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Research Article

Application of ionic-liquid-supported magnetic dispersive solid-phase microextraction for the determination of acaricides in fruit juice samples

In this study, ionic liquid (IL) supported magnetic dispersive solid-phase microextraction was developed and a systematic investigation was conducted on imidazolium ILs for their extraction performance. This nano-based pretreatment procedure was then applied for the determination of acaricides in fruit juice samples for the first time. A feature of this technique is that the commonly laborious chemical modification of magnetic nanoparticles (MNPs) was skillfully circumvented. Because of the combination of ILs, dispersive liquid–liquid microextraction, and dispersive MNP solid-phase microextraction, the extraction efficiency can be significantly improved using commercial MNPs. Parameters of the extraction method were investigated by one-factor-at-a-time approach. The optimal experimental conditions were as follows: emulsification for 2 min by sonication with the addition of 50 μL $[C_6MIM][NTf_2]$ in the dispersive liquid–liquid microextraction step and vortexing for 90 s after adding 40 mg spherical barium ferrite nanoparticles (20 nm). The desorption time was 2 min. Good linearity (0.5–500 ng/mL) and detection limits within the range of 0.05–0.53 ng/mL were achieved. The application of the proposed method was demonstrated by the analysis of real fruit juice samples, in which recoveries between 85.1 and 99.6% were obtained.

Keywords: Acaricides / Ionic liquids / Magnetic nanoparticles / Sample preparation / Ultrasound
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1 Introduction

Acaricides such as clofentezine, chlorfenapyr, and fenpyroximate have been developed to control insects and acarid pests [1–3]. In spite of the therapeutically effective practices in combating these pests, discrepancies in the regulation of acaricide applications (doses, administration method, suppression period) as well as its worldwide utilization have inevitably resulted in the direct contamination of food products [4]. Therefore, maximum residue levels (0.5 μg/L) have been set by the European Commission to protect consumers from exposure to unacceptable levels of clofentezine, chlorfenapyr, and fenpyroximate in fruit vegetable and juices (http://www.ec.europa.eu/food/plant/protection/pesticides/index_en.htm). Besides, indirect pesticide application can also contaminate soil, air, and water [5]. The presence of the aforementioned residues decreases food quality, therefore, suitable analytical methods are needed to confirm and quantify contaminant concentrations [6]. For instance, the application of highly sensitive analytical systems such as GC–MS/MS [7] and LC–MS [8] are powerful options. Nevertheless, a sample preconcentration step is still necessary considering the low concentrations and complexity of the targets in sample matrix. It is in this context an ultrasensitive, timesaving, and highly efficient method for environmental and food monitoring for acaricides has become indispensable. Lately, a successful attempt was made by comparison of two ultrasound-enhanced microextraction steps for preconcentration and determination of six acaricides in water samples [9].

Magnetic nanoparticles (MNPs) have emerged as one of the primary nanomaterials for bioseparation applications in terms of their distinct advantages: (i) MNPs possess favorable magnetic properties, low toxicity, and high chemical stability [10]; (ii) MNPs can be synthesized and functionalized in large quantities using a wide range of techniques [11]; (iii) their adsorption capacity can be expected to be high with the large surface area of nanoparticles (NPs) [12]. Therefore,

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Abbreviations: **DLLME**, dispersive liquid–liquid microextraction; **D-μ-SPE**, dispersive solid-phase microextraction; **IL**, ionic liquid; **MNP**, magnetic nanoparticle; **NP**, nanoparticle; **S-BaFe**, spherical barium ferrite NPs

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research involving MNPs to improve conventional analytical performance and create unprecedented functions for nanomaterials is flourishing [13]. Examples include 1,5-diphenylcarbazide-doped MNPs for the extraction of Hg^{II} [14], carbon-based MNPs for the preconcentration of lanthanides [15], and ionic liquid (IL) modified MNPs for the adsorption of proteins from aqueous samples [16].

