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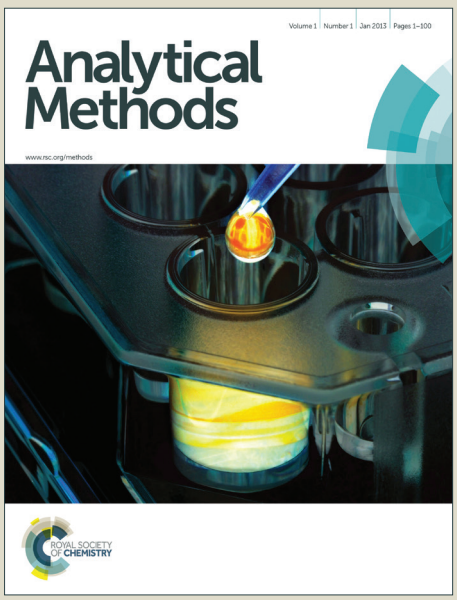

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ARTICLE TYPE

Determination of sulfonylurea herbicides in soil by ionic liquid-based ultrasonic-assisted extraction high-performance liquid chromatography

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A high-performance liquid chromatography method for determination of sulfonylurea herbicides in soil has been developed. Prior to the determination, the sample preparation was performed by ionic liquid-based ultrasonic-assisted extraction (IL-based UAE). The dried powder of soil was mixed with a room temperature ionic liquid [C_6MIM][BF_4] to form a suspension, and then the ultrasonic extraction was performed in a water bath at ambient temperature. The chromatographic separation was performed on a C18 chromatographic column with gradient elution mode. The method was validated by evaluating the repeatability, linearity, precision, applicability. The limits of detection ranged from 7.7 ng g^{-1} to 11.3 ng $g^{-1}$and the limits of quantification were between 25.6 ng g^{-1} and 37.6 ng g^{-1}.The calibration curves showed good linear relationship (r>0.9990) in the concentration range of 50.0-25000 ng g^{-1} for nicosulfuron and 50.0-5000 ng g^{-1} for metsulfuron-methyl, bensulfuron-methyl and pyrazosulfuron-ethyl. The recoveries range from 81.1 to 100.1% with relative standard deviations lower than 7.44%. The IL-based UAE is free of volatile organic solvent, and consumes less sample, time and solvent, compared with regular ultrasonic and Soxhlet extractions. There was no obvious difference in the extration recoveries of sulfonylurea herbicides obtained by the three methods.

1 Introduction

Herbicides are often used in the agricultural fields and widely distributed in the environment due to the great consumption every year. However, they are often in the center of health and safety consideration due to their toxicity or potential adverse influence on ecosystem. Sulfonylurea herbicides are systemic weed control products and frequently used to weed among crops, such as corn, wheat, barley, canola, and potato. They have been used at low application rates for weed control in cereals because of their high herbicidal activity and low mammalian toxicity [1]. They represent potential environment pollutants in soil and water. Because the concentrations of sulfonylurea residues are low, improvement of limit of detection is necessary in the environmental analysis. Different chromatographic methods for the determination of sulfonylurea herbicides, including HPLC [2-5], capillary electrophoresis (CE) [6-8], gas chromatography (GC) [9], and high-performance liquid chromatography-tandem quadrupole mass spectrometry (HPLC-MS/MS) [10-12], have been established. However, most of the methods reported are time consuming and need complicated pretreatment steps to obtain effective isolation of analyte from the matrices, especially from complicated matrices, such as soil. As the analytical technique has rapidly developed, there has been a trend towards less (organic) solvent consumption, shorter extraction time and miniaturization in the extraction. The application of ionic liquids (ILs) during the separation step is due to their properties, such as high thermal and chemical stability, negligible vapor pressure, low toxicity and good electrical conductivity [13]. ILs are melting salts which consist of organic cations and organic or inorganic anions. Those ILs, whose melting points are lower than 25□, are known as Room Temperature Inoic Liquids (RTILs) and their

particular properties (i.e. polarity, viscosity, solvent miscibility or hydrophobicity) can be changed by means of simple chemical modifications[14-15]. Currently, the RTILs have attracted increasing interest and are used more and more as attractive alternatives to environmentally unfriendly solvents in sample preparation [16-21].

