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A new disposable ionic liquid based coating for headspace solid-phase microextraction of methyl tert-butyl ether in a gasoline sample followed by gas chromatography–flame ionization detection

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ABSTRACT

A new ionic liquid (IL) based solid-phase microextraction (SPME) fiber was investigated and used for headspace (HS) extraction of methyl tert-butyl ether (MTBE) in a gasoline sample. Using the new IL coated HS-SPME fiber with the combination of gas chromatography–flame ionization detection (GC–FID); sub-to-low $\mu g\,L^{-1}$ concentrations of MTBE were detected. Four different ILs including 1-butyl-3-methylimidazolium tetraflouroborate ($[C_4C_1IM]$ $[BF_4]$), 1-octyl-3-methylimidazolium tetraflouroborate ($[C_8C_1IM]$ $[BF_4]$), 1-octyl-3-methylimidazolium hexaflourophosphate ($[C_8C_1IM]$ $[PF_6]$) and 1-ethyl-3-methylimidazolium ethylsulphate ($[C_2C_1IM]$ $[ETSO_4]$) were synthesized and examined for extraction, preconcentration and determination of MTBE. It was observed that $[C_8C_1IM]$ $[BF_4]$ showed the highest extraction efficiency and possessed the best extractability for MTBE. The fiber coating takes up the compounds from the sample by absorption in the case of liquid coatings. The calibration graph was linear in a concentration range of 1–120 $\mu g\,L^{-1}$ ($R^2 > 0.994$) with the detection limit of 0.09 $\mu g\,L^{-1}$ level. The new IL-coated fiber was applied successfully for the determination of MTBE in a gasoline sample with good recoveries between 90 and 95%.

1. Introduction

Several different coatings are commercially available for solid-phase microextraction (SPME) analysis. These include polydimethylsiloxane (PDMS), polyacrylate (PA), Carboxen (CAR), divinylbenzene (DVB), and Carbowax (CW) [1–3]. These fibers are available in different thicknesses with single coatings, mixtures, or co-polymers and are suitable for the analysis of both polar and non-polar organic compounds such as phenols, alcohols, ketones, nitroaromatics, benzene, toluene, ethylbenzene, and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs), pesticides [2,3]. However, 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]. Therefore, it is of interest to develop a novel low cost SPME coating with desired analytical characteristic which can be easily prepared [4]. Several approaches have been proposed to overcome these drawbacks. Supelco (Bellefonte, PA, USA) has developed metal fiber assemblies in which the fiber core is made of metal alloy to extend the lifetime of the fiber assembly, and to improve durability and the reproducibility of the extraction [2]. While the sol–gel technology was adopted to prepare SPME fibers [6–24], also disposable usage of technical grade optical fibers as SPME fiber was proposed [25]. Another alternative is to employ liquid-phase microextraction (LPME) performed by using a single drop of solvent [26–29] or a small length of porous hollow fiber protecting the solvent [29,30]. Unfortunately, LPME suffers from relatively low sensitivity and inconvenient in performance compared with SPME [29].

Room temperature ionic liquids (RTILs), resulting from the combination of organic cations and various anions that are liquids at room temperature [29,31] are gaining widespread recognition as potential environmentally compatible solvents. Good thermal stability, negligible vapor pressure, tunable viscosity and natural liquid nature at room temperature, merit the ILs as good candidates for SPME coatings. Also, their miscibility with water and organic solvents [29,31], as well as good extractability for various organic compounds [29–35] and metals ions [29,36–41], merit their consideration as potential absorbents for SPME/LPME.

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Recently, Jiang and coworkers reported the use of 1-octyl-3-methylimidazoluim hexafluorophosphate [C_8C_1IM] [PF_6] as a disposable coating for headspace (HS) SPME of BTEX in paint samples [29]. Anderson and coworkers developed a SPME sorbent coating based on a polymeric IL for the selective HS-extraction of different analytes [42]. Another group used fused-silica capillaries coated ILs for the SPME of PAHs [43]. A kind of reusable IL-based SPME fiber was prepared for the first time by fixing 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 [44].

