Nanoporous array anodic titanium-supported co-polymeric ionic liquids as high performance solid-phase microextraction sorbents for hydrogen bonding compounds

Jing Jia a,b, Xiaojing Liang a, Licheng Wang a, Yong Guo a, Xia Liu a,*, Shengxiang Jiang a

a Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
b University of Chinese Academy of Sciences, Beijing 100039, China

A R T I C L E   I N F O

Article history:
Received 15 May 2013
Received in revised form 11 October 2013
Accepted 11 October 2013
Available online 22 October 2013

Keywords:
Nanoporous array anodic titanium
Polymeric ionic liquids
Solid-phase microextraction
Polar compounds
Alcohols
Volatile fatty acids

A B S T R A C T

A nanoporous array anodic titanium-supported co-polymeric ionic liquids (NAAT/PILs) solid-phase microextraction (SPME) fiber was prepared in situ on the titanium wire. NAAT was selected as the substrate, in view of its high surface-to-volume ratio, easy preparation, mechanical stability, and rich titanol groups on its surface which can anchor silica coupling agent containing vinyl and then introduce ionic liquid copolymers as sorbents. In this work, 1-vinyl-3-nonanol imidazolium bromide ([C9OHVIm]Br) and 1,4-di(3-vinylimidazolium) butane dibromide ([[(VIM)2C4]2[Br]]) were synthesized and used as monomer and crosslinker, respectively. Extraction properties of the NAAT/PILs fiber for polar alcohols and volatile fatty acids (VFAs) in aqueous matrix were examined using gaseous sampling–SPME (GS–SPME) and headspace SPME (HS–SPME) mode, respectively. Combining the superior properties of NAAT substrate and the strong hydrogen bond interaction of PILs to polar compounds, the NAAT/PILs fiber showed much higher adsorption affinity to aliphatic alcohols than bare NAAT and pure PILs fibers. The detection limits (LOD) of established GS–SPME–GC–FID method are in the range of 0.35–17.30 ng mL−1 with a linear range from 0.01 to 500 ng mL−1. Also, it showed high extraction performance toward volatile fatty acids (VFAs) compounds from aqueous matrix. Under the optimized SPME conditions, wide linear ranges were obtained with correlation coefficients (R2) greater than 0.99 and limits of detection were in the range of 0.85–8.74 ng mL−1. Moreover, real-world samples were analyzed and good results were obtained.

© 2013 Published by Elsevier B.V.

1. Introduction

Solid-phase microextraction (SPME), as a universal sample preparation technology, is being developed and has attracted considerable attention due to its integration of sampling, extraction, concentration and sample introduction in a single process [1–3]. However, it is well known that the analysis of polar compounds like alcohols remains as a challenge due to the strong interactions of these compounds with the aqueous matrix. In many cases, on or post fiber-derivatization is employed to accelerate the extraction of polar compounds [4,5]. Hence, enhancement in SPME for extraction of polar analytes has been a focus of further improvement and might be achieved thanks to the improvements in sorbent material, coating technology and format technology.

Djozan and co-workers [6] developed anodized aluminum wire as the SPME coating (~20 μm thickness) for the extraction of some aliphatic alcohols and BTEX from gaseous samples. Due most probably to the porous layer of Al2O3, which is formed on the metal surface, this coating can adsorb a wide range of the compounds. Similarly, Zhang and coworkers [7] prepared anodized aluminum wire as the SPME coating by a two-step anodization technology for the extraction of biological volatile organic compounds. Maleki and coworkers [8] introduced a sol–gel titania for headspace sampling of aliphatic alcohols from non-alcoholic beer samples. In summary, the high extraction efficiency of these coating toward polar analytes was mainly attributed to strong donor–acceptor interactions. In addition, other sorbent materials such as cycloextrim [9], methacrylic acid trimethylolpropanetricarboxylate co-polymers [10], calix[4]arene [11], MWCNT [12], and polyaniline [13] were developed and used for the extraction of polar analytes through hydrogen bonding interaction or else.

Among all the coating materials ionic liquids (ILs) attracted more and more attention owing to their very unique properties. ILs possess wide liquid ranges, low volatilities, good thermal stability, electrolytic conductivity, tunable viscosity and miscibility, outstanding designability characteristic, reusability and so on. Moreover the remarkable “dual nature” solvation characteristic makes them interact with apolar compounds like a nonpolar...
stationary phase while interacting with polar compounds like a polar stationary phase [14]. ILs can also be designed to exhibit high solubility of organic compounds while also being tuned to be water immiscible. Thus far, ILs and polymeric ionic liquids (PILs) have been widely used as sorbent materials in SPME concerning the extraction of non-polar or medium-polar analytes [15–17] and a small number of reports also investigated their extraction performances for polar analytes [18–20].

