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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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## ARTICLE INFO

### Article history:

Received 20 March 2013

Received in revised form

3 June 2013

Accepted 10 June 2013

Available online 14 June 2013

### Keywords:

Ionic liquid

Liquid–liquid microextraction

Acaricides

Surface tension

Ultrasound irradiation

## 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<sub>6</sub>MIM][NTf<sub>2</sub>]), 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 μg L<sup>-1</sup> for chlorfenapyr and fenpyroximate and 0.5–600 μg L<sup>-1</sup> 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 μg L<sup>-1</sup>. Real fruit juice samples (at fortified levels of 10 μg L<sup>-1</sup> and 30 μg L<sup>-1</sup>) were successfully analyzed using the proposed method. The relative recoveries and enrichment factors were in the range of 92–104%.

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## 1. Introduction

Chlorfenapyr, spirodiclofen and fenpyroximate are excellent broad-spectrum acaricides that have been developed to control insects such as acarid pests on vegetables and fruit trees [1,2]. Although spraying chemical acaricides is 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<sup>-1</sup> 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) are a 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 synthesize 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<sub>6</sub>MIM][NTf<sub>2</sub>] 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. Acetonitrile and methanol for spectroscopy were obtained from Dikma Limited (China) and the deionized water (< 18 cm MΩ resistivity) was purified by a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). 1-Butyl-3-methylimidazolium chloride [C<sub>4</sub>MIM]Cl, 1-butyl-2,3-dimethylimidazolium chloride [C<sub>4</sub>MMIM]Cl, 1-hexyl-3-methylimidazolium chloride [C<sub>6</sub>MIM]Cl, 1-hexyl-2,3-dimethylimidazolium chloride [C<sub>6</sub>MMIM]Cl, 1-octyl-3-methylimidazolium chloride [C<sub>8</sub>MIM]Cl, 1-octyl-2,3-dimethylimidazolium chloride [C<sub>8</sub>MMIM]Cl and 1-decyl-3-methylimidazolium chloride [C<sub>10</sub>MIM]Cl were purchased from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). Li[NTf<sub>2</sub>] 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<sub>n</sub>MIM][NTf<sub>2</sub>]) ionic liquids and three 1-alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>n</sub>MMIM][NTf<sub>2</sub>]) 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<sub>2</sub>] with equal amounts of the desired cation ([C<sub>n</sub>MIM]Cl and [C<sub>n</sub>MMIM]Cl, n=4, 6, 8 or 10). After purification, the final products were characterized by nuclear magnetic resonance (NMR) spectroscopy. The <sup>1</sup>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<sup>-1</sup>) 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 < ± 0.05 mN m<sup>-1</sup>.

Chromatographic analysis was carried out by an Agilent 1200 HPLC system equipped with a variable wavelength 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<sup>-1</sup>. The variable wavelength detector was

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