Methyl tert-butyl ether (MTBE) is a volatile and suspected/potential carcinogenic organic compound; therefore its determination is of great importance for both the environment and human being. 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 thereby it reduced the emission of compounds such as carbon monoxide and ozone [45–47]. MTBE has become a priority groundwater pollutant over the last decade, thus new methods for the determination of MTBE are of great importance. Many analytical methods have been used for the detection of MTBE including direct aqueous injection (DAI) [47–52], purge and trap [47–50], headspace generation [53–55] and SPME in combination with gas chromatography/mass spectrometry detection (GC–MS) [50–56].

In this study, we reported a 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 headspace SPME of MTBE from a gasoline sample. Four different RTILs were synthesized and applied to the HS-SPME of MTBE. [C_8C_1IM] [BF_4] showed the best extractability. Optimization of different factors on the headspace extraction of MTBE was performed. Simplicity, easy preparation, low consumption of IL and solvent, and much lower cost per determination than the commercial SPME fibers, are the main advantages of the proposed disposable IL-coated fibers.

2. Experimental

2.1. Chemicals and standards preparation

All chemicals used for the synthesis of the four ILs; i.e., 1-butyl-3-methylimidazolium tetraflouroborate ([C_4C_1IM] [BF_4]), 1-octyl-3-methylimidazolium tetraflouroborate ([C_8C_1IM][BF_4]), 1-octyl-3-methylimidazolium hexaflourophosphate ([C_8C_1IM] [PF_6]), 1-ethyl-3-methylimidazolium ethylsulphate ([C_2C_1IM] [$EtSO_4$]) and dichloromethane were purchased from Merck (Darmstadt, Germany) as analytical reagent grade chemicals and used without further purification. Dichloromethane was used for the dilution of the ILs prior to the modification of SPME fibers. 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). All stock and standard solutions were prepared each day.

2.2. Synthesis of ILs

ILs were synthesized similar to those reported in the literature [57,58]. Briefly, the syntheses were as follows:

2.2.1. [RMIM] [Cl]

The IL [RMIM] [Cl] was prepared according to the synthesis method described [57]. Equal molar amounts of chloroalkyl (*R*: C_8, C_4) and 1-methylimidazole (Merck, 99%) were added to a round-bottomed flask fitted with a reflux condenser for 4 h at 70 °C with stirring under nitrogen atmosphere until two phases formed. After cooling to room temperature, the reaction mixture was washed four times using ethyl acetate in order to remove any unreacted material. The product was dried under vacuum at 70 °C for 8 h. 1-Alkyl-3-methylimidazolium chloride ([RMIM] [Cl]), was obtained as a pure product.

[C_4C_1IM] [Cl] ^{1}H NMR (300 MHz; $CDCl_3$): δ (ppm): 0.93 (3H, t, N-$(CH_2)_3CH_3$), 1.36 (2H, m, N-$(CH_2)_2CH_2CH_3$), 1.86 (2H, m, N-$CH_2CH_2CH_2CH_3$), 4.09 (3H, s, N-CH_3), 4.3 (2H, t, N-$CH_2(CH_2)_2CH_3$), 7.44 (1H, s, H-4), 7.59 (1H, s, H-5), 10.63 (1H, s, H-2). ^{13}C NMR (75.4 MHz; $CDCl_3$): δ (ppm): 13.33, 19.3, 32.04, 36.38, 49.58, 122.02, 123.7 and 137.5.

[C_8C_1IM] [Cl] ^{1}H NMR (300 MHz; $CDCl_3$): δ (ppm): 0.75 (3H, t, N-$(CH_2)_7CH_3$), 1.17–1.2 (10H, m), 1.8 (2H, m), 4.03 (3H, s, N-CH_3), 4.2 (2H, t, N-$CH_2(CH_2)_6CH_3$), 7.41 (1H, s, H-4), 7.65 (1H, s, H-5), 10.46 (1H, s, H-2). ^{13}C NMR (75MH, $CDCl_3$): δ (ppm): 13.9, 22.39, 26.07, 28.78, 28.84, 30.19, 31.48, 36.37, 49.85, 121.90, 123.78 and 137.47.

2.2.2. [C_8C_1IM] [PF_6]

To a solution of 20.6 g of [C_8C_1IM] [Cl] dissolved in 40 mL distilled water, 18.2 g of KPF_6 dissolved in 25 mL distilled water was added and the mixture was stirred for about 5.5 h at room temperature. A two phase mixture was formed. After leaving the mixture for 30 min, the aqueous phase was separated from the organic phase. The aqueous phase was then washed two times with dichloromethane, each time with 50 mL. The combined organic phase was then added to the IL phase. The organic phase was washed three times with distilled water, each time with 50 mL and was dried over magnesium sulfate. The suspension was filtered and its solvent was evaporated. The final product was dried completely at 70 °C under vacuum to give 27 g of product with 90% yield.

