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A hydroxyl functionalized ionic liquid-based ultrasound-assisted surfactant-enhanced emulsification microextraction to determine herbicides in water samples

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Abstract: The paper described a hydroxyl functionalized ionic liquid (FIL), 1-hydroxyl hexyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl] imide [HHyMIMTf₂N] as extraction solvent for extraction and preconcentration of seven herbicides from water samples by ultrasound-assisted surfactant-enhanced emulsification microextraction combined with high-performance liquid chromatography. The FIL was dispersed into the aqueous samples by the assistance of ultrasound. Meanwhile, the addition of a surfactant as an emulsifier enhance the speed of the mass-transfer from aqueous samples to the FIL, on the other hand, it avoided FIL to stick to the centrifuge tube wall. The effects of experimental parameters, such as FIL volume, the type and concentration of surfactant, ultrasound extraction and centrifugation time, sample pH and salt addition were investigated and optimized for the method. Under the optimized conditions, the linear correlation coefficient ranged from 0.9904 to 0.9998 for concentration levels of 0.2–400 µg L⁻¹. The good recoveries (66.7–102.3%) of the target analytes were obtained from the water samples. The relative standard deviations (RSDs, n=6) ranged from 1.5–10.3%, and the limits of detection (LODs) for the herbicides were between 0.005 µg L⁻¹ and 0.084 µg L⁻¹. The applicability of the proposed method was evaluated by the extraction and determination of seven herbicides from several real water samples.

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Introduction

Separation and pre-concentration procedures are considered of great importance in pesticide analysis as they eliminate or minimize matrix effects and concomitants, lower the detection limit of detection techniques towards pesticides and their degradation. However, traditional liquid/liquid extraction (LLE) is still the most popular procedure in routine sample preparation. LLE is recognized as an effective method for screening tests of unknown pesticides [1, 2] because of its simplicity, robustness, minimal operator training, efficiency, and a wealth of available analytical data. However, this technique is time-consuming and requires large-volumes of organic hazardous solvents which cause environmental pollution, health hazards to laboratory personnel.

So the current trend is towards simplification and miniaturization of the sample-preparation steps and decrease in the quantities of organic solvents used. In this sense, a great effort has been made since the 1990s, when solid-phase microextraction (SPME) appeared as a miniaturized technique directly derived from solid phase extraction (SPE) [3]. From then, SPME has become one of the most valuable alternative techniques to classical approaches for sample preparation. Likewise, several liquid-phase microextraction (LPME) techniques have emerged from LLE as an attempt to miniaturize and improve this technique. Single-drop micro-extraction (SDME) [4-6], headspace SDME[7], continuous-flow microextraction(CFME)[8], hollow-fiber LPME (HF-LPME)[9], Dispersive liquid–liquid microextraction (DLLME)[10], solidification of floating organic drop liquid phase microextraction (SFODME)[11] procedures of micro-LLE have been applied in
The DLLME technology was first introduced by Assadi et al [10] and based on the dispersion of the extraction solvent into the aqueous sample. This method has many advantages including simplicity, rapidity, low sample volume, low cost, high recovery and high enrichment factors. DLLME has been widely used for the extraction of many pesticides, such as, organochlorine pesticides[18], organophosphorus pesticides[19], carbamate pesticides[20], triazine herbicides[21], phenylurea herbicides[22] and so on[23,24]. In DLLME technique, the extraction solvent should be hydrophobic and possess a higher density than water. Chlorinated solvents such as chlorobenzene, carbon tetrachloride and tetrachloroethylene are used as extractants. These solvents are highly toxic and produce environmental pollution, hazards to laboratory personnel. New extraction solvents shall be explored to replace these solvents in DLLME technology.