In this study, IL-based ultrasonic-assisted extraction (UAE) was developed for the extraction of sulfonylurea herbicides from soil, based on the advantages of ionic liquid and ultrasound. The presented method greatly simplified the sample pretreatment step, and the results were satisfactory. For the comparison, the UE and Soxhlet extraction (SE) were also applied. To evaluate the new extraction method, the SE is often adopted as a reference method.

2 Experimental

2.1 Reagents and apparatus

Nicosulfuron, metsulfuron-methyl, bensulfuron-methyl, and pyrzaosulfuron-ethyl were obtained from Chinese Drug Biological Product Qualifying Institute (Beijing, China). The chemical structures of the analytes are shown in Fig. 1. The standard stock and working solutions were prepared in acetonitrile. Chromatographic grade acetonitrile was obtained from Fisher Scientific (Pittsburgh, Pennsylvania, USA). Ionic liquids (purity > 99%), including $[C_2MIM][BF_4]$, $[C_4MIM][BF_4]$, $[C_6MIM][BF_4]$, $[C_8MIM][BF_4]$, $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$, and $[C_8MIM][PF_6]$ were purchased from Cheng-Jie Chemical Co. LTD (Shanghai, China). Water was purified with a distillator (Rong-hua Co. LTD, Jiangsu, China) and filtered through a 0.45 μm membrane.

KQ-2200E ultrasonic generator(Kunshan, Jiangsu, China) and SH-36 Mixer(Zhenghui, Shanghai, China) were used in the extraction step. RE-52 AA vacuum rotatory evaporator (Yarong, Shanghai, Chian) was employed.

2.2 Sample preparation procedure

The surface layer of soils (20 cm) were taken from Haerbin, Heilongjiang Province (Northeast of China) and used as the samples. The soils were first dried in the atmosphere, ground and screened through a 60-mesh sieve to remove stones, plant roots and other large particles. The soils then were triturated with a pulverizer, passed through a 120 mesh stainless steel sieve and stored in a desiccator. The spiked soil samples were prepared by adding appropriate volume of working standard solution of the pesticides in the samples. To ensure the standard solution to be well distributed, a reasonable amount of methanol was added to moisten the sample and careful agitation was performed followed by an air-drying for 24 h at ambient temperature before sample analysis. 150 μL of [$[C_6MIM][BF_4]$ were placed in 2 mL centrifuge tube. 0.100 g 120 mesh sample was added into the tube. The ionic liquid and the sample were mixed with a rapid mixer. Then the tubes containing the homogeneous mixture were placed in the water bath of ultrasonic generator, whose power was 400 W. The extraction was performed for 5 min at 20 ℃. The suspensions were filtered through a 0.45 μm membrane filter. The resulting solution was referred to as the sample solution and was introduced into an auto sampler vial for HPLC injection.

2.3 HPLC analysis

Chromatography separation was carried out on a Agilent 1290 series chromatograph equipped with Agilent HPLC XDB-C18 column (4.6 mm ×250 mm, 5 μm particle size). The mobile phase was composed of water (phase A) and acetonitrile (phase B). The flow rate of the mobile phase was 1.0 mL min^{-1} and 5.0 μL of sample solution was injected in each case. The gradient program was as follows: 0–12 min, phase B was from10%(V/V) to 40%(V/V); 12–20 min, phase B was from 40%(V/V) to 45%(V/V) ; 20–30 min, phase B was from 45%(V/V) to 65%(V/V) ; then phase B was returned to 10%(V/V) in 5.0 min. Finally, 10%(V/V) phase B was maintained for 0.8 min for reconditioning the column prior to the next injection. The absorbance was measured at a wavelength of 239 nm. The temperature of the column was controlled at 30 ℃.

2.4 Ultrasonic and Soxhlet extraction

1.000 g of sample powder was put into an Erlenmeyer flask equipped with a stopper, in which 50 mL of acetonitrile was added accurately. The flask was weighed afterwards. Then

ultrasonic extraction was performed for 40 min. After cooling, the flask was weighed again, and the loss weight was made up with acetonitrile. After shaken up, the resulting solution was filtered with a 0.45 μm membrane filter and the resulting solution was referred to as the sample solution.

