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In-situ metathesis reaction combined with ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction method for the determination of phenylurea pesticides in water samples

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ABSTRACT

A novel microextraction technique, named in-situ metathesis reaction, combined with ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction was developed for the determination of five phenylurea pesticides (i.e., diuron, diflubenzuron, teflubenzuron, flufenoxuron, and chlorfluazuron) in environmental water samples. In the developed method, 360 μL $LiNTf_2$ aqueous solution (0.162 g/mL) was added to the sample solution containing a small amount of $[C_6MIM]Cl$ (0.034 g) to form a water-immiscible ionic liquid, $[C_6MIM]NTf_2$, as extraction solution. The mixed solutions were placed in an ultrasonic water bath at 150 W for 4 min and centrifuged at 3500 rpm for 10 min to achieve phase separation. After centrifugation, fine droplets of the extractant phase settled to the bottom of the centrifuge tube and were directly injected into the high-performance liquid chromatography system for analysis. The quantity of $[C_6MIM]Cl$, the molar ratio of $[C_6MIM]Cl$ and $LiNTf_2$, ionic strength, ultrasound time, and centrifugation time, were optimized using a Plackett–Burman design. Significant factors obtained were optimized by employing a central composite design. The optimized technique provides good repeatability (RSD 2.4 to 3.5%), linearity (0.5 μg/L to 500 μg/L), low LODs (0.06 μg/L to 0.08 μg/L) and great enrichment factor (244 to 268). The developed method can be applied in routine analysis for the determining of phenylurea pesticides in environmental samples.

1. Introduction

Since the 1940s and the 1950s, phenylurea pesticides have been introduced as the "second generation of pesticides" [1]. After several decades of development, these herbicides are still used in large quantities for selective control of broad-leaf and grass weeds and as algicides in paints and coatings throughout the world [2]. However, the remaining low concentration residues of these compounds in soil can affect the groundwater system. Due to their residual activity and extensive use, phenylurea pesticides are frequently detected in surface water in concentrations exceeding the EU limit value of 0.1 μg/L for pesticides in drinking water [3–5]. Moreover, their prolonged usage may cause toxicological effects in the environment and serious hazards to human health through accumulation in the food chain at toxic levels [6,7]. Therefore, rapid, simple, sensitive, and "green" analytical methods are essential for monitoring these compounds in the environment.

Several analytical methods, such as micellar electrokinetic chromatography [8], immunoassay [9], gas chromatography [10], high-performance liquid chromatography (HPLC) [11], and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [12,13] have been developed to determine phenylurea pesticides in the environment and in plant samples. However, sample preconcentration and pretreatment procedures are often needed prior to instrumental analysis because most of the herbicides exist at trace levels in the environmental system. The most popular pretreatment techniques are solid-phase extraction [14,15] and liquid–liquid extraction [16]. Although these methods offer high reproducibility and high sample capacity, they are time-consuming and labor-intensive. Furthermore, a large amount of toxic organic solvents are used to elute the analyte in the analysis. Recently, research on sampling approaches focused on the development of efficient and economical techniques requiring less organic solvents. Such methods include solid-phase microextraction (SPME) [17], liquid-phase microextraction (LPME) [18], single-drop microextraction (SDME) [19], hollow fiber-based liquid-phase microextraction (HF-LPME) [20], and liquid–liquid microextraction (LLME) [21]. Compared with the older types of preconcentration and matrix isolation techniques, the more recent sampling methods are miniaturized, automated,

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consuming less organic solvent, and easy to conduct. However, several drawbacks still exist in the newer methods, such as declining performance with time and sample carry-over problems [22].

A new microextraction technique, namely, dispersive liquid–liquid microextraction (DLLME), was developed by Rezaee et al. [23] to enable sample extraction and preconcentration to be done in a single step. The basic principle of this method involves the dispersion of a non-water-miscible extraction solvent assisted with a water-miscible disperser solvent in an aqueous solution to generate a very high contact area between the aqueous phase and the extraction solvent. Based on the DLLME method, Zhou and co-workers performed the most preferred modifications, namely, ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME) [24]. In this modified method, emulsification of a microvolume of the extraction solvent in the aqueous sample solution is enhanced by the assistance of ultrasound energy, in which the analytes are more easily extracted into the fine droplets of the emulsified extraction phase. It was successfully applied for the preconcentration of pesticides [25], pollutants [26], drugs [27], antibiotic [28], and metal ions [29], etc.

