



Ultrasonic nebulization headspace ionic liquid-based single drop microextraction of flavour compounds in fruit juices

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ABSTRACT

The ultrasonic nebulization headspace ionic liquid-based single drop microextraction was developed for the extraction of flavour constituents from fruit juices. The GC–MS was applied to the separation and detection of the constituents. The parameters affecting extraction performance, such as microdrop volume, extraction time, enrichment time, extraction temperature, and position of microdrop, were investigated and optimized. The optimized system was: ionic liquid, 1-hexyl-3-methylimidazolium tetrafluoroborate; solvent microdrop volume, 12.5 μ L; extraction time, 5 min; enrichment time, 20 min; extraction temperature, 80 $^{\circ}$ C; the height of the microdrop above the solution surface, 1 cm; and, the pH value of sample solution did not affect the species, and solubility of analytes. The recoveries were in the range of 80.4–115.0%, and the relative standard deviations were lower than 9.1%. The present method is a simple and sensitive method for the determination of flavour constituents in fruit juices.

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1. Introduction

The fruit juice industry has become one of the world's major agricultural businesses with world trade in fruit juices annually exceeding \$ 10 billion. Aroma is a decisive criterion for evaluating fruit juice quality [1]. Volatile flavour constituents directly affect the sensorial quality of fresh and processed fruit products [2]. A considerable amount of methods have been developed for characterizing flavour compounds.

The sample pretreatment is a critical step for the determination of flavour compounds. The methods to extract flavour compounds usually involved distillation, extraction, combination of distillation and extraction, and solvent assisted flavour evaporation [1]. Recently, some enrichment methods have been proposed for the determination of volatile compounds. The solid-phase extraction (SPE) [3], solid-phase microextraction (SPME) [4–6], and single drop microextraction (SDME) [7] have been developed. SDME has the advantages of simplicity, rapidity and inexpensiveness, and was applied in extracting analytes from spice [8], water [9], vegetable [10], and so on [11]. To meet a variety of analytical requirement, SDMEs were divided into direct immersion (DI)-SDME [12] and headspace (HS)-SDME. In HS-SDME, the microdrop was suspended in the headspace of extraction vessel, and the extraction efficiency for each constituent in

sample depends on its volatility and distribution ratio between the gas phase and the suspended solvent. So, HS-SDME, which was usually combined with stirring extraction, ultrasonic extraction and microwave assisted extraction, is an effective method to extract flavour constituents from foodstuffs. When the HS-SDME was applied, the nonvolatile compounds were not extracted, which is of crucial importance in flavor compound isolation from such matrices as foodstuffs [13]. The HS-SDME was applied for the extraction of volatile aldehydes from cucumber [14] and flavors from clove buds [15]. HS-SDME was applied for the extraction of 2,4,6-trichloroanisole and 2,4,6-tribromoanisole in wine samples [16] and volatile sulphur compounds in beer and beverage [17]. Ionic liquid-based-SDME coupled with ion mobility spectrometry (IMS) was applied for the determination of 2,4,6-trichloroanisole in water and wine samples [18].

HS-SDME coupled with ultrasonic nebulization extraction was first studied for extraction of the essential oil from *Cuminum cyminum* L [19]. The description of ultrasonic nebulization extraction has been reported in literature [20,21]. These experiments confirmed that HS-SDME coupled with ultrasonic nebulization extraction is a feasible and alternative method for the extraction of active constituents from samples.

The ionic liquids (ILs) are semi-organic molten salts which consist of organic cations and organic or inorganic anions. The ILs emerge as possible “green” solvents [22–24], because they have the advantages of immeasurably low vapor pressure, high stability, large viscosity, moderate dissolvability of organic compounds, as well as adjustable miscibility and polarity [25–27].

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ILs were recently proposed as the hopeful substitutes of extraction solvents. In recent years, the ILs have attracted increasing interest and are used more and more as attractive alternatives to environmentally friendly solvents in sample preparation [28–30]. ILs are promising solvents in the preparation of various active constituents from medicinal plants, such as essential oils [31], alkaloids [32,33], terpene lactones [34], and polyphenolic compounds [35].

Because IL has immeasurably low vapor pressure, the evaporation of the ILs are difficult. If GC is going to be applied after SDME, the ILs can contaminate the GC column. This drawback limits the application of the IL-based SDME in GC analysis [36].

In this paper, the ionic liquid 1-hexyl-1-3-methylimidazolium tetrafluoroborate ($[\text{C}_6\text{MIM}][\text{BF}_4]$), which is hydrophilic, was used as extraction solvent in SDME. However, the IL is not suitable to be introduced into the GC system, because the IL can contaminate the GC column. With the aim of contributing to exploiting the advantages of ILs as extraction solvents for the microextraction of flavour in fruit juices, the present work focuses on the development of a simple and available approach for the use of IL-based SDME prior to GC system.

2. Experimental

2.1. Chemicals and sample preparation

Fruit juices (samples 1, 2 and 3) used in this experiment were purchased from local supermarkets in Changchun, Jilin Province, China. Sample 1, 2 and 3 are orange, mango and peach juices, respectively. The content of fruit juice in sample 1 is higher than 10%. Sample 2, 3 contain 30 and 36% fruit juices, respectively. The pH value of the three samples is 2.5. The samples were kept at 4 °C before analysis. In this study, all experiments were carried out with sample 1 except for the experiment mentioned in Section 3.2.2 in which the three samples were used.