Surface modification is one of the most commonly used techniques when applying MNPs for the determination of various analytes. A feature of this technique lies in the fact that NPs can be stabilized and functionalized through selective ion uptake. Substantial progress has been made in this area to achieve targeted purposes [17–19]. For example, Hu and co-workers spent more than 13 h on the preparation of Fe_3O_4@SiO_2@IDA microspheres for the trace analysis of Cd, Mn, and Pb in environmental samples [20]. Over 24 h are required to synthesize uranyl-imprinted silica-coated MNPs, for the selective extraction of uranyl ions [21]. Notwithstanding, it is evident that relatively time-consuming and arduous work has to be done compared with their pretreatment processes. In this sense, the development of timesaving and easy-to-operate microextraction techniques should be considered.

Very recently, a new mode of magnetic extraction technique, which is termed as dispersive liquid–liquid microextraction (DLLME) coupled with dispersive solid-phase microextraction (D-μ-SPE) was developed [22]. The procedure proves that hydrophobic MNPs could be employed to retrieve the extractant of 1-octanol in the D-μ-SPE step, while the analytes were extracted by 1-octanol in the DLLME step. Through the combination of these two procedures, laborious modification can be eliminated while satisfactory recovery can be easily realized. To expand the two-step microextraction with more extensive extractants and solvents with higher densities than water, we applied $[C_6MIM][NTf_2]$ to preconcentrate and determined pyrethroids in honey samples. The introduction of ultrasound can further improve the efficiency of this method and avoid the use of a dispersive solvent [23]. However, the adsorption behaviors of MNPs with ILs with different side chains are still unknown. Thus, this study follows the discussion on imidazolium ILs and is a continuation of our systematic study on the possible application of the two-step method in the extraction of acaricides.

The goal of this work is to assess the suitability of six ILs for the extraction of acaricides with different carbon atoms and side chains in the IL-supported magnetic dispersive solid-phase microextraction (IL-MSPME) step. It is worth noting that the nano-based technique was first introduced for the determination of acaricides. Generally in this work, ILs without the addition of any disperser were directly utilized to extract the compounds of interest in the ultrasonic-assisted DLLME step, and thereafter unmodified MNPs were added to re-extract ILs in D-μ-SPE. Different factors that affect the extraction efficiency, such as the volume and type of ILs, sonication time, and desorption time, were evaluated using the one-factor-at-a-time approach. Under the optimized conditions, the present nano-based method was successfully applied for analyzing acaricides in fruit juice samples.

2 Materials and methods

2.1 Chemicals and samples

Clofentezine (99% purity) was purchased from Aladdin (Shanghai, China). Chlorfenapyr, fenpyroximate, pyridaben, and spirodiclofen (98% purity) were obtained from the Agricultural Environmental Protection Institution, Tianjin, China. The acetonitrile for spectroscopy was purchased from Dikma (Beijing, China), and the deionized water was purified using a Milli-Q SP Reagent Water System-(Millipore, Bedford, MA, USA). 1-Butyl-3-methylimidazolium chloride ($[C_4MIM]Cl$), 1-butyl-3-ethylimidazolium chloride ($[C_4MMIM]Cl$), 1-hexyl-3-methylimidazolium chloride ($[C_6MIM]Cl$), 1-hexyl-3-ethylimidazolium chloride ($[C_6MMIM]Cl$), 1-octly-3-methylimidazolium chloride ($[C_8MIM]Cl$), and 1-octyl-3-ethylimidazolium chloride ($[C_8MMIM]Cl$) were purchased from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). Lithium bis(trifluoromethanesulfonimide) was purchased from Zhejiang Jiuzhou Pharmaceutical (Zhejiang, China). Sodium chloride (analytical grade) was purchased from Beijing Chemical Reagent Company. Stock solutions of spherical barium ferrite NPs (S-BaFe; 30–50 nm) were purchased from Aladdin. Standard stock solutions were prepared in acetonitrile at a final concentration of 100 mg/L. Working standard solutions were freshly prepared by dilution of an appropriate amount of the standard stock solutions in deionized water.