1.000 g of sample powder was placed in a thimble-holder of the Soxhlet extractor, and 150 mL acetonitrile was added into the distilling flask of Soxhlet extractor. The extraction was carried out for 4 h. Then the extract was evaporated to dryness under reduced pressure at 40 ℃. The residue was dissolved in 1.0 mL of acetonitrile. After filtration with a 0.45 μm membrane filter, the resulting solution was referred to as the sample solution.

3 Results and discussion

3.1 Sample preparation optimization

The effects of experimental parameters, such as type and amount of the IL, sample amount, extraction power and time on the extraction recoveries of the analytes were investigated. All the experiments were performed in triplicate.

3.1.1 Selection of IL

The structures of ILs have significant influence on their physicochemical properties, which might greatly affect the extraction recoveries of the target analytes. For the ILs with the same anion, the viscosity of the ILs increases with increase of the alkyl chain length, and the polarity of the ILs increases with increase of the alkyl chain length from ethyl to hexyl and decreases from hexyl to octyl. For the ILs with the same cation, the viscosity of ILs with $[PF_6]^-$ is higher than that with $[BF_4]^-$, and the the polarity of ILs with $[PF_6]^-$ is stronger than that with $[BF_4]^-$. In order to evaluate the performance of the ILs, seven kinds of ILs, including, $[C_2MIM][BF_4]$, $[C_4MIM][BF_4]$, $[C_6MIM][BF_4]$, $[C_8MIM][BF_4]$, $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$, and $[C_8MIM][PF_6]$ were used as the extraction solvents to treat the sample, The experimental results are shown in Fig 2. When the anion was $[BF_4]^-$, with increase of alkyl chain length the recoveries of the target analytes first increased and then slightly decreased. When the anion was $[PF_6]^-$, with increase of alkyl chain length the recoveries of the target analytes first increased and then dramatically increased. When the extraction solvents were $[C_6MIM][BF_4]$, and $[C_8MIM][PF_6]$, the recoveries were almost the same. This phenomenon could be attributed to the fact that the polarity of the two ILs and sulfonylurea herbicides is nearly the same. Considerating of the high viscosity of $[C_8MIM][PF_6]$, $[C_6MIM][BF_4]$was used in the following experiments.

3.1.2 Selection of UAE power and time

The effect of extraction power and time were also investigated. As shown in Fig. 3. The recoveries dramatically increased with the increase of extraction power ranging from 160 to 280W，and slowly increased when the extraction power was higher than 280W, So the extraction power was chosen as 400 W.

The effect of the extraction time, including 2, 5, 10, 15 and 20 min, on the recoveries was investigated. The results shown in Fig.4 indicate that the optimal irradiation time is 5 min.

3.1.3 Selection of sample amount

The effect of sample amount on recoveries of target analytes was investigated. When the amount of the sample powder was 100 mg, the recoveries of the analytes were the highest. Therefore, 100 mg of sample powder was used in the work.

3.1.4 Selection of volume of $[C_6MIM][BF_4]$

The effect of ILs volume on recoveries of the target analytes was investigated. Experimental results showed that there was little change of the extraction recoveries when the volume of $[C_6MIM][BF_4]$ increased from 150 to 500 μL. Besides, the volume lower than 150 μL made collection of IL difficult. So 150 μL of $[C_6MIM][BF_4]$ was used in this study.

3.2 Method validation

The newly developed method was validated. For validation of the analytical method, the selectivity, linearity, accuracy, precision, and limit of detection and quantification were discussed[22-27].

3.2.1 Selectivity

The target analytes were identified by comparing their retention times with those of the authentic standard analytes. Chromatograms of the blank sample, the standard solution and

the spiked sample are shown in Fig. 5. It can be seen from Fig. 5 that the retention times are 14.48 min for nicosulfuron, 16.59 min for metsulfuron, 22.79 min for bensulfuron-methyl, and 26.45 min for pyrazosulfuron-ethyl. There are not interference peaks at retention times of analytes, and the present method is specific to sulfonyluren herbicides[28].

