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Ionic liquid-based totally organic solvent-free emulsification microextraction coupled with high performance liquid chromatography for the determination of three acaricides in fruit juice

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ABSTRACT

A novel, totally organic solvent-free emulsification microextraction (TEME) technique using ionic liquids (ILs) is proposed in this study. Seven bis(trifluoromethylsulfonyl)imide ionic liquids were synthesized. After comparing the physicochemical properties of the ionic liquids and their application to microextraction experiments, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_6MIM][NTf_2]$), which has moderate surface tension and viscosity, was selected as the extraction solvent. The dispersion of ILs and mass transfer were accelerated by ultrasound irradiation and temperature control processes. Therefore, no dispersive organic solvent was needed. Several variables, such as ionic liquid volume, duration of the ultrasound extraction, dispersion temperature, ionic strength and centrifugation time were investigated and optimized. Under the optimum conditions, the calibration curve was linear in the range of 0.1–600 $\mu g\ L^{-1}$ for chlorfenapyr and fenpyroximate and 0.5–600 $\mu g\ L^{-1}$ for spirodiclofen, with correlation coefficients of 0.9994–0.9999. The enrichment factors were between 261 and 285. The limits of detection (LODs) were 0.02–0.06 $\mu g\ L^{-1}$. Real fruit juice samples (at fortified levels of 10 $\mu g\ L^{-1}$ and 30 $\mu g\ L^{-1}$) were successfully analyzed using the proposed method. The relative recoveries and enrichment factors were in the range of 92–104%.

1. Introduction

Chlorfenapyr, spirodiclofen and fenpyroximate are excellent broad-spectrum acaricides that have been developed to control insects such asacarid pests on vegetables and fruit trees [1,2]. Although spraying chemical acaricidesis the most efficient method to control tick populations, the widespread use of these compounds has resulted in environmental contamination. Furthermore, acaricide residues in fruits raise public health concerns because many people eat fruit and drink commercial fruit juice on a daily basis. The Association of the Industry of Juices and Nectars (AIJN) and the European Union (EU) Directive on Fruit Juice Quality (396/2005/EC) established a maximum allowable concentration of 0.010 mg kg^{-1} for total pesticides [3,4]. Because of this legal limit, simple , environmentally friendly and sensitive analytical techniques are imperative for monitoring trace levels of acaricide pesticides.

Current methods for the detection of pesticide residue in real water and fruit juice samples require sample preparation prior to instrument analysis. Good sample preparation should not only clean up the sample but also preconcentration and extraction. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are two of the most commonly used sample preparation methods. Nevertheless, the significant disadvantages of these methods are the large quantities of solvent utilized and the multiple operation steps that are needed [5]. Recently, research has been oriented towards the efficient development of miniaturized pretreatment methods. Such methods include solid-phase microextraction (SPME), liquid-phase microextraction (LPME), hollow fiber-based liquid-phase microextraction (HF-LPME) and single-drop microextraction(SDME) [6]. However, these methods have several drawbacks, including the need for expensive laboratory consumables, declining performance with time and sample carry-over [7]. Compared with the aforementioned preconcentration and matrix isolation techniques, dispersive liquid–liquid microextraction (DLLME) and ultrasound-assisted emulsification microextraction (USAEME) are not only miniaturized but also easy to conduct. Both of these methods are based on the formation of miniature extractant droplets in the sample solution, which accelerates the mass transfer. Following the pioneering research of Assadi et al. [8] and Garcia-Jares et al. [9], many studies have demonstrated good extraction efficiencies for various analytes using these microextraction techniques [10–15].

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ILs are defined as salts with melting points at or below 100 °C. ILs exhibit a unique combination of intrinsic physicochemical properties, making them highly promising substances in many fields. Room-temperature ionic liquids (RTILs) area subset of ionic liquids that are liquid at room temperature (~25 °C). Since the first report in 1982 [16], RTILs have attracted increasing interest and have been more frequently applied in analytical chemistry for sample preparation. Although there is increasing interest in the replacement of organic solvent with RTILs during the extraction procedure, the use of organic solvent cannot be completely avoided in these recently developed methods. For DLLME, the water-immiscible extraction solvent must dissolve in a water-miscible organic dispersive solvent. Even the extraction solvent can be replaced by an ionic liquid, organic dispersive solvents such as acetonitrile, acetone and 1,4-dioxane are still required. In contrast to DLLME, the use of a dispersive solvent is not needed for USAEME, but ultrasonic energy cannot disrupt common hexafluorophosphate ionic liquids, and they produce very fine emulsions. Therefore, toxic halogenated hydrocarbons are commonly selected as extraction solvents for USAEME.

