Chinese Chemical Letters 25 (2014) 465–468

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Determination of spices in food samples by ionic liquid aqueous solution extraction and ion chromatography

Hai-Bao Zhu [a,*], Yun-Chang Fan [b], Ya-Ling Qian [a], Hong-Fang Tang [a], Zheng Ruan [a], Dan-Hua Liu [a], Han Wang [a]

[a] Zhejiang Academy of Medical Sciences, Hangzhou 310013, China
[b] College of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454003, China

ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form 14 November 2013
Accepted 20 November 2013
Available online 8 December 2013

Keywords:
Spices
Ionic liquid
Food
Ion chromatography

ABSTRACT

In the present work, a novel method to extract three kinds of spices, namely vanillin, ethyl vanillin and ethyl maltol from food products such as biscuit, chocolate and milk powder was developed. 1-Octyl-3-methylimidazolium chloride ([Omim]Cl) aqueous solution was selected as the extracting medium. A 0.5 g powder of food product was extracted by 5.0 mL of [Omim]Cl aqueous solution (0.3 mol/L, pH 6.0) under ultrasonication at 50 °C, and then the extract was centrifuged for 10 min at 4000 rpm. The extract was filtered through a syringe filter and injected into ion chromatography system for analysis. The separation of the three spices was carried out on an anion exchange column. The detection wavelength was set at 280 nm. Compared with traditional extraction solvents, [Omim]Cl aqueous solution displayed particular advantages. The applicability of the proposed method to real sample was confirmed. Under the optimal conditions, good reproducibility of extraction performance was obtained, with the relative standard deviation (RSD) values ranging from 1.9% to 6.3%. The recoveries of spiked samples were between 79.8% and 95.8%. The detection limits (LOD, $S/N = 3$) of vanillin, ethyl vanillin and ethyl maltol were in the range of 20–45 μg/kg. The use of ionic liquid aqueous solution as extraction solvent was operationally easy and environmental-friendly.

1. Introduction

Vanillin, ethyl vanillin and ethyl maltol are extensively used as spices in food industry to improve the taste of the products of interest. However, excessive usage of spices might be harmful. So, it is of great importance to monitor the level of the three spices in food samples. High performance liquid chromatography (HPLC) [1], capillary electrophoresis [2] and spectrometric methods [3] were developed for this purpose. However, few methods were reported using ion chromatography (IC). The three spices investigated in the present work are weak organic acids. Therefore, they could be separated by anion-exchange chromatography. However, suitable sample pretreatment procedure is a prerequisite for the determination of the three spices in food samples by ion chromatography.

Extraction methods for spices in different food samples predominantly consist of solid phase extraction (SPE), solvent extraction and matrix solid phase expression (MSPE) [4,5]. Organic solvents were usually used in these conventional methods. They pose a threat to the environment and human health. Thus developing a relatively simple and environmentally benign extraction method for the determination of spices in food samples is urgent. Recently, ionic liquids (ILs) have attracted extensive interest owing to their potential use as environmentally benign solvents to replace traditional volatile organic solvents in many applications, including some extraction processes like liquid-phase microextraction [6,7], solid-phase microextraction [8,9] and microwave-assisted extraction [10,11].

It has been reported that a series of ILs based on the 1-alkyl-3-methylimdazolium salts act as short chain cationic surfactants in aqueous solution and form aggregations above critical aggregation concentration [12,13]. Therefore, IL-based aqueous solution is also a good medium for the extraction of polycyclic aromatic hydrocarbons from sediments.

The main purpose of the present work was to evaluate the possibility of using an IL aqueous solution, 1-octyl-3-methylimidazolium chloride ([Omim]Cl), to replace traditional organic solvents to extract vanillin, ethyl vanillin and ethyl maltol from biscuit, chocolate and milk powder. After investigating the parameters affecting the extraction efficiency, the optimal extraction conditions were established for the IC-UV/vis determination of vanillin, ethyl vanillin and ethyl maltol. Because of the

* Corresponding author.
E-mail address: chem-zhuhaibao@163.com (H.-B. Zhu).

1001-8417/$ – see front matter © 2013 Hai-Bao Zhu. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
http://dx.doi.org/10.1016/j.cclet.2013.12.001

nonvolatility of the IL, the proposed method was environmentally friendly with good reproducibility and spiked recoveries.

2. Experimental

2.1. Reagents and samples

Vanillin, ethyl vanillin and ethyl maltol standard agents were obtained from Dingfu Chem. Co. (Shanghai, China). HPLC-grade acetonitrile was purchased from Tedia Co. (USA). 1-Chlorooctane (99.5%) was purchased from Bangcheng Chem. Co. (Shanghai, China). 1-Methylimidazole (99.0%) was obtained from Kaile Chem. Co. (Zhejiang, China). Analytically pure sodium hydroxide was purchased from Sinopharm Chem. Reagent Co., Ltd. (Beijing, China). Deionized (18.2 MΩ/cm) water generated by a Millipore Milli-Q Plus system (Millopore, Milford, USA) was used throughout.

Working solutions of vanillin, ethyl vanillin and ethyl maltol were obtained by appropriate dilution of the corresponding standard solutions (1000 mg/L) with deionized water. Ionic liquids [Omim]Cl was prepared according to the reported literature [14,15].

