

# Reevaluation of headspace solid-phase microextraction and gas chromatography–mass spectrometry for the determination of methyl *tert*-butyl ether in water samples

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## Abstract

A headspace solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS) method has been reevaluated for the determination of methyl *tert*-butyl ether (MTBE) in water. Factors affecting method performance were examined. The internal standard, deuterated MTBE, is necessary because it allows normalization of the calibration since the deuterated MTBE and MTBE experience the same extraction efficiency. The method detection limit was 6.6 ng/l, with a linear range up to 160 µg/l. SPME extraction efficiency and detection sensitivity for MTBE decreased in the presence of gasoline matrix. However, reliable measurement of MTBE was possible in the background matrix concentration of 0.97 mg/l gasoline using deuterated internal standard. Reproducibility was 4.5% at the spiking level of 47 ng/l. The average recoveries of MTBE in spiked fountain water, tap water, and snow at 60 ng/l and in spiked rainwater at 580 ng/l ranged from 101 to 105%. The method was successfully applied to the analysis of trace levels of MTBE in various water samples, including rain and snow samples collected in Albany, NY, USA.

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## 1. Introduction

Methyl *tert*-butyl ether (MTBE) is the most commonly used fuel oxygenate, and is added to gasoline to enhance the octane number of gasoline. Because large amount ( $8.8 \times 10^9$  kg in 1997) of MTBE have been produced in the USA [1], and because a number of investigations have shown that MTBE may pollute the aquatic and atmospheric environment, its environmental fate has led to concern. MTBE is present at relatively high concentrations in some urban air due to its use as a gasoline additive. The high solubility of MTBE in water, combined with its high concentration in some gasoline, can result in high concentrations of MTBE in surface water, ground water, and storm water [2,3]. In fact,

MTBE was reported as the second most frequently detected chemical (after chloroform) in shallow groundwater [3,4]. Currently, the most common method for the determination of MTBE is purge-and-trap pre-concentration, followed by gas chromatography (GC) analysis. Purge-and-trap/gas chromatographic instrumentation is expensive, technically sophisticated, and time-consuming to operate. Therefore, an alternate method for analyzing trace levels of MTBE from small volumes of sample with relatively high method sensitivity is necessary.

Solid-phase microextraction (SPME), a relatively new extraction technique, was introduced by Pawliszyn and co-workers [5,6]. The SPME technique integrates sampling, extraction, and concentration into a single step. Furthermore, this solvent-free sample preparation technique is advantageous when field analysis is being performed [7]. Recently, a few papers were published that describe the use of SPME–GC–MS to determine MTBE concentrations in water

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[1,8–13]. Method detection limits (MDLs) of 8–14 ng/l and 1 µg/l were reported, indicating an advantage in sensitivity when trace analysis is necessary. These MDLs are generally better than the MDLs of 0.2–1.1 µg/l for standard US Environmental Protection Agency (EPA) purge-and-trap GC methods [14]. Although MTBE in river water and wastewater have been analyzed successfully using SPME method [12], to date, most of the MTBE analysis using SPME has focused on the extraction of standards spiked into relatively clean water [1,8–10]. Among the published papers, only two investigated the possible matrix effects arising from the presence of monoaromatic compounds [11,13].

Recently, the limitations of Carboxen–polydimethylsiloxane (CAR–PDMS) fiber in quantitative analysis have been discussed [11,15]. Black and Fine [11] found that the response of the deuterated internal standards of MTBE and *tert*-butyl alcohol (TBA) dropped by more than 65% when the sample contained total aromatic compounds above 1 ppm. They suggested that if SPME methods are used, internal standards should be considered a necessity along with monitoring of internal standard peak areas and total aromatic content. Dewsbury et al. [13] described a SPME method for the analysis of MTBE, TAME (*tert*-amyl methyl ether), and TBA in petroleum fuel-contaminated groundwater with MDL of 1 µg/l for MTBE. They reported that accurate measurement of MTBE could be obtained in a background matrix containing up to 300 mg/l of total BTEX (benzene, toluene, ethylbenzene, and xylenes) concentration provided the internal deuterated MTBE standard is used in the analysis. Murray [15] also observed that the competitive extraction of volatile organic sulfur compounds on CAR–PDMS fiber resulted in erratic calibration curves. Cho et al. [16] investigated the CAR–PDMS fiber for the analysis of BTEX in water and found reduced extraction efficiency under multi-component conditions due to competitive replacement. These results demonstrate the limitations of CAR–PDMS fiber for the quantitative analysis of multi-component samples and suggest that a deuterated isotope analog is needed for each component analyzed.

