



A novel reusable ionic liquid chemically bonded fused-silica fiber for headspace solid-phase microextraction/gas chromatography-flame ionization detection of methyl *tert*-butyl ether in a gasoline sample

Ramin Amini^a, Ahmad Rouhollahi^{a,b,*}, Mina Adibi^c, Ali Mehdinia^d

^a Department of Chemistry, Faculty of Science, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran, Iran

^b Department of Chemistry, York University, 4700 Keele St., Toronto, ON, Canada M3J 1P3

^c Department of Specialty Chemical, Division of Chemical and Petrochemical, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-137, Tehran, Iran

^d Department of Marine Living Resources, Iranian National Center for Oceanography, P.O. Box 14155-4781, Tehran, Iran

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ABSTRACT

A novel ionic liquid (IL) bonded fused-silica fiber for headspace solid-phase microextraction (HS-SPME)/gas chromatography-flame ionization detection (GC-FID) of methyl *tert*-butyl ether (MTBE) in a gasoline sample was prepared and used. The new proposed chemically bonded fiber has better thermal stability and durability than its corresponding physically coated fiber. Another advantage is that no spacer was used for the purpose of bonding the IL to the surface of the fused-silica. The latter advantage makes the preparation of these fibers easier with lower cost than those prepared using sol-gel method. The ionic liquid 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis(trifluoromethylsulfonyl) imide was synthesized and cross linked to the surface of the fused-silica fiber. Then, the chemically IL-modified fibers were applied to the headspace extraction of MTBE. The chemically IL-modified fibers showed improved thermal stability at temperatures up to 220 °C relative to the physically IL-modified fibers (180 °C). The chemically bonded IL film on the surface of the fused-silica fiber was durable over 16 headspace extractions without any significant loss of the IL film. The calibration graph was linear in a concentration range of 2–240 $\mu\text{g L}^{-1}$ ($R^2 = 0.996$) with the detection limit of 0.1 $\mu\text{g L}^{-1}$ level. The reproducibility (RSD %, $n = 6$) of the new IL bonded fused-silica fiber (8.9%) was better than the physically coated fiber (12%) suggesting that the proposed chemically IL-modified fiber is more robust than the physically IL-modified fiber. The optimum extraction conditions were the followings: 40 °C extraction temperature, 12 min extraction time, 30 s desorption time and sample agitation at 200 rpm.

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1. Introduction

There are many commercially available SPME fibers including Polydimethylsiloxane (PDMS), Polyacrylate (PA), Divinylbenzene (DVB), Carboxen (CAR), and Carbowax (CW) [1–3]. These fibers are available in different thicknesses with single coatings, mixtures, or co-polymers and are suitable for the application of solid-phase microextraction (SPME) to the analysis of non-polar organic compounds, for example benzene, toluene, ethylbenzene, and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs), pesticides, etc., and polar organic compounds such as phenols, alcohols, ketones, nitroaromatics [2]. However, these fibers suffer from a low operating temperature, the breakage of the fiber, the stripping of the coatings, relatively high thickness of the conventional fibers, and

instability of them in organic solvents [2,3]. Up to now, several commercial coatings are all based on fused-silica fiber, which is fragile and must be handled with great care. Commercial coatings are relatively expensive and difficult to prepare in a routine laboratory [4]. Additionally, lot-to-lot variations of the fibers often result in relatively poor extraction reproducibility [5]. Recently, sol-gel technology was adopted to prepare SPME fibers [6–24]. However, Some of the drawbacks of the commercial SPME fibers including the low operating temperature, instability, and stripping of the coatings can be overcome by chemically bonding of a class of new coating materials, i.e., room temperature ionic liquids (RTILs) which are resulted from the combination of organic cations and various anions [25,26]. RTILs exhibit dual nature retention. That is, they separate polar molecules such as a polar phase and nonpolar molecules as if they are nonpolar phases [27,28]. This distinguished advantage extends the use of RTILs to the area of separating both polar and nonpolar compounds. RTILs are gaining widespread recognition as potential environmentally compatible solvents. Good thermal stability, negligible vapor pressure, tunable viscosity, natural liquid

* Corresponding author at: Department of Chemistry, York University, 4700 Keele St., Toronto, ON, Canada M3J 1P3. Tel.: +1 416 736 2100x77723; fax: +1 416 736 5936. E-mail addresses: rouholla@yorku.ca, rouhollahi@kntu.ac.ir (A. Rouhollahi).

nature at room temperature, miscibility with water and organic solvents which is highly depends on the ILs structures, and also good extractability for various organic compounds [25–31] and metals ions [26,32–37], merit their consideration as potential absorbents for SPME/LPME.