3.2.2 *Linearity*

The standard solutions containing nicosulfuron, metsulfuron-methyl, bensulfuron-methyl and pyrazosulfuron-ethyl were prepared and diluted to appropriate concentrations for the construction of calibration curves. Six concentrations of each analyte were injected in triplicate, and then the calibration curve was constructed by plotting the peak area (A) versus the concentration (c) of each analyte. The regression equation, linear range, correlation coefficient, limit of detection (LOD), and limit of quantification (LOQ) are listed in (Table 1).

3.2.3 *Limits of Detection and Quantification*

To obtain the LOD and LOQ, the blank sample was analyzed 12 times and the standard deviations of the blank signals were obtained. The LODs were the concentration of analytes that can yield a signal-to-noise of 3. The LODs for nicosulfuron, metsulfuron-methyl, bensulfuron-methyl, and pyrazosulfuron-ethyl were 10.2, 11.3, 8.5 and 7.7 ng g^{-1}, respectively. The LOQs were the concentrations of analytes that can yield a signal-to-noise ratio of 10. The LOQs for nicosulfuron, metsulfuron-methyl, bensulfuron-methyl and pyrazosulfuron-ethyl were 34.0, 37.6, 28.3 and 25.6 ng g^{-1}, respectively.

3.2.4 *Applicability and Precision*

To evaluate the applicability and precision of the present method three soil samples (samples 1–3) obtained from different areas were analyzed. The results indicated that nicosulfuron, metsulfuron-methyl, bensulfuron-methyl and pyrazosulfuron-ethyl in three soil samples were not detectable. The spiked samples were analyzed. The results are showed in Table 2.

The precision of the present method was expressed as relative standard deviation (RSD). The intra-day precision was obtained by analyzing the samples five times in one day and the inter-day precision was obtained by analyzing the sample once each day over five consecutive days. The intra-day and inter-day RSDs for nicosulfuron, metsulfuron-methyl, bensulfuron-methyl and pyrazosulfuron-ethyl are 3.00-7.56% and 3.00- 7.93%, respectively. Therefore, the reproducibility of the present method was acceptable.

3.2.5 *Accuracy*

To evaluate the accuracy of the present method, spiked samples were analyzed (Table 3) and the analytical results obtained by different methods were compared (Table 4). The recoveries were from 81.1 to 100.1%. It can be seen that the recoveries are related to the kinds the analytes. Because $[C_6MIM][BF_4]$ has different capabilities to extract nicosulfuron, metsulfuron-methyl, bensulfuron-methyl, and pyrazosulfuron-ethyl, the recoveries of nicosulfuron and pyrazosulfuron-ethyl are slightly higher than those of metsulfuron-methyl, bensulfuron-methyl.

3.2.6 *Comparison of extraction methods*

In order to evaluate the performances of IL-based UAE, UE and SE were also applied. The results are shown in Table 4. From those results, it can be seen that there is little difference in recoveries obtained by the three methods. The results indicate that the accuracy of the present method is satisfactory. Compared with the conventional UE and SE, only a small amount of the solvent (0.15 mL) was used in the present method. The extraction time of the present method (5 min) was shorter than those of UE (40 min) and SE (240 min). Considering the expenditure of sample amount, time and extraction solvent, IL-based UAE should be a comparatively satisfactory method.

Conclusions

A green and effective method IL-based UAE has been developed for simultaneous extraction of nicosulfuron, metsulfuron-methyl, bensulfuron-methyl, and pyrazosulfuron-ethyl in soil. The calibration curves showed good linear relationship ($r > 0.9990$). The recoveries were between 81.1% and 100.1% with RSDs lower than 7.44 %. Compared with UE and SE, the present method expends less sample, extraction time and solvent. The present method should a promising prospect in the extraction of pesticides in soil.

Notes and references

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Figure captions

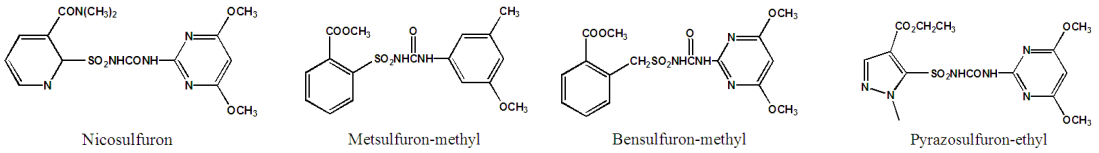
Fig. 1. Chemical structures of pesticide standards.