In traditional UA-DLLME, the extraction and disperser solvents are usually toxic organic solvents, such as chlorobenzene, carbon tetrachloride, acetonitrile, and acetone. Consequently, the development of new extraction and disperser solvents is an important issue in DLLME evolution. Room temperature ionic liquids (ILs), noted as "green" solvents, are promising and suitable solvents that may be used in ionic liquids dispersive liquid–liquid microextraction (IL-DLLME) procedures. In fact, 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]) have been successfully applied as extraction phases for the determination of several insecticides in our previous studies [30,31]. Nevertheless, an organic dispersive solvent is also required both in typical DLLME and IL-DLLME to assist in the formation of fine droplets in the extraction solvent during dispersion. To further improve and expand the applications of the IL-DLLME method, Baghdadi et al. and Yao et al. introduced a modified IL-DLLME method involving in situ solvent formation [32,33]. In these methods, a small amount of a hydrophilic IL was dissolved completely in the aqueous sample solution, after the addition of an ion-pairing reagent, a cloudy solution with fine microdroplets of the water-immiscible IL (1-butyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide, [C_4MIM]-NTf_2) was formed (Scheme 1). The extraction and metathesis reaction are accomplished in one step and result in an efficient and excellent extraction performance. The advantages of in-situ metathesis reaction-assisted IL-DLLME are the exclusion of the requirement for utilizing a disperser solvent and the remarkable increase in surface area of the IL extraction solvent.

In the present study, in-situ metathesis reaction combined with UA-IL-DLLME method (in-situ UA-IL-DLLME) in conjunction with HPLC was introduced and applied to determine five phenylurea pesticides in several environmental samples. In the extraction procedure, a hydrosoluble IL (1-hexyl-3-methylimidazolium chloride, [C_6MIM]Cl) and an ion-exchange reagent (lithium bis[(trifluoromethane)sulfonyl]imide, $LiNTf_2$) were added to the aqueous solution in sequence and a novel hydrophobic IL (1-hexyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide [C_6MIM]-NTf_2) was formed as extraction solvent (Fig. 1). Furthermore, experimental factors, such as the quantity of [C_6MIM]Cl, the molar ratio of [C_6MIM]Cl and $LiNTf_2$, ionic strength, ultrasound time, and centrifugation time were assessed and optimized with the aid of response surface methodology based on statistical design of experiments (DOE). A Plackett–Burman (P–B) factorial design was developed to define the significant experimental variables, after which a central composite design (CCD) was employed in finding the optimum conditions for the in-situ UA-IL-DLLME.

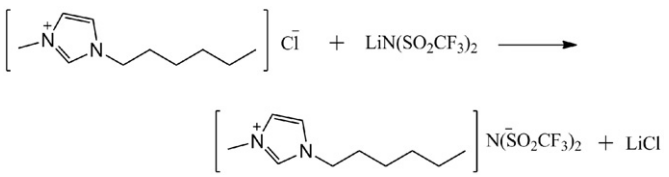

Fig. 1. Formation of [C_6MIM]-NTf_2 by in situ reaction.

2. Materials and methods

2.1. Reagents

Five phenylurea pesticides (diuron, diflubenzuron, teflubenzuron, flufenoxuron, and chlorfluazuron, 98% to 99% purity) and humic acid sodium salt were purchased from Aladdin Reagent Corporation (Shanghai, China). The methanol for spectroscopy was obtained from Dikma Limited (China) and the deionized water was purified from a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). Sodium chloride (analytical grade) was obtained from Beijing Chemical Reagent Company. 1-Hexyl-3-methylimidazolium chloride [C_6MIM]Cl was obtained from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). $LiNTf_2$ was purchased from Zhejiang Jiuzhou Pharmaceutical (Zhejiang, China).

The stock standard solutions of 3000 mg/L for each insecticide were dissolved in HPLC-grade methanol and stored at 4 °C in the refrigerator, protected from light. A mixed standard solution of 3 mg/L of each pesticide was prepared in methanol. Chromatograms and peak areas were obtained for quality control. Calculation of enrichment factors (EF) and recoveries (%*R*) was performed by injecting mixed standard solutions into the instrument system five times a day. The working standard aqueous solutions were prepared daily by serial dilution of the mixed standard solution with ultrapure water before extraction. River water, reservoir water and lake water collected from Xiaoyue River (Haidian, Beijing), Shangzhuang Reservoir (Haidian, Beijing), and Baiyang Lake (Baoding, Heibei), respectively were used for method validation. The environmental water samples were stored in glass containers at 4 °C and filtered through a 0.22 μm membrane (Agla, USA) prior to analysis. The soil sample was collected from the experimental field of our campus (China Agricultural University, Beijing). Twenty grams of soil were weighted into 200 mL distilled water and followed by ultrasound radiation for 10 min. After the centrifugation at 4000 rpm for 5 min, the supernatant was filtered through a 0.22 μm membrane and stored in glass containers at 4 °C.