[C_8C_1Im] [PF_6] ^{1}H NMR (300 MHz; $CDCl_3$): δ (ppm): 0.88 (3H, t), 1.28 (10H, m), 1.87 (2H, t), 3.91 (3H, s), 4.14 (2H, t), 7.32 (1H, s), 7.34 (1H, s), 8.46 (1H, s).

2.2.2.1. [C_8C_1IM] [BF_4]. To a solution of 20.0 g of [C_8C_1IM] [Cl] dissolved in 40 mL distilled water, 12.4 g of $NaBF_4$ dissolved in 25 mL distilled water was added dropwise, while the temperature was kept below 5 °C throughout the addition. The mixture was then stirred for 7 h at room temperature. After the reaction was completed, vacuum distillation was used to remove the water content of the mixture. Dichloromethane was added to the residual and the mixture was dried over magnesium sulfate. The mixture was filtered and its solvent evaporated. The final product was dried under vacuum at 70 °C to give 20.8 g of the IL with 84% yield. [C_8C_1IM] [BF_4] ^{1}H NMR (300 MHz; $CDCl_3$): δ (ppm): 0.76 (3 H, t), 1.14-1.20 (10H, m), 1.76 (2H, t), 3.84 (3H, s), 4.06 (2H, t), 7.30 (1H, s), 7.34 (1H, s), 8.64 (1H, s).

2.2.2.2. [C_4C_1IM] [BF_4]. The same procedure was used as for [C_8C_1IM] [BF_4] with the substitution of [C_4C_1IM] [Cl] for [C_8C_1IM] [Cl]. The final product was obtained with the yield of 85%. [C_4C_1IM] [BF_4] ^{1}H NMR (300 MHz; $CDCl_3$): δ (ppm): 0.67 (3H, t), 1.09 (2H, m), 1.61 (2H, m), 3.69 (3H, s), 3.95 (2H, t), 7.22 (1H, s), 7.24 (1H, s), 8.44 (1H, s).

2.2.3. [C_2C_1IM] [$EtSO_4$]

To a solution of 4.92 g of 1-methylimidazole in toluene (8 mL), 9.25 g (60 mmol) of freshly distilled diethyl sulfate was added dropwise, keeping the temperature at 10 °C throughout the addition. The mixture was stirred for about 4 h at room temperature. A two-phase mixture was detected and separated. The IL phase was washed 3 times with fresh toluene, each time with 10 mL. The residual toluene in the IL was then removed under vacuum at 70 °C to give 13.5 g of the IL with 95% yield [54]. [C_2C_1IM] [$EtSO_4$] ^{1}H NMR

(300 MHz; $CDCl_3$): δ (ppm): 1.25 (3H, t), 1.53 (3H, t), 3.99 (3H, s), 4.07 (2H, m), 4.3 (2H, m), 7.49 (2H, s), 9.49 (1H, s).

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 μm was used for the 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 180 °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, 50 °C min^{-1} to 250 °C, and finally 250 °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 5973 N 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. A 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 180 °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).

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. (Urmia, Iran).

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

2.4. Preparation of the ionic liquid-coated fibers

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 [5,59–61]. The fibers were then washed with dichloromethane followed by a 2-min conditioning step in the GC injection port at 160 °C under helium.

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 1:5 (v/v). The conditioned bare fused-silica fiber was dipped into the IL solution, held for 15 min, and removed from the coating solution and allowed to dry in the air for 10 min. It was found that the above type of coating method achieved better homogeneous film thickness. 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 IL-modified SPME fibers for the headspace extraction.