Room temperature ionic liquids (ILs) are a group of new organic salts consisting of a combination of organic cations and various anions that are liquids at room temperature. Most ILs are generally regarded as “green” solvents due to their unique physicochemical properties, such as broad liquid ranges, negligible vapor pressures, good thermal stabilities, and good extractabilities for various organic compounds and metal ions. By changing the combination of cation and anion, their miscibilities with water and organic solvents and the viscosities of ILs can be tuned [3, 25]. Their high density is also a favorable property as it facilitates phase separation. Consequently, ILs have been proposed as extraction solvent in DLLME, and successfully applied for determination of pesticides [26-31]. In the traditional IL-DLLME, the partitioning of analytes in organic extractants may decrease due to the increased solubility of analytes in the aqueous phase as larger volumes of dispersive solvent are used. In order to overcome this disadvantage, an
ultrasound-assisted emulsification microextraction (USAEME) has been developed by Garcia-Jares and co-workers [32], which based on the emulsification of a microvolume of organic extractant in an aqueous sample by ultrasound radiation without using any dispersive solvent. The result is a very efficient for analytical extraction. Very recently, Ionic liquid-based ultrasound-assisted emulsification microextraction [IL-USAEME] has been successfully applied to the analysis of some pesticides [33-35], however, the extraction time in USAEME is usually significantly longer than that needed in conventional DLLME.

Lately, a new sample pre-treatment method called ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) [36-38] was developed with which the analysis time was greatly shortened. It is well known that surfactants are amphiphilic molecules which contain both hydrophobic and hydrophilic groups. Therefore, they can be readily dissolved in both organic phase and water phase. Surfactant could serve as an emulsifier to enhance the dispersion of the water-immiscible phase into the aqueous phase and accelerate the formation of fine droplets from the extraction solvent in an aqueous sample solution under ultrasound radiations, thus decreasing the extraction time. We found that surfactant used in IL-based ultrasound-assisted emulsification microextraction (IL-USAEME) technique, acted as an emulsifier not only to enhance the speed of the mass-transfer from aqueous samples to the IL, but also to avoid IL to stick to the centrifuge tube wall. After extraction, two phases can be readily separated by centrifugation.

Presently, the most popular ILs used as extraction solvent in IL-based microextraction techniques for determination of pesticides is 1-alkyl-3-methylimidazolium hexafluorophosphate ([RMIMPF6] [26-31, 33, 34], which can extract most nonpolar or low polar compounds. In this study, we introduced a functional hydroxyl group into the structure of ILs, synthesized from
1-hydroxylhexyl-3-methy-limidazolium bis [(trifluoromethyl) sulfonyl] imide ([HHyMIMTf₂N]),
and investigated its extraction efficiency to seven polar herbicides.

This paper, for the first time, reported the use of [HHyMIMTf₂N] as a solvent for extraction
and preconcentration polar herbicides with UASEME, (named FIL-UASEME). The study aimed
to assess the suitability of [HHyMIMTf₂N] in extraction and preconcentration of polar herbicides
in water samples. The effect of different experimental parameters on the extraction efficiency
were also examined and optimized.

2. Experimental

2.1 Reagents and materials

The herbicide standards (simazine, atrazine, isoproturon, linuron, diuron, ametryn,
prometryne) were purchased from Agricultural Environmental Protection Institution in Tianjin,
China, with the purities from 98% to 99%. Stock standard solutions of individual herbicides
(1,000 mg L⁻¹) were prepared in methanol and stored in freezer. The working solutions of mixed
standard were obtained by diluting with methanol before use. N-methylimidazole and
6-chloro-1-hexanol was obtained from Shanghai Cheng Jie Chemical Co. Ltd. HPLC grade
methanol was obtained from DIMA Technology Inc. (Richmond Hill, USA). Deionized water was
obtained from the Milli-Q SP Reagent Water system (Millipore, Bedford, MA, USA). All the
solvents and solutions were filtered through a 0.22-µm cellulose filter before use. Analytical-grade
sodium chloride and acetic acid were obtained from Beijing Chemical and Reagent Ltd., Beijing,
China. Chemically pure surfactants (NP, Triton X-100, Tween80 and Tween 20) were purchased
from Beijing Chemical Reagents Company (Beijing, China).

Tap water, river water, and field water used for the method validation were collected in glass
bottles from Beijing, Tianjin, Hebei provinces, respectively, which was stored at 4°C and filtered through a 0.45 µm membrane before analysis.

2.2 Instrumentation

An Agilent 1100 series high-performance liquid chromatography (Agilent, Palo Alto, CA, USA) consists of a binary high-pressure pump for mobile-phase delivery, DAD detector, an automatic sample injector and Agilent ChemStation. The herbicides were separated by an Extend C\textsubscript{18} column (150 mm×4.6 mm×5 µm; Zorbax, Agilent). The analysis was conducted in gradient modes at ambient temperature at a flow rate of 1 ml min\textsuperscript{-1}. The initial mobile phase was held for 1 min with 40 % methanol, increased to 60 % methanol from 1 to 10 min, then to 80 % methanol between 10 and 20 min, and decreased to 40 % methanol from 20 to 25 min. The system was re-equilibrated at the initial conditions (40 % methanol) from 25 to 30 min. The injection volume was 20µL. The analytes were monitored at 230 nm.