2.2. Instruments

Chromatographic analysis was carried out on an Agilent 1200 HPLC system (California, USA) equipped with variable-wavelength detection (VWD). A high-pressure injection valve fitted with a 20 μL loop was used for the sample injection. The analytical column was Agilent Eclipse Plus C18 column (5 μm, 4.6 mm × 250 mm). A Baiyang 52A (Baoding, China) centrifuge was used for centrifugation. A KQ3200DE ultrasonic water bath (Kunshan Ultrasonic Instrument Co. Ltd., Kunshan, China) (150 W and 40 kHz) was applied to emulsify the IL. All glassware used in the experiments were washed with deionized water and acetone and then dried at room temperature.

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

Variables	Level	
	Low (−1)	High (+1)
(Q) the quantity of [C_6MIM]Cl (g)	0.028	0.034
(R) the molar ratio of [C_6MIM]Cl and LiNTf2	1:1	1:1.6
(I) ionic strength (NaCl concentration; w/v) (%)	0	8
(UT) ultrasound time (min)	0	4
(CT) centrifugation time (min)	5	20

2.3. Determination of target compounds by HPLC

The flow rate of mobile phase was kept at 1 mL/min. The mobile phase A and B were methanol and water, respectively. The gradient conditions are as follows: 0–10.5 min, 77% A; 10.5–15 min, 77–83% A; 15–30 min, 83% A; 30–35 min, 83–77% A. The temperature of column was controlled at 25 °C. The monitoring wavelength was 240 nm for diuron and 254 nm for diflubenzuron, teflubenzuron, flufenoxuron and chlorfluazuron.

2.4. In-situ UA-IL-DLLME procedure

A total of 0.034 g of [C_6MIM]Cl was added into a 15 mL glass conical centrifuge tube. A total of 10 mL of spiked water was placed into the tube. Then, the tube was shaken gently to disperse and dissolve the IL into the water sample. After quickly adding 360 μL $LiNTf_2$ of aqueous solution (0.162 g/mL) to the water sample, the mixed solution was vibrated using an ultrasonic water bath at 150 W for 4 min. A turbid cloudy solution was formed. The solution was then centrifuged at 3500 rpm for 10 min to achieve phase separation. The upper aqueous phase was removed with a syringe. The volume of the sedimented phase collected after removal of the aqueous phase was approximately 37 μL. From the remaining sedimented phase, 10 μL was aspirated into a 50 μL microsyringe (Agilent, USA) and directly injected into the HPLC system for analysis.

2.5. Optimization strategy

Several factors may affect extraction performance, such as the quantity of [C_6MIM]Cl, the molar ratio of [C_6MIM]Cl and $LiNTf_2$, and ultrasound time. P–B design was used for variable screening to define the significant experimental variables of in-situ UA-IL-DLLME for the extraction of phenylurea pesticides from the water samples. After determining the variables that mainly affect the extraction process, CCD was performed to derive the corresponding response surface equation and investigate the interaction among these variables. The experimental design matrix and data analysis were performed using MINITAB version 16 software.

2.6. Calculation of EF and R%

EF is the ratio between the analyte concentration in the sediment phase (C_{sed}) and the initial concentration in the analyte (C_0). To evaluate the effect of experimental conditions on the extraction efficiency, EF and *R*% were calculated according to the following equations:

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

$$R\% = \frac{C_{sed} V_{Sed}}{C_0 V_{aq}} \times 100 = Ef \times \frac{V_{sed}}{V_{aq}} \times 100 \quad (2)$$

where C_{sed} is obtained from the calibration graph of the direct injection of standard solution in methanol in the range of 0.1 mg/L to 12 mg/L and V_{sed} and V_{aq} are the volume of the sediment phase and the volume of the sample, respectively.

3. Results and discussion

In previous studies on IL-DLLME, single-dimensional searches were usually performed to optimize the parameters relevant to the extraction process. However, univariate searches are laborious, time-consuming, and proceed without considering the interactive effects of the test variables. To resolve these problems, P–B design and CCD, which combines screening and optimization, were used in the developed method to determine the optimal experimental conditions. These chemometric methods allow a simultaneous varation in whole factors and facilitate the quantification of linearity, correlation coefficients, and the interactive effects of the tested variables.

3.1. P–B design

P–B design was used to identify the factors having significant effects on the extraction efficiency among a large number of variables. In the present study, based on the literature and the previous experience of the current authors [32–34], the influence of five factors, namely, quantity of [C_6MIM]Cl, molar ratio of [C_6MIM]Cl and $LiNTf_2$, ionic strength, ultrasound time, and centrifugation time at two levels, were selected. To evaluate the main effects of these five factors, a matrix of the P–B design was developed consisting of 12 experiments and performed randomly to eliminate the effects of extraneous or nuisance variables. Their levels and the corresponding symbols are depicted in Table 1. Each of the trials was performed in triplicate and the mean of the corresponding recoveries were treated as responses. ANOVA test was used to determine the main effects using the *t*-test with a 95% probability [35].