It should be pointed out that ILs still possess shortcomings, like limited extraction efficiency and weak specificity. Motivated by the rapid development and widespread application of one dimensional nanostructure, there is a drive to search the action of support substrate in ILs SPME fiber which seem to be expected to enhance extraction performance of ILs SPME coating. As a matter of fact, one dimensional nanostructure material including nanowire, nanoparticle, nanorod and nanotube have been an important development trend in SPME fiber coating [7,21–23] owing to its amazing properties such as high surface area and special optical, electrical property and especially gas absorption property [7].

Nanoporous array anodic titanium (NAAT) as a kind of one dimensional nanomaterial has been widely used as the template material for the fabrication of other one dimensional nanomaterials [24], and the support of catalysts [25] and sensors [26]. In general, NAAT can be prepared by a one-step [27] or two-step [28] anodic oxidation method using the high-purity titanium as anode in the proper electrolytes. And the surface of NAAT is porous and has numerous titanium groups [29] which can react with other active groups. All of these aspects inspire us and lay the foundation for our research group to develop nanostructure/task-specific polymeric ionic liquid-based SPME coatings for the extraction of polar compounds.

In present paper, the NAAT layer served a multiple purpose: it enlarged the surface area of titanium wire, functionalized the titanium wire with titanol groups, and played as an efficient coating composition coupled with PILs. Surface morphology of the prepared NAAT/PILS SPME fiber was investigated by scanning electron microscope (SEM). Extraction performance of the fiber for aliphatic alcohols was evaluated in GS–SPME coupled to GC. For comparison purposes, bare NAAT and pure PILS SPME fibers were also used to extract the same analytes. In addition to performing the extraction in an aqueous matrix, VFAs was also employed as the analytes to investigate the selectivity of the NAAT/PILS SPME coatings from aqueous matrix using HS–SPME–GC mode. Four real samples were collected to test the reliability of the proposed method, and results were also acceptable.

2. Experimental

2.1. Chemicals and reagents

Titanium wire (120 mm × 0.127 mm o.d., 99.9% in purity) was obtained from the Alfa Aesar (Ward Hill, MA, USA). 1-Vinylimidazole, 3-methacryloxypropyl trimethoxysilane (MPTMS), 1,4-dibromobutane, benzene, toluene, ethylbenzene, o-xylene, m-xylene and n-heptanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 9-Bromo-1-nonanol was purchased from Isomersyn Technology (Beijing, China). Azodiisobutyronitrile (AIBN) was obtained from Shandong Chemical Co. (Shanghai, China) and purified through recrystallization before use.

Methanol, ethanol, n-propanol, iso-butanol, 1-pentanol, isopentanol, n-hexanol, n-octanol, cyclohexanol, tetrahydrofurfuryl alcohol, benzyl alcohol, phenethyl alcohol and benzaldehyde were purchased from the Tianjin Chemical Reagent Plant (Tianjin, China). Valeric acid, hexanoic acid, heptanoic acid, octanoic acid and nonanoic acid were purchased from the British Drug Houses (England). Acetonitrile, acetone, n-hexane, diethyl ether and ethylene glycol were purchased from Rionlon Bohua (Tianjin) Pharmaceutical & Chemical Co., Ltd. (Tianjin, China); hydrofluoric acid (HF) and ammonium fluoride (NH4F) were purchased from Shanghai Qingxi Chemical factory (Shanghai, China). All chemicals are analytical reagents.

Stock solutions of alcohols were prepared in n-hexane with concentration at 2.5 mg mL−1. Working solutions were prepared by diluting appropriate amount of the stock solution up to 10 mL hexane and then 1.0 μL of it was introduced into 25 mL sealed glass vial as extraction sample. A stock standard solution mixture of 10 mg mL−1 of each fatty acid was prepared in acetone. The VFAs aqueous solutions were prepared daily by diluting the stock solution with water and used throughout the experiments. Stock and working solutions were all stored at 4 °C until use.