Recently, Jiang et al. reported the use of 1-octyl-3-methylimidazolium hexafluorophosphate [C_8C_1IM] [PF_6] as a disposable coating for headspace (HS) SPME of BTEX in paint samples [26]. Anderson et al. developed a SPME sorbent coating based on a polymeric IL for the selective HS-extraction of different analytes [38]. He et al. prepared a kind of reusable IL-based SPME fiber for the first time by fixing ionic liquid (IL) via cross-linking of IL on the surface of a fused-silica fiber and applied to the forensic determination of methamphetamine (MAP) and amphetamine (AP) in human urine samples [39]. A large number of applications of ILs in the field of separation have been recently reported in the literature [40–43].

Methyl *tert*-butyl ether (MTBE) is a volatile and suspected/potential carcinogenic organic compound widely employed as an additive in gasoline. MTBE was originally used to increase the octane index number when tetraethyl lead was withdrawn from gasoline. Later, it was used to increase the efficiency of combustion and achieve a cleaner burning process and thereby reduce the emission of compounds such as carbon monoxide and ozone [43–46]. Some other fuel oxygenates used as additives in gasoline are ethyl *tert*-butyl ether (ETBE), *tert*-amyl ether (TAME), and diisopropyl ether (DIPE). MTBE is highly soluble in water, is highly mobile, and is sparingly biodegradable [4,47]. The combination of these properties together with the high content of this compound in some gasolines may account for the appearance of elevated concentrations of MTBE in surface waters, ground waters, and even in rain and snow [45]. Some studies [45,48,49] have shown that gasoline spills and unburned fuel components used in boats are the main sources of pollution of surface waters.

Different analytical methods including direct aqueous injection (DAI) [46,49], purge and trap [46–50], headspace generation [51–53] and SPME in combination with gas chromatography/mass spectrometry detection (GC–MS) [49–55], have been used for the detection of MTBE. Several papers reporting the determination of MTBE and other ethers in water [51,56–58] and gasoline [59–62] were also published. In recent years, MTBE was sampled by headspace SPME (HS-SPME) and analyzed by GC/MS [63,64]. Recently, Alizadeh et al. reported a HS-SPME-ion mobility spectrometry method with dodecylsulfate-doped polypyrrole film as a new fiber for the quantification of MTBE in water and gasoline samples without sample cleanups [65]. Achten and Püttmann reported a new method development based on SPME for the determination of MTBE in surface water at sub-ppb concentrations [58]. They obtained the best results with a cooled (5 °C) 75 μ m poly(dimethylsiloxane)/Carboxen (PDMS/Carboxen, black) fiber at a sample temperature of 18–19 °C and a sodium chloride concentration of 25%. Also, Tabar-Heydar et al. described the development of HS-SPME extraction employing a new designed sample vial with special features such as cooling the HS and low HS volume for the extraction and determination of MTBE in water samples [66].

In this study, we reported a chemical bonding method for fabricating IL-modified SPME fibers based on the surface modification of fused-silica fibers. Then the fibers coupled with GC were used for HS-SPME of MTBE from a gasoline sample. Two similarly prepared SPME fibers were employed and compared to each other. These were chemically IL-modified and physically IL-modified fused-silica fibers. The first one, i.e., the chemically IL-modified SPME fiber showed better thermal stability (220 °C) and durability than the physically IL-modified SPME fiber. Simplicity, much lower cost than the commercial SPME fibers, easy preparation, high operating temperature, and low consumption of IL and solvent are

the main advantages of the proposed reusable IL-modified SPME fibers.

2. Experimental

2.1. Chemicals and standards preparation

All chemicals used for the synthesis of the ionic liquid, i.e., 1-methyl-3-(3-trimethoxysilyl propyl)imidazolium bis(trifluoromethyl sulfonyl)imide and dichloromethane were purchased from Merck (Darmstadt, Germany) as analytical reagent grade chemicals and used without further purification. Dichloromethane was used for dilution of the IL prior to the modification of HS-SPME fiber. MTBE was supplied by Acros Organics (Geel, Belgium). Methanol (Merck, Darmstadt, Germany) was used for standard preparation. MTBE-standards were made from a 10 mg L⁻¹ stock solution (diluted in methanol). The stock solution and the different standard solutions should be fresh prepared each day.