The standardized effects for the P–B design are illustrated in a Pareto chart in Fig. 2. Given that all analytes showed similar results, only the chart of diflubenzuron was chosen as a representative example of the phenylurea pesticides. Variables significant at 5% level ($P < 0.05$) were considered to have greater influence on recoveries. Considering that the bar length was proportional to the significance in Fig. 2, the quantities of both [C_6MIM]Cl and ultrasound time were statistically important, and the quantity of [C_6MIM]Cl was the most significant factor. Centrifugation time was another significant variable next to ultrasound time. Moreover, as shown in Fig. 2, ionic strength and the molar ratio of [C_6MIM]Cl and $LiNTf_2$ revealed no

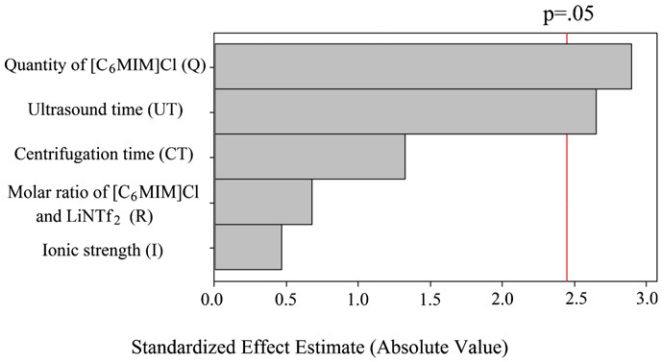

Fig. 2. Pareto chart of the main effects obtained from the Plackett–Burman design for phenylurea pesticides.

significant effect on extraction efficiency. Consequently, NaCl concentration was fixed at 0%, supporting our previous results. After the reaction equilibrium between [C_6MIM]Cl and $LiNTf_2$, an extra quantity of $LiNTf_2$ acts the role of NaCl in the present study. Therefore, to ensure 100% completion of in-situ metathesis reaction without unnecessary wastage, the molar ratio of [C_6MIM]Cl and $LiNTf_2$ was chosen at 1:1.2 as a compromise value. Finally, the factors considered in the next optimization step were the quantity of [C_6MIM]Cl, ultrasound time, and centrifugation time, while the molar ratio of [C_6MIM]Cl and $LiNTf_2$ was fixed at 1:1.2 with no salt addition.

3.2. CCD design

The next step in the present research was the optimization of the three factors chosen from the first screening design. Many experimental designs, such as Box–Wilson and CCD, can be found in the literature to perform the optimization. In the present study, a circumscribed CCD was employed and constructed using several superimposed designs. The CCD used consists of a factorial design ($2f$) augmented with star points ($2f$) and central points (C), where f is the number of variables to be optimized and C is the number of running times [36]. The star points are located at $+\alpha$ and $-\alpha$ from the center of the experimental domain. The value of α was selected as 1.682 to establish the rotatability condition of the CCD [37]. In the current study, f and C were set to 3 and 6, respectively, which meant that twenty experiments were required in this design and performed randomly, for the same reasons as mentioned for the P–B design.

The CCD allowed a quadratic model fit to the data and permitted the response to be modeled by a polynomial fit, which can be expressed in the following equation:

$$y = \beta_0 + \beta_1 Q + \beta_2 UT + \beta_3 CT + \beta_{12} Q \times UT + \beta_{13} Q \times CT + \beta_{23} QT \times UT + \beta_{11} Q^2 + \beta_{22} UT^2 + \beta_{33} CT^2$$

where β_0 is the intercept, β_1 to β_{33} represent the regression coefficients, and y is the response function (recovery, in the present study). The CCD model consists of three main effects, three two-factor interaction effects, and three curvature effects. This mathematical model was obtained by applying the Minitab program to perform the multivariate regression analysis on the chromatographic data for each design point. The results obtained from the CCD, namely, the parameter estimates, the Students t distribution, and p values, are listed in Table 2. The experimental data shows a good fit with second-order polynomial equations. The coefficient value of determination (R^2), which measures the amount of variation around the mean explained by the model, was 0.917. The adjusted R^2 is an adjustment for the number of terms in the respective model, and higher adjusted R^2 values indicate a better accordance with the experimental data and the fitted model. In the current work, the adjusted R^2 was 0.842.

Table 2
Analysis of variance (ANOVA) for central composite design.