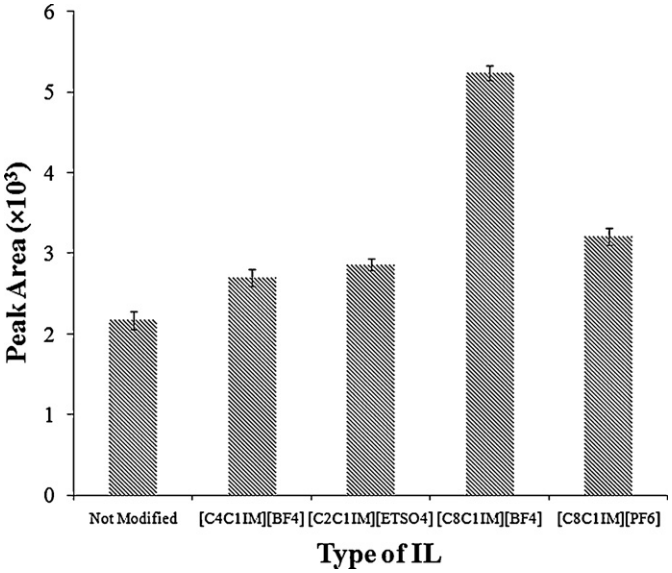

Fig. 1. Effect of four different ILs on the extraction efficiency of the MTBE. MTBE concentration: 80 μg L^{-1}, extraction time: 8 min, extraction temperature: 30 °C, desorption time: 30 s, stirring rate: 400 rpm.

2.5. Headspace solid phase microextraction

HS-SPME was conducted for MTBE standard solutions. Different factors including the effects of concentration, extraction time and temperature, and solution 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 with a hot plate equipped with a magnetic stirring bar at different temperatures beginning at room temperature 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.

2.6. 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. Selection of the IL and optimization of the coating procedure

The effects of four different synthesized ILs on the extraction efficiency of MTBE were tested. As shown in Fig. 1, among the four synthesized ILs, $[C_8C_1IM]$ $[BF_4]$ was the best of all for MTBE preconcentration and possessed the best extractability for MTBE. Due to the hydrophobic interactions of the MTBE with the ionic liquid coated on the fused-silica surface, a complex adsorption/desorption mechanism increases the extraction efficiency [5]. 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) [62].

In order to obtain the best volumetric ratio of the IL to dichloromethane, eight different volumetric ratios of IL to dichloromethane were prepared. These were 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7 and 1:8 (v/v). Our experiments showed that the best volumetric ratio of IL to dichloromethane is 1:5 (v/v). Less than 1:5

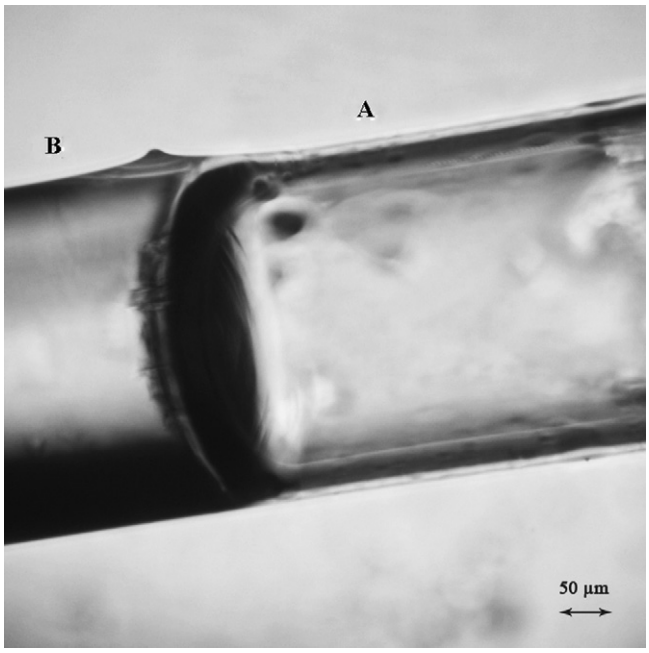

Fig. 2. Optical microscopic images of the fused silica fiber after removing the polyimide layer, surface treatment and conditioning (A) and the same fiber after coated with [OMIM] [BF_4] (B) at a total magnification of 400.

(v/v) leads to inhomogeneous and thick IL film on the fibers while more than 1:5 (v/v) makes a very thin IL film on the fibers that is not capable of extracting a significant amount of MTBE. Because the GC injection temperature was set to 180 °C and also bearing in mind that viscosity of the ILs drop rapidly at high temperatures, an optimum homogeneous film thickness of the IL on the fibers was required.