2.2. Synthesis of the IL

IL was synthesized similar to that reported in the literature [67]. Briefly, the synthesis was as follows:

1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride was synthesized by the reaction of 12.4 g (0.15 mol) of freshly distilled 1-methylimidazole with 46.3 g (0.23 mol) of (3-chloropropyl) trimethoxysilane with total reflux under nitrogen atmosphere at 90 °C for 20 h. The reaction mixture was cooled down to room temperature and the organic upper phase was separated, leaving behind a yellow viscous ionic liquid phase. The ionic liquid phase was then washed thoroughly with Et₂O (2 × 50 mL). Finally, the obtained product was dried at 70 °C for 8 h. The structure was confirmed by ¹H NMR:

¹H NMR (300 MHz, CDCl₃, 25 °C): δ (ppm): 0.22 (m, CH₂Si), 1.59 (m, CH₂CH₂N), 3.2 (s, SiOCH₃), 3.7 (s, CH₃N), 3.92 (t, CH₂N), 7.20 (s, H5), 7.47 (s, H4), 9.97 (s, H2).

To a solution of 22 g (0.078 mol) of the synthesized chloride salt dissolved in 100 mL acetone, 22.5 g (0.078 mol) of lithium LiNTf₂ was added and the mixture was left under stirring for five days at room temperature under nitrogen atmosphere. After concentrating under vacuum the solid was solubilized in 100 mL CH₂Cl₂ and washed with water till AgNO₃ test was negative. The organic phase was then dried over anhydrous MgSO₄, filtrated and its solvent was evaporated. The obtained product was dried under vacuum for 3 h at 60 °C. The ¹H NMR data were as follows:

¹H NMR (300 MHz, CDCl₃, 25 °C): 0.54 (m, CH₂Si), 1.87 (m, CH₂CH₂N), 3.46 (s, SiOCH₃), 3.83 (s, CH₃N), 4.08 (t, CH₂N), 7.29 (s, H4, H5), 8.53 (s, H2).

2.3. Instrumentation

NMR analyses were acquired with a Bruker AVANCE 300 spectrometer. GC analyses were performed using a Shimadzu GC-14B gas chromatograph (Kyoto, Japan) with a split-splitless injector and a flame ionization detector (FID). The Chromanit software provided by Shimadzu was used to monitor the chromatograms. A CBP1 fused-silica column (Shimadzu capillary column Hicap series) with dimensions of 25 m length × 0.32 mm I.D. and film thickness of 0.5 μ m was used for GC analyses. Helium (99.995% pure) was used as the carrier gas with a flow rate of 1.3 mL min⁻¹. The injector port was operated in the splitless mode at 200 °C. The detector temperature was maintained at 250 °C. The column was used with the following temperature program: initial temperature of 40 °C for 1 min, 20 °C min⁻¹ to 100 °C, 30 °C min⁻¹ to 200 °C, and finally 200 °C for 0.5 min. Hydrogen and air were used as detector gases.

GC–MS analysis was performed using an Agilent HP-6890N GC–MS (Wilmington, DE, USA) equipped with a 5973N mass-selective detector using the electron impact (70 eV) mode. The MS was operated in the total ion current (TIC) mode, scanning from 5 to 100 m/z. Chromatographic data were recorded using an HP Chemstation, which was controlled by Windows NT (Microsoft) and equipped with Wiley 275 mass spectral library. An HP-5MS crosslinked 5% diphenyl–95% dimethylpolysiloxane column (30 m × 0.32 mm I.D., 1.0 μm film thickness) was used. Helium (>99.999% pure) was used as carrier gas with flow rate of 1.3 mL min⁻¹. The injector temperature was 200 °C and operated in the splitless mode. The interface temperature was maintained at 250 °C. The column was used with the following temperature program: 35 °C for 4 min, 25 °C min⁻¹ to 200 °C, 40 °C min⁻¹ to 230 °C, and 230 °C for 1 min.

Optical microscopic images were obtained on an Axioskop 2 plus Zeiss microscope (Hamburg, Germany) equipped with a Canon powershot G6 camera (Tokyo, Japan). The images were obtained with total magnification of 400.

SPME device (the diameter of the outer needle: 0.81 mm and the diameter of the inner needle: 0.53 mm) was purchased from Azar Electrode Co. (Urumia, Iran).

All the sample solutions were agitated using a hot plate equipped with a magnetic stirring bar (Heidolph, Schwabach, Germany).

2.4. Fiber preparation

Fused-silica fibers coated with polyimide polymer were cut into 2-cm pieces. SPME fibers were prepared by removing the polyimide polymer from the last 1 cm segment of the fibers using microflame torch similar to those reported in the literature [5,68–70]. The fibers were then washed with dichloromethane followed by a 2-min conditioning step in the GC injection port at 160 °C under helium.