In the last few years, an in-situ metathesis reaction combined with ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction (in-situ UA-IL-DLLME) was developed in which fine microdroplets of water-immiscible ILs are formed without dispersive solvents. Bis[(trifluoromethane)sulfonyl]imide ionic liquids, as common products of these in-situ metathesis reactions, are considered “green solvents” and have provided a foundation for the improvement of modern microextraction methods. Because of the low surface tension of this type of ionic liquid, it is interesting to synthetize these ILs before the extraction procedure and apply them to USAEME. Furthermore, the direct use of bis[(trifluoromethane)sulfonyl]imide ionic liquids in USAEME can also overcome the three main drawbacks for in-situ UA-IL-DLLME, which are dilution of the sample solution, introduction of extra impurities and increased salt strength.

In most of the published papers cited above, dispersive solvents and sonication were used to assist the formation of submicron droplets. Nevertheless, the interactions between the properties of the extraction solvent and dispersion approaches remain unclear, thus significantly hindering further exploration of liquid–liquid microextraction methods. Additionally, data regarding extractant surface tension, which is important in the dispersion process and in the formation of a stable emulsion, are rare or not existent.

Therefore, the main aims of this work were to synthesize seven bis[(trifluoromethane)sulfonyl]imide ionic liquids, select the best ionic liquid by comprehensive comparison of its physical properties and apply it to microextraction experiments. As a result, a new extraction method, named “totally organic solvent-free emulsification microextraction (TEME),” was developed and has the advantages of USAEME, including temperature-controlled extraction and the use of an ionic liquid. In this method, the environmental friendly TEME procedure using [C_6MIM][NTf_2] as the IL extraction solvent was directly conducted. A primary ultrasound-assisted, temperature-controlled process and a secondary ultrasound-assisted process were applied to enhance the dispersion. Various factors affecting extraction efficiency were evaluated and optimized. Using the optimized conditions, the proposed method was successfully applied for the simultaneous determination of three acaricides in three real fruit juice samples.

2. Experimental

2.1. Reagents and materials

Chlorfenapyr, spirodiclofen and fenpyroximate (98% purity) were obtained from Agricultural Environmental Protection Institution, Tianjin, China. Acetonitrileand methanol for spectroscopy were obtained from Dikma Limited (China) and the deionized water (< 18 cm MΩ resistivity) was purified bya Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). 1-Butyl-3-methylimidazolium chloride [C4MIM]Cl, 1-butyl-2,3-dimethylimidazolium chloride [C_4MMIM]Cl, 1-hexyl-3-methylimidazolium chloride [C_6MIM]Cl, 1-hexyl-2,3-dimethylimidazolium chloride [C_6MMIM]Cl, 1-octyl-3-methylimidazolium chloride [C_8MIM]Cl, 1-octyl-2,3-dimethylimidazolium chloride [C_8MMIM]Cl and 1-decyl-3-methylimidazolium chloride [C_{10}MIM]Cl were purchased from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). Li[NTf_2] was purchased from Zhejiang Jiuzhou Pharmaceutical (Zhejiang, China). Sodium chloride (analytical grade) was purchased from the Beijing Chemical Reagent Company. The glassware and polytetrafluoroethylene containers were thoroughly cleaned by soaking in nitric acid (10%, v/v) for at least 24 h and rinsed with ultra-high-purity deionized water.

Four 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nMIM][NTf_2]) ionic liquids and three 1-alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nMMIM][NTf_2]) ionic liquids were prepared by a metathesis reaction according to procedures similar to those described elsewhere [17]. Briefly, the bis(trifluoromethylsulfonyl)imide ionic liquids were prepared by mixing the lithium salt of the desired anion, Li[NTf_2] with equal amounts of the desired cation ([C_nMIM]Cl and [C_nMMIM]Cl, $n=4$, 6, 8 or 10). After purification, the final products were characterized by nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H NMR spectra confirmed the desired structures.

The fruit juice (grape, peach and orange) samples were purchased from a local supermarket (Beijing, China). Fruit juice samples were stored in refrigerator at 4 °C. A 30 mL aliquot of fresh juice was centrifuged at 4000 rpm for 10 min. Then, the supernatant was filtered through a 0.22 μm membrane (Agla, USA) prior to being processed by the TEME procedure.

