the acceptable recovery of insecticides. In the case of 5, 8, and 10 min, the EF and recovery had minimal difference, and they were maintained at a constant level. To separate the two phases more sufficiently, 10 min, not 8 min, was used as the optimal condition for the procedure.

3.7 Evaluation of method performance

The *in situ* IL-DLLME technique was evaluated according to linearity, LODs, precision, EFs, and recoveries under the optimized condition. Linearity was observed in the range of 5–200 µg/L for all insecticides with their correlation coefficient (R^2) ranging from 0.9990 to 0.9999. Precision was obtained by conducting six replicates of ultrapure water at a spiked level of 20 µg/L. The RSDs of the insecticides ranged from 2.9 to

4.6%. The LODs were in the range of 0.98–2.54 µg/L, which were determined as the analyte concentration that gave a signal-to-noise ratio of 3 as calculated by the instrument software. The validated results are shown in Table 1. Besides, extraction and determination of studied insecticides by the proposed method was compared with other methods [42–46] and the results are shown in Table 2. It can be seen that a small sample volume (8 mL) is adequate for the analysis owing to the high EFs (over 260), and simple operation makes the sample preparation easy and fast; only 1.5 min are needed before instrumental analysis.

3.8 Real water sample analysis

The applicability of *in situ* IL-DLLME was validated by performing extractions in four real water samples, including tap water, reservoir water, river water, and bottled mineral water, at a spiked level of 20 µg/L. The recoveries and RSDs are shown in Table 3. Results show that the recoveries were between 92 and 120% in the four performed water samples.

Table 1. Performance of the proposed method

Insecticide	Linear range (µg/L)	Linearity	R^2	LODs (µg/L)	RSD (%)	Enrichment factor	ER (%)
Methoxyfenozide	5–200	$Y = 2.42x + 6.50$	0.9997	2.54	4.1	326	102
Thiamethoxam	5–200	$Y = 4.04x + 16.84$	0.9990	1.40	3.7	264	83
Tetrachlorvinphos	5–200	$y = 5.70x + 14.31$	0.9999	0.98	4.6	280	88
Diafenthion	5–200	$y = 3.78x + 14.25$	0.9996	1.95	2.9	260	82

Table 2. Comparison of *in situ* DLLME-HPLC with other methods for determination of studied insecticides

Insecticides	Methods	Sample volume (mL)	Extraction time	LODs	Linear range	References
Tetrachlorvinphos	SPE-GC-MS	10	> 50 min	0.1 µg/L	0.5–500 µg/L	[42]
Thiamethoxam	SPE-HPLC-DAD	~5	–	3 µg/kg	6–100 µg/kg	[43]
Diafenthion	SPE-HPLC-UV	10	> 35 min	0.2 mg/kg	0.7–13 mg/kg	[44]
Tetrachlorvinphos	SBSE-GC-MS/MS ^{a)}	100	14 h	< 1 µg/kg	10–500 µg/kg	[45]
Tetrachlorvinphos	SPME-GC-MS ^{b)}	18	45 min	11 ng/L	25–250 ng/L	[46]
Methoxyfenozide, tetrachlorvinphos, thiamethoxam, and diafenthion	Represented method	8	1.5 min	0.98–2.54 µg/L	5–200 µg/L	Represented method

a) Stir bar sorptive extraction.

b) Solid-phase microextraction.

Table 3. Relative recoveries of the four insecticides in four real water samples at a spiked level of 20 µg/L

Analytes	Reservoir water		River water		Tap water		Bottled mineral water	
	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
Methoxyfenozide	120	2.8	120	9.2	103	5.1	102	5.1
Thiamethoxam	115	0.9	106	7.7	104	3.1	103	4.5
Tetrachlorvinphos	117	0.9	110	4.0	97	2.8	104	5.6
Diafenthion	119	0.7	111	2.4	92	3.7	103	3.7

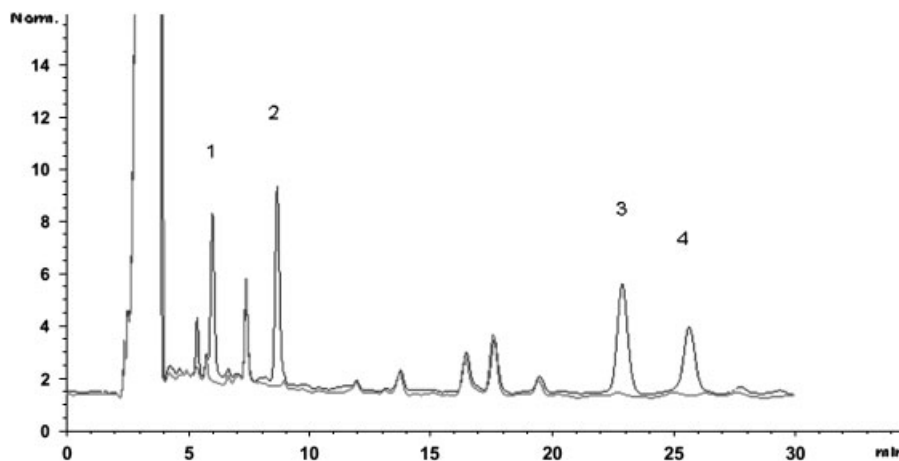


Figure 4. Chromatograms of the four studied insecticides in reservoir water sample preconcentrated using the proposed IL-DLLME method (blue = spiked with the four studied insecticides; red = blank) with HMIM-Cl mass of 0.027 g, LiNTf₂ solution volume of 1280 μ L (0.03 g/mL), sample volume of 8 mL, injection volume of 10 μ L, extraction time of 1 min, centrifugation time of 10 min, and sample concentration of 20 μ g/L.

The RSDs were between 0.7 and 9.2%. These results indicate that the matrix complexity had little effect on the *in situ* IL-DLLME method. Hence, the method has a wide range of applicability in the preconcentrations of insecticides in water samples. The typical chromatogram of the reservoir water samples is presented in Fig. 4.

4 Concluding remarks

In the present study, IL-DLLME, using *in situ* halide exchange reaction to form a turbid mixed system, was used to determine four insecticides in aqueous samples. The formation of the immiscible IL extract phase and transfer process of the analytes proceeded simultaneously. This simultaneity and the use of ice-bath enhanced the efficiency and sufficiency of the extraction procedure and greatly shortened the operation time. Furthermore, the extraction process was conducted without the use of an organic dispersive solvent. Only LiCl salt remained in the aqueous solution after extraction, making the pretreatment method more environment-friendly. The method was proven fast, simple, and sensitive. It is expected to be widely applied in screening target compounds for aqueous sample extraction in the future.

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The authors have declared no conflict of interest.

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