2.5. Preparation of the physically IL-coated fibers

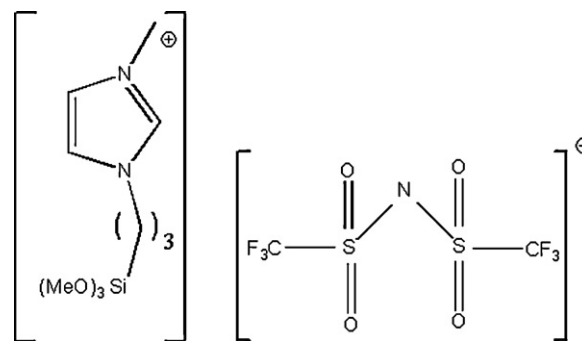
To make the IL amendable to coating as a thin film on the fused-silica fiber, a solution was prepared by mixing the IL in dichloromethane at a ratio of 1:7.5 (v/v). The dipping conditions were optimized (data not shown here) and the optimum dipping condition was obtained. The conditioned bare fused-silica fibers were dipped vertically into the coating solution 2 times, each time held for 3 min, and removed from the coating solution and allowed to dry in the air for 2 min. Prior to performing headspace extractions, the coated fibers were conditioned at 120 °C under helium stream in the GC injection port for 5 min to eliminate residual solvents from the fibers. This procedure was repeated each time before utilizing physically IL-modified SPME fibers for the headspace extractions.

2.6. Preparation of the chemically IL-coated fibers

After fiber preparation step, the fibers were put into a solution comprising of 5% of 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis (trifluoromethylsulfonyl) imide. The system was refluxed for 24 h under nitrogen atmosphere. Then the fibers were washed several times with chloroform in order to remove the excess amount of reactant which was not coated chemically to the surface of the fibers. After the reaction was completed, the fibers were kept in air for drying and used in HS extractions [71].

2.7. Headspace solid phase microextraction

Headspace SPME was conducted for MTBE standard solutions. Different factors including the effects of concentration, extraction



Scheme 1. Structural formula of 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis(trifluoromethylsulfonyl) imide.

time and temperature, desorption time and temperature, and stirring rate were tested and optimized in order to obtain the best possible conditions for headspace analysis of the gasoline sample. MTBE standard solutions (5 mL) were placed in a 10 mL glass vial equipped with a PTFE–silicon septum. All the vials were sealed with aluminum caps. All the sample solutions were agitated using a hot plate equipped with a magnetic stirring bar at different temperatures during the extraction process while allowing the analytes to equilibrate between the organic phase and the headspace. Each determination was repeated three times. The mean values were adopted and the standard deviations were shown as error bar in the figures.

2.8. Real sample

A gasoline sample as a real sample was collected at a local refinery at Kermanshah city, Iran.

3. Results and discussion

3.1. Comparison of the extraction efficiency and thermal stability of chemically coated and physically coated fibers

Scheme 1 shows the structural formula of the synthesized IL. As shown in Fig. 1, the chemically IL-modified fiber showed durability for over 16 consecutive extractions while the physi-

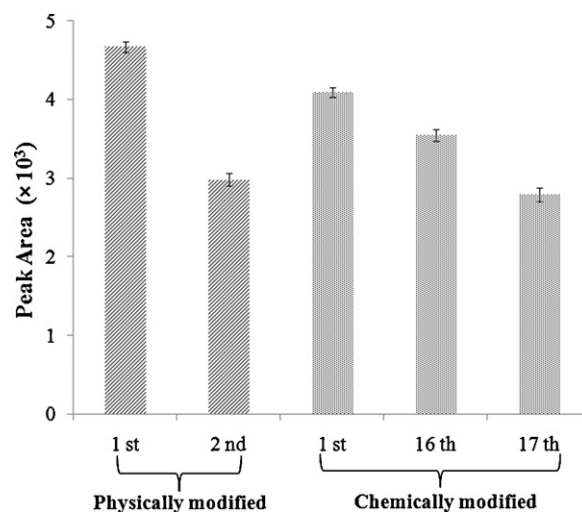
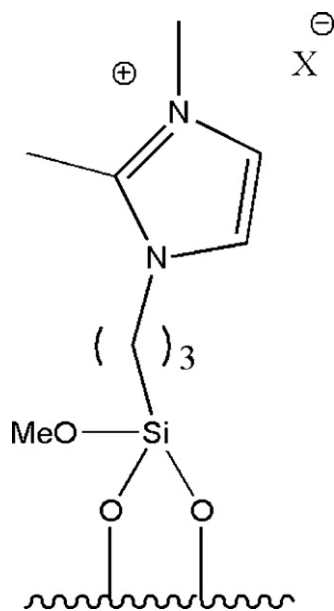


Fig. 1. Extraction efficiencies (MTBE peak area) related to the physically and chemically modified fibers. MTBE concentration: 70 μg L⁻¹, extraction time: 3 min, desorption time: 25 s, stirring rate: 300 rpm (1st: first extraction, 2nd: second extraction, 16th: sixteenth extraction, 17th: seventeenth extraction).