The standards, hexyl acetate (99%) and geranyl acetate (98%) were purchased from Acros Company (New Jersey, USA). The standard Limonene (> 98%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). *n*-Decane was used as internal standard and purchased from Acros Company (New Jersey, USA). 1-Ethyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_2\text{MIM}][\text{BF}_4]$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{MIM}][\text{BF}_4]$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_6\text{MIM}][\text{BF}_4]$) were obtained from Chengjie Chemical Co., Ltd. (Shanghai, China). Chromatographic grade *n*-hexane was purchased from Fisher Scientific Company (UK).

The standard stock solutions of target compounds and internal standard were prepared by dissolving the compounds in *n*-hexane. These stock solutions were stored in the dark at 4 °C. Pure water was obtained with Milli-Q water purification system (Millipore Co., USA). The other reagents purchased from Beijing Chemical Factory (Beijing, China) are all of analytical grade.

2.2. Instruments and apparatus

The extraction and concentration system was assembled in our laboratory. A schematic diagram of the system is shown in Fig. 1. An ultrasonic humidifier (Beijing Branson Ultrasound Co. Ltd., China) working at 1.7 MHz with maximum output power of 35 W was employed as the ultrasonic source. The extraction vessel was a self-made glass flask (100 mL). The port on the bottom of the extraction vessel was sealed with the PVC film and the size of the port was the same as that of the piezocrystal. The space between the ultrasonic nebulization extraction and the piezocrystal was full of coupling water. A heating tape connected with a

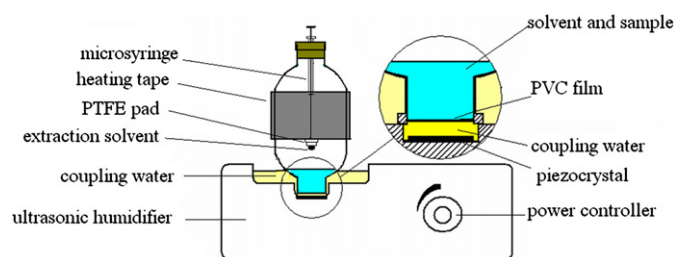


Fig. 1. UN-HS-IL-SDME system.

thermocouple sensor (XMTD-2001 Xinghua AOTE Temperature Instrument Co., Xinghua, China) was used for heating the extraction vessel and can regulate the heating temperature. A 25 μL microsyringe (Zhenhaisan'ai Instrument Co. Ltd, Ningbo, China) was used for microextraction and sample injection. It is not possible to suspend a large volume of microdrop of $[\text{C}_6\text{MIM}][\text{BF}_4]$ from the tip of a bare needle. In order to suspend a large volume of drop on the needle of the microsyringe, the tip of the microsyringe needle was sheathed with a polytetrafluoro-ethylene (PTFE) pad as shown in Fig. 1. In this way, the probability of drop detachment decreased and a large volume of microdrop can be suspended at the tip of syringe with good stability.

2.3. GC–MS analysis

The sample solution was analyzed using a GC–MS QP 2010 (Shimadzu, Kyoto, Japan). Chromatographic separation was conducted with a DB-5MS capillary column (30 m \times 0.25 mm I.D., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA). Ultra-high-purity helium (99.999%) was used as the carrier gas at a constant flow of 1.0 mL min^{-1} . The temperature program was set initially at 60 °C for 2 min to 140 °C at a rate of 10 °C min^{-1} (held for 1 min), and then to 220 °C at a rate of 3 °C min^{-1} (held for 1 min). The injector temperature was maintained at 250 °C, and the injection volume was 1.0 μL in the split mode (split ratio 1:5). The ion source temperature, interface temperature, and electron impact ionization energy were 200 °C, 250 °C, and 70 eV, respectively. The mass spectrometer was operated in a selected ion monitoring (SIM) mode for quantitative analysis. Full-scan MS data were acquired in the range of m/z 50–550 to obtain the fragmentation spectra of the target analytes.

2.4. UN-HS-IL-SDME

Fruit juice was centrifuged at 3000 rpm for 5 min before extraction. 5 mL of fruit juice and 5 mL of water were added into the extraction vessel shown in Fig. 1. The needle of the 25 μL microsyringe was passed through the plug and was clamped at a fixed position in the extraction vessel. The height of the tip of the microsyringe above the surface of the sample solution was approximately 1 cm. The extraction vessel was wrapped with a heating tape and the extraction temperature was controlled at 80 °C. When the nebulizer was switched on, the ultrasonic energy was transferred through coupling water to the sample solution and the sample solution spurted up from the bottom of the extraction vessel. The “ultrasonic fountain” appeared and the extraction vessel was full of aerosol. The analytes in fruit juice were transferred from extraction solvent to headspace by the help of ultrasonic fountain. Ultrasonic nebulization can be used to produce very fine aerosol, and the analytes can be enriched and accumulate in the aerosol [37]. All the experiments were performed in triplicate. In the headspace, the analytes were transferred from the aerosol into the gas phase due to the gas–liquid distribution equilibrium. After ultrasonic nebulization extraction

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