A 40 kHz and 75W ultrasonic water bath with temperature control (Shenhua Co., China) was applied to emulsify the IL. The 1H-NMR spectra of [HHyMIM\textsubscript{2}N\textsubscript{2}] were measured using DPX-400 (Bruker, Optics Inc., Ettlingen, Germany). An RJ-TDL-40B low-speed desktop centrifuge was purchased from Jiangsu Ruijiang Co., Ltd., China. ILs was weighted with an AUY220 electronic balance (Shimadzu, Kyoto, Japan)

2.3 Synthesis of [HHyMIM\textsubscript{2}N\textsubscript{2}]

0.11 mol 6-chloro-1- hexanol was slowly added into three -necked flask filled with 0.1 mol N-methylimidazole and 50ml ethyl acetate from dropping funnel at 50°C. The mixture was maintained for 48 hour after dripping is finished. The resulting viscous liquid was slowly cooled to room temperature, followed by heating the solution under vacuum at 80°C to remove the
remaining solvent and reagent, washed three times with sulfuric (30 mL), and then was dried under vacuum at 70° for 24 h.

Preparation of [HHyMIMTf₂N] was then carried out by mixing equimolar amount of [HHyMIMCl] and Lithium bis(trifluoromethanesulphonyl)imide [LiTf₂N] in 100mL water. The mixture was continuously stirred for 5 h at room temperature. After that, the ionic liquid phase in the bottom of the beaker was washed with water until chloride ion was not detected using a silver nitrate test. The obtained [HHyMIMTf₂N] was concentrated in a rotary evaporator at 80°, and then was dried under vacuum at 80° for 24 h.

¹H-NMR (D₂O, 500 MHz), δH: 1.21~1.34 (m, 4H), 1.38~1.43 (m, 2H), 1.75~1.81 (m, 2H), 3.37(t, 2H), 3.84(s, 3H), 4.16(t, 2H), 4.34(s, 1H), 7.68(s, 1H), 7.75(s, 1H), 9.07(s, 1H).

2.4 FIL7 based ultrasound-assisted emulsification microextraction procedure

100µL IL was added into a 10 mL glass centrifuge tube, then 5.0 mL spiked water (the pH value was adjusted by adding 0.5 M HAC or 0.5 M NaOH ) and 20 µL of 10 mmol L⁻¹ Tween 80 as emulsifier and anti-sticking agent (the concentration of Tween 80 in sample solution was 0.04 mmol L⁻¹) were added into the centrifuge tube with screw cap. The centrifuge tube was immersed in an ultrasonic bath for 2 min at 30 °C ± 2 °C. During ultrasonication, the FIL was dispersed into the aqueous solution as fine droplets and a homogenous solution was achieved. Afterwards, the test tubes were cooled in an ice water for 5 minutes. In this step, the herbicides were extracted into fine droplets of [HHyMIMTf₂N]. The resulting cloudy solution was centrifuged at 3800 rpm for 5 min to disrupt the emulsions and separate the FIL from the aqueous phase, while the IL precipitated at the bottom of the conical test tube (25±1 µL). The upper aqueous phase was removed with a syringe, and the residue was dissolved in 200 µL methanol. 20 µL of the residue
sample was injected into the HPLC system for analysis.

3. Results and discussion

3.1. Optimization of extraction conditions

In order to reach optimum experimental conditions for quantitative extraction of herbicides via FIL-USAEME, the influence of different parameters such as functionalized ionic liquid amounts, type and concentration of surfactant, sonication time, salt concentration and sample pH were investigated. In the experiment, 5.0 mL of double-distilled water spiked with 20.0 µgL⁻¹ each of the seven herbicides was used to study the extraction performance under different experimental conditions. All the experiments were performed in six replicates and the means of the results were used for optimization.

The enrichment factor (EF) and extraction recovery (ER) values were used to evaluate the extraction efficiency. The enrichment factor was defined as the ratio between the concentration of analyte in the sediment phase \(C_{sed}\) and the initial concentration of analyte \(C_0\) in the aqueous sample.