Scheme 2. Most probable pattern of the IL chemically bonded to the surface of the fiber. X^- : bis (trifluoromethylsulfonyl) imide.

cally IL-modified fiber can be used for only the first time after its modification and has to be modified before every extraction. This suggests that the synthesized IL was bonded successfully to the surface groups of the fused-silica fibers. However, after the 16th consecutive extraction by the fiber, a significant decrease in extraction efficiency occurred. Scheme 2 illustrates the most probable proposed chemically bonded reaction between the IL and the functional groups on the fiber surface. Due to the hydrophobic interactions of the MTBE with the ionic liquid bonded onto the fused-silica surface groups, a complex adsorption/desorption mechanism increase the extraction efficiency [5]. On the other hand, the ionic liquid film acts like a sponge, concentrating the analytes by absorption/adsorption processes. Extraction is based on a similar principle to chromatography, based on gas–liquid or liquid–liquid partitioning. Kinetics of the SPME extraction process depends on a number of parameters (e.g. film thickness, agitation of the sample, etc). For further investigation, both of the chemically and physically IL-modified fused-silica fibers were exposed to elevated temperatures. According to the chromatograms (Fig. 2), the chemically IL-modified fused-silica fibers could tolerate temperatures up to 220 °C and are more resis-

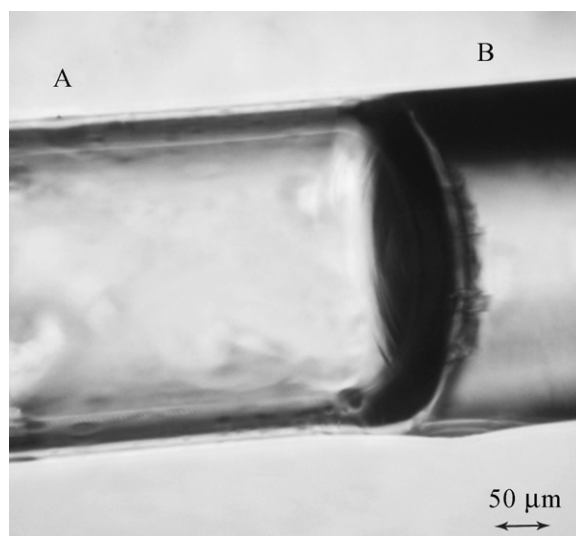


Fig. 3. Optical microscopic image of a fused-silica fiber after removing the polyimide layer, surface treatment and conditioning (A) and the same fiber after chemically coated with 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis(trifluoromethylsulfonyl) imide (B) at a total magnification of 400.

tant to extreme temperatures than the physically IL-modified fused-silica fibers (180 °C). The detector response at 220 °C for the chemically IL-modified fiber was such low that no significance loss of the IL film from the fiber occurred. Fig. 3 shows the micrograph image of a fused-silica fiber after removing its polyimide polymer, surface treatment and conditioning (A), and after it has been chemically coated with the synthesized IL. The mean coated film thickness of IL on the fiber was estimated as 11 μm .