Model term	Parameter estimate (coefficients)	t	P
Constant	88.250	131.954	0.000
Q	2.1368	4.815	0.001
UT	2.417	5.448	0.000
CT	−1.5367	−3.463	0.006
Q × UT	0.338	0.582	0.573
Q × CT	1.986	3.428	0.006
UT × CT	1.738	2.997	0.013
Q^2	−0.627	−1.452	0.177
UT^2	−1.387	−3.212	0.009
CT^2	−1.706	−3.949	0.003

Ultrasound time, with the smallest p-value, is obviously the most significant factor. The quantity of [C_6MIM]Cl is highly significant when compared with centrifugation time. Interaction effects between ultrasound time and centrifugation time and the quadratic term of UT^2 and CT^2 were also significant at 95% confidence level.

Fig. 3 depicts the response surface plots of the extraction recovery modeling for the quantity of [C_6MIM]Cl, ultrasound time, and centrifugation time. Based on the analysis and plots presented in Fig. 3A, while keeping the centrifugation time at 12.5 min, the recovery increased with prolonged ultrasound time

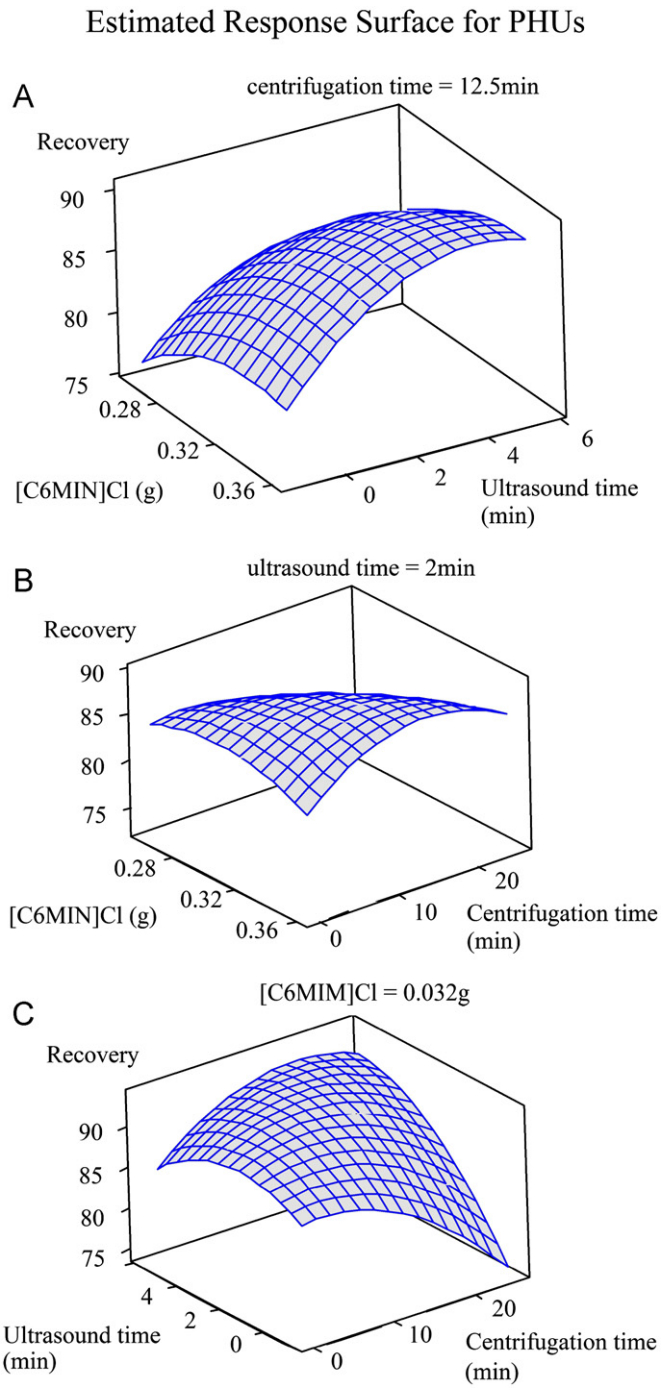

Fig. 3. Response surfaces for phenylurea pesticides using the central composite design obtained by plotting the: (A) quantity of [C_6MIM]Cl vs ultrasound time, (B) quantity of [C_6MIM]Cl vs centrifugation time, and (C) ultrasound time vs centrifugation time.