The main purposes of the present study are to reevaluate the headspace SPME–GC–MS method for the determination of MTBE in water samples, and to investigate the feasibility and limitations of CAR–PDMS fiber for quantitative analysis of MTBE in complex water samples such as gasoline-contaminated water.

## 2. Experimental

### 2.1. Chemicals and materials

SPME fiber assemblies and SPME fiber holder were obtained from Supelco (Bellefonte, PA, USA). Glass vials (10 ml) with holed screw cap and silicone–polytetrafluoroethylene septum were obtained from National Scien-

tific (Lawrenceville, GA, USA). MTBE and [<sup>2</sup>H<sub>3</sub>]MTBE (MTBE-d<sub>3</sub>) were obtained in the highest commercially available purity (>99%) from Aldrich. The calibration standards (certified standard solutions; AccuStandard catalog no. M-502D/E/F) used for BTEX/TMBs (trimethylbenzenes) were purchased from AccuStandard (New Haven, CT, USA). Automotive gasolines were obtained from local gasoline stations in Albany, NY, USA. All of the other solvents used were nanograde. The water used for preparing the aqueous solution was distilled water, which was passed through a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA).

### 2.2. Preparation of standards

A concentrated standard (stock) solution with a concentration of 6.51 mg/ml for MTBE or 5.46 mg/ml for MTBE-d<sub>3</sub> was prepared separately by weighing MTBE or MTBE-d<sub>3</sub> and dissolving it in methanol in a volumetric flask. All of the stock solutions were stored at 4 °C and used within a month. Additional diluted stock solutions were also made by appropriate dilution in methanol. Diluted aqueous MTBE standards of various concentrations (working solutions) were made from the appropriate stock solution daily using distilled/deionized water. A 2 ng/ml aqueous mix of BTEX/TMBs calibration standard (AccuStandard catalog no. M-502D/E/F) and MTBE calibration standard (100 µg/ml, prepared in the laboratory) was prepared for gasoline (100 ng/ml in aqueous solution) characterization.

### 2.3. Headspace solid-phase microextraction

For the SPME determinations, a manual SPME holder and fibers were used. The fibers were conditioned as recommended by the manufacturer. Two blank injections were performed before the actual analysis. Between uses, fibers were kept sealed from ambient air by piercing the tip of the SPME needle into a small piece of septum to prevent accidental contamination. The sampling procedure involved placing 7 ml of sample into a 10 ml vial containing 2.33 g NaCl (25% (w/w)) and sealing with a screw-top septum containing cap. The sample was then spiked with a 7 µl aliquot of methanol containing 4.37 mg/l of MTBE-d<sub>3</sub> as an internal standard. The vial was placed in a water bath maintained at 40 ± 0.1 °C for 15 min to establish phase equilibrium. The vial and SPME holder were clamped into a stand that allowed the vial to be immersed in the water bath only up to the level of the liquid in the vial. The SPME needle was then inserted through the septum into the headspace so as to locate the tip of the exposed fiber approximately 0.5 cm from the top of the liquid; the fiber was allowed to equilibrate for 30 min. The fiber was then retracted, removed from the vial, and placed immediately into the injector of the GC system. The SPME holder was adjusted so that the exposed fiber tip was positioned about halfway (1.5 in.; 1 in. = 2.54 cm) into the GC injector

port liner when extended from the protective needle. Injection was accomplished by extending the fiber in the heated inlet for 2 min, and the splitter was opened after 0.50 min. The additional 1.5 min of exposure time in the injector port allowed the fiber to be cleaned of any compounds that were not desorbed in the initial 0.5 min. Preliminary studies indicated that the above procedure allowed for reproducible, quantitative transfer of MTBE into the injector port of the GC system. Method blanks containing internal standards were run at the beginning and at the end of the sample queue. Triplicates of each sample were extracted by the SPME technique.