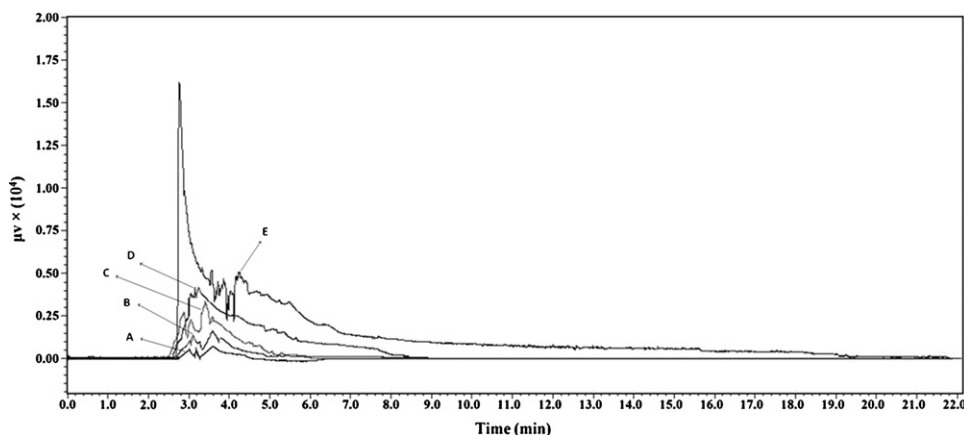
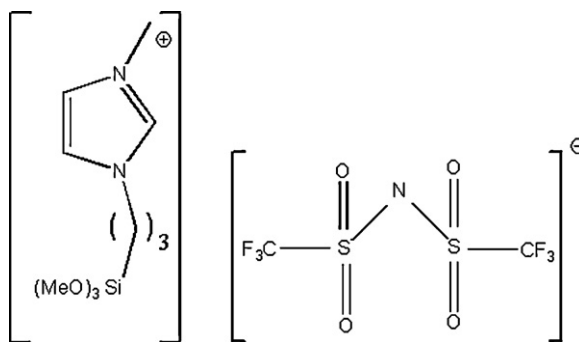


Fig. 2. Typical chromatograms related to the physically modified IL-coated fused-silica fiber at D) 180 °C and chemically modified IL-coated fused-silica fiber in four different elevated temperatures (A) 180 °C, (B) 220 °C, (C) 230 °C and (E) 240 °C.

Table 1

The effect of an interfering compound^a on the extraction efficiency of MTBE^b by the proposed reusable IL-modified SPME fiber.

Interfering compound concentration (mg L ⁻¹)	Reduced percentage of MTBE peak area
1	8.3
5	15.6
10	28.1
15	30.3
20	30.4

^a Interfering compound: benzene.

^b MTBE concentration: 10 μg L⁻¹

3.2. Matrix competition effect

While absorption is a non-competitive process, adsorption is by definition competitive, and a molecule with higher affinity for the surface can replace a molecule with lower affinity. Thus, the amount of the analyte extracted by the fiber from a sample can be significantly affected by sample matrix composition [72]. To further study the properties of the proposed reusable IL-modified SPME fiber, a water sample spiked with one concentration of MTBE was studied and the extraction efficiency was investigated using headspace extraction. Table 1 illustrates the effect of an interfering compound on the extraction efficiency of MTBE peak area for the proposed reusable IL-modified SPME fibers. In this experiment, the concentration of the interfering compound (benzene) was varied between (1 and 20) mg L⁻¹. It can be observed from the table that the presence of the interfering compound caused a reduction on the extraction efficiency of MTBE extracted by the reusable IL-modified fibers.

3.3. Optimization of HS-SPME conditions

Extraction and desorption times and temperatures and solution stirring rate were optimized. Fig. 4 shows the effects of different extraction times and temperatures on the MTBE peak area. The optimum values for temperature and time were obtained as 40 ± 1 °C and 12 min, respectively. The extraction temperature has a dual effect on the extraction of analytes in the headspace [26,73,74]. Two effects, the diffusion coefficient of the analyte from the liquid medium to the headspace and partition coefficient of the analyte in the fiber coating compete to each other. High temperatures increase

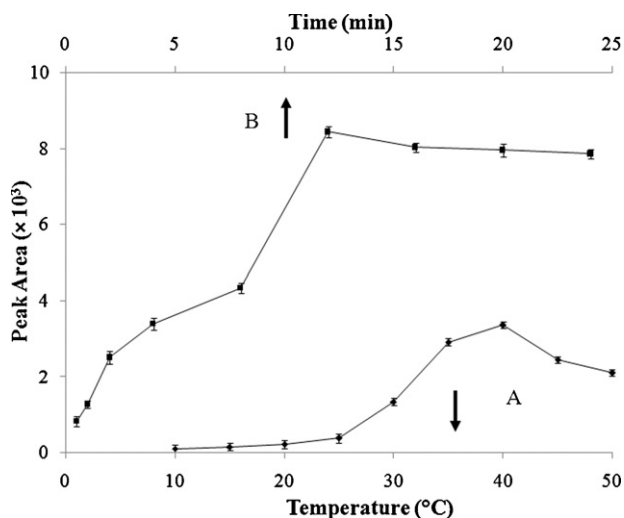


Fig. 4. (A) Effect of extraction temperatures (at extraction time of 3 min) and (B) extraction times (at extraction temperature of 40 °C). MTBE concentration: 70 μg L⁻¹, desorption time: 25 s, stirring rate: 300 rpm.