Stock solutions (200 mg mL^{-1}) of chlorfenapyr, spirodiclofen and fenpyroximate were prepared by dissolving appropriate amounts of their solids in acetonitrile. All of the stock solutions were stored in a refrigerator at 4 °C. Working solutions containing all the target acaricides were prepared daily by serial dilutions of the stock solutions with ultra-high-purity deionized water. The calibration curve for each acaricide was obtained by fitting the concentration of each acaricide versus its HPLC peak area to a linear regression model, and the concentration of analytes in the sample was calculated based on the calibration curves.

2.2. Instrumentation

The viscosities of synthesized ionic liquids were measured using a coaxial cylinder rotational rheometer with a controlled shear rate (Brookfield R/S-CC, Germany) at 25 ± 0.1 °C. The density was determined by adding 50 μL of IL into a weighed vial with a 100 μL HPLC microsyringe to quantify its weight. The surface tension measurements were performed using the pendant drop method with a data physics OCA 20 (Data physics Instruments GmbH, Filderstadt, Germany). The compartment containing the ionic liquid droplet was thermostated at 273.00 K with a stability of ± 0.03 K. The uncertainty of the surface tension measurement was estimated to be $< \pm 0.05$ mN m^{-1}.

Chromatographic analysis was carried out by an Agilent 1200 HPLC system equipped with a variable wavelength detector detector (VWD) system (California, USA) and an automatic sample injector. Separation of the analytes was carried out on a Spursil C18 column (5 μm, 4.6 × 250 mm, Dikma Limited) with Spursil C18 Guard Cartridges (5 μm, 2.1 × 10 mm, Dikma Limited). An acetonitrile and water mixture (78:22, v/v) was used as the mobile phase at a flow rate of 1 mL min^{-1}. The variable wavelength detector was first set at 260 nm to detect chlorfenapyr, and it was changed to 230 nm after 10.0 min to detect spirodiclofen and fenpyroximate. Data collection and analysis were performed using Agilent ChemStation. Centrifugation was performed in a 52a centrifuge that was purchased from the Baiyang Centrifuge Factory (Baoding, China). The samples were ultrasonically irradiated in a water bath at 150 W and 40 kHz using an ultrasonic instrument (KQ3200DE; Kunshan Ultrasonic Instrument Co. Ltd., Kunshan, China).

2.3. *Totally organic solvent-free emulsification microextraction procedure*

Ten milliliters of homogeneous sample solution containing the target analytes were placed in a 15 mL screw-cap conical bottom polytetrafluoroethylene tube. After rapidly and vigorously injecting 53 μL of [C6MIM][NTf2] into the sample solution using a 100 μL syringe, the conical tube was subjected to ultrasonic treatment for 2 min, and a slightly cloudy solution was formed in the test tube. Then, the conical tubes were heated in a temperature-controlled water bath set at 60 °C for 2 min, which made the ionic liquids almost completely disperse in the solution. Afterward, the tubes were cooled with ice water and simultaneously underwent additional 2 min ultrasonic treatment for full extraction the analytes from the very fine droplets. The mixture was then centrifuged at 4000 rpm for 10 min. The upper aqueous phase was carefully removed, and the ionic liquid (approximately 37 μL) was easily withdrawn with a syringe. Finally, 10 μL of the IL phase was injected into the HPLC system for analysis.

3. Results and discussion

3.1. *Effect of the type of ionic liquid*

Recently, ionic liquids have received much attention because of their unique physical and chemical properties such as low volatility, high thermal stability and wide liquid range. Furthermore, their good dissolubility with organic compounds, moderate surface tension and viscosity make them promising candidates for use with various extraction methods. Among these properties, the importance of surface tension has been addressed by various studies. According to Ozcan et al.'s research, a lower surface tension of the extractant would enable a stronger cavitation under ultrasound irritation and hence a higher efficiency in emulsion formation [18]. The same conclusion was also drawn from a study that was conducted by Chen et al. in which CCl$_4$ had the lowest surface tension, thus enabling it to disperse in the presence of an emulsifier, which resulted in a higher extraction capability [19]. However, limited measured surface tension data for bis(trifluoromethylsulfonyl)imide ionic liquids are available. To address these fundamental challenges, we attempted to measure the surface tension and other important properties for the synthesized bis(trifluoromethylsulfonyl)imide ionic liquids in this study. The results and a comparison with hexafluorophosphate ionic liquids and common organic solvents are listed in Table 1.