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

The extraction recovery was defined as the percentage of the total amount of analyte \(n_0\) extracted to the sediment phase \(n_{sed}\)

\[
ER = \frac{n_{sed}}{n_0} \times 100 = \frac{C_{sed}V_{sed}}{C_0V_{aq}} \times 100 = EF \times \frac{V_{sed}}{V_{aq}} \times 100 \quad (2)
\]

where \(C_{sed}\) is calculated from the calibration curve of the herbicide standard solution in the extraction, and \(V_{sed}\) and \(V_{aq}\) are the volumes of the sediment phase and the aqueous sample, respectively.

3.2 Compare with FIL [HHyMIMTf2N] and traditional IL
[HMIMPF6], [OMIMPF6] and [BMIMTf2N] were most employed in DLLME. To evaluate the advantage of [HHyMIMTf2N] extraction efficiency in UASEME, it would be significantive to provide the comparison with three traditional IL. The solubility of [HMIMPF6], [OMIMPF6], [BMIMTf2N], [HHyMIMTf2N] in water were 7.5 g L⁻¹, 2.0 g L⁻¹, 8 g L⁻¹ [33], 12 g L⁻¹ respectively.

Various volumes of the ionic liquids, 70 µL [HMIMPF6], 45 µL [C8mim][PF6], 75µL [BMIMTf2N], 100 µL [HHyMIMTf2N] according to their solubility, were added to 5 mL aqueous solutions containing 20 µg L⁻¹ herbicides. The volume of the sedimented phase was near 25 µL for the four ionic liquids added. As can be seen in Fig 1, the extraction efficiencies of using [HHyMIMTf2N] as extraction solvent were higher than that using the other three traditional IL as extraction solvent, although the volume of [HHyMIMTf2N] required was higher than that of the other traditional IL to achieve a constant volume of sedimented phase. Because of the structure of the hydroxyl groups of [HHyMIMTf2N], hydrogen bonding or electrostatic interactions between the ionic liquid and the target analytes may be present and also contribute to the extraction efficiency. Basing on the results, it is evident that [HHyMIMTf2N] is superior to the other three traditional IL in enrichment polar herbicides from water samples and the volume of reagent consumed.
The volume of extraction solvent has been found to significantly influence the extraction performance in liquid phase microextraction. To examine the effect of FIL volume on the extraction efficiency, different volumes of FIL ranging from 50 to 140µL were subjected to the same procedure. The results are shown in Fig. 2. The peak area increased with the increase of volume of IL from 50 to 100µL, and decreased above 100µL. Therefore, 100µL FIL was selected in the further experiments.

3.3 Compare with Effect of type and concentration of surfactant

Due to the high viscosity of ILs, some of the IL-phase sticks to the wall of the centrifuge tube after centrifugation. In order to overcome this problem, non-ionic surfactants were added to the sample solutions. In the presence of non-ionic surfactants, molecules of the surfactant surrounded the fine droplets of IL during phase separation. Hence, interactions of IL with the wall of the centrifuge tube decreased and consequently, the IL-phase hardly stuck to the wall of the centrifuge tube. At the same time, the surfactant serves as an emulsifier, accelerating the IL into the aqueous samples under ultrasound radiation. Therefore, in this method, the surfactant functions as not only emulsifier, but also anti-sticking agent. Four types of non-ionic surfactant (Triton X-100, NP-10, Tween20, Tween80) were investigated. The relevant data were given in Fig. 3. The results showed that the highest value was obtained for Tween 80.
The surfactant concentration was also a critical parameter which could affect extraction efficiency. Four different surfactant (Tween 80) concentrations at 0, 0.02, 0.03, 0.04, 0.05 mmol L$^{-1}$ were investigated. Based on the obtained data, we can conclude that the peak area of analytes reached a plateau at 0.04 mmol L$^{-1}$ and decreased after that. This can be explained by the fact that when the surfactant concentration was lower than the CMC (0.038 mmol L$^{-1}$), the increase of free surfactant monomer generated an improved dispersion procedure; meanwhile, when the surfactant concentration was higher than the CMC, a fraction of the analytes can be incorporated into the micelles, leading to a low extraction efficiency. Based on the results, the concentration of Tween80 was selected at 0.04 mmol L$^{-1}$.