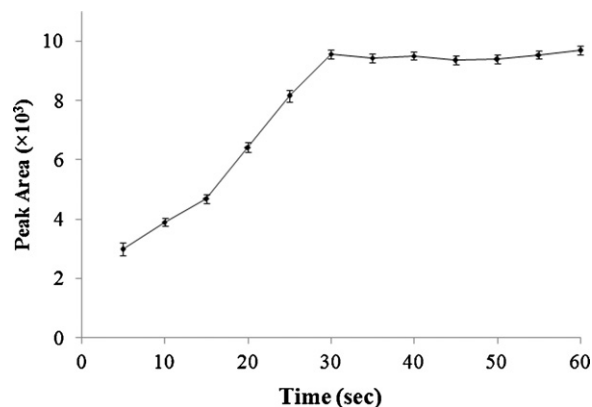


Fig. 5. Effect of desorption times on the extraction of MTBE. MTBE concentration: 70 μg L⁻¹, extraction temperature: 40 °C, extraction time: 12 min.

the former which leads to shorter extraction times and higher extraction efficiencies while decreasing the latter in the fiber coating and thereby decreasing extraction efficiencies. Fig. 5 illustrates the effect of different desorption times. The optimum value was obtained as 30 s. Less than 30 s leads to an incomplete desorption of MTBE while more than that did not have any further effect. The effect of different stirring rates is shown in Fig. 6 with the optimum value of 200 rpm.

3.4. Analytical performance of the method

In order to evaluate the linearity of the headspace SPME/GC-FID method, a calibration curve over a concentration range of 2–240 μg L⁻¹ of MTBE was obtained. All the experiments were carried out in triplicate at each concentration point. Linear dynamic range (LDR), coefficient of determination (R^2), limit of detection (LOD), limit of quantification (LOQ) and relative standard deviation (RSD %) are shown in Table 2. Also, a comparison of the proposed reusable IL-modified SPME fiber with the physically IL-modified SPME fiber and different commercial SPME fibers and methods was made and is shown in Table 2. Regression equation was obtained as $y = 138.09(\pm 0.03)x - 19.68(\pm 0.37)$. LOD and LOQ were calculated as three and ten times of base-line noise, respectively. Six repeated determinations of a standard solution containing 30 μg L⁻¹ of MTBE were done to calculate the precision (RSD).

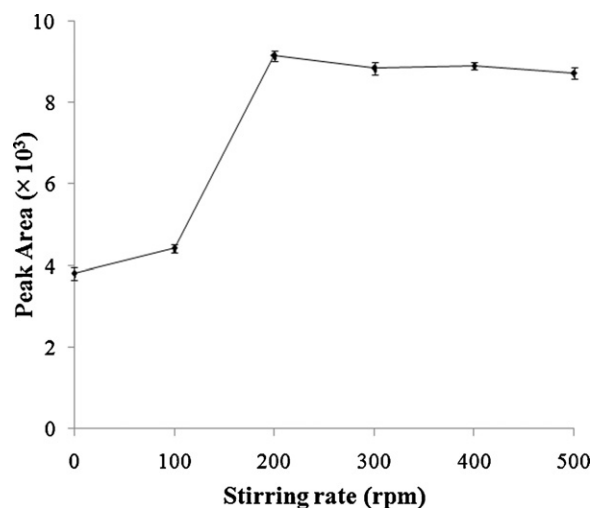


Fig. 6. Effect of different stirring rates on the extraction of MTBE. MTBE concentration: 70 μg L⁻¹, extraction temperature: 40 °C, extraction time: 12 min, desorption time: 25 s.

Table 2

Analytical performance data of the proposed reusable IL-modified SPME fiber and its comparison with the physically IL-modified SPME fiber and different commercial SPME fibers and methods.

Fiber type	Linear range ($\mu\text{g L}^{-1}$)	Coefficient of determination (R^2)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	RSD% ($n=6$)
11 μm Chemically IL-modified SPME fiber ^a	2–240	0.996	0.1	0.33	8.9
Physically IL-modified SPME fiber ^a	1–130	0.994	0.1	0.33	12
65 μm PDMS-DVB ^a [51]	5–500	0.999	0.45	–	6.3
75 mm PDMS/Carboxen ^a [75]	–	–	0.27	–	7.7
Headspace GC–MS (in ground water)	0.01–10	0.9993	0.01	–	10.9

^a HS-SPME-GC/FID.