2.2 Synthesis of the ILs

All ILs were synthesized by the anion exchange method from the corresponding chloride salt of the imidazolium cation with one equivalent of lithium bis(trifluoromethylsulfonyl)amide in deionized water. The obtained higher density hydrophobic IL phase was decanted and washed with water six to eight times. The product was then dried at 50°C for at least 48 h. After purification, the final products were characterized by NMR spectroscopy. The ^1H NMR spectra confirmed the desired structures.

2.3 Instrumentation

Chromatographic analysis was performed on an Agilent 1200 HPLC system (CA, USA) equipped with a variable wavelength detector and an automatic sample injector. The separation of the analytes was performed on a Spursil C_{18} column (5 μm, 4.6 × 250 mm, Dikma) with Spursil C_{18} Guard Cartridges (5 μm, 2.1 × 10 mm, Dikma). The mobile phase was an acetonitrile/water mixture (77:23, v/v) delivered at a flow rate of 1 mL/min, and the column temperature was 25°C. The

variable wavelength detector was set at 270 nm to detect clofentezine and changed to 260 nm after 12 min to detect chlorfenapyr, fenpyroximate, and then changed to 230 nm after 18 min to detect pyridaben and spirodiclofen. A high-speed refrigerated centrifuge (Baiyang 52A, Baoding, China), a vortex shaker (QL-861, Haimen, China), and ultrasonic equipment (KQ3200DE, Kunshan, China) were used. All glassware used in the experiments were washed with deionized water and acetone and then dried at room temperature.

2.4 Preparation of fruit juice samples

Fruit juice samples were purchased from local supermarkets (grape, apple, and pear). The samples were stored at room temperature before use. Once opened, they were stored in the specific food containers at 4°C and analyzed within three days. Fifty microliters aliquot of fresh juice was centrifuged at 3500 rpm for 10 min, and then the supernatant was filtered through a 0.45 μm membrane filter into 100 mL conical flask. Before extraction, 45 mL of filtrate was diluted at 1:1 ratio with deionized water in a volumetric flask of 100 mL.

2.5 Extraction procedure

2.5.1 IL-DLLME step

Aliquots of 50 μL of $[C_6MIM][NTf_2]$ were quickly injected into a conical-bottomed test tube that contained 10 mL of water to form an emulsified solution by shaking. This solution was then sonicated for 2 min to accelerate the formation of the fine droplets of the extraction solvent and enhance the transfer of the analytes.

2.5.2 D-μ-SPE step

Forty milligram of S-BaFe MNPs (20 nm) was added to the tube, which was vigorously shaken using a vortex agitator for 90 s at 2800 rpm. The MNPs were successfully able to extract the $[C_6MIM][NTf_2]$ after the high-speed stirring process. A magnet was subsequently held around the test tube to concentrate the NPs. After all of the MNPs were sedimented within 30 s, the sample solution was carefully removed using a drip tube and microsyringe. Acetonitrile (50 μL) was injected into the test tube to desorb the IL from the MNPs by sonication for 2 min. Finally, the NPs were isolated from the solution with a magnet, and 10 μL of organic solvent was collected and injected into the HPLC system for analysis.

3 Results and discussion

3.1 Comparison of IL-MSPME with DLLME and selection of the IL

The proposed method allows the application of unmodified MNPs to attain satisfactory extraction efficiency in a relatively short time due to the rapid mass transfer between MNPs and ILs. Suitable MNPs are critical for the extraction efficiency in terms of their important role in the D-μ-SPE procedure. Considering the best performance of S-BaFe (30–50 nm) in our previous study [23], S-BaFe MNPs were chosen for the subsequent experiments.