2.2. Instrumentation

An Agilent 7890A series gas chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a flame ion detector (FID) was used. The separations of alcohols and VFAs were carried out on an FFAP capillary column (25 m × 0.32 mm i.d. × 0.33 μm film thickness). Ultrapure nitrogen (>99.999%) was used as the carrier and make-up gas at 1 mL min−1 and 30 mL min−1, respectively. The temperatures of injector and detector were fixed at 195°C and 300°C, respectively. Desorption of the fibers into the injection port was carried out in splitless mode for 5 min. Separation of short-chain alcohols was achieved using a temperature program as follows: the column temperature was initially held at 35°C for 5 min, and programmed at 10°C min−1 to 160°C, being held for 5 min. For the separation of VFAs, the column temperature was programmed as follows: initial temperature was held at 150°C and programmed at 5°C min−1 to 165°C, held 2 min, and then programmed at 0.8°C min−1 to 180°C. For the separation of mixture of other analytes like benzene homologues and aromatic compounds with polar group (cyclohexanol, tetrahydrofurfuryl alcohol, benzyl alcohol, phenethyl alcohol and benzoaldehyde), OV1701 capillary column (25 m × 0.32 mm i.d. × 0.33 μm film thickness) was used. The temperature program used for benzene homologues separation was as follows: 45°C for 6 min and then programmed at 3.5°C min−1 to 65°C, holding for 5 min, then programmed at 25°C min−1 to 200°C. The temperature program for other analytes separation was as follows: initially held at 110°C for 11.5 min and then programmed at 30°C min−1 to 180°C.

The linear adjustable DC power supply used for the titanium wire anodization process was an LW10J2 system (Liyou, Shanghai, China) with adjustable voltage in the range of 0–20 V, providing currents in the range of 0–2 A.

1H NMR (UNITY INOVA-400 MHz) and Ion Trap MS (ITMS) were used to confirm the formation of monocationic IL monomer and dicationic imidazolium crosslinker. Surface properties of the proposed fiber were characterized by a scanning electron microscope (SEM, JSM-6701F, JEOL Ltd., Japan).

2.3. Preparation of SPME fiber

2.3.1. Synthesis of ionic liquid monomer

The synthesis of 1-vinyl-3-nonanol imidazolium bromide ([C9OHVIm]Br) IL monomer was carried out according to the following procedure: equimolar mixture of 1-vinylimidazole and 9-bromo-1-nonanol was reacted in acetonitrile at 60°C for one day. The solvent was eliminated after reaction. The obtained [C9OHVIm]Br was recrystallized in cold diethyl ether and dried under vacuum, giving a white solid powder. The structure was confirmed by 1H NMR and MS (see supplementary
Fig. 1. Preparation schema of the poly [C4OHVIm][ViM]2C4[Br] coated NAAT fiber. (a) Synthesis of ionic liquid monomer and (b) functionalization of the titanium wire and the polymerization.

The dicatonic cross-linker, namely 1,4-di[3-vinylimidazolium]butane dibromide ([ViM]2C4[Br]2) was synthesized by reacting two molar equivalents of 1-vinylimidazole with one molar equivalent of 1,4-dibromobutane in acetone at 50 °C for 36 h in a dark environment. The obtained dicatonic product was then purified by acetone and was dried under vacuum at 50 °C for 2 days. The structure was confirmed by 1H NMR and MS (see supplementary material). 1H NMR (DMSO-d6, 400 MHz): δ9.674 (s, 1H), 8.262 (s, 1H), 7.985 (s, 1H), 7.294–7.355 (q, 1H), 5.972–6.011 (d, 1H), 5.390–5.412 (d, 1H), 4.183–4.219 (t, 2H), 3.323–3.355 (t, 2H), 1.806–1.822 (t, 2H), 1.353–1.367 (t, 2H), 1.225 (m, 11H). (IT-MS) m/z [ViM]+ = 237.3 amu.

2.3.2. Pretreatment of titania nwire substrate

Before anodization, the titanium wire was thoroughly washed with ethanol, acetone, and distilled water in an ultrasonic bath for 10 min in sequence. Then the titanium wire was anodized by a two-step anodization procedure as reported by Wang [30]. The first anodization was carried out in ethylene glycol electrolyte containing 0.5 wt% NH4F at 20 V for about 2 h, then the TiO2 nanotube films were easily peeled off in 1 M HCl under ultrasonication, resulting in bowl-like footprints on the wire surface. Afterwards, the titanium wire was reanodized under the same conditions, with the addition of 0.5% HF in the electrolyte, for about 10 min to obtain highly ordered TiO2 NTs. The fiber was pulled out from the electrolyte, washed with water gently and dried.

2.3.3. Preparation of PILs coated fiber

After the above treatments, the metal wire support was modified according to the scheme as shown in Fig. 1. The as-prepared fiber was immersed into 5 mL of a MPTMS solution containing 80% methanol/water (volume ration 95:5) for 30 min to incorporate vinyl functionality onto the wire surface. After that, the fiber was immersed into pre-polymerization mixture with 3 mL dimethyl sulfoxide as solvent containing equivalent amounts of (50 mg mL−1) monocationic IL monomer and dicatonic IL cross-linker and 1% AIBN. Then the polymerization was performed at 70 °C under N2 protection for 6 h. After the reaction the fiber was pulled out from polymerization solution and dried under indoor environment.