of as long as 4 min and the 0.34 g [C_6MIM]Cl provided the best extraction result. Indeed, sufficient ultrasound time accelerates the formation of a fine dispersive mixture and results in higher recoveries, whereas the extension of ultrasonic treatment time can also result in the loss of volatile analytes and extractants due to heat generation. Fig. 3B demonstrates a significant positive effect of centrifugation time from 0 min to 10 min and indicates that the short time allotted was not enough to break down the cloudy solution and to achieve total sediment phase. This figure also reveals that the recovery of large analytes increased when the quantity of [C_6MIM]Cl increased from 0.026 g to 0.034 g and then decreased with the continuous increase in the quantity of [C_6MIM]Cl. This finding may probably be due to a larger quantity of [C_6MIM]Cl forming an extra amount of [C_6MIM]NTf_2 after the in-situ metathesis reaction, which accelerated the settlement at the bottom of the tube. Fig. 3C shows the extraction recovery three-dimensional response surface yielded by the model for ultrasonic treatment time and centrifugation time, at a constant value of the quantity of [C_6MIM]Cl. Same as Fig. 3A and B, both the ultrasonic time and centrifugation time produced positive influences at early stage, however the prolong time with ultrasonication and centrifugation decreased the extraction of analytes. Overall, and according to the results of the optimization study, the optimum conditions selected for in-situ UA-IL-DLLME are as follows: 10.0 mL sample solution with no salt addition, 0.034 g of [C_6MIM]Cl and 360 μL $LiNTf_2$ aqueous solution (0.162 g/mL) for the extraction solvent, 4 min ultrasonic treatment time, and 10 min centrifugation at 3500 rpm.

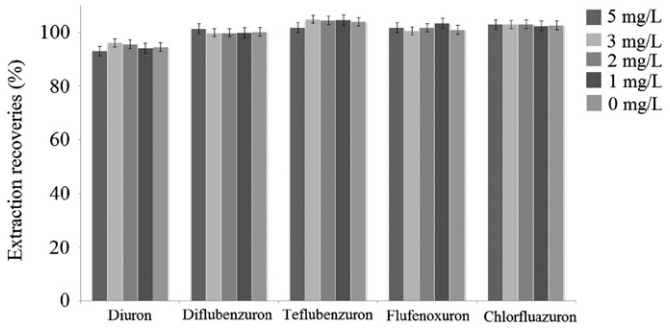

Fig. 4. The matrix effect on the extraction recoveries. Extraction conditions as follows: 10.0 mL sample solution with different humic acid concentrations (0–5 mg/L) and no salt addition, 0.034 g of [C_6MIM]Cl and 360 μL $LiNTf_2$ aqueous solution (0.162 g/mL) for the extraction solvent, 4 min ultrasonic treatment time, and 10 min centrifugation at 3500 rpm.

3.3. Martix effect

Compounds with high molecular mass can affect the ionization of lower mass molecules in complex matrices [38]. To study the influence of the matrix on the extraction procedures, standard solutions with humic acid (a principal component of humic substances, which exists in environmental matrices) were extracted under the optimized conditions. Fig. 4 showed the extraction recoveries were in the range of 93.1–106.1% for all the studied phenylurea pesticides at different humic acid concentrations (0–5 mg/L). These results indicated there was no significant matrix effect on the extraction efficiencies under in-situ metathesis reaction combined with ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction.

3.4. Evaluation of the method performance

Under the above-mentioned optimal conditions, quality factors including the limits of detection (LODs), limits of quantitation (LOQs), linear calibration ranges, regression equations, and other characteristics of the method were investigated to evaluate the analytical performance of the proposed method. Three replicate extractions were performed for each concentration level. The results are listed in Table 3. The linearity of the method was evaluated using water samples spiked with phenylurea pesticides at nine different concentrations ranging from 0.5 μg/L to 500 μg/L. The results showed good linearity within the concentration range studied for all the five phenylurea pesticides, with the correlation coefficients (r) ranging from 0.9996 to 0.9997. Satisfactory precisions (RSD: 2.4% to 3.5%, $n=6$) were calculated at a concentration level of 5 μg/L of each phenylurea pesticide. The limits of detection (LODs) and limits of quantitation (LOQs)

Table 3
The performance characteristics of the proposed method combined with HPLC-VWD.

Compound	Linearity equation	Linearity (μg/L)	r	RSD (%)	Enrichment factors	LOD (μg/L)	LOQ (μg/L)	Recovery (%)
Diuron	Y=11.486X-6.1887	0.5–500	0.9996	2.7	244	0.07	0.23	92.6
Diflubenzuron	Y=7.919X-14.535	0.5–500	0.9997	3.4	262	0.06	0.20	99.0
Teflubenzuron	Y=4.542X-8.739	0.5–500	0.9997	3.5	263	0.07	0.23	99.7
Flufenoxuron	Y=5.351X-14.099	0.5–500	0.9997	3.4	268	0.08	0.28	101.8
Chlorfluazuron	Y=7.484X-19.783	0.5–500	0.9996	2.4	265	0.06	0.18	100.6

RSD: relative standard deviation; LOD: limits of detection (S/N=3); LOQ: limits of quantitation (S/N=10).

Table 4
Comparison of in-situ UA-IL-DLLME with other methods for the determination of PHUs.