#### 2.4. Instrumentation

The GC–MS analyses were performed on a Hewlett-Packard 6890 gas chromatograph fitted with a 60 mm  $\times$  0.32 mm i.d., 1.8  $\mu$ m film thickness Rtx-502.2 column (Restek, Bellefonte, PA, USA). The injection port was equipped with a Merlin Microseal septum (Hewlett-Packard, Avondale, PA, USA) and a 0.75 mm i.d. injector liner (Supelco) designed to optimize recovery in SPME analysis. The injection port was operated in the splitless injection mode, with the split/splitless purge valve opened at 0.50 min after injection. The injector port temperature was 310  $^{\circ}$ C, with a helium head pressure maintained at 5.0 psi. (1 psi = 6894.76 Pa). The GC oven temperature was maintained at 40  $^{\circ}$ C for 4 min, and then temperature-programmed at a rate of 10  $^{\circ}$ C/min to 120  $^{\circ}$ C, and then at 25  $^{\circ}$ C/min to 250  $^{\circ}$ C, which was held for 10 min. MTBE was detected with an HP 5972 mass spectrometry detector (Hewlett-Packard), which uses electron impact ionization for fragmentation. For increased sensitivity and specificity, the MS detector was operated in the selected-ion monitoring (SIM) mode. Data analysis was performed with HP MSD Productivity ChemStation Software. The GC–MS–SIM chromatograms of the headspace SPME of a standard solution containing MTBE and MTBE- $d_3$  with their corresponding full-scan mass spectra are shown in Fig. 1. Confirmation ions at  $m/z$  73 and 57 and a quantitation ion at  $m/z$  73 for MTBE, and confirmation ions at  $m/z$  76 and 57 and a quantitation ion at  $m/z$  76 for the internal standard, MTBE- $d_3$ , are shown.

#### 2.5. Gasoline characterization

For gasoline characterization experiments, the scan mode was used, with a scan range of 50–550  $m/z$ . MTBE and BTEX/TMBs concentrations in gasoline were determined using EPA Method 502.2, purge and trap (O.I. Analytical) gas chromatography (Varian Star 3400) with photoionization detection (Tracor Instruments 703 photoionization detector), following the calibration procedures and quality control (QC) measurements outlined in the method. An Rtx-502.2 column (Restek) with 105 m  $\times$  0.53 mm i.d., 3.0  $\mu$ m film thickness was used. The laboratory that deter-

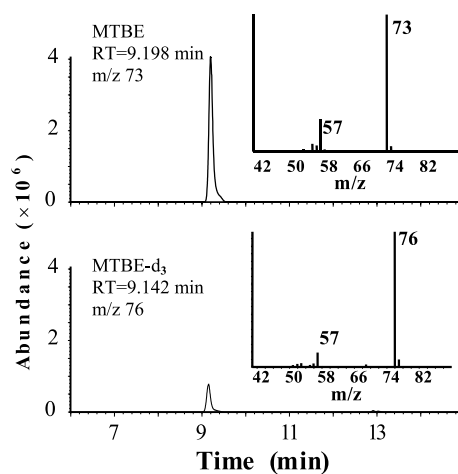


Fig. 1. SIM chromatograms for a standard containing 32.5  $\mu$ g/l MTBE and 4.37  $\mu$ g/l MTBE- $d_3$  (internal standard) and their corresponding full-scan mass spectra after headspace-SPME extracted for 30 min in 25% (w/w) NaCl.

mined the MTBE and BTEX/TMBs concentrations in the gasoline is accredited by NELAP (National Environmental Laboratory Accreditation Program) for the analysis of volatile organic compounds using EPA Method 502.2. The laboratory routinely participates in NELAP proficiency testing programs and has successfully analyzed the proficiency samples for BTEX/TMBs and MTBE.