Biscuit, chocolate and milk powder were randomly purchased from local supermarket.

2.2. Equipment

IC analysis was performed on a Dionex 500 ion chromatographic system (Dionex, USA) consisting of a quaternary pump, a manual injector with a 15 μL loop and an ultraviolet detector setting at 280 nm. An AS18 column equipped with an AG18 guard column (Dionex, USA) was used for the separation of the three spices extracted in the IL phase. Chromeleon 6.5 software was used to acquire data and control the instrumentation.

TDL-60B ultrasonic machine from Anting Instrument Co. (Shanghai, China) was used to facilitate the extraction of the three spices from solid matrices. TG16-W centrifugal machine from Weierkang Xiangying Centrifuge Co., Ltd. (Changsha, China) was used to clarify and simultaneous separate the liquid phase.

2.3. Chromatographic conditions

A mixture of 25 mmol/L sodium hydroxide–acetonitrile (85:15, v/v) was used as mobile phase by pneumatic means, *i.e.* by putting the high-density polyethylene (HDPE) bottles in a chamber pressurized at 250 psi with nitrogen. The flow rate of the eluent was 0.25 mL/min.

2.4. Extraction procedure

Typically, 0.5 g of sample, which was crushed into powders, was weighed into a 10-mL plastic conical bottom tube, and then 5.0 mL IL aqueous solution (0.3 mol/L) was added. After extraction for 20 min under ultrasonic irradiation, the mixture was centrifuged for 10 min at 4000 rpm. The extract was filtered through a syringe filter (pore size 0.45 μm) and injected into the IC system for analysis.

3. Results and discussion

3.1. Influence of IL concentration

To evaluate the IL concentration effect on the extraction efficiency, additional experiments were performed using different concentrations of [Omim]Cl. Biscuit sample spiked with 80 mg/kg of vanillin, ethyl vanillin and ethyl maltol was used as a representative in the experiment. The result in Fig. 1 shows that the extraction recoveries of vanillin, ethyl vanillin and ethyl maltol increased with the IL concentration up to 0.3 mol/L and plateaued above this level.

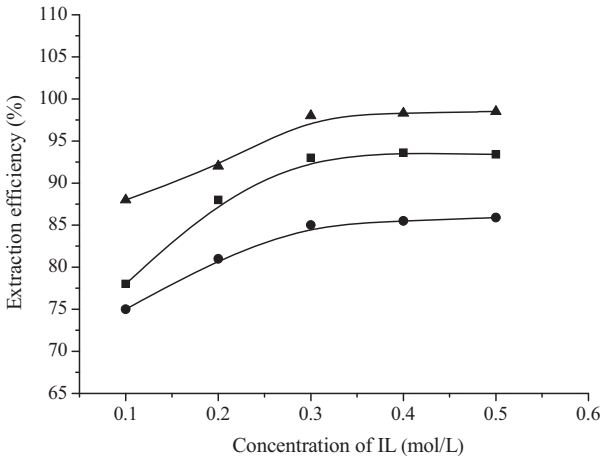

Fig. 1. Effect of IL concentration on extraction efficiency. (▲) Ethyl vanillin;(■) ethyl maltol; (●) vanillin. Condition: 0.5 g biscuit sample spiked with 80 mg/kg of vanillin, ethyl vanillin and ethyl maltol was extracted with 5.0 mL extractant for 20 min under ultrasonication.

3.2. Effect of volume of IL

In order to investigate the effect of IL volume on extraction efficiency, 0.5 g of biscuit sample spiked with 80 mg/kg of vanillin, ethyl vanillin and ethyl maltol was extracted with different volumes of extractant (2–7 mL) for 20 min. The results shown in Fig. 2 demonstrate that the recoveries of the three spices are almost constant with the volume of [Omim]Cl ranging from 5.0 to 7.0 mL. Since unnecessary IL aqueous solution was not used to avoid an excessive dilution of the sample, 5.0 mL was then selected as the extractant volume.

3.3. Effect of pH value

The effect of pH value on the efficiency of extraction was studied using 2 mol/L hydrochloric acid or 1 mol/L sodium hydroxide regulating the pH values of extraction phase. Results showed that, in the pH 3–8 range, the extraction efficiency of the IL aqueous solution on the three spices did not vary with the change of pH values. However, the extraction efficiency decreased significantly when the pH value was above 8. A reasonable explanation for this phenomenon is that the hydroxyl groups (–OH) of the three spices exist in neutral forms (–OH) and thus can form hydrogen bonds with the IL [6]. Thus, the extraction efficiency of the [Omim]Cl was higher under acidic conditions than in alkaline environments. Considering the fact that the pH value of deionized water is very close to 6, pH 6 was then selected. Additionally, the pK_a values of three spices were in the following order: ethyl vanillin > ethyl maltol > vanillin, therefore, the percentages of the neutral form for the three spices were also in the same order, which explained why the extraction efficiency decreased in the following sequence: ethyl vanillin > ethyl maltol > vanillin.

3.4. Effect of temperature

In this study, the effect of extraction temperature on extraction efficiency was examined in the range of 40–70 °C. The results showed that, the extraction efficiency at 50 °C is higher than the