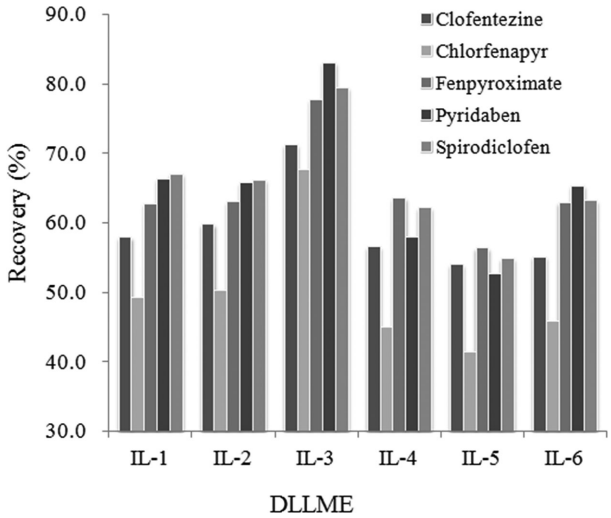

Figure 1. Recovery of acaricides in DLLME. The extraction conditions were as follows: water sample volume, 10.00 mL; IL1–IL6, ($[C_4MIM][NTf_2]$, $[C_4MMIM][NTf_2]$, $[C_6MIM][NTf_2]$, $[C_6MMIM][NTf_2]$, $[C_8MIM][NTf_2]$, and $[C_8MMIM][NTf_2]$), 50 μL; sonication time, 2 min; centrifugation time (3800 rpm), 15 min; no salt addition; concentration level, 50 μg/L.

According to the last investigation on the performance of direct D-μ-SPE and the two-step method, IL-SPME showed a higher extraction efficiency. This is because the DLLME step was a contributing factor in the enhancement of the two-step process. However, the performance of IL-SPME compared with classical DLLME is still unknown. A series of experiments was therefore conducted and the pertinent data are shown in Figs. 1 and 2. The observations suggest that the re-extraction of the IL through adding MNPs by vortex is comparable with centrifugation. It is in this way that microextraction time is significantly saved through the elimination of centrifugation.

The selection of an appropriate extractant is a key step in the optimization of IL-MSPME conditions. Room-temperature ILs have been gaining exposure for their potential use as green solvents and as alternatives to traditional volatile organic solvents for a variety of bioseparation applications. Nevertheless, ILs often require the addition of a toxic dispersive solvent to reduce their high viscosity, which commonly decreases the partition coefficient of analytes [24]. The ILs used in this work may provide a potential platform for developing unique extraction techniques. To systematically study the affinity of MNPs toward ILs, ILs with different carbon atoms and side chains were employed. As shown in Fig. 2, IL3 ($[C_6MIM][NTf_2]$) had the best performance for the extraction of acarides. Therefore, $[C_6MIM][NTf_2]$ was applied in the following study.

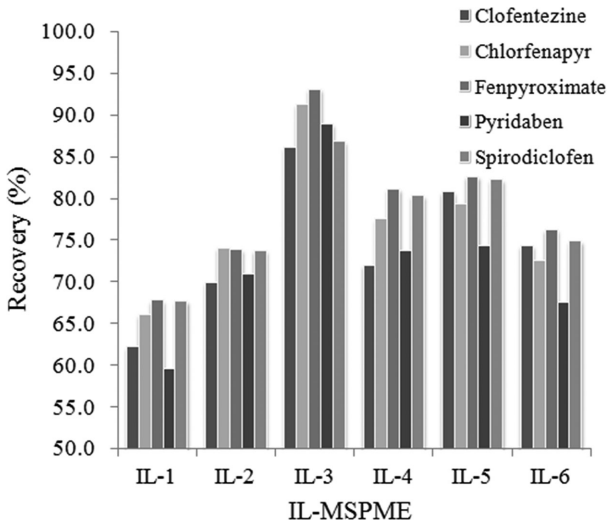

Figure 2. Recovery of acaricides in IL-MSPME. The extraction conditions were as follows: water sample volume, 10.00 mL; IL1–IL6, ([C_4MIM][NTf_2], [C_4MMIM][NTf_2], [C_6MIM][NTf_2], [C_6MMIM][NTf_2], [C_8MIM][NTf_2], and [C_8MMIM][NTf_2]), 50 μL; sonication time, 2 min; MNPs dosage, 40 mg; vortex time, 60 s; desorption solvent (acetonitrile), 50 μL; desorption time, 2 min; no salt addition; concentration level, 50 μg/L.

