



# Preparation of a polymeric ionic liquid-based adsorbent for stir cake sorptive extraction of preservatives in orange juices and tea drinks



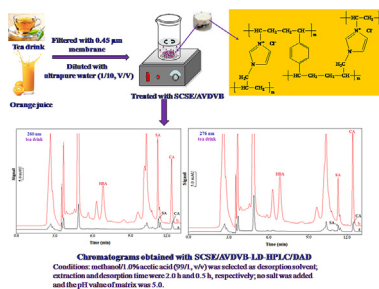
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## HIGHLIGHTS

- A new polymeric ionic liquid-based adsorbent was prepared.
- The adsorbent was used as the extractive medium of SCSE.
- The multiply interactions involved the extraction of preservatives.
- Method of determination of preservatives in juice and tea drinks was developed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, a new polymeric ionic liquid-based adsorbent was prepared and used as the extraction medium of stir cake sorptive extraction (SCSE) of three organic acid preservatives, namely, *p*-hydroxybenzoic acid, sorbic acid and cinnamic acid. The adsorbent was synthesized by the copolymerization of 1-allyl-3-vinylimidazolium chloride (AV) and divinylbenzene (DVB) in the presence of a porogen solvent containing 1-propanol and 1,4-butanediol. The effect of the content of monomer and the porogen solvent in the polymerization mixture on the extraction performance was investigated thoroughly. The adsorbent was characterized by infrared spectroscopy, elemental analysis, scanning electron microscopy and mercury intrusion porosimetry. To obtain the optimal extraction conditions of SCSE/AVDVB for target analytes, key parameters including desorption solvent, adsorption and desorption time, ionic strength and pH value in sample matrix were studied in detail. The results showed that under the optimized conditions, the SCSE/AVDVB could extract the preservatives effectively through multiply interactions. At the same time, a simple and sensitive method by combining SCSE/AVDVB and high-performance liquid chromatography with diode array detection was developed for the simultaneous analysis of the target preservatives in orange juices and tea drinks. Low limits of detection ( $S/N = 3$ ) and quantification limits ( $S/N = 10$ ) of the proposed method for the target analytes were achieved within the range of 0.012–0.23  $\mu\text{g/L}$  and 0.039–0.42  $\mu\text{g/L}$ , respectively. The precision of the proposed method was evaluated in terms of intra- and inter-assay variability calculated as relative standard deviation (RSD), and it was found that the values were all below 10%. Finally, the proposed method was used to detect preservatives in different orange juice and tea drink samples successfully. The recoveries were in the range of 71.9–116%, and the RSDs were below 10% in the all cases.

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## 1. Introduction

For complicated samples, sample preparation is an unavoidable step in the whole analytical procedure. Suitable sample preparation can concentrate target analytes and reduce the matrix interferences. In the past decades, many efforts have been devoted to developing simple, cost-effective and environmentally friendly sample pre-treatment methodologies. According to the different extraction phases concerned, sample-preparation procedure can be divided into solvent-based and adsorbent-based extraction [1]. Compared with solvent-based extraction, adsorbent-based extraction has received wide acceptance because it can circumvent the disadvantages of consuming large amounts of organic solvents. In the past two decades, various adsorbent-based extraction formats such as solid-phase extraction (SPE) [2], magnetic solid-phase extraction (MSPE) [3], solid-phase microextraction (SPME) [4], stir bar sorptive extraction (SBSE) [5] and stir cake sorptive extraction (SCSE) [6] have been developed. In the all kinds of extraction formats in adsorbent-based extraction, the core is the extraction medium (adsorbent). Different adsorbents possess different extraction performance for analytes. Rapid, more selective extraction and high enrichment of analytes have been the desirable objectives of selection of appropriate adsorbents. So far, a great variety of adsorbents has been reported and part of them has been commercially available. Surface-modified silicas (C8, C18) [2], porous monolithic materials [7], graphene-based materials [8], carbon nanotubes [9], polymeric ionic liquids (PILs) [10], metal-organic frameworks (MOFs) [11] and boronate affinity materials [12] et al. have been developed and widely used to extract all kinds of compounds from environmental, biological and food samples. Although many new materials are emerging, developing adsorbents with promising structural and chemical reactive properties for sample preparation is highly desired.