3.4 Effect of temperature and sonication time

Temperature has a significant effect on the solubility and mass transfer. The effect of different temperatures on the extraction was evaluated from 20 to 60 °C. The extraction recoveries increased with the increase of temperature from 20 to 30 °C, and decreased above 30 °C. The extraction temperature of 30 °C was chosen in this study.

FIL-UASEME is a type of equilibrium extraction, and the optimal extraction efficiency is obtained once the equilibrium is established. Hence, the effect of sonication time on extraction efficiency was investigated 1 min, 2 min, 3 min, 5 min. The experimental results indicated that the highest extraction efficiencies were obtained at 2 min of sonication time, and at further increase of sonication time, the peak area of analytes decreased. It is likely that the surface area between the extraction solvent (HHyMIMNTf$_2$) vesicle and the aqueous phase is large after IL was dispersed.
by ultrasonic agitation to form vesicles. Thus, the transfer of the analytes from aqueous phase to extraction phase was fast. Therefore, FIL-UASEME is a kind of fast equilibrium extraction procedure with a short extraction time. 2 min was chosen for the dispersive procedure.

3.5 Effect of centrifugation time

Centrifugation was applied to separate FIL containing the analytes from the aqueous phase. The ionic liquid phase was settled at the bottom of the tested tube during this process. The centrifugation time was studied in the range 2–15 min at 3800 rpm. The results indicated that the peak area increased from 2 to 5 min while a slight decrease was observed after 5 min. Longer centrifugation times may have resulted in overheating inside the centrifuge chamber, causing some of the FIL phase to re-dissolve back to the aqueous phase and a loss of sensitivity. Therefore, 5 min was chosen as optimum.

3.6 Effect of salt concentration

The salting-out effect has been frequently used in LLE and LPME. Generally, the addition of salt can decrease the solubility of analytes in the aqueous phase and promote the transfer of the analytes to the organic phase. Conversely, ultrasound waves can be absorbed and dispersed in a viscous medium as calorific energy; thus, the cavitation process can be withdrawn reducing the emulsification phenomenon [39]. In this experiment, the effect of the concentrations of NaCl (0, 2%, 4%, 6%, 8%, 10%, w/v) on extraction efficiency of target analytes was investigated. The results showed that when sodium chloride was added, the extraction efficiency of the analytes decreased. Therefore, no sodium chloride was added to the samples for further studies.

3.7 Effect of sample pH

The pH of the sample solution is an important factor that affects the composition of the
analytes. The analytes were present in different forms in the water samples when the pH was varied. The instantaneous form of the analytes affected the extraction efficiency of the target analytes. In the present study, the extractions were performed under different pH conditions ranging from pH 3 to 8. The pH value was adjusted by adding 0.5 M HAC or 0.5 M NaOH in spiked water. The results are shown in Fig. 4. The recovery of all analytes was best at pH 7. Therefore, pH 7 was selected as the optimum pH value.

3.8 Comparison of IL-UASEME with ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME)

In the present work, for comparison, an IL-DLLME method was also explored for herbicides determination according to our group work [40]. Methanol (0, 0.3 mL, 0.5 mL, 0.8 mL, 1 mL, as dispersive solvent) containing 100µL [HHyMIMTf$_2$N] (as extraction solvent) was rapidly injected into water sample by using a 1.0-mL syringe and then sonicated for 1min. The test tubes were cooled in an ice water for 5 min. The cloudy solution was centrifuged for 5min at 3800rmp and the dispersed fine droplets of FIL were settled to the bottom of centrifuge tube. The sediment phase was collected and diluted with 200 µL methanol. Subsequently, the extract was injected into the HPLC system for analysis. The extraction efficiency decreased slightly with an increasing amount of methanol, but to compare with surfactant as emulsifier, methanol was not beneficial in improving of extraction efficiency. We concluded that IL-UASEME is preferred to IL-DLLME for target herbicides determination in the present work.

3.9 Validation of the method

Under optimal conditions, the detection limits, precisions, and linear ranges were important parameters to evaluate the proposed method FIL-UASEME. Linear ranges were investigated over...
a concentration range of 0.2–40 µg L$^{-1}$ with respect prometryne, 1–200 µg L$^{-1}$ for simazine, atrazine and ametryn, 2–400 µg L$^{-1}$ for isoproturon, diuron and linuron, respectively with samples spiked at six different concentrations with six replicates. The precisions were obtained by six replicates extractions of deionized water at spiked level 20 µg L$^{-1}$. The results are shown in Table 1.