Fig. 2 shows micrograph images of a fused-silica fiber after removing its polyimide layer, surface treatment and conditioning (A), and after it has been coated with [C_8C_1IM] [BF_4] (B). The mean coated film thickness of IL on the fiber was estimated as 12.7 μm.

For optimization of the coating procedure, the coating time was optimized in the range of 1–30 min. Also, the effect of different coating conditions including 1 time for 2 min (dipping in the coating solution for 2 min and then 1 min in air to allow the dichloromethane to evaporate, namely, 1×2 min), 1×4 min, 1×6 min, 2×2 min, 2×6 min, 3×2 min, 3×4 min, 3×6 min were tested. These are all illustrated in Fig. 3. It is obvious from Fig. 3 that the resulted MTBE peak area was significantly higher when the fibers were dipped in the coating solution for 15 min than those with shorter times or different conditions. More than 15 min did not have any further effect on the MTBE peak area.

3.2. Optimization of HS-SPME conditions

To obtain the optimum extraction temperature, nine different temperatures within the range of 20–65 °C were studied. According to literature [29,63,64], the extraction temperature has a dual effect on the extraction of analytes in the headspace. 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 with each other. High temperatures increase the former which leads to shorter extraction times and higher extraction efficiencies while decreasing the latter in the fiber coating, thereby decreasing extraction efficiencies. Fig. 4A illustrates the effect of extraction temperatures on the extraction efficiencies of MTBE. As can be seen, increased peak areas of MTBE in the range of 20–45 °C with the highest MTBE peak area at 45 °C were obtained.

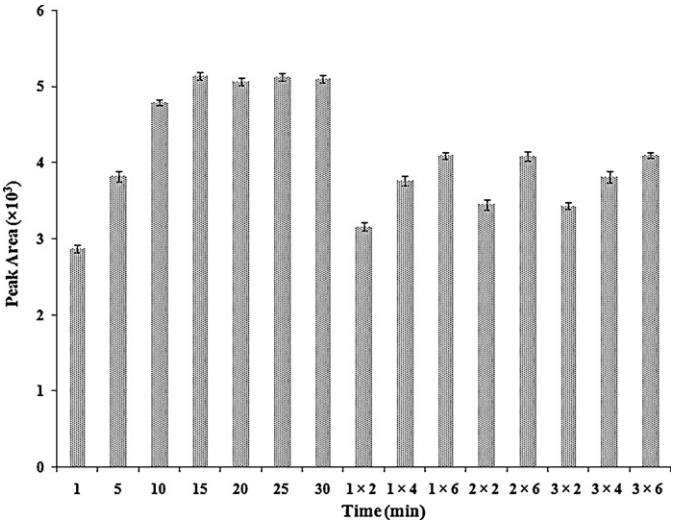

Fig. 3. Effect of different coating times and conditions on the MTBE peak area. (1×2 means, dipping in the coating solution 1 time for 2 min). MTBE concentration: 60 μg L^{-1}, extraction time: 8 min, extraction temperature: 30 °C, desorption time: 30 s, stirring rate: 400 rpm.

At temperatures higher than 45 °C, decreased MTBE peak areas were seen.

The extraction times were also optimized in the range of 0.5–30 min. Fig. 4B shows that the MTBE peak areas increased in the range of 0.5–18 min and remained nearly constant with prolonged extraction times suggesting that the optimum extraction time was 18 min.

Fig. 5 shows the effect of different stirring rates on the extraction efficiency of MTBE. The optimum value for solution stirring rate was obtained as 300 rpm.

Our experiments showed that desorption of MTBE was almost completed in about 10 s. This rapid and complete desorption is another advantage of the proposed fiber. Less than 10 s leads to an incomplete desorption of MTBE while more than that did not have any further effect. It is noteworthy that at GC injector temperatures higher than 180 °C, significant loss of the IL film occurred.