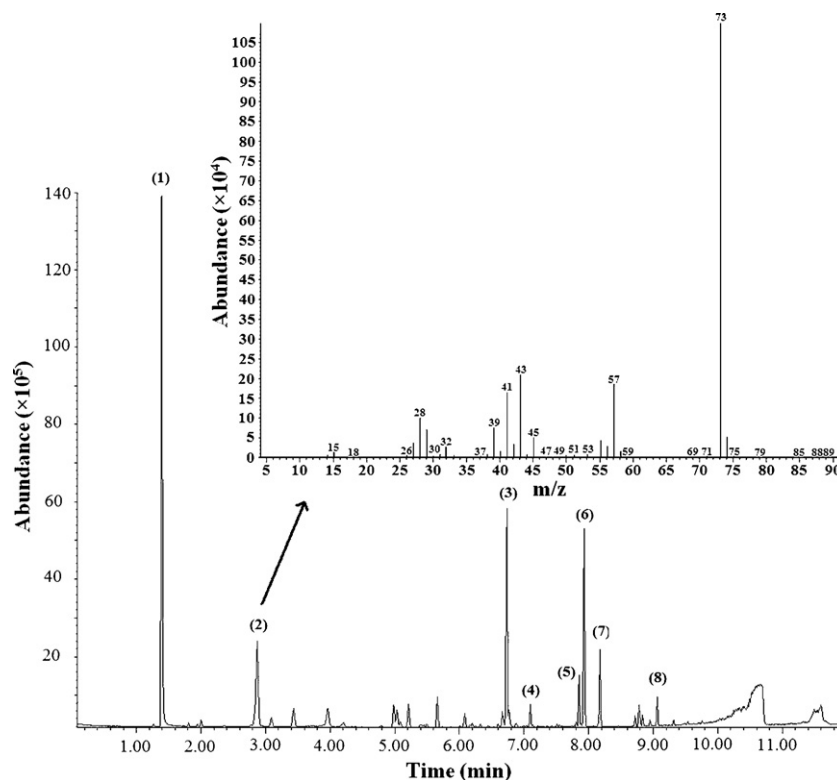


Fig. 7. Typical total-ion chromatogram of a gasoline sample with the use of the reusable chemically modified IL-coated fiber. Peaks: (1) methanol, (2) MTBE, (3) toluene, (4) *n*-octane, (5) 1-buten-3,3-dicarbonitrile, (6) isopropylidenmalonitrile, (7) spiro (2,4)heptadiene-(2,4), (8) 1-bromoethyl benzene. Inset: mass spectrum of MTBE detected in the gasoline sample.

3.5. Real sample analysis

An aliquot of 10 μL of a gasoline sample was added to a 100 mL volumetric flask, and was diluted with methanol. 5 mL of the diluted solution was transferred to a 10 mL headspace vial equipped with a PTFE–silicon septum and headspace SPME was conducted for the diluted real sample. The amount of MTBE was determined as 75.9 ± 0.3 ($\pm\text{SD}$) $\mu\text{g L}^{-1}$ in the diluted solution. The gasoline sample was spiked with three concentration levels of MTBE solutions including 4, 20 and 40 $\mu\text{g L}^{-1}$ and good spike recoveries including 91.6%, 95.8%, and 94.2% were obtained, respectively.

For further confirmation of the MTBE presence in the real sample, GC–MS analysis was performed. The total ion current of the gasoline sample and mass spectrum of MTBE are shown in Fig. 7.

4. Conclusion

A new reusable IL-bonded fused-silica SPME fiber was prepared and investigated for the determination of MTBE in a gasoline

sample by HS-SPME/GC-FID. The proposed reusable chemically IL-modified SPME fibers have been successfully applied to the rapid preconcentration of MTBE. High operating temperature, easy preparation, stability and durability of the coating are some of the main advantages of the chemically crosslinked IL-SPME fibers. The chemically bonded IL film on the surface of the fused silica fiber was durable over 16 headspace extractions without any significant loss of the IL film. Compared to the widely used commercially available SPME fibers, these proposed task-specific IL-coated fibers have much lower cost, comparable reproducibility, and no carryover between the determinations. The calibration graph was linear in a concentration range of 2–240 $\mu\text{g L}^{-1}$ ($R^2 = 0.996$) with the detection limit of 0.1 $\mu\text{g L}^{-1}$ level. The reproducibility (RSD %, $n=6$) of the new IL bonded fused-silica fiber (8.9%) was better than the physically coated fiber (12%) suggesting that the new chemically IL-modified fiber is more robust than the physically IL-modified fiber. The proposed reusable IL-modified fused-silica fibers showed improved thermal stability at temperatures up to 220 $^{\circ}\text{C}$ relative to the physically modified fibers (180 $^{\circ}\text{C}$).

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