Fig.2. Effect of IL type, 1. $[C_2MIM][BF_4]$; 2. $[C_4MIM][BF_4]$; 3. $[C_6MIM][BF_4]$; 4. $[C_8MIM][BF_4]$; 5. $[C_4MIM][PF_6]$; 6. $[C_6MIM][PF_6]$; 7. $[C_8MIM][PF_6]$; Sample amount: 100 mg; volume of IL: 150 μL; ultrasonic power: 400 w; ultrasonic time: 5 min.

Fig. 3. Effect of ultrasonic power, Sample amount: 100 mg; volume of IL: 150 μL; ultrasonic power : 400 w; ultrasonic time: 5min.

Fig. 4. Effect of ultrasonic time, Sample amount: 100 mg; volume of IL: 150 μL; ultrasonic power: 400 w; ultrasonic time: 5 min.

Fig. 5. Chromatograms of blank sample (a), spiked sample (b) and standard solution (c), Peak 1. Nicosulfuron ; Peak 2. Metsulfuron-methyl ; Peak 3. Bensulfuron-methyl ; Peak 4. Pyrazosulfuron-ethyl



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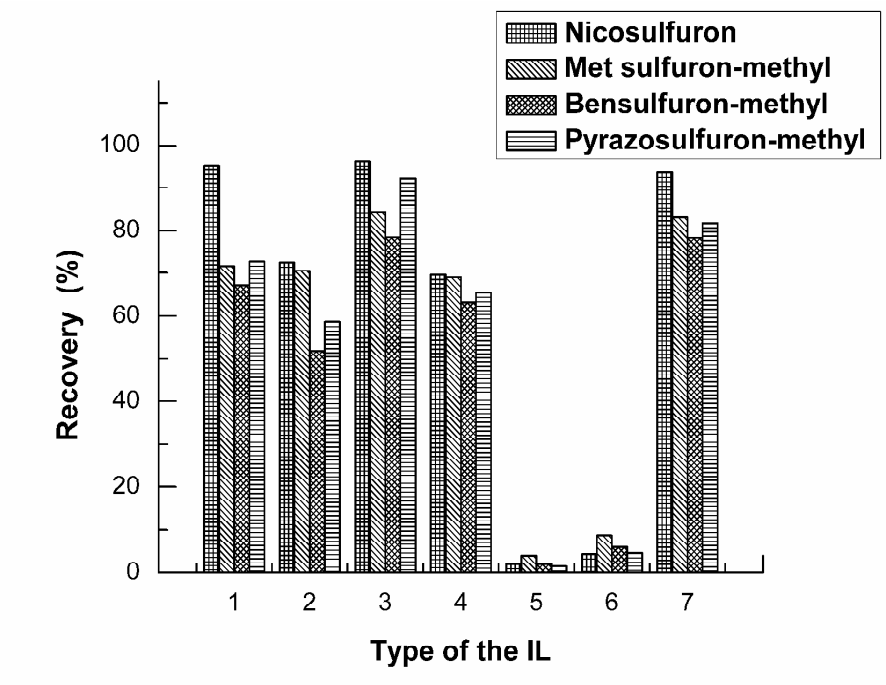

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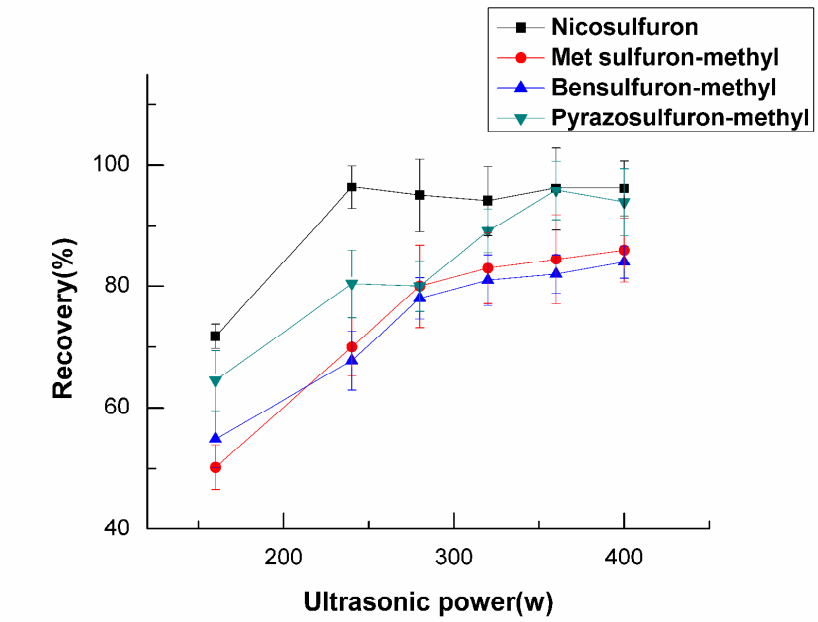