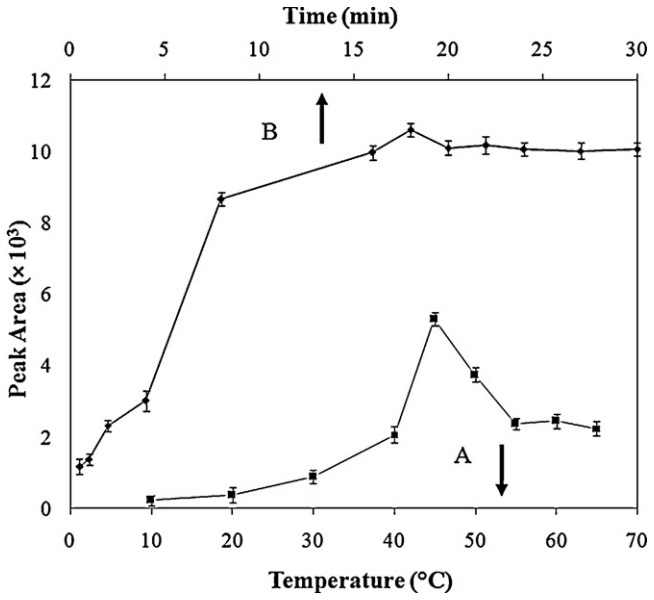

Fig. 4. (A) Effect of the extraction temperatures (extraction time: 8 min) and (B) the extraction times on the extraction of MTBE (extraction temperature: 45 °C). MTBE concentration: 80 μg L^{-1}, desorption time: 10 s, stirring rate: 400 rpm.

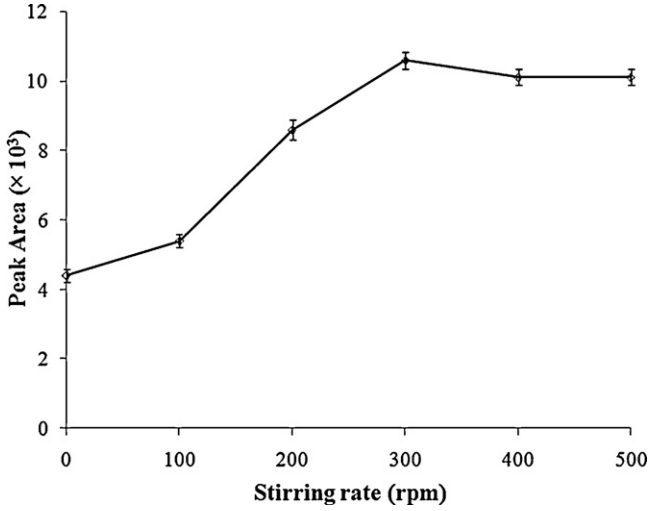

Fig. 5. Effect of different stirring rates on the extraction of MTBE. MTBE concentration: 80 μg L^{-1}, extraction temperature: 45 °C, extraction time: 18 min, desorption time: 10 s.

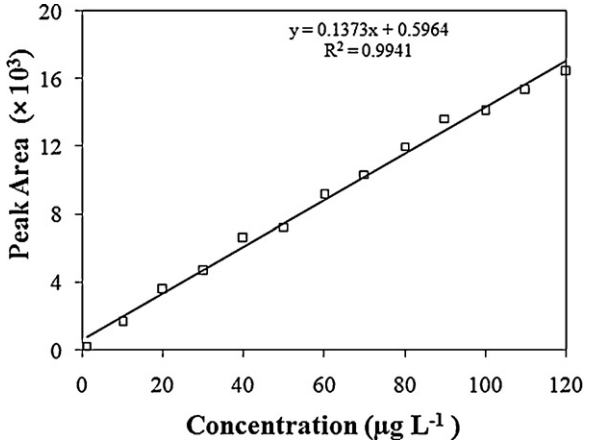

Fig. 6. Calibration curve of MTBE determination. MTBE concentration range: 1–120 μg L^{-1}, extraction temperature: 45 °C, extraction time: 18 min, desorption time: 10 s, stirring rate: 400 rpm

This limitation of the IL film makes it useful only for volatile and semi volatile compounds.

3.3. 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 1–120 μg L^{-1} of MTBE was obtained. All the experiments were carried out in triplicate at each concentration point. This gave a linear regression with a correlation coefficient (R^2) of 0.9941 (Fig. 6). Linear dynamic range (LDR), correlation coefficient (R^2), limit of detection (LOD), limit of quantification (LOQ) and relative standard deviation (RSD%) are shown in Table 1. Also, a comparison of the disposable IL-coated SPME fiber with two different commercial SPME fibers was made and is shown in Table 1. 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%).