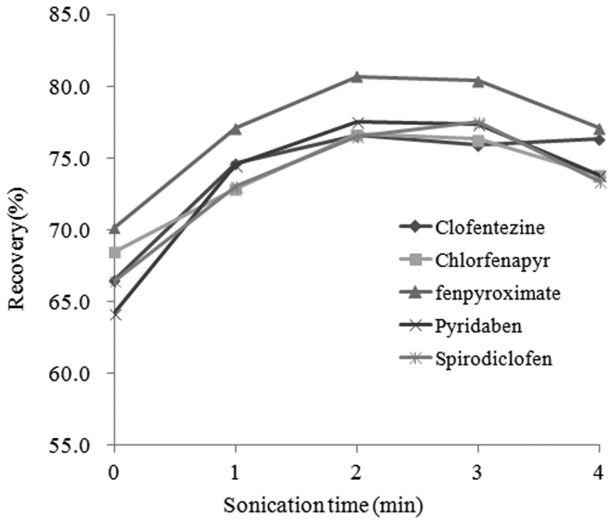

Figure 3. Effect of sonication time on recovery. Extraction conditions: water sample volume, 10.00 mL; [C_6MIM][NTf_2], 50 μL; MNPs dosage, 40 mg; vortex time, 30 s; desorption solvent (acetonitrile), 30 μL; desorption time, 1 min; no salt addition; concentration level, 50 μg/L.

3.2 Effect of the volume of IL

In order to study the effect of IL volume, experiments were conducted in which [C_6MIM][NTf_2] varied in the range of 30–70 μL in 10 μL intervals. In this study, the efficiency increases with the addition of ILs until 50 μL (at a volume of 30–50 μL, recoveries increase from 48.1–54.5 to 67.7–76.8%), while it remains almost constant at volumes >50 μL. Thus, 50 μL of [C_6MIM][NTf_2] was selected as the optimal volume for further study.

3.3 Effects of the dosage of MNPs

To evaluate the effects of the dosage of MNPs, MNPs from 10 to 50 mg were investigated. For all the model compounds, a relatively higher response was obtained using 40 mg of MNPs, indicating that 40 mg of MNPs is enough to retrieve the ILs and can be effectively desorbed by the acetonitrile. Consequently, 40 mg of MNPs was selected.

3.4 Sonication time

Sonication is an effective way to improve the mass transfer process in analytical procedures. In acoustically emulsified media, bubbles can be collapsed to produce intense shock waves in the surrounding liquid and high-velocity liquid jets. This can promote emulsification by generating smaller droplets, thus accelerating the equilibrium [25]. However, prolonged time may result in heat generation and analyte degradation [26]. The sonication time was optimized in the range of 0–4 min (Fig. 3). The results indicated that extraction rates increased along with increased sonication times and it appeared that equilibrium was attained for all acaricides after only 2 min. Thus, it was decided to fix the sonication time at 2 min in the following experiments.

3.5 Effect of vortex time

The purpose of the use of a vortex agitator is to create fluid fields in which MNPs could extract ILs toward equilibrium faster because of the shorter diffusion distance and larger specific surface area [26]. Additionally, it is worth noting that a vortex can result in the breakup of ILs into smaller droplets and prevent aggregation. The dual effects of vortex are very favorable for equilibrium. Considering the limitation of our agitator (rotational speed remains constant at 2800 rpm), different vortex times (30, 60, 90, 120, 150 s) were investigated. In the current study, the extraction rates increased with increasing vortex extraction times and it appears that equilibrium is attained for all target analytes after only 90 s. Based on the above, a 90 s vortex time was chosen, enabling extraction at equilibrium conditions and resulting in increased precision and sensitivity.