### 3. Results and discussion

#### 3.1. Fiber evaluation

At present, nine different SPME fibers are available from Supelco. There are four adsorbent-type fibers, including the nonpolar PDMS with three different coating thicknesses of 7, 30, and 100  $\mu$ m, and a polar 85  $\mu$ m polyacrylate (PA). The adsorbent-type fibers contain divinylbenzene (DVB) and/or Carboxen 1006. Depending upon the desired polarity, the DVB fibers are available suspended in either PDMS or Carbowax (CW), a moderately polar phase. Carboxen is only one available suspended in PDMS. Two additional adsorbent-type fibers available are a bare fused silica fiber and a combination of DVB–PDMS layered over CAR–PDMS fiber. For most volatile organic compounds (VOCs), PDMS fibers are the first choice. This coating shows a high affinity for non-polar compounds under most conditions. PA fiber shows a high affinity for polar compounds, such as phenols and polar pesticides. It has been shown that the mixed phase coating is more suitable for small-molecule compounds [17]. Based on these considerations, six different fibers (five coating types) were evaluated to determine which fiber most effectively extracted MTBE from water samples.

The relative extraction efficiencies of MTBE (expressed by peak areas in the chromatograms) for the six fibers were

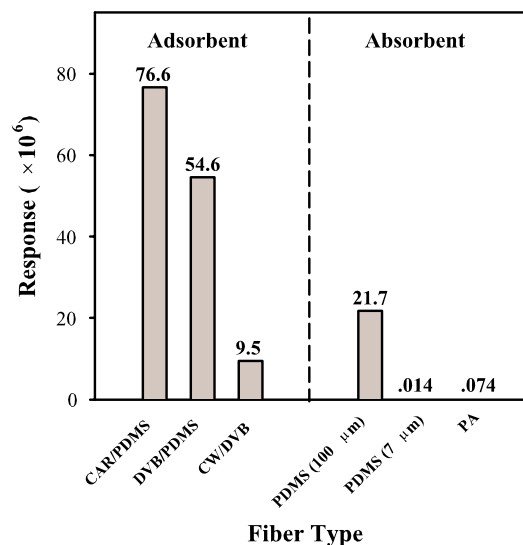


Fig. 2. Comparison of area responses (triplets of each data point) of 100 and 7  $\mu\text{m}$  PDMS, 85  $\mu\text{m}$  PA, 85  $\mu\text{m}$  CAR–PDMS, 65  $\mu\text{m}$  DVB–PDMS, and 65  $\mu\text{m}$  CW–DVB fibers for headspace–SPME extraction of 58  $\mu\text{g/l}$  MTBE solution.

compared under identical experimental conditions (adsorption/absorption time 30 min, headspace static mode, 40  $^{\circ}\text{C}$  and 25% (w/w) NaCl added), rather than under the optimum conditions for each fiber. The results of the experiments on the 100 and 7  $\mu\text{m}$  PDMS fibers, 85  $\mu\text{m}$  PA fiber, 85  $\mu\text{m}$  CAR–PDMS fiber, 65  $\mu\text{m}$  DVB–PDMS fiber, and 65  $\mu\text{m}$  CW–DVB fiber are summarized in Fig. 2. The area responses were obtained from the average of three replicates. These results show that, of the fibers evaluated, the CAR–PDMS fiber is the most effective at extracting MTBE, as stated earlier [1], followed by the DVB–PDMS fiber, and then the 100  $\mu\text{m}$  PDMS and CW–DVB fibers, and finally the PA and 7  $\mu\text{m}$  PDMS fibers. It can be seen that CAR–PDMS fiber extracted amounts of MTBE 2.2-, 5.7-, and 13-fold higher than did the DVB–PDMS, 100  $\mu\text{m}$  PDMS, and CW–DVB fibers, respectively. The CAR–PDMS fiber extracted a quantity of MTBE up to three orders of magnitude greater than did the PA fiber. The 100  $\mu\text{m}$  PDMS fiber extracted a quantity three orders of magnitude higher than did the 7  $\mu\text{m}$  PDMS fiber. This is as expected, because sensitivity increases as the volume of coating increases [18]. The CAR–PDMS fiber is composed of a porous carbon with a surface area of 720  $\text{m}^2/\text{g}$ , optimal for small molecules ( $\text{C}_2$ – $\text{C}_6$  analytes) [17]. The micropores of the CAR–PDMS fiber retain smaller analytes such as MTBE better than do the other fibers; thus, it would be expected to show high sensitivity to MTBE. The CAR–PDMS fiber was therefore chosen for further method development.