For comparison, the original titanium wire without anodization treatment was also modified as the same as the above-mentioned preparation procedure and repeated the polymerization process to obtain a thicker PILs coating. Before SMPE experiment, all the fibers were aged for 20 min in GC injector.

2.4. SPME procedure

The prepared SMPE fiber was equipped into a home-made SMPE holder [31] modified from a 5 μL microinjector. Sampling of all compounds was carried out by non-invasion sampling technique. Sampling the mixed standard of aliphatic alcohols by the modified titanium SPME fiber coating was carried out as follows. One
microliter aliquot of the working solution was introduced into a 25 mL sealed glass vial and a gaseous sample containing 40 ng mL$^{-1}$ of each alcohol was prepared. Then the conditioned SPME fiber coating was pushed out from the holder cartridge followed by headspace exposure for appropriate moment at the ambient temperature. The extraction parameters containing exposure time and relative humidity were investigated. In addition, the sampling of benzene homologues, cyclohexanol, tetrahydrofurfuryl alcohol, benzyl alcohol, phenethyl alcohol and benzaldehyde was carried out according to the similar procedure.

An appropriate amount of the VFAs stock solution and NaCl were introduced into certain volume water. Following the dissolution of NaCl, the pH of solution was adjusted by 1 M HCl to requisite value and complemented with water to fill up the volumetric flask. As for the sampling of VFAs, 15 mL of the prepared aqueous solution with a concentration of 1 μg mL$^{-1}$ was placed into the sample vial. The fiber coating was suspended in headspace of aqueous solution. Agitation was performed at 900 rpm using a magnetic stir bar to accelerate the extraction. The extraction was performed under optimized conditions (ionic strength, pH, extraction temperature and time). After extraction, the fiber coating was retracted into needle and introduced into GC inlet for thermal desorption.

2.5. Enrichment factors (EFs)

The enrichment factors (EFs), defined as the ratio of the chromatographic peak area response for the SPME extraction to that from direct liquid injection [19], were used to evaluate the pre-concentration of the analytes to the prepared SPME fiber coating in this study. The concentration of aliphatic alcohols and aromatic analytes with polar group (cyclohexanol, tetrahydrofurfuryl alcohol, benzyl alcohol, phenethyl alcohol and benzaldehyde) and compared ones without any polar group (benzene, toluene, ethylbenzene, o-xylene, and m-xylene) was 0.5 μg mL$^{-1}$ in hexane solutions for SPME fibers. The SPME extraction time was 40 min. The direct liquid injection experiments were carried out by injection of 1.0 μL of the standard solution in hexane containing 0.5 μg mL$^{-1}$ of each analyte using splitless injection mode and the same SPME inlet liner. All injection carried out by SPME and by direct liquid injection to calculate EF was performed by quadruplicate. Furthermore, the mixed standard solution containing toluene, ethylbenzene, n-heptanol, n-octanol, cyclohexanol and phenethyl alcohol was used as extraction solution to investigate the fiber extraction selectivity.

3. Results and discussion

3.1. Design and characterization of the SPME fiber

Usage of metal substrate wires has become one of the most important trends to develop the SPME fiber technology owing to its great mechanic strength [32,33]. However, the major difficulty in metal-based SPME coatings is improvement of fiber selectivity because free metal fibers themselves do not offer enough selectivity and the lack of proper chemical bonding of sorbents with the metal surface. Nanoporous array anodic titanium (NAAT) is a kind of one dimensional nanostructure material and has excellent gas absorption property owing to high surface area. Furthermore, the activated surface could provide rich titanol groups [29] which could act as active center to anchor other groups like silica coupling agent. In this regard, the NAAT can be used as starting material for the introduction of MPTMS on the surfaces and the included vinyl can introduce ionic liquid copolymers as the SPME coatings. Fig. 2 shows the scanning electron microscope (SEM) images of the proposed NAAT/PILs fiber. As shown in Fig. 2a, uniform PILs coating

![Fig. 2. SEM images of (a and b) as-prepared NAAT/PILs/titaniu...magnification.](image-url)
is formed on the surface with numerous protuberant nanoblocks, which greatly help to increase the surface area to volume ratio. From Fig. 2b–d, it can be seen that the NAAT/PILs coating has a much rougher surface than the pure PILs coating. Average thickness of the NAAT/PILs coating was merely 3 μm.

As prepared PILs sorbents in this work combine a monomer containing polar hydroxyl group ([C₂OHVIm]Br), which promotes hydrophilic interactions through hydrogen-bonding ability, and a crosslinking monomer ([VIM]₂C₄)Br, which helps to increase the specific surface area [34], and bromide anion contained in both monomers, which possess hydrogen-bonding ability [35]. Additionally, in our previous work, the crosslinking copolymerization coating technique was verified to effectively enhance thermal properties of the resulting polymer [18]. Thus, the prepared NAAT/PILs SPME fiber was considered to possess outstanding properties which bare NAAT and PILs cannot be compared to, and will exhibit excellent extraction performance.

