Analytica Chimica Acta 803 (2013) 66–74

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Silica-based ionic liquid coating for 96-blade system for extraction of aminoacids from complex matrixes

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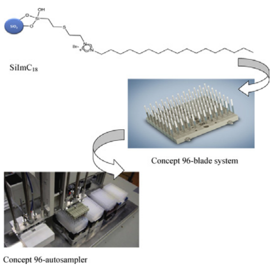
HIGHLIGHTS

- Silica-based 1-vinyl-3-octadecylimidazolium bromide ionic liquid was synthesized and characterized.
- The synthesized polymer was immobilized on the stainless steel blade using polyacrylonitrile glue.
- $SiImC_{18}$-PAN 96-blade SPME was applied as an extraction phase for extraction of highly polar compounds in grape matrix.
- This system provides high extraction efficiency and reproducibility for up to 50 extractions from tartaric buffer and 20 extractions from grape pulp.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 February 2013
Received in revised form 10 June 2013
Accepted 4 July 2013
Available online 9 July 2013

Keywords:
Silica-based ionic liquid
High throughput analysis
LC–MS/MS
96-Blade SPME
Aminoacids
Grape pulp

ABSTRACT

1-Vinyl-3-octadecylimidazolium bromide ionic liquid $[C_{18}VIm]Br$ was prepared and used for the modification of mercaptopropyl-functionalized silica (Si-MPS) through surface radical chain-transfer addition. The synthesized octadecylimidazolium-modified silica ($SiImC_{18}$) was characterized by thermogravimetric analysis (TGA), infrared spectroscopy (IR), ^{13}C NMR and ^{29}Si NMR spectroscopy and used as an extraction phase for the automated 96-blade solid phase microextraction (SPME) system with thin-film geometry using polyacrylonitrile (PAN) glue. The new proposed extraction phase was applied for extraction of aminoacids from grape pulp, and LC–MS–MS method was developed for separation of model compounds. Extraction efficiency, reusability, linearity, limit of detection, limit of quantitation and matrix effect were evaluated. The whole process of sample preparation for the proposed method requires 270 min for 96 samples simultaneously (60 min preconditioning, 90 min extraction, 60 min desorption and 60 min for carryover step) using 96-blade SPME system.

Inter-blade and intra-blade reproducibility were in the respective ranges of 5–13 and 3–10% relative standard deviation (RSD) for all model compounds. Limits of detection and quantitation of the proposed SPME-LC–MS/MS system for analysis of analytes were found to range from 0.1 to 1.0 and 0.5 to 3.0 $\mu g L^{-1}$, respectively. Standard addition calibration was applied for quantitative analysis of aminoacids from grape juice and the results were validated with solvent extraction (SE) technique.

1. Introduction

Ionic liquids (ILs) are organic/inorganic salts with a melting point below 100 °C. These compounds have some special properties, such as negligible vapor pressure, high thermal stability (~250–400 °C), variable viscosity, and capability of undergoing

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http://dx.doi.org/10.1016/j.aca.2013.07.005

multiple solvation interactions [1]. The popularity of ILs is due to their applications in green chemistry; however, their usage also has been extended to other research areas. ILs are also used in different areas of separation techniques, including: gas chromatography (GC), liquid chromatography (LC) and, electrophoretic methods. In LC, ILs are used as the mobile phase additives to eliminate the destructive effect of stationary phase on the retention of basic analytes. Moreover, ILs have been applied as the stationary phase for LC columns through using synthesized silica based ionic liquid (SiIL) particles [2–9].

Four various methods have been reported in the literature for synthesizing SiIL. The first method begins with the attachment of bromoalkyl-1-trichlorosilane to silica; followed by the synthesized compound being endcapped with chlorotrimethyl silane. Finally, the reaction between the endcapped modified silica and ionic liquid produces SiIL [10–16]. The second method uses 3-mercaptopropyltrimethoxysilane (MPS), to modify activated silica; afterwards, the reaction of the product with the allyl group of imidazole is utilized in the presence of azodiisobutyronitrile (AIBN) as an initiator [17–20]. The third method uses a silane-coupling agent, such as 3-chloropropyltrimethoxysilane, for the modification of activated silica. The reaction is completed through the reaction of the product by imidazole [21–28]. The fourth method synthesizes ionic liquid via the reaction of 3-bromopropyl-triethoxysilane and 1-alkylimidazole. Finally, the reaction of synthesized ionic liquid with silica produces SiIL [29]. In the current work, the second method was used for synthesizing SiIL.

Solid phase microextraction (SPME), a popular sampling technique introduced by Pawliszyn in the early 1990s, is a simple, quick, cost effective and solventless technique, which integrates sampling and sample preparation into one step [31,32]. Automated high-throughput analysis is necessary to provide fast and precise sample preparation for analysis in various fields of clinical, pharmaceutical, food, and environmental sciences. In-house 96-coated SPME fiber using automated robotic unit was used to access high-throughput analysis via automation of SPME coupled with LC–MS/MS for parallel analysis of drugs in human blood and plasma by Pawliszyn's group in 2008 [33].