Fig. 3. Effect of ultrasonic power, Sample amount: 100 mg; volume of IL: 150 μL; ultrasonic power : 400 w; ultrasonic time: 5min.

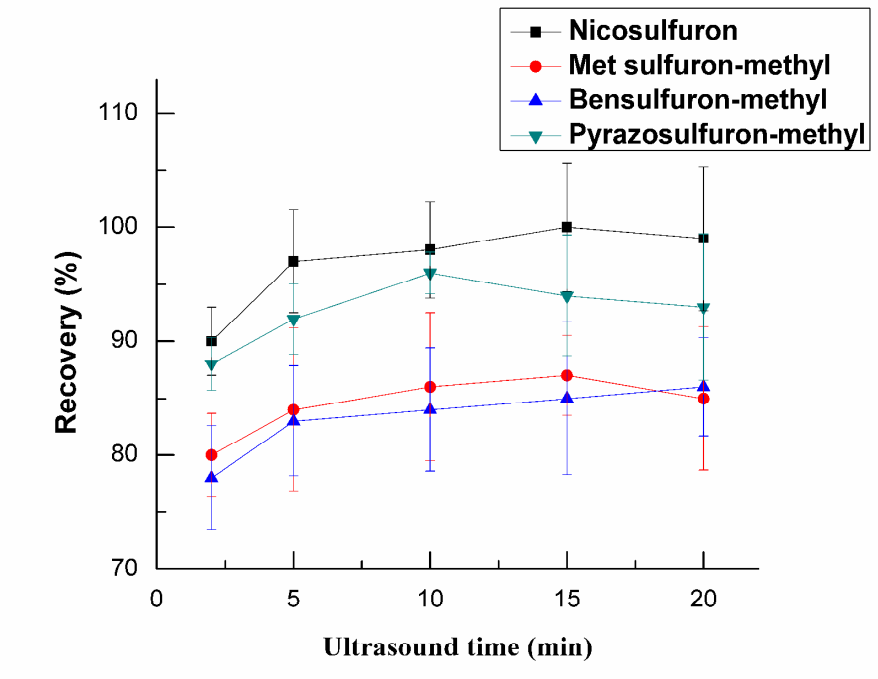

Fig. 4. Effect of ultrasonic time, Sample amount: 100 mg; volume of IL: 150 μL; ultrasonic power: 400 w; ultrasonic time: 5 min.