### 3.2. Optimization of SPME conditions

The extraction time profile for MTBE was established by plotting the relative response versus the extraction time (Fig. 3a). The CAR–PDMS fiber reached equilibrium in

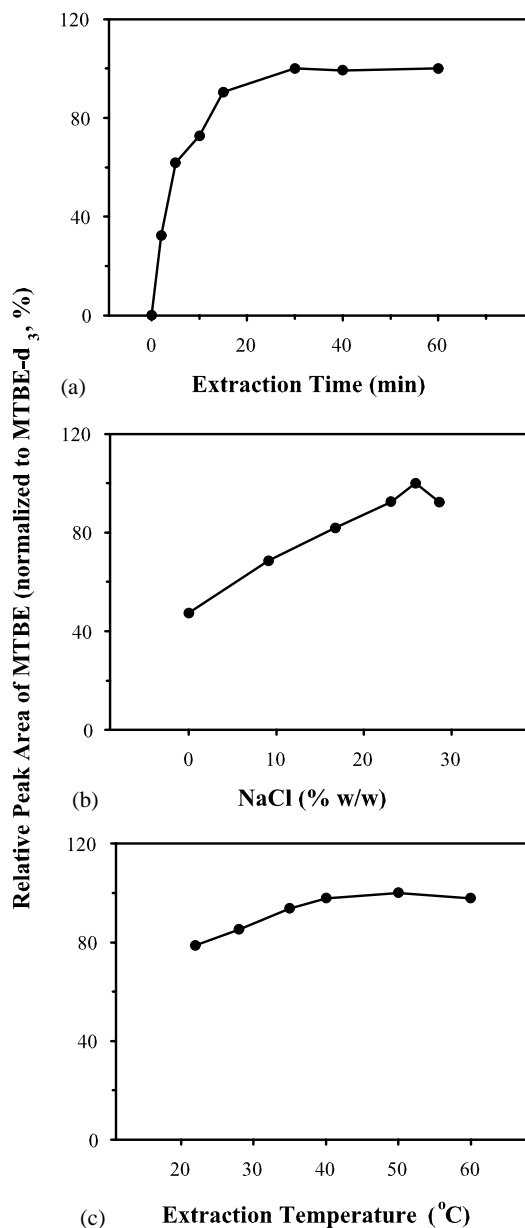


Fig. 3. Extraction yield (triplets of each data point) in headspace SPME of distilled water spiked with MTBE at a concentration of 10  $\mu\text{g/l}$ . (a) Influence of extraction time; (b) influence of NaCl concentration; (c) influence of sample temperature.

about 30 min for MTBE. Note that a significantly shorter extraction time can be used if reduced sensitivity can be tolerated. SPME quantitation is feasible before adsorption equilibrium is reached. To maximize the sample throughput, an extraction time of 30 min was chosen, since it matches the GC analysis cycle time of 34 min (27 min for analysis plus 7 min for cooling).

NaCl and other salts are commonly used as matrix modifiers in headspace analyses to increase the amount of analyte that partitions into the headspace. The effect of addition of NaCl was investigated by conducting headspace SPME experiments from an aqueous MTBE solution of 57.8  $\mu\text{g/l}$

containing various concentrations of NaCl. Our results show that the extraction yield of MTBE increases with increasing NaCl concentration, up to 25% (Fig. 3b). Upon further addition of NaCl, the extraction yield decreased again. Therefore, NaCl (25% (w/w)) was used as a matrix modifier in all subsequent analyses. Because the SPME extraction is conducted by headspace instead of direct immersion in a concentrated salt solution, the problem due to salt crystallization on the fiber after a hot injection, which occasionally contributes to premature breakage of the fiber, can be avoided [8].