### 3.2. Optimization of SPME

#### 3.2.1. Aliphatic alcohols

In GS–SPME, extraction conditions such as exposure time and relative humidity, which influence the alcohols extraction efficiency were investigated to obtain the highest extraction efficiency.

Exposure time of fiber in gaseous samples is an important parameter in achieving distribution equilibrium of analytes between fiber coating and sample; it is therefore a decisive factor for improving the extraction efficiency. For this investigation, extractions were carried out at different times, ranging from 20 to 60 min followed by thermal desorption and GC analysis of analytes. As shown in Fig. 3, for most of analytes, the approximate extraction equilibrium is reached at 40 min. Further extractions were therefore performed at 40 min.

In this work, the effect of humidity was determined at 25 °C by preparing a mixture standard sample of 40 ng mL⁻¹ concentration in a 25 mL sample vial and progressively adding 0.5–5 μL of water to increase the humidity. Each 0.5 μL added ~10% relative humidity to the standard. An equilibration time of 15 min was used. For this investigation, standard samples providing relative humidity of 10–100% were prepared, and the amounts of analytes extracted monitored by GC–FID. The results are shown in Fig. 4. It can be observed from the figure that the presence of water vapor in the gaseous samples has little effect on extraction efficiency of the alcohols studied when the water vapor is more than 20%. However, the presence of less than 20% water vapor in the gaseous samples decreases the analytes peak areas (amount of analytes extracted) effectively. It means that the amount of water in vapor may have dual effect adsorption of alcohols. Therefore, the proposed fiber is a steady adsorbative fiber for sampling from air samples with a relative humidity of more than 20% and the highest extraction can be achieved when the water vapor is about 20%.

#### 3.2.2. VFAs

Many factors can affect the extraction efficiency of VFAs in HS–SPME. The extraction performance of the NAAT/PIL coating was optimized using a “one-variable-at-a-time” procedure in terms of ionic strength, pH of the aqueous solution, extraction temperature, and extraction time.

Generally, ion strength would affect the solubility of analytes in aqueous phase as adding salt to water solution, which are going to be present in the headspace. In this work, ion strength of working solution was adjusted by NaCl. As shown in Fig. 5, the highest extraction efficiencies are obtained with content of NaCl at 30% (w/v) (30% is close to the saturated level of NaCl in water) for all VFAs. Hence, content of NaCl in working solution for VFAs was set at 30% (w/v).

![Fig. 3. Effect of extraction time on extraction efficiency. Extraction conditions: extraction temperature, room temperature. Concentration of analytes: 40 ng mL⁻¹. Error bars were obtained based on four replicates.](image1)

![Fig. 4. Effect of relative humidity at 25 °C on the adsorption of analytes from 40 ng mL⁻¹ gaseous standard. Experimental conditions: as in Fig. 3. Error bars were obtained based on four replicates.](image2)

![Fig. 5. Effect of content of NaCl on extraction efficiency. Extraction conditions: extraction time, 45 min; extraction temperature, 40 °C; pH value of the working solution, 2. Concentration of analytes: 1 μg mL⁻¹. Error bars were obtained based on four replicates.](image3)
Given the fact that only the neutral species are going to be present in the headspace to be efficiently extracted by the SPME coating, it is necessary to adjust the pH of the aqueous solution especially the analytes to be extracted are in ionic form. Several experiments were carried out at different pH values, using aqueous solutions containing 30% (w/v) NaCl. These data are shown in Fig. 6. The results suggested that a pH value of 1 was more efficient for all VFAs studied, so the pH value of the aqueous sample was fixed at 1 for following experiments.

The effect of temperature on the SPME extraction is two-fold: a higher temperature is required to elevate the mass transference and accelerate the extraction rate, but it would decrease the distribution coefficient of analytes between the extraction coating and sample solution. Herein, the selection of a proper temperature is quite important. Extraction temperature profiles for VFAs ranging from 25 to 90 °C were investigated. As shown in Fig. 7, peak areas of most analytes reach the highest values at 40 °C. Hence, the extraction temperature of 40 °C was chosen for the following experiments.

Sorption-time profiles of all VFAs were constructed by performing extractions in 30% (w/v) NaCl solutions at pH 1 and 40 °C at various time intervals. Based on the data in Fig. 8, 55 min was chosen as an adequate extraction time for most of VFAs.