All the selected herbicides exhibited good linearity with correlation coefficients ranged from 0.9804 to 0.9998. Satisfactory precisions (RSD: 6.12%–9.37%, n=6) were presented. The limit of detections (LODs) was calculated from deionized water samples at spiked level of 2 µg L$^{-1}$ with a signal-to-noise (S/N) of 3. The LODs ranged from 0.005 to 0.084 µg L$^{-1}$.

3.10 Application of real samples

The proposed FIL–UASEME–HPLC method was applied to the preconcentration and determination of target herbicides in three real samples. In order to validate the accuracy of the FIL–UASEME procedure, each sample was spiked with target species at three different concentration levels of 2, 10, 20 and 50 µg L$^{-1}$ and analyzed in six replicates using the proposed method. Fig. 5 shows the typical chromatogram of target herbicides after FIL–UASEME in spiked water. No analytes were detected in these three samples. The analytes recoveries of samples are shown in Table 2. The recoveries are in the ranges of 65.5–98.8%, 65.9–102.7% and 64.7–101.2% for tap water, river water and field water sample, respectively. The recoveries of analytes did not vary significantly at different spiking concentration levels of 2, 10, 20 and 50 µg L$^{-1}$. The values of recoveries have confirmed the validity of the proposed method. The obtained RSD for three real samples were fairly low at different spiking concentrations. These results indicated that the matrices of the real samples had little effect on the proposed FIL–UASEME method for preconcentration of herbicides from water samples.
4. Conclusion

In this study, a rapid, sensitive, efficient, and environmentally friendly method based on FIL-UASEME coupled with HPLC was developed to determine herbicides in water samples. In the FIL-UASEME technique, a hydroxyl functionalized [HHyMIMTf$_2$N] ionic liquid was synthesized and used as extraction solvent and surfactant tween80 was used as an emulsifier to enhance the speed of the mass-transfer, decrease the extraction time, and to avoid FIL to stick to the centrifuge tube wall. This proposed FIL-UASEME method was compared to other methods in Table 3. Compared with SPE, SPME and HF-LPME methods, which required longer extraction time, the other DLLME methods used chlorinated solvents as extractants. These solvents are highly toxic and produce environmental pollution. The extraction time for the FIL-UASEME procedure was very short, and the ionic liquid is used as the extraction solvent, which is safe and environmental friendly. The extraction system can be employed for fast and effective separation and preconcentration of herbicides. Results demonstrated that the proposed FIL–UASEME–HPLC method provided good reproducibility, wide linear range and short analysis time, especially improved extraction efficiency for some polar herbicides in comparing with traditional IL. The performance of method in the extraction and determination of herbicides from tap water, river water and field water sample were excellent showing a recovery of 64.7–102.7% and RSD of Fig.5. The chromatograms of a blank river and spiked at 2μg L$^{-1}$ (1) simazine (2) atrazine, (3) isoproturon (4) diuron (5) ametryn (6) linuron (7) prometryne
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Reference


Table 1 Analytical performance data for the herbicides by the FIL-UASEME technique

<table>
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<tr>
<th>Herbicide</th>
<th>LR (µg L(^{-1}))</th>
<th>Linearity</th>
<th>R(^2)</th>
<th>RSD(%)</th>
<th>Recovery(%)</th>
<th>LOD (µg·L(^{-1}))</th>
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<td>simazine</td>
<td>1-200</td>
<td>(y=2603x-3.288)</td>
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<td>8.34</td>
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<td>0.9998</td>
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<td>86.3</td>
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Table 2

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Table 3 Comparsion of the FIL-UASEME with other methods