The increase in the water temperature causes an increase of the concentration of target compounds in the headspace, but a simultaneous decrease in the adsorption distribution on the fiber. Therefore, the vial was submerged only as far as necessary to submerge the liquid phase of the sample to help to keep the SPME fiber cool, which is a desired condition for SPME. This is because, as the temperature of the fiber increases the partition coefficient decreases [19]. The adsorption-temperature profile obtained using a CAR-PDMS fiber at the MTBE concentration of 5.45  $\mu\text{g/l}$  showed that the amount of MTBE adsorbed increased with increasing temperature of extraction from 20 to 40  $^{\circ}\text{C}$ , and then leveled off (Fig. 3c). The effect of temperature in the headspace SPME is more complex than in the liquid SPME. At higher temperatures, diffusion and mass transfer are accelerated, but the main reason for the increase in response is the increase in the concentration of analyte in the headspace. Increasing the temperature increases the Henry's law constant of MTBE, resulting in a higher analyte partial vapor pressure in the headspace. In summary, for headspace SPME, a higher temperature not only speeds up the kinetics of the process but also affects the thermodynamics. The effects of temperature on both the Henry's law constant and the distribution constant of coating/gas play important roles in the adsorption of MTBE onto the fiber.

In the previous studies in which CAR-PDMS or DVB-CAR/PDMS fiber was used for MTBE extraction, desorption temperatures of 220–280  $^{\circ}\text{C}$  were used [1,8–10,13], with the exception of the study by Black and Fine [11], in which the desorption temperature was 320  $^{\circ}\text{C}$ . We investigated the effect of desorption temperatures on the desorption efficiency of MTBE and found nearly complete desorption of MTBE from CAR-PDMS fiber at 310  $^{\circ}\text{C}$  for 0.5 min desorption, compared with only 93% MTBE recovery at 250  $^{\circ}\text{C}$  for 1 min desorption. Increasing the desorption time to 4 min at 250  $^{\circ}\text{C}$  led to recovery of only 4% more MTBE, leaving 3% of the MTBE not desorbed. Therefore, an injection port temperature of 310  $^{\circ}\text{C}$  was set for all of the subsequent experiments. Possible carryover of unknown compounds having high affinities for the fiber, present in real samples, can be easily removed when a split/splitless injector is used. The sample introduction is performed in the splitless mode. After desorption of the MTBE, the fiber is kept in the injector for an additional time, operating in the injector in the split mode (purge on). Normally, SPME

desorption time would be determined by investigating the amount of analyte desorbed versus the length of time that the fiber was exposed in the injector. However, long exposure times produce peak tailing in the GC. Therefore, the SPME fiber desorption time was determined by the shortest duration of purge-off in the split/splitless injector that yielded maximal MTBE recovery and minimal peak tailing. This value was determined to be 30 s. After this time, the purge was turned on while the fiber was left exposed for an additional 90 s. This also had the effect of eliminating carryover of analytes on the fiber, since purge gas swept the fiber clean. After a desorption time of 2 min, no memory effects were observed.

### 3.3. Blanks

MTBE has been quantified by the ion at  $m/z$  73. Unfortunately, in GC-MS analysis, the ion at  $m/z$  73 is one of the predominant ions associated with the degradation of both polysiloxane-based stationary phases and septa, because both are made from polysiloxane polymers. To reduce the bleed from septa, Merlin Microseal septa should be used. Even with a new capillary column and liner and thorough cleaning of the ion source, it is still impossible to completely eliminate the ion at  $m/z$  73 from the analytical system. Our investigations revealed an average background concentration of ions at  $m/z$  73 for about 1–2 ng/l in the blanks; these values were much lower than MDL of MTBE.