### 3.3. Performance of the SPME fiber

Generally, extraction performances of SPME fiber are largely determined not only by the nature of adsorbent including property and content of sorbent material but also the dimensional structure of the coating like porosity and surface morphology. In our work, the extraction capacity of NAAT/PILs fiber coating was evaluated based on the mixed standard of aliphatic alcohols including methanol, ethanol, n-propanol, isobutanol, 1-pentanol, isopentanol, n-hexanol, n-heptanol and n-octanol. For comparative purposes, pure NAAT and plain PILs fibers were also used to extract these aliphatic alcohols under the same conditions. From chromatograms showed in Fig. 9, it can be observed that while under the same conditions NAAT/PILs fiber exhibited excellent extraction efficiency compared with pure NAAT and PILs fibers, which indicated that both the property of fiber substrate and its grafting materials on adsorbent play important roles in the adsorption of aliphatic alcohols. And the extraction capacity increased with the order of increasing of their alkyl chain. This improved performance was due to the synergistic advantages of a large specific surface area of NAAT and the strong affinity of prepared imidazolium (contained a long alkane hydroxyl chain)/halide anions-based PILs to hydrogen bond acidity groups. In addition, it is necessary
to highlight the differences in coating thickness among these fibers. The pure PILs fiber possesses a thicker coating (20 μm) than NAAT/PILs fiber (3 μm) (shown in Fig. 2) but still showed weaker extraction capacity. In fact, higher coating thicknesses in SPME are usually accompanied by higher extraction efficiencies. These data suggested that NAAT as a kind of one-dimensional nanomaterial was an effective scattered support material to enhance the specific surface area of the outer coating and increase the adsorption stress of coating material to metal substrate.

In order to explore the extraction capacity and selectivity of NAAT/PILs SPME fiber coating, extraction of another kind of analytes with polar hydrogen bonding group including cyclohexanol, tetrahydrofurfuryl alcohol, benzyl alcohol, phenethyl alcohol, benzaldehyde and apolar analytes containing benzene, toluene, ethylbenzene, α-xylene, m-xylene were also performed by GS–SPME mode. The enrichment factors (EFs) of each analyte were defined as the ratio of the chromatographic peak area response for the SPME extraction to that from direct liquid injection [19] and the results were listed in Table 1. The essential difference between the two kinds of analytes is whether a polar hydroxyl or aldehyde group in its molecule structure. Although the log Kow values of analytes with polar group (−0.11 to 1.48) are very close to compared analytes (2.13–3.20), but their extraction results were quite different. The smallest EF value of analytes containing hydrogen bonding group is over 900, but the biggest EF value for compared ones is less than 9. Furthermore, the NAAT/PILs fiber was used to extract all analytes in the mixed standard solution containing toluene, ethylbenzene, n-heptanol, n-octanol, cyclohexanol and phenethyl alcohol to investigate the fiber extraction selectivity further. The extraction chromatogram was shown in Fig. 10 and from it we can see that the NAAT/PILs fiber can selectively extract n-heptanol, n-octanol, cyclohexanol and phenethyl alcohol and nearly no extraction of toluene and ethylbenzene. The above results indicated that the NAAT/PILs fiber showed benign extraction capacity and selectivity to analytes containing polar hydroxyl or aldehyde group. This fact could perhaps be attributed to the physical–chemical properties of the as-prepared fiber sorbent. On the one hand, bromide anion in both IL monomer can offer strong interactions with polar and hydrogen bond donating analytes due to its hydrogen bond basicity. On the other hand, the hydroxyl group in 1-nonanol group can also interact with polar analytes through hydrogen-bonding ability.

3.4. Analytical performance

Under the optimized conditions, the proposed GS–SPME–GC–FID method was evaluated by testing the analytical parameters of alcohols. As shown in Table 2, the method shows wide linear ranges (0.01–500 μg L−1) with correlation coefficients (R²) ranging from 0.9943 to 0.9999. The repeatability of one fiber was conducted by extracting standard mixture of the nine alcohols with 40 ng mL−1 concentrations for five replicate extractions and the RSD oscillated between 2.56 and 9.78%. RSDs obtained from five different fibers are from 7.18 to 13.29%. Limits of detection (LODs) were calculated as three times the signal-to-noise ratio, and values of LODs are in the range of 0.35–17.3 ng L−1. LODs with other PILs-based and commercial fibers for some analytes were also listed in Table 2. Compared with the other PILs-based fibers [19,36], LODs in this work are much lower. In addition, based on the experimental investigations, the obtained extraction material is stable enough for more than 120 replicate extraction cycles.