3.6 Salt addition

Further investigation was performed on the effect of salt concentration on the extraction efficiency. Sodium chloride was added in the range of 0–8% w/v. In this study, the addition of NaCl has a negative effect on the extraction efficiency as a result of increase in solubility of [C_6MIM][NTf_2] in the aqueous phase. In addition, at higher salt concentration, the density of

Table 1. Performance characteristics of the IL-MSPME method combined with HPLC

Acaricides	Linearity equation	Linearity (ng/mL)	*r*	RSD (%)[a)]	LODs (ng/mL)[b)]	Recovery (%)
Clofentezine	$Y = 5.2093X + 10.861$	0.5–500	0.9998	3.3	0.28	88.0
Chlorfenapyr	$Y = 2.3877X + 10.998$	0.5–500	0.9981	2.7	0.53	95.1
Fenpyroximate	$Y = 3.5964X - 16.599$	0.5–500	0.9976	2.1	0.42	99.3
Diafenthiuron	$Y = 5.5297X - 18.698$	0.5–500	0.9990	1.4	0.05	98.9
Spirodiclofen	$Y = 3.4542X + 3.6891$	0.5–500	0.9999	1.7	0.08	97.0

a) RSD that was calculated by five extraction reduplicates ($n = 5$) at the spiked level of 50 μg/L.
b) LOD: S/N = 3.

the aqueous solution became higher, which is unbeneficial for vortex mixing. Herein, salt was not added in the following experiments.

3.7 Effect of desorption time

The effect of desorption time over the range of 0–4 min at intervals of 1 min was evaluated. It has been observed that all the acaricides were desorbed almost completely within 2 min, and no significant change in chromatographic signals was observed. According to our experiments, the desorption time was maintained up to 2 min for further study.

Based on the above discussion, the optimal extraction conditions for the IL-MSPME method are as follows: 50 μL $[C_6MIM][NTf_2]$, 40 mg S-BaFe (20 nm) MNPs, sonication time at 2 min, a vortex mixing at 2800 rpm for 90 s, acetonitrile as the desorption solvent, and 2 min for the desorption. No salt was added to the sample solution.

3.8 Method validation

Under the optimized experimental conditions, quantitative analysis was performed to evaluate the sensitivity and stability of the proposed method. The results are illustrated in Table 1. All the analytes exhibited good linearity with a correlation coefficient (R) >0.9976. LODs, determined at a S/N of 3, ranged between 0.05 and 0.53 ng/mL. These excellent results indicated that the present approach was a simple and sensitive procedure to determine acaricides at trace levels.

3.9 Analysis of fruit juice samples

The practical performance of the present method was validated with three fruit juice samples, grape, pear, and apple juice, obtained from a local market. As listed in Table 2, the recoveries of the five analytes from the three fruit juice samples were in the range of 85.1–99.6% with the RSDs <5.3%. Typical chromatograms of the acaricides in spiked and blank honey samples are illustrated in Fig. 4. The results demonstrate that the precision and accuracy of the present method were acceptable.

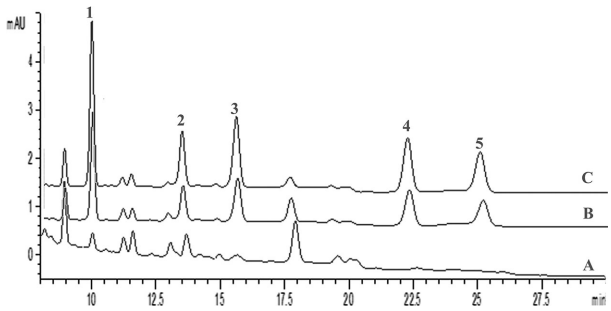

Figure 4. Typical chromatograms of acaricides in the spiked and blank fruit juice samples from the local market: (1) clofentezine; (2) chlorfenapyr; (3) fenpyroximate; (4) diafenthiuron; (5) spirodiclofen. Chromatograms A–C: spiked levels were 0, 10, and 30 μg/L, respectively.