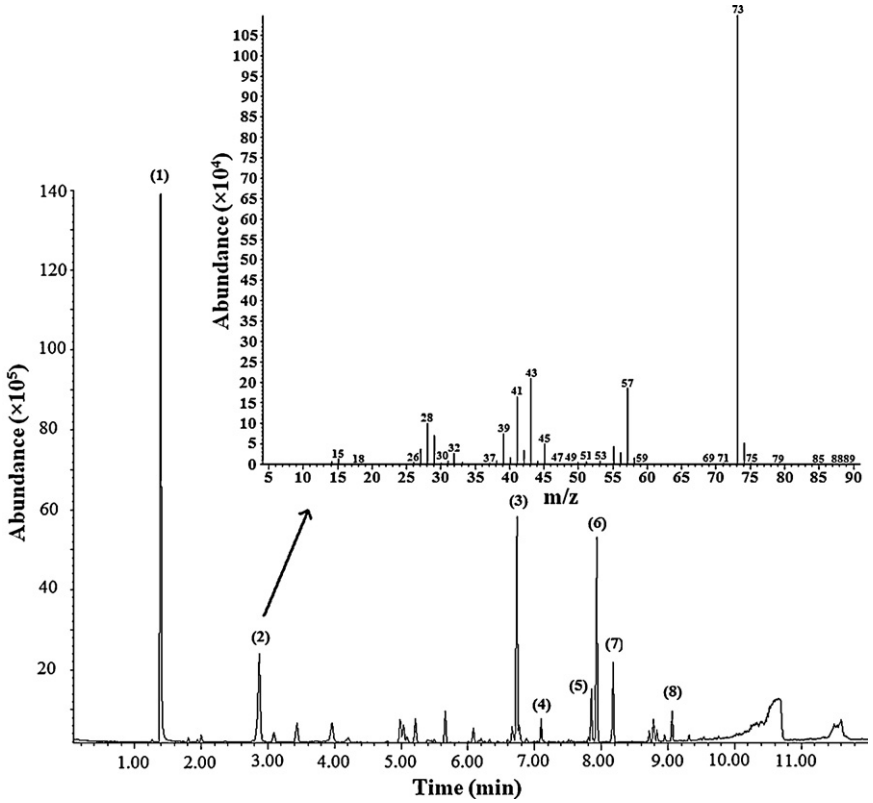

Fig. 7. Typical total-ion chromatogram of a gasoline sample with the use of the new disposable modified IL-coated fiber. Peaks: (1) methanol, (2) MTBE, (3) toluene, (4) *n*-octane, (5) 1-buten-3,3-dicarbonitrile, (6) isopropylidenmalonitrile, (7) spiro (2,4)heptadiene-(2,4), (8) 1-bromoethyl benzene.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

Table 1
Analytical performance data of the proposed IL-coated fiber.

Fiber type	Linear range ($\mu g\,L^{-1}$)	Correlation coefficient (R^2)	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	RSD% ($n=6$)
12.7 μm IL modified fused-silica capillary[a]	1–120	0.9941	0.09	0.3	8.3
65 μm PDMS–DVB[a] [53]	5–500	0.999	0.45	–	6.3
75 mm PDMS/Carboxen[a] [65]	–	–	0.27	–	7.7

[a] HS-SPME–GC/FID.

3.4. 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 70.5 ± 0.4 (± SD) $\mu g\,L^{-1}$ in the diluted solution. The gasoline sample was spiked with two concentration levels of MTBE solutions including 2 and 30 $\mu g\,L^{-1}$ and good spike recoveries including 90.6% and 94.3% were achieved, respectively.

For further confirmation of 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

Four different ILs have been synthesized and used for the first time for the determination of MTBE by HS-SPME/GC–FID. The proposed disposable IL-coated fibers have been successfully applied to the rapid preconcentration of MTBE in a gasoline sample. Large viscosity, involatility and good thermal stability of the IL will keep it staying on the fiber while the analyte is thermally desorbed in the injection port of GC. Compared to the widely used commercially available SPME fibers, these proposed task-specific IL-coated fibers have much lower cost, comparable reproducibility (RSD = 8.3%), and no carryover between the determinations. The calibration graph was linear in a concentration range of 1–120 $\mu g\,L^{-1}$ ($R^2 > 0.994$) with the detection limit of 0.09 $\mu g\,L^{-1}$ level.

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