Method	Extraction time (min)	Extraction solvent	Analytical ranges	LODs	Ref.
PLE[a] LC-MS/MS	30	Dichloromethane/acetone	10–50 μg/kg	1.9–3.9 μg/kg	[12]
QuEChERS LC-MS/MS	20	Acetonitrile	5–500 μg/L	0.7–0.14 μg/L	[13]
SPME-LC	40	–	5–100 μg/L	0.7–4.6 μg/L	[39]
SPME-GC-NPD	60	–	1–250 μg/L	0.04–0.10 μg/L	[40]
FDME[b]-HPLC	25	1-dodecanol	0.01–10.0 mg/L	5–10 μg/L	[41]
DLLME-HPLC	4	Acetone	1–200 μg/L	0.01–0.5 μg/L	[42]
In-situ UA-IL-DLLME HPLC	4	[C_6MIM]NTf2	0.5–500 μg/L	0.05–0.08 μg/L	Present work

[a] Pressurised liquid extraction;
[b] Floated organic drop microextraction.

Table 5
Relative recovery and RSD values (five replicates) of PHUs studied in environmental samples.

Samples	PHUs	Added (μg/L)	Recovery ± RSD %	Samples	PHUs	Added (μg/L)	Recovery ± RSD %
River water (Xiaoyue River, Haidian, Beijing)	Diuron	1.5	94.1 ± 3.7	Reservoir water (Shangzhuang Reservoir, Haidian, Beijing)	Diuron	1.5	94.1 ± 2.9
		30	93.3 ± 2.8			30	94.6 ± 1.9
		300	92.7 ± 2.0			300	94.7 ± 2.1
	Diflubenzuron	1.5	96.7 ± 4.0		Diflubenzuron	1.5	97.6 ± 3.8
		30	100.2 ± 3.1			30	100.9 ± 2.2
		300	98.3 ± 3.5			300	100.5 ± 3.6
	Teflubenzuron	1.5	106.5 ± 3.5		Teflubenzuron	1.5	104.8 ± 4.1
		30	106.0 ± 3.5			30	104.3 ± 2.8
		300	103.5 ± 3.0			300	104.8 ± 2.9
	Flufenoxuron	1.5	104.6 ± 3.7		Flufenoxuron	1.5	103.3 ± 4.1
		30	101.0 ± 3.3			30	101.2 ± 3.1
		300	103.6 ± 2.4			300	103.5 ± 2.5
	Chlorfluazuron	1.5	100.0 ± 2.8		Chlorfluazuron	1.5	101.9 ± 3.7
		30	102.6 ± 3.3			30	103.3 ± 3.1
		300	104.6 ± 2.2			300	104.7 ± 2.7
Lake water (Baiyang Lake, Baoding, Heibei)	Diuron	1.5	94.2 ± 2.9	Field soil (China Agricultural University, Haidian, Beijing)	Diuron	1.5	95.1 ± 3.0
		30	94.6 ± 1.9			30	93.4 ± 2.9
		300	92.4 ± 1.7			300	92.4 ± 2.3
	Diflubenzuron	1.5	100.0 ± 4.9		Diflubenzuron	1.5	100.0 ± 4.1
		30	101.3 ± 3.0			30	100.9 ± 3.1
		300	104.8 ± 3.5			300	104.8 ± 2.6
	Teflubenzuron	1.5	106.5 ± 3.2		Teflubenzuron	1.5	104.8 ± 2.6
		30	104.3 ± 4.6			30	102.9 ± 3.2
		300	103.8 ± 2.9			300	103.8 ± 3.3
	Flufenoxuron	1.5	104.6 ± 2.4		Flufenoxuron	1.5	102.1 ± 3.7
		30	99.8 ± 4.2			30	102.2 ± 3.2
		300	103.6 ± 2.8			300	103.6 ± 3.3
	Chlorfluazuron	1.5	103.8 ± 2.6		Chlorfluazuron	1.5	100.0 ± 4.4
		30	103.3 ± 2.0			30	101.3 ± 2.1
		300	104.8 ± 2.3			300	104.8 ± 2.5