Table 1
Physicochemical properties of bis(trifluoromethylsulfonyl)amide ionic liquids, hexafluorophosphate ionic liquids and selected organic solvents.

Ionic liquid	Density (g mL^{-1})	Water solubility (g 100 mL^{-1})	Viscosity (mPa s)	Surface tension (mN m^{-1})
[C$_4$mim][NTf$_2$]	1.42	0.79	34.6	32.2
[C$_4$mmim][NTf$_2$]	1.40	0.56	67.4	33.4
[C$_6$mim][NTf$_2$]	1.36	0.26	50.8	31.1
[C$_6$mmim][NTf$_2$]	1.34	0.22	89.8	31.6
[C$_8$mim][NTf$_2$]	1.31	0.10	70.1	30.3
[C$_8$mmim][NTf$_2$]	1.30	0.09	122.1	30.8
[C$_{10}$mim][NTf$_2$]	1.26	0.07	72.0	30.1
[C$_4$mim][PF$_6$]	1.38	1.88	393	48.8
[C$_6$mim][PF$_6$]	1.30	0.75	560	43.4
[C$_8$mim][PF$_6$]	1.23	0.20	710	37.7
Chloroform	1.49	0.75	0.56	28.9
Tetrachloromethane	1.59	0.08	0.97	32.3
1,1,2,2-Tetrachloroethane	1.60	0.29	1.77	34.7

It is well known that surface tension is defined as the force that is required to close a cut of unit length in the surface of a liquid. Therefore, the lower the surface tension of the liquid, the easier the formation of tiny droplets. As indicated in Table 1, the surface tension of bis(trifluoromethylsulfonyl)imide ionic liquids is in the range of 30.1–33.4 mN m^{-1}, which is considerably lower than corresponding hexafluorophosphate ionic liquids. On the other hand, the high surface tension of hexafluorophosphateionic liquids indicates that this type of IL is not suitable for USAEME. In comparison with common extraction organic solvents, the surface tension of most bis(trifluoromethylsulfonyl)imide ionic liquids is lower than that of tetrachloromethane and 1,1,2,2-tetrachloroethane. As observed in Table 1, the surface tension of bis(trifluoromethylsulfonyl)imide ionic liquids decreases with the length of the alkyl chain of the cation. Conversely, the viscosity increases from [C$_4$mim][NTf$_2$] to [C$_{10}$mim][NTf$_2$]. Using our specific TEME procedures, we determined that [C$_6$mmim][NTf$_2$] (viscosity: 89.8 mPa s) and [C$_8$mmim][NTf$_2$] (viscosity: 122.1 mPa s) were unlikely to be efficient for extraction without acetonitrile dilution because of their higher viscosity. It is well understood that low viscosity is another essential condition for the development of a totally organic solvent-free emulsification microextraction method. Because of its surface tension, viscosity and water solubility, [C$_6$mim][NTf$_2$] is the best candidate for the TEME procedure. As expected, under the selected chromatographic conditions, [C$_6$mim][NTf$_2$] had higher analyte recoveries compared with the other five bis(trifluoromethylsulfonyl)imide ionic liquids ([C$_{10}$mim][NTf$_2$] which presented an overlap peak which affects the analysis of spirodiclofen). The results are shown in Fig. 1.

3.2. *Effect of ionic liquid volume*

The volume of extraction solvent was another crucial parameter that could affect the extraction efficiency. To study this effect, solutions containing different volumes of [C$_6$mim][NTf$_2$] were compared in this experiment. The results are shown in Fig. 2. By increasing the volume of extraction solvent from 38 to 58 μL, the volume of sedimented phase increased correspondingly from 21 to 42 μL, and the maximum extraction efficiency was reached when using 53 μL [C$_6$mim][NTf$_2$]. Consequently, 53 μL was used as the optimum volume for the extraction in further experiments.

3.3. *Effect of the duration of the first ultrasound extraction*

In this study, because [C$_6$mim][NTf$_2$] was directly injected to the solution, the first ultrasound irradiation played an important role in emulsification and mass transfer. The effect of the duration of the first ultrasound extraction was studied over a time range from 0 to 4 min. The results (Fig. 3) indicate that the extraction efficiencies are increased by prolonging the ultrasound irradiation time up to 2 min. As discussed in the study of Zhou et al. [20], sufficient treatment time accelerates the formation of a fine dispersive mixture; after that, extending the duration of the ultrasonic treatment can also result in the loss of volatile analytes due to heat generation. The same trend was observed in our experiments; thus, a 2 min duration for the first ultrasound irradiation was chosen for the following study.