To eliminate the limitation of the previous design [33], a 96-blade system coated with thin film geometry was developed, and commercial SPE particles including C_{18}, PS-DVB-WAX, and PBA were used as the stationary phase on the stainless steel blade for 96-blade system using polyacrylonitrile (PAN) as a biocompatible binder [34,35]. These extractive phases provide high extraction recovery in the case of extraction of nonpolar compounds, but it is needed to introduce new extraction phase for extraction of polar compounds.

Based on the author's knowledge, until now ionic liquids immobilized on silica have not been applied to the stationary phase for SPME as the sample preparation technique for high-performance liquid chromatography. According to Refs. [36–38], molecular interactions such as strong hydrogen bonding, hydrophobic, ion-dipole, and strong ion-pairing exist in ionic liquid, which provide sufficient interaction with polar compounds. Due to these considerations, we synthesized a new stationary phase based on N-methylimidazolium cation group attached on the silica surface, and then immobilized it on the stainless steel blade with PAN glue; finally, the new extraction phase was applied for direct extraction of aminoacids as a group of polar compounds from complex food matrix.

An essential active compound available in food and beverages is aminoacids, which affect the food quality through taste, aroma, and color. Since these compounds are considered vital elements of human diet, their determination has an important role in food industry [39]. Most methods for analysis of this group of compounds usually require derivatization by derivatization agents to increase their detectability. However, these methods have some disadvantages, such as instability of derivatives, side reactions, reagent interferences, and significant time consumption. Thus, a reliable, rapid, and accurate method of analysis is needed for performing qualitative and quantitative analysis of aminoacids to investigate food quality for nutritional and regulatory purposes and overcome the drawbacks of determined in aminoacid analysis techniques based on pre- or post-column derivative methods [40].

The objective of this study is to introduce a new coating for SPME coupled with LC–MS/MS for extraction of aminoacids as the high polar compounds from grape pulp without sample pretreatment. The chemical structure of understudied aminoacids is shown in Supplementary Figure S-1.

2. Experimental

2.1. Chemicals and materials

1-Vinylimidazole (99%), 3-mercaptopropyltrimethoxysilane, 2,2-azobisisobutyronitrile (AIBN) (98%), and polyacrylonitrile (PAN) were purchased from Sigma–Aldrich (MO, U.S.). 1-Bromooctadecane, (96%) was purchased from Fisher Scientific (ON, Canada). Silica gel with 60 Å average diameter was purchased from SiliCycle Inc. (Quebec, Canada). Arginine, aspartic acid, glutamic acid, isoleucine, histidine, leucine, lysine, phenylalanine, proline, threonine, tryptophan, tyrosine L-(+)-tartaric acid and potassium-L-tartrate monobasic were purchased from Sigma–Aldrich (MO, U.S.). Acetonitrile (HPLC grade), methanol (HPLC grade), and N,N-dimethylformamide (DMF) were purchased from Caledon Laboratories (ON, Canada). Polypropylene Nunc U96 Deep Well plates were purchased from VWR International (ON, Canada).

2.2. Liquid chromatography and mass spectrometry conditions

Chromatographic separation was performed by Discovery HS F5 column, 2.1 mm × 15 cm, 3 μm particle size (Supelco, Bellefonte, PA, USA) using gradiant condition. Flow rate was 200 μL min^{-1}, and mobile phases A and B consisted of water/formic acid (99.9/0.1, v/v) and acetonitrile/formic acid (99.9/0.1, v/v). The chromatographic elution and a 40 min gradient program was optimized for separating the model compounds as follows: 100% A (0–3 min), linear gradiant from 100 to 10% A (3–25 min), linear gradiant held at 10% A from 25 to 34 min, the column reached to equilibrium for 6 min by applying gradiant 10% A to 100% A. Quantitative analyses of compounds were performed using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, CA, U.S.) equipped with TurboIonSpray source. A CTC PAL autoinjector from Leap Technologies (CTC Analytics, NC, U.S.) was used for the injection of samples into the LC–MS/MS system (20 μL injection volume). The MS/MS analysis was performed in positive mode under multiple reaction monitoring (MRM) conditions. The summary of MS/MS parameters is given in Table 1, and extracted ion chromatograms of aminoacids are shown in Supplementary Figure S-2.

2.3. SPME procedure using automated Concept 96-blade SPME

The Concept 96-blade SPME device and autosampler prepared by Professional Analytical System (PAS) Technology (Magdala, Germany) controlled by concept software was used to provide reproducibility and high-throughput for the analysis. The detailed description of automated 96-blade SPME system is reported in Refs. [34,35]. This system has 4 stations: preconditioning, extraction, wash, and desorption steps. Red seedless grapes, purchased from a local market in Waterloo (ON, Canada), were manually stemmed, washed with deionized water, dried, and crushed using