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<tr>
<th>Method</th>
<th>LOD (µgL⁻¹)</th>
<th>Recovery(%)</th>
<th>RSD (%)</th>
<th>Extraction time (min)</th>
<th>Extraction solvent and volume</th>
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<tr>
<td>SPE-HPLC-UV [41]</td>
<td>4.9-16.7</td>
<td>76.0-97.4</td>
<td>0.2-3.1</td>
<td>80</td>
<td>methanol, 11.5mL</td>
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<td>SPME-GC-MS [42]</td>
<td>0.002-0.017</td>
<td>1.8-7.9</td>
<td>60</td>
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<td>SPE-HPLC-DAD(MS)[43]</td>
<td>0.021-0.042</td>
<td>70-90</td>
<td>5-20</td>
<td>60</td>
<td>acetonitrile, 8mL</td>
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<td>SPME-HPLC-UV[44]</td>
<td>0.5-5.1</td>
<td>85-113</td>
<td>0.4-5.9</td>
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<td>HF-LPME-HPLC-UV[45]</td>
<td>0.1-1.0</td>
<td>64-97</td>
<td>1.7-2.1</td>
<td>180</td>
<td>1-octanol , 12µL</td>
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<td>DLLME-HPLC-PAD [46]</td>
<td>0.01-0.5</td>
<td>88-109</td>
<td>3.0-7.8</td>
<td>&lt;1</td>
<td>carbon disulfide and toluene, 148µL</td>
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<td>DLLME-GC-MS [21]</td>
<td>0.021-0.12</td>
<td>24.2-115.6</td>
<td>1.36-8.67</td>
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<td>SA-DLLME-HPLC-UV [47]</td>
<td>0.0023- 0.018</td>
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<td>1.3-8.3</td>
<td>0.5</td>
<td>chloroform,73µL</td>
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<td>p-DLLME-HPLC-UV [48]</td>
<td>0.10-0.28</td>
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<td>0.4-5.9</td>
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<td>dichloromethane, 60µL</td>
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<td>FIL-UASEME (this method)</td>
<td>0.005-0.084</td>
<td>64.7-102.7</td>
<td>1.5-10.3</td>
<td>2</td>
<td>[H3NIM(Tf2N)], 100µL</td>
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Figure captions

Fig.1. Compare with FIL [H-HyMIMTf₂N] and traditional IL. Concentration of the standard mixed solution: 20 µgL⁻¹; sample volume: 5 mL; surfactant (Tween 80) concentration: 0.03mmolL⁻¹; extraction time: 3min; room temperature; error bars represent the standard deviation of the mean enrichment factors for n = 3 replications.

Fig.2. Selection volume of extraction solvent [H-HyMIMTf₂N]. Concentration of the standard mixed solution: 20 µgL⁻¹; sample volume: 5 mL; surfactant (Tween 80) concentration: 0.03mmolL⁻¹; extraction time: 3min; room temperature; error bars represent the standard deviation of the mean enrichment factors for n = 3 replications.

Fig.3. Selection of surfactant. Concentration of the standard mixed solution: 20 µgL⁻¹; sample volume: 5 mL; extractant volume: 100µL; extraction time: 3min; surfactant (Tween 80) concentration: 0.03mmolL⁻¹; room temperature; error bars represent the standard deviation of the mean enrichment factors for n = 3 replications.

Fig.4. Effect of sample pH . Concentration of the standard mixed solution: 20 µgL⁻¹; sample volume: 5 mL; extractant volume: 100µL; surfactant: Tween 80 0.04mmolL⁻¹; extraction time: 2min; temperature 30°C; error bars represent the standard deviation of the mean enrichment factors for n = 3 replications.

Fig.5. The chromatograms of a blank river and spiked at 2 µgL⁻¹. (1) simazine (2) atrazine, (3) isoproturon (4) diuron (5) ametryn (6) linuron (7) prometryne
Fig 1

![Bar chart showing peak areas for different pesticides. The chart includes peaks for simazine, atrazine, isoproturon, diuron, ametryn, linuron, and prometryne. The x-axis represents different ILs: [HMIMPF6], [OMIMPF6], [BMIIMTf2N], [HHyMIMTf2N]. The y-axis represents peak area ranging from 0 to 250.](image-url)
Fig 2

![Graph showing the relationship between Peak Area and Volume of IL (µL). The graph includes lines for simazine, atrazine, isoproturon, diuron, ametryn, linuron, and prometryne.](image-url)
Fig3

$\text{Peak area}$

- simazine
- atrazine
- isoproturon
- diuron
- ametryn
- linuron
- prometryne

NP-10  Triton X-100  Tween 20  Tween80
Fig4

![Graph showing the peak area vs. pH for various pesticides](image)

- Simazine
- Atrazine
- Isopturon
- Diuron
- Ametryn
- Linuron
- Prometryne
Fig 5

[Graph showing peaks labeled 1 to 7 with "blank" and "spiked" annotations.]