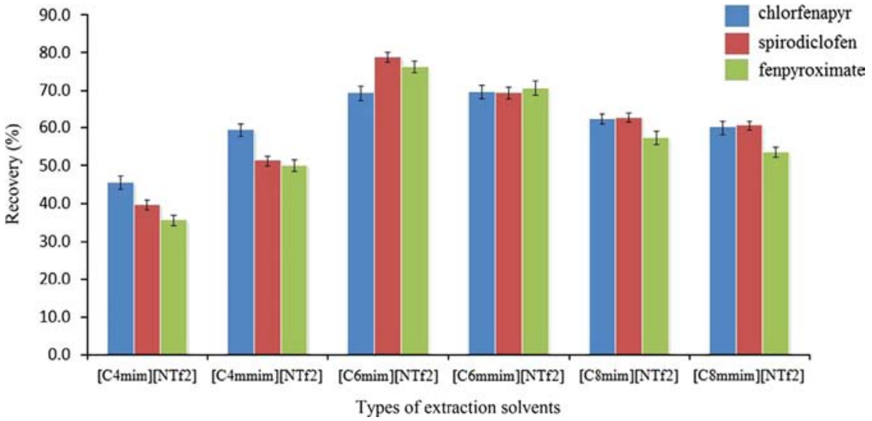

Fig. 1. Effect of various ionic liquids on recoveries. Extraction conditions as follows: sample volume, 10.0 mL; extraction solvent volume for each IL was varied to keep sediment phase as 30 μL; the first ultrasound irradiation time, 1 min; dispersion temperature, 50 °C; the second ultrasound irradiation time, 1 min; centrifugation time, 10 min; concentration level, 10 μg L^{-1}.

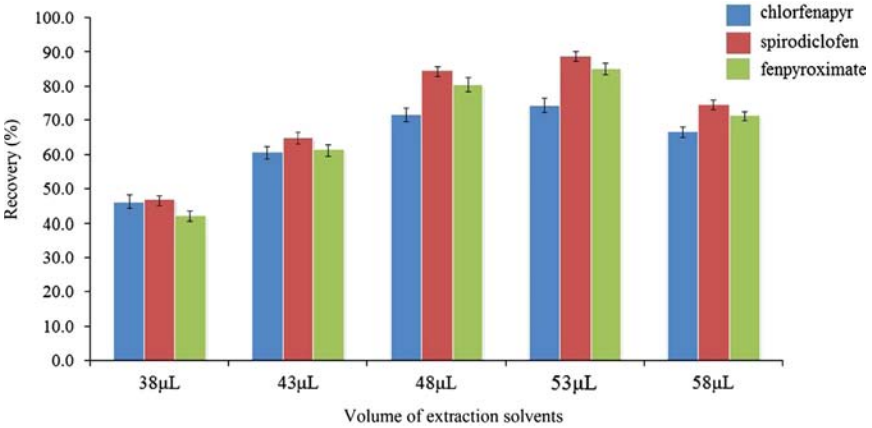

Fig. 2. Effect of ionic liquid volume on recoveries. Extraction conditions as follows: sample volume, 10.0 mL; extraction solvent: $[C_6mim][NTf_2]$. The other extraction conditions: as in Fig. 1.

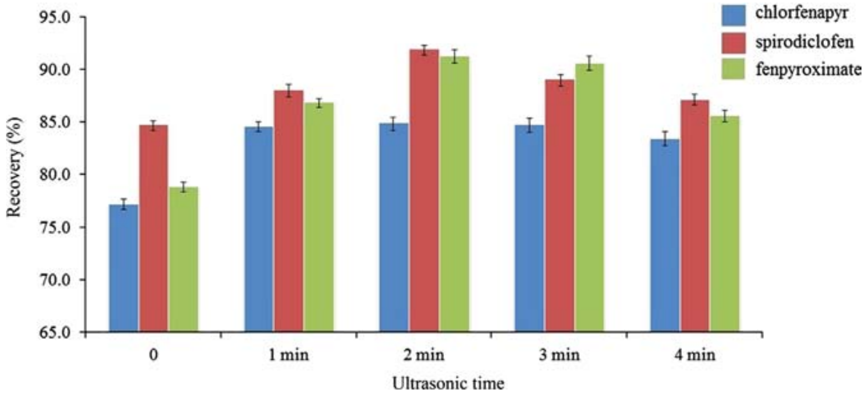

Fig. 3. Effect of the first ultrasound irradiation time on recoveries. Extraction conditions as follows: sample volume, 10.0 mL; extraction solvent: 53 μL $[C_6mim][NTf_2]$. The other extraction conditions: as in Fig. 1.