Furthermore, the proposed HS–SPME–GC method was monitored by testing the analytical parameters of five VFAs in aqueous sample. The figures of merit of the calibration curves, limits of detection, estimation coefficients (R²) and the repeatability were performed under the conditions optimized above for the five VFAs including valeric acid, hexanoic acid, heptanoic acid, octanoic and nonanoic acid. The results are shown in Table 3. The linear range was 0.01–50 000 μg L−1 for five VFAs with estimation coefficients all greater than 0.999. The LODs (S/N=3) ranged from 0.85 to 8.74 ng L−1 for overall VFAs with precision ranging from 3.15 to 7.32% and 4.03 to 12.45% for one fiber and different fibers, respectively. Given the fact that analytes with higher hydrophobicity were given lower LODs and higher sensitivities, we can see that hydrophobic interactions still existed besides the polar interactions and one-dimensional nanostructure material effect during extractions. Analytes with lower solubility and higher hydrophobicity kept stronger affinity with the long chain of monomers, which was favorable for their extraction.

3.5. Application

In order to evaluate the practical applications, the proposed NAAT/PILs fiber was applied in the extraction of aliphatic alcohols from four different alcoholic beverages. Two microliter aliquot of the unspiked alcoholic samples was introduced into extraction vial and then analyzed by the proposed GS–SPME–GC–FID method, and their typical chromatograms are presented in Fig. 11. As can be seen, nine aliphatic alcohols (methanol, ethanol, n-propanol, isobutanol, 1-pentanol, isopentanol, n-hexanol, n-heptanol and n-octanol) detected in alcoholic samples 1 and 2. Contents of ethanol in these samples were 49%, 42%, 10.4% and 2.8% (v/v), respectively, which were in good correspondence with label indications (52%, 39%, 10% and 3%). The concentration of methanol, n-propanol, isobutanol, 1-pentanol, isopentanol, n-hexanol, n-heptanol and n-octanol present in sample 1 were 18.05, 16.21, 7.40, 26.81, 21.88, 869.26, 71.22 and 59.30 μg mL−1, respectively. The contents of methanol, n-propanol, isobutanol, 1-pentanol, isopentanol, n-hexanol, n-heptanol and n-octanol present in sample 2 were 8.48, 8.57, 6.97, 19.57, 11.42, 135.948, 22.65 and 34.49 μg mL−1, respectively. The contents of methanol, n-propanol, isobutanol, 1-pentanol, isopentanol, n-hexanol, n-heptanol and n-octanol present in sample 3 were 5.67, 1.71, 8.59, 10.06, 2.62, 6.35 and 2.35 μg mL−1, respectively. Other aliphatic alcohols containing methanol, propanol, isobutanol, isopentanol, n-heptanol and n-octanol were detected at the concentration of 2.67, 1.37, 5.54, 1.06, 17.7 and 2.98 μg mL−1, respectively, for sample 4.
Table 1
Enrichment factors (EFs) for the different compounds on NAAT/PILs-coated fiber.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>log $K_{ow}$</th>
<th>log $K_{aw}$</th>
<th>EFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanol</td>
<td><img src="cyclohexanol.png" alt="Structure" /></td>
<td>1.23</td>
<td>-3.745</td>
<td>5752.1</td>
</tr>
<tr>
<td>Tetrahydrofurfuryl alcohol</td>
<td><img src="tetrahydrofurfuryl.png" alt="Structure" /></td>
<td>-0.11</td>
<td>-6.777</td>
<td>907.3</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td><img src="benzyl.png" alt="Structure" /></td>
<td>1.10</td>
<td>-4.861</td>
<td>5681.5</td>
</tr>
<tr>
<td>Phenethyl alcohol</td>
<td><img src="phenethyl.png" alt="Structure" /></td>
<td>1.46</td>
<td>-4.980</td>
<td>2131.7</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td><img src="benzaldehyde.png" alt="Structure" /></td>
<td>1.48</td>
<td>-2.962</td>
<td>1450.3</td>
</tr>
<tr>
<td>Benzene</td>
<td><img src="benzene.png" alt="Structure" /></td>
<td>2.13</td>
<td>-0.644</td>
<td>8.5</td>
</tr>
<tr>
<td>Toluene</td>
<td><img src="toluene.png" alt="Structure" /></td>
<td>2.73</td>
<td>-0.566</td>
<td>7.2</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td><img src="ethylbenzene.png" alt="Structure" /></td>
<td>3.15</td>
<td>-0.49</td>
<td>7.9</td>
</tr>
<tr>
<td>o-Xylene</td>
<td><img src="oxylene.png" alt="Structure" /></td>
<td>3.12</td>
<td>-0.674</td>
<td>8.0</td>
</tr>
<tr>
<td>m-Xylene</td>
<td><img src="mxylene.png" alt="Structure" /></td>
<td>3.20</td>
<td>-0.532</td>
<td>8.9</td>
</tr>
</tbody>
</table>

$log K_{ow}$, octanol/water partition coefficients; $K_{aw}$, air-to-water partitioning coefficients.