The characteristic data of the present method were compared with those reported in the literature. As evident in Table 3, the proposed method is superior to those reported methods in the following ways: (i) a nano-based microextraction technique was introduced to monitor acaricide residues in fruit juice samples for the first time; (ii) ILs were applied as extractants without adding any toxic dispersive solvents; (iii) a symmetrical study on imidazolium ILs was investigated in the IL-MD-μ-SPE method; (iv) recoveries and LODs are comparable to other SPME techniques. In general, we have demonstrated that the present method is a simple, rapid, and effective pretreatment procedure.

4 Concluding remarks

In this study, a novel nano-based technique (IL-MSPME), was developed and for the first time applied for the determination of acaricides in fruit juice samples. Six imidazolium ILs with different carbon atoms and side chains were prepared to systematically study IL-MSPME. Under optimal parameters, the proposed method was applied and compared with other methods, indicating that it is robust, simple, and sensitive. The simplicity and efficiency of the present approach may render it applicable to the environmental remediation of other pesticides.

Table 2. Results of the determination of fruit juice samples spiked with acaricides

	Spiked level (μg/L)	Grape juice		Apple juice		Pear juice	
		Recovery (%)	RSD%[a)]	Recovery (%)	RSD%	Recovery (%)	RSD%
Clofentezine	0	ND[b)]		ND		ND	
	10	88.7	1.2	88.8	3.8	89.8	1.5
	30	87.1	3.6	89.2	2.2	88.9	3.0
Chlorfenapyr	0	ND		ND		ND	
	10	92.2	3.7	92.7	4.1	93.0	3.0
	30	89.2	2.5	91.5	4.4	92.0	2.8
Fenpyroximate	0	ND		ND		ND	
	10	93.6	3.9	90.1	2.2	87.0	3.1
	30	90.8	1.8	92.5	5.1	92.5	2.7
Diafenthiuron	0	ND		ND		ND	
	10	96.5	4.1	95.7	5.3	85.1	4.1
	30	94.3	2.6	87.1	1.8	90.8	2.2
Spirodiclofen	0	ND		ND		ND	
	10	91.5	3.8	90.8	2.6	99.6	2.4
	30	88.3	2.5	93.5	4.6	94.4	3.5

a) RSD that was calculated by five extraction reduplicates ($n = 5$).
b) ND stands for not determined.

Table 3. Comparison of the IL-MSPME with other methods for the determination of acaricides

Methods	Extractant/coatings	MNPs	Time (min)	Analytical range	LODs	Recoveries (%)	Ref.
SPME-GC/MX	Polyacrylate fiber	—	55	—	2–18 (ng/g)	89–111	[8]
SPE-HPLC	C_{18}	—	35	0.015–0.1 (μg/g)	0.001–0.2 (μg/g)	60–104	[3]
LLE-HPLC	Hexane–propanol-2–ammonia	—	25	0.05–0.5 (mg/kg)	0.0015–0.06 (mg/kg)	86.2–102.8	[1]
US-DLLME-HPLE	[C8MIM][PF6] + methanol	—	20	1–500 (μg/L)	0.04–0.14 (μg/L)	89.5–101.1	
IL-D-μ-SPE-HPLC	$[C_6MIM]NTf_2$	S-BaFe	10	0.5–500 (μg/L)	0.05–0.53 (μg/L)	85.1–99.6	Present work

http://www.paper.edu.cn/en_releasepaper/content/4501732

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The authors have declared no conflict of interest.

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