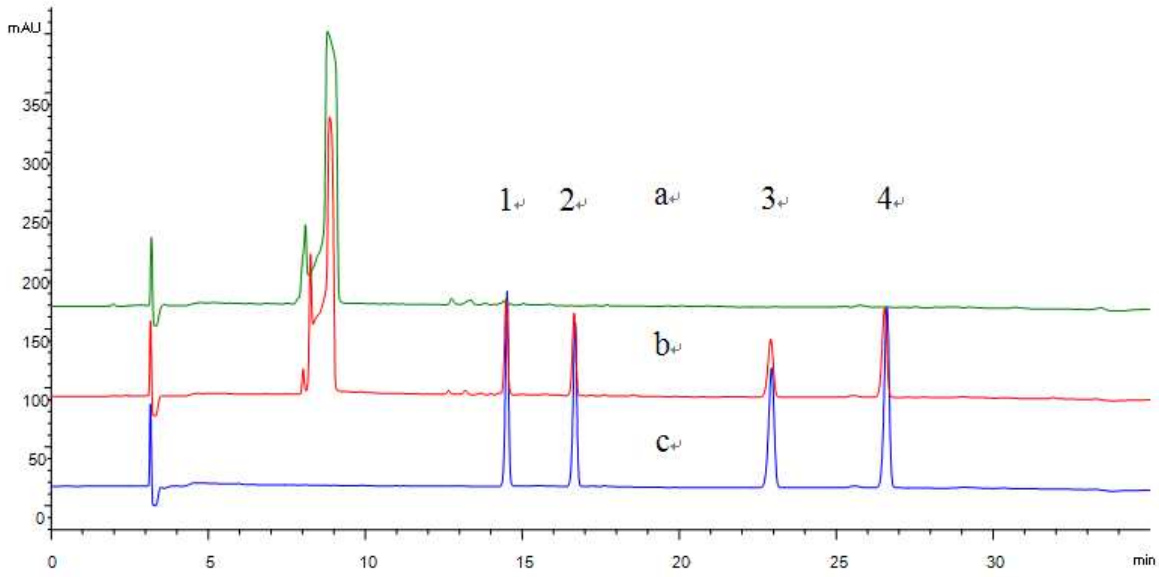

Fig. 5. Chromatograms of blank sample (a), spiked sample (b) and standard solution (c), Peak 1. Nicosulfuron；Peak 2. Metsulfuron-methyl；Peak 3. Bensulfuron-methyl；Peak 4. Pyrazosulfuron-ethyl

Table 1. Analytical performances for the determination of analytes

Analyte	Regression equation	Linear range ($ng\ g^{-1}$)	r	LOD ($ng\ g^{-1}$)	LOQ ($ng\ g^{-1}$)
Nicosulfuron	A = 0.0115C+5.9144	50.0-25000	0.9993	10.2	34.0
Metsulfuron-methyl	A = 0.0120C-0.1496	50.0-5000	0.9990	11.3	37.6
Bensulfuron-methyl	A = 0.0102C+5.8300	50.0-5000	0.9996	8.5	28.3
Pyrazosulfuron-ethyl	A = 0.0192C+8.1213	50.0-5000	0.9993	7.7	25.6

Table 2. Analytical results of samples

Analyte	Spiked level/(ng g^{-1})	Intra-day RSD/(%, n=5)	Inter-day RSD/(%, n=5)
Nicosulfuron	125	5.97	7.29
	2500	3.00	5.94
Metsulfuron-methyl	125	6.55	6.63
	2500	5.92	7.93
Bensulfuron-methyl	125	6.40	5.20
	2500	4.17	5.32
Pyrazosulfuron-ethyl	125	7.28	7.15
	2500	7.56	3.00

Table 3. Recovery for the analyte

Sample	Analyte	Spiked level/(ng g^{-1})	Recovery/(%)	RSD/(%, n=3)
1	Nicosulfuron	125	96.4	4.94
		2500	98.3	4.70
	Metsulfuron-methyl	125	87.8	4.95
		2500	90.5	3.70
	Bensulfuron-methyl	125	81.3	2.22
		2500	89.8	2.24
	Pyrazosulfuron-ethyl	125	99.1	7.44
		2500	100.1	2.33
2	Nicosulfuron	125	94.1	4.20
		2500	99.4	6.31
	Metsulfuron-methyl	125	81.1	5.41
		2500	92.1	1.30
	Bensulfuron-methyl	125	83.9	2.51
		2500	88.4	1.67
	Pyrazosulfuron-ethyl	125	93.6	3.90
		2500	99.5	3.22
3	Nicosulfuron	125	96.4	2.37
		2500	98.5	3.15
	Metsulfuron-methyl	125	92.2	4.68
		2500	90.3	3.35
	Bensulfuron-methyl	125	89.2	3.61
		2500	90.6	5.20
	Pyrazosulfuron-ethyl	125	94.9	5.09
		2500	100.0	1.35

Table 4. Comparison of extraction methods

	IL-based UAE	UE	SE
Sample amount (mg)	100	1000	1000
Solvent	$[C_6MIM][BF_4]$	acetonitrile	acetonitrile
Volume of solvent (mL)	0.15	50.0	150.0
Extraction time (min)	5	40	240
Recovery (%)	81.1～100.1	76.4～104.1	76.8～102.3