Table 2
Analytical merits of the proposed gaseous-sampling-SPME–GC–FID method for the determination of aliphatic alcohols.\(^\text{a}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>EFs</th>
<th>Linear range (µg L(^{-1}))</th>
<th>$R^2$</th>
<th>LOD(^\text{a}) (ng L(^{-1}))</th>
<th>Repeatability (n=5, %) (single fiber)</th>
<th>Reproducibility (n=5, %) (fiber-to-fiber)</th>
<th>LOD of poly $[C_\text{poly}]/[Br-]$ (µg L(^{-1}))</th>
<th>LOD of other PILs fibers (µg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>758.5</td>
<td>0.01–500</td>
<td>0.998</td>
<td>2.08</td>
<td>6.98</td>
<td>10.12</td>
<td>20</td>
<td>10 [36]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>545.8</td>
<td>0.01–500</td>
<td>0.995</td>
<td>1.91</td>
<td>6.82</td>
<td>7.18</td>
<td>15</td>
<td>10 [36]</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>600.5</td>
<td>0.01–500</td>
<td>0.999</td>
<td>12.50</td>
<td>6.04</td>
<td>9.45</td>
<td>5</td>
<td>5 [36]</td>
</tr>
<tr>
<td>Iso-butanol</td>
<td>530.7</td>
<td>0.01–500</td>
<td>0.999</td>
<td>17.30</td>
<td>2.56</td>
<td>10.03</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Isopentanol</td>
<td>640.5</td>
<td>0.01–500</td>
<td>0.995</td>
<td>4.82</td>
<td>9.78</td>
<td>12.43</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>724.8</td>
<td>0.01–500</td>
<td>0.997</td>
<td>2.46</td>
<td>3.84</td>
<td>7.67</td>
<td>1.5</td>
<td>4.8 [19]</td>
</tr>
<tr>
<td>n-Hexanol</td>
<td>797.6</td>
<td>0.01–500</td>
<td>0.994</td>
<td>0.85</td>
<td>2.99</td>
<td>12.02</td>
<td>0.5</td>
<td>2.1 [19]</td>
</tr>
<tr>
<td>n-Heptanol</td>
<td>719.4</td>
<td>0.01–500</td>
<td>0.995</td>
<td>0.42</td>
<td>3.37</td>
<td>13.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octanol</td>
<td>576.8</td>
<td>0.01–500</td>
<td>0.997</td>
<td>0.35</td>
<td>4.02</td>
<td>12.45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Experimental conditions: extraction temperature, room temperature; extraction time, 40 min; desorption temperature 195 °C; desorption time, 10 min.
\(^{b}\) Correlation coefficient.
\(^{c}\) LODs were estimated as the concentrations where S/N=3.

Table 3
Analytical merits of the proposed HS–SPME–GC–FID method for the determination of VFAs.\(^\text{a}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linear range (µg L(^{-1}))</th>
<th>$R^2$</th>
<th>LOD(^\text{a}) (ng L(^{-1}))</th>
<th>Repeatability (n=5, %) (single fiber)</th>
<th>Reproducibility (n=5, %) (fiber-to-fiber)</th>
<th>LOD of poly $[VHlm^-]/[NTf_2^-]$ (µg L(^{-1}))</th>
<th>LOD of poly $[VHlm^-]/[Cl^-]$ (µg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valeric acid</td>
<td>0.01–50 000</td>
<td>0.999</td>
<td>8.74</td>
<td>6.94</td>
<td>6.55</td>
<td>4.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>0.01–50 000</td>
<td>0.999</td>
<td>2.42</td>
<td>7.32</td>
<td>9.38</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>0.01–50 000</td>
<td>0.999</td>
<td>1.38</td>
<td>3.15</td>
<td>12.45</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>0.01–50 000</td>
<td>0.999</td>
<td>0.85</td>
<td>5.88</td>
<td>11.58</td>
<td>0.3</td>
<td>0.02</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>0.01–50 000</td>
<td>0.999</td>
<td>1.07</td>
<td>5.67</td>
<td>4.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Experimental conditions: 30% NaCl (w/v); pH 1; extraction temperature, 50 °C; extraction time, 55 min; desorption temperature 195 °C; desorption time, 10 min.
\(^{b}\) Correlation coefficient.
\(^{c}\) LODs were estimated as the concentrations where S/N=3.
components in alcoholic beverages. This new SPME fiber was also available for preconcentration of VFAs from water sample by HS–SPME–GC mode. Furthermore, the practical aspects of NAAT/PILs demonstrated in this study suggested the important role of NAAT as support material, which will further open up the possibility of applying the similar NAAT-based adsorbents for extraction of broad analyte ranges.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (21105107 and 21175143) and National Science & Technology Major Project of China (2011ZX05010 and 2011ZX05011) are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2013.10.042.

References