3.4. Effect of the dispersion temperature

The water solubility of RTIL typically varies greatly because of its stronger ionic bond. Therefore, in the proposed method, the heating temperature was another key factor and also the driving force for the complete dispersion of ionic liquid into aqueous solution. The effect of the dispersion temperature was studied within a temperature range of 50–90 °C, and the results are shown in Fig. 4. It was determined that the best extraction performance was achieved at 60 °C.

3.5. Effect of duration of the second ultrasound extraction in an ice-bath

To make extractants re-form submicron droplets, an ice-water sonicated bath was employed. Using this method, the low temperature

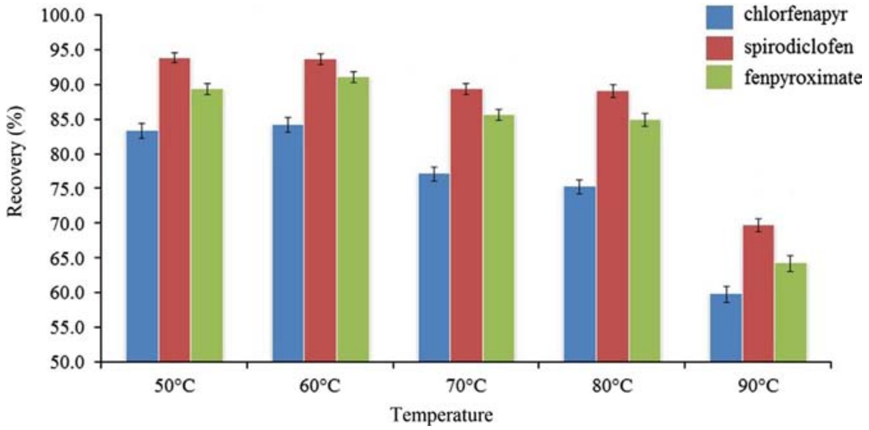

Fig. 4. Effect of the dispersion temperature on recoveries. Extraction conditions as follows: sample volume, 10.0 mL; extraction solvent, 53 μL [C_6mim][NTf_2]; The first ultrasound irradiation time, 2 min. The other extraction conditions: as in Fig. 1.

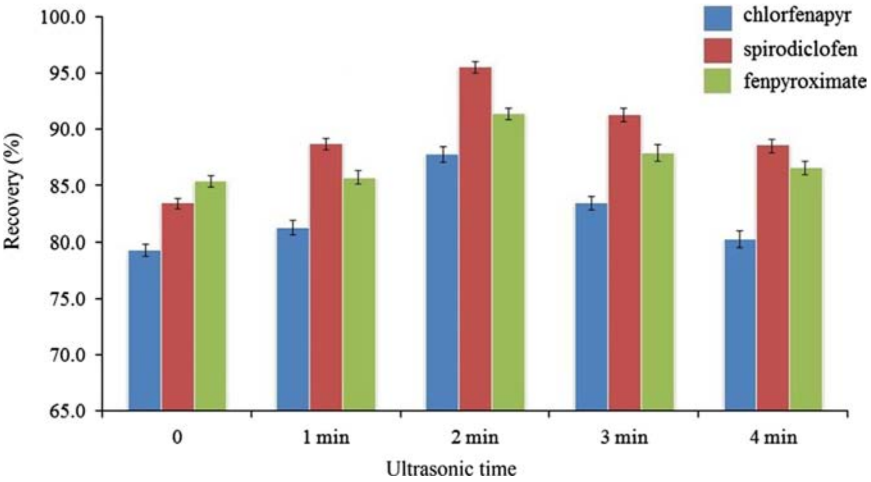

Fig. 5. Effect of ionic liquids on recoveries. Extraction conditions as follows: sample volume, 10.0 mL; extraction solvent, 53 μL [C_6mim][NTf_2]; The first ultrasound irradiation time, 2 min; dispersion temperature, 60 °C; centrifugation time, 10 min; concentration level, 10 μg L^{-1}.

can significantly reduce the solubility of the ionic liquid in water, and ultrasound irradiation re-disperses the droplets, which leads to an increase in the extraction efficiency of the procedure in a minimum amount of time. The effect of the duration of the second ultrasound in an ice-bath was investigated for 0–4 min. The results indicated that a 2 min time period is enough for efficient extraction, and no significant change was observed with longer extraction times. Thus, to reduce the total analysis time and avoid potential analyte loss over a longer extraction time, 2 min was selected as the optimal extraction time Fig. 5.