PILs refer to a special type of polyelectrolytes which carry an ionic liquid species in each of the repeating units. PILs combine the unique properties of ILs and the macromolecular architecture together with intrinsic polymer characteristics such as mechanical stability, improved processability, durability and spatial controllability [13]. Based on these advantages, PILs have stirred great interests in sample pretreatment. So far, several kinds of adsorbents based on PILs have been synthesized and used as the extraction phases of SPME [14–18], multiple monolithic fiber solid-phase microextraction (MMF-SPME) [19], SCSE [6] and MSPE [20]. The previous results well indicate that PILs are ideal alternatives for adsorbents. Developing new PILs-based extraction materials are interesting for sample preparation.

With the rapid development of food industry, preservatives such as *p*-hydroxybenzoic acid (HBA), sorbic acid (SA) and cinnamic acid (CA) are used extensively to maintain the nutritional value and other properties of food products. However, the excessive use of these preservatives may be harmful to consumers and cause some adverse effects such as urticaria, intolerance, and hyperpnea in humans [21]. In many countries, the maximum permitted concentrations of preservatives in different kinds of food have been regulated [22,23]. Therefore, developing a simple and accurate method for the simultaneous analysis of preservatives is necessary for food safety. Among the analytical methodologies of preservatives, chromatographic methods such as gas chromatography (GC) [24], high-performance liquid chromatography (HPLC) [25], and capillary electrophoresis [26] are the most popular techniques because of their effective power in qualification and quantification. However, food matrices are generally diverse and complex, to enrich the target analytes and clean up the sample matrices, a suitable sample pretreatment technique is necessary before the analysis. So far, several sample pretreatment technologies such as

liquid–liquid extraction (LLE) [27], liquid-phase microextraction (LPME) [28], SPE [29], SPME [30] and SBSE [31] have been successfully applied to the extraction of preservatives from all kind of food samples. However, the LLE technique requires large volumes of poisonous solvent. SPE needs multi-step laborious and time consuming procedures. For SBSE, the friction between stir bar and the bottom of the vial during extraction can easily cause the loss of coating and extraction performance. The extraction capacity is limited for LPME and SPME because low extractant is employed. Therefore, developing simple, high extraction performance, cost-effective and environmentally friendly sample pretreatment methods to analyze preservatives in food is necessary.

Organic acid preservatives such as HBA, SA and CA belong to polar compounds. The  $\log K_{o/w}$  values for HBA, SA and CA are 1.33, 1.58 and 2.33, respectively. Therefore, they can produce intense interactions with water molecules in aqueous solutions. To extract HBA, SA and CA effectively, new adsorbent combines with suitable extraction format should be developed. Considering the distinctive properties of PILs, an ionic liquid 1-allyl-3-vinylimidazolium chloride (AV) was in-situ copolymerized with divinylbenzene (DVB) to get a PIL-based adsorbent (AVDVB). The new adsorbent was combined with SCSE to extract HBA, SA and CA in orange juices and tea drinks. SCSE is a new extraction format developed in our groups [32], it possesses many advantages such as simple operation, high extractive capacity, good flexibility, cost-effectiveness, satisfactory life-span, and environmental friendliness. After the optimization of preparation and extraction parameters of SCSE/AVDVB, a simple and sensitive methodology combining SCSE and liquid desorption (LD), followed by HPLC with diode array detection (SCSE/AVDVB-LD-HPLC/DAD) for the direct analysis of trace preservatives in orange juice and tea drink samples was developed.

## 2. Experimental

### 2.1. Chemicals

AV (99%) was purchased from Cheng Jie Chemical Co. LTD (Shanghai, China); DVB (80%) were supplied by Alfa Aesar Ltd. (Tianjin, China); Azobisisobutyronitrile (AIBN) (97%, re-crystallized before use), 1-propanol (97%) and 1,4-butanediol (98%) were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA); Water used throughout the study was purified using a Milli-Q Reference water-purification system (Merck Millipore, Germany).

HBA (99%), SA (99%) and CA (98%) were purchased from China Medicine (group) of the Shanghai Chemical Reagent Corporation (Shanghai, China). The chemical structures,  $pK_a$ , and  $\log K_{o/w}$  values of the targeted preservatives are presented in Table S1 in Supplementary materials. They were prepared as 100  $\mu\text{g}/\text{mL}$  mixtures in methanol and stored at 4 °C in the dark. The sample solution was spiked with these standard stock solutions to the desired concentration for each experiment.

### 2.2. Instruments

HPLC analyses were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was carried out using a RE3725i manual sample injector with a 20  $\mu\text{L}$  loop (Rheodyne, Cotati, CA, USA), all experiments were performed at room temperature.

The morphologies of monolithic materials were examined by a Model XL30 scanning electron microscopy (SEM) instrument

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