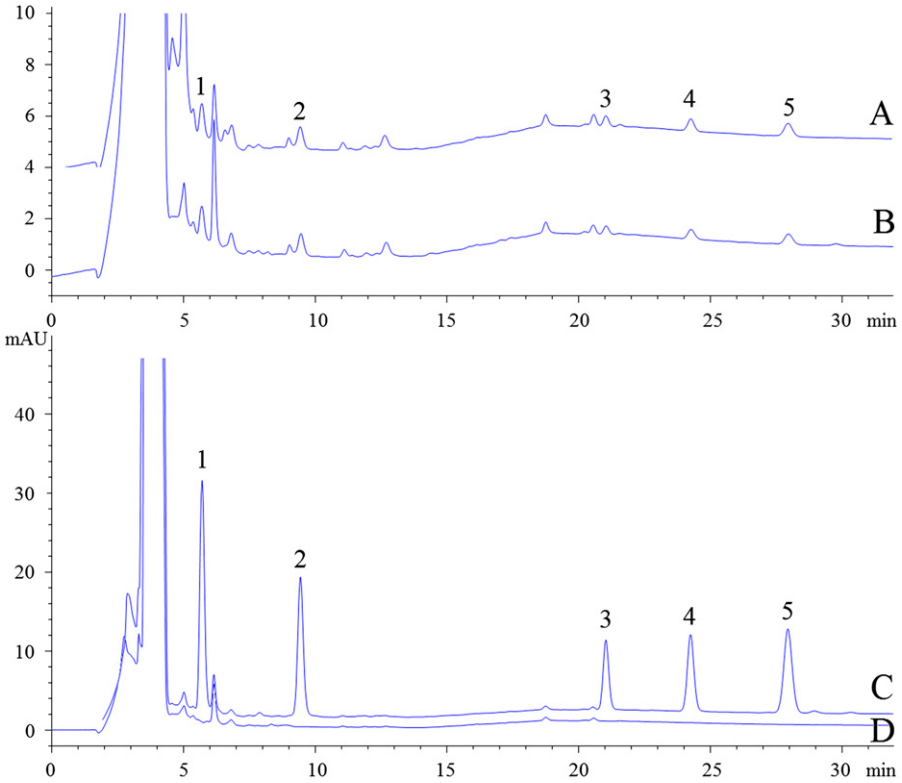

Fig. 5. The HPLC chromatogram of blank and spiked environmental samples under the optimal extraction condition. (A) and (B) were field soil and lake water samples spiked with 1.5 μg/L of each analyte. (C) and (D) were blank and spiked (30 μg/L) lake water samples. 1, Diuron; 2, diflubenzuron; 3, teflubenzuron; 4, flufenoxuro; 5, chlorfluazuron.

were calculated from pure water samples with spiked levels of 1.5 μg/L and a signal-to-noise ratio (S/N) of 3 and 10, respectively. The LODs ranged from 0.06 μg/L to 0.08 μg/L, and LOQs ranged from 0.18 μg/L to 0.23 μg/L. The extraction recoveries and enrichment factors of this method were high and ranged from 92.6% to 101.8% and 244 to 268, respectively.

A comparison with other relevant methods for the analysis of phenylurea pesticides (Table 4) shows that the proposed method exhibits better linearity and precision, adequately low detection limits, and low sample consumption. Moreover, the in-situ UA-IL-DLLME used $[C_6MIM]NTf_2$ instead of a volatile organic solvent as extraction solvent and did not require the utilization of a disperser organic solvent in the extraction procedures. Therefore, in-situ UA-IL-DLLME is, a simple, fast, easy to perform, and environmentally friendly technique.

3.5. Analysis of real samples

In-situ UA-IL-DLLME was applied in real environmental samples, including lake, reservoir, lake water and soil, for the determination of the five phenylurea pesticides to study the applicability of the proposed method. Results show that diuron, diflubenzuron, teflubenzuron, flufenoxuron, and chlorfluazuron residues were below the detectable level in all samples (as shown in Fig. 4(a)). For the recovery experiment, environmental samples were spiked with standards of the five phenylurea pesticides at concentrations of 1.5 μg/L, 30 μg/L and 300 μg/L, respectively. The results are summarized in Table 5 and the chromatogram of a lake water sample spiked with 1.5 μg/L and 30 μg/L of phenylurea pesticides was displayed in Fig. 4(c) and (b). As can be seen, relative recoveries were between 92.1% and 104.8%, and RSD values were between 1.8% and 4.9% for all the phenylurea pesticides in the spiked samples. These results indicate that the in-situ UA-IL-DLLME method is feasible for the determination of phenylurea pesticides in environmental samples Fig. 5

4. Conclusions

A novel microextraction technique based on ILs, named in-situ metathesis reaction, combined with UA-IL-DLLME was successfully applied in the determination of five phenylurea pesticides in environmental samples, whicn including lake, reservoir, lake water and soil. In the developed method, forming the immiscible IL extraction phase and the transfer of analytes proceeded simultaneously. The ultrasonication process promoted $[C_6MIM]NTf_2$ to disperse into the sample solution and accelerated the extraction. Optimization of the experimental variables was performed using response surface methodology and experimental designs. The resulting technique provides good repeatability, linearity range and enrichment factor for each compound, and matrix effects do not interfere with the quantification process. Therefore, the proposed method is recommended as a fast, simple, sensitive, and environment friendly sample preparation technique.

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