3.6. Effect of ionic strength and centrifugation time

To evaluate the possibility of any observable salting-out effect, experiments were performed at different concentrations of NaCl (0–8%, w/v). In the proposed method, no significant changes in extraction recoveries were observed with increased salt concentration. This finding suggests that the salting-out effect was negligible. During the TEME procedure, centrifugation was used to disrupt the cloudy solution after extraction and to deposit the sediment phase in the tubes. The effect of centrifugation time on the extraction recoveries was assayed in the range of 5–25 min. Based on the experimental results, the extraction efficiency for the analytes was lower when the centrifugation time was short (5 min), while longer centrifugation times had no significant effect on the extraction efficiency. To save time, 10 min was selected as a centrifugation time.

3.7. Application of TEME in fruit juice samples

3.7.1. Method validation

Under the most favorable extraction conditions that were determined as described above, a series of working solutions containing chlorfenapyr, spirodiclofen and fenpyroximate at 11 different concentration levels (0.1–600 μg L^{-1}) were prepared to establish the calibration curve. For each level, six replicate extractions and determinations were performed. The results shown in Table 2 indicate that the calibration curve was linear from 0.1 to 600 μg L^{-1} for chlorfenapyr and fenpyroximate and 0.5–600 μg L^{-1} for spirodiclofen. Good linearity with squared regression coefficients of approximately 0.9994 and 0.9999 were observed. The limits of detection (LODs), determined at a signal-to-noise ratio of 3, for TEME were between 0.02 and 0.06 μg L^{-1}. The resultant repeatabilities expressed as relative standard deviations (RSDs) varied from 1.9 to 3.3%. The extraction recoveries and enrichment factors of this method were high, ranging from 94 to 103% and 261 to 285, respectively.

3.7.2. Comparison of TEME and other methods

A comparison of the proposed TEME method with published methods for the extraction and determination of acaricides is summarized in Table 3. The TEME method is superior to the other solid-phase extraction, liquid-phase extraction, and conventional liquid-phase microextraction methods with regard to the

Table 2
The performance characteristics of the proposed method combined with HPLC-VWD.

Compound	Linearity equation	Linearity (μg L^{-1})	r	RSD (%)	Enrichment factors	LOD (ng L^{-1})	Recovery (%)
Chlorfenapyr	$Y=9.364X-0.382$	0.1–600	0.9999	1.9	261	28.1	94.1
Spirodiclofen	$Y=4.255X+5.246$	0.5–600	0.9994	3.3	285	61.4	102.9
Fenpyroximate	$Y=5.863X+0.977$	0.1–600	0.9999	3.4	274	21.1	98.6

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

Table 3
Comparison of in-situ UA-IL-DLLME with other methods for the determination of PHUs.

Method	Extraction solvent	Analytical ranges	LODs	RSD (%)	Ref.
LPME	Isooctane	0.5–100 μg L^{-1}	50.0 ng L^{-1}	9.0	[1]
DLLME	$[C_6MIM][PF_6]$	2–100 μg L^{-1}	1.1 μg L^{-1}	10.5	[21]
UADLLME	Tetrachloromethane	0.6–1520 μg L^{-1}	0.1–0.3 μg L^{-1}	1.1–3.6	[22]
SPME	–	0.01–0.1 mg L^{-1}	0.17 μg L^{-1}	3.0	[23]
TEME	$[C_6MIM]NTf_2$	0.1–600 μg L^{-1}	21.1–61.4 ng L^{-1}	1.9–3.4	Present work

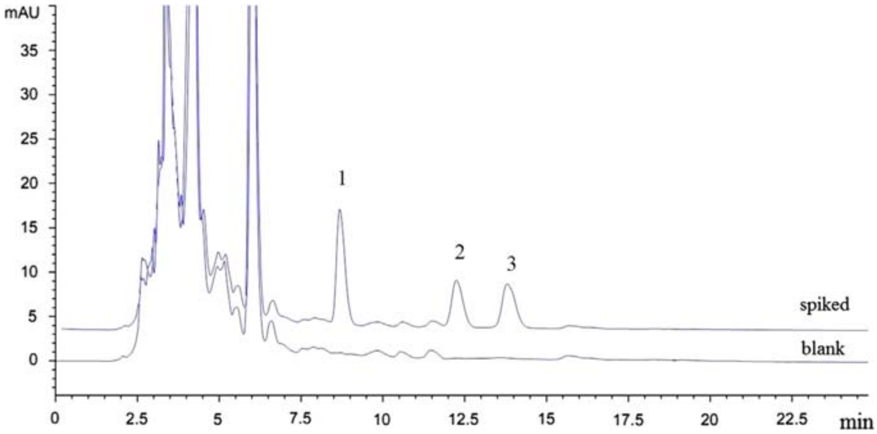

Fig. 6. The typical chromatograms of acaricides in spiked and blank grape juice sample. (1) Chlorfenapyr; (2) spirodiclofen; (3) fenpyroximate.

following: (i) A lack of organic solvent during the entire extraction procedure, which is safer and more environmentally friendly; (ii) better relative standard deviations (1.9–3.4%) because of the non-volatile nature of the ionic liquid extractant; (iii) good analytical ranges (0.1–600 μg L^{-1}) and extraction efficiency (recovery: 94–103%) because of the high dispersion state of $[C_6mim][NTf_2]$ caused by ultrasound irradiation and temperature control; and (iv) high enrichment factors (261–285) and low LODs (21.1–61.4 ng L^{-1}) due to the high partition coefficient of analytes between $[C_6mim][NTf_2]$ and water. In conclusion, the TEME method is a simple, reliable and environmentally friendly micro-extraction method that can serve as a complementary technique for DLLME and USAEME.

3.7.3. *Analysis of real fruit juice samples*

To evaluate the applicability and accuracy of the proposed method in real samples, the optimized TEME method was applied to the extraction of acaricides in three types of fruit juice samples (grape, peach and orange juice). The results show that chlorfenapyr, spirodiclofen and fenpyroximate residues were below the detectable level in all samples (Fig. 6). For the recovery experiment, five replicates of real samples were spiked with standards of pesticides at concentrations of 10 and 30 μg L^{-1}. The relative recoveries of the three acaricides in the spiked samples ranged from 92 to 104% with a precision of 2.1–4.8% (RSD). These data are listed in Table 4 and the chromatogram of a juice sample spiked with 10 μg L^{-1} of acaricides is displayed in Fig. 6.

Table 4
Relative recovery and RSD values of acaricides studied in three fruit juice samples.

Samples	Acaricides	Added (μg L^{-1})	Recovery (%)	RSD (%) ($n=5$)
Grape juice	Chlorfenapyr	10	94.5	3.8
		30	96.8	2.7
	Spirodiclofen	10	98.9	4.1
		30	96.8	2.3
	Fenpyroximate	10	103.7	2.1
		30	96.2	3.9
Peach juice	Chlorfenapyr	10	94.9	3.0
	Spirodiclofen	30	91.9	2.2
		10	100.0	4.8
		30	100.0	3.9
	Fenpyroximate	10	103.7	3.4
		30	93.7	3.6
Orange juice	Chlorfenapyr	10	93.8	3.6
	Spirodiclofen	30	95.6	3.5
		10	98.1	2.0
		30	97.1	2.6
	Fenpyroximate	10	96.7.	3.5
		30	96.8	3.8

4. Conclusion

In this work, seven bis[(trifluoromethane)sulfonyl]imide ionic liquids were synthesized using metathesis reactions. Physicochemical properties such as surface tensions and viscosities were measured systematically. By comparing these properties and their application to microextraction experiments, [C_6mim][NTf_2] was selected as the extractant in the totally organic solvent-free emulsification microextraction procedure. The dispersion of the extraction solvent was accelerated by the ultrasound irradiation and temperature control process. Under the optimum condition, wide linearity, high recoveries, good repeatability and a great enrichment factor were obtained. Furthermore, the proposed method is a completely organic solvent-free emulsification microextraction procedure and is therefore environmentally friendly. Finally, the robust results of the experiments using real fruit juice samples indicate that the TEME method is a viable option for the determination of acaricide residues in real aqueous samples for future studies.

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