### 3.4. Method detection limit and calibration

The MDL for MTBE was determined by the EPA procedure [20]. The MDL was obtained from a two-tailed  $t$ -test analysis of seven replicate analyses carried out at 47 ng/l, yielding six degrees of freedom. The MDL, as  $t$  (3.14) times the standard deviation of seven replicate runs, was 6.6 ng/l. The average recoveries of MTBE in spiked fountain water, tap water, and snow at 60 ng/l and in spiked rainwater at 580 ng/l ranged from 101 to 105%, indicating that MTBE was quantitatively recovered. Precision was 4.5%, expressed as percent relative standard deviation (R.S.D.), and was calculated from the replicate analyses used to determine the MDL.

The linearity of the method was investigated by determining the calibration curves over the concentration range of interest. The concentration ranges were chosen to bracket typical USA federal or state government action levels of MTBE in drinking water, typically in the low-ppb range. Calibration standards containing MTBE at concentrations from 0 (blank) to 3250  $\mu\text{g/l}$  were prepared. Calibration standards with added deuterated internal standards (MTBE- $\text{d}_3$ ) were extracted and analyzed in the same manner as the samples. Detector response was averaged over triplicate runs using the peak area. Calibration curves were prepared by plotting relative peak area of MTBE (versus MTBE- $\text{d}_3$ ) against total MTBE concentration. The line of best fit for the relation-

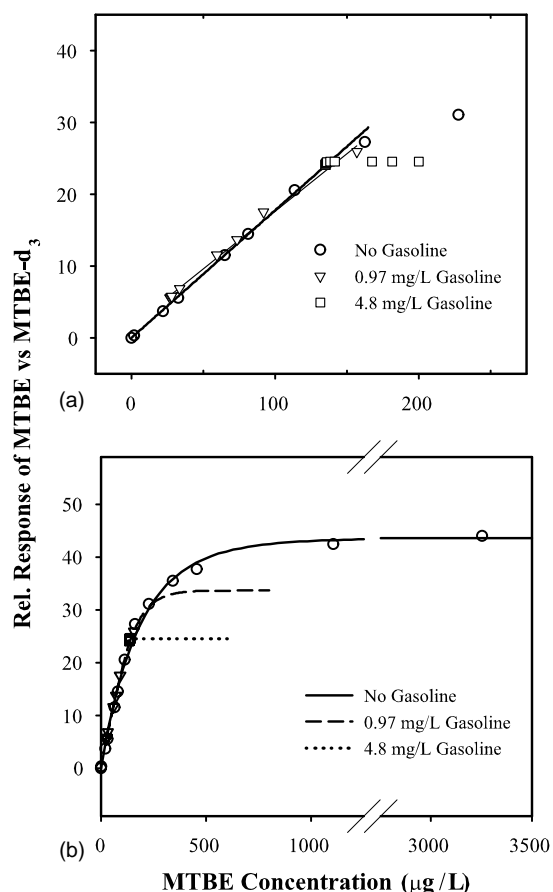


Fig. 4. Calibration curves for MTBE using the SIM mode, obtained by plotting the relative area of ion at  $m/z$  73 vs. ion at  $m/z$  76 for the gasoline-free aqueous samples and the aqueous samples containing 0.97 and 4.8 mg/l gasoline after SPME extraction.

ship between relative response and concentration of MTBE in the sample was determined by linear regression. The calibration curve (Fig. 4a) was found to have good linearity, characterized by a correlation coefficient of  $r^2 = 0.998$ . The linear range is 0.05–160  $\mu\text{g/l}$ .

The capacity of CAR–PDMS fiber and linear range of MTBE using SPME–GC–MS method were more complex when analytes additional to MTBE (multi-component) were extracted simultaneously. The presence of interfering compounds can affect the extraction. Therefore, the single-component standard may not be valid for the analysis of multi-component mixtures. For adsorbent-type fibers, the number of sites or pores is limited. Analytes may compete for the same site. As the concentration of a mixture of analytes is increased, the sites will eventually become occupied. At this point no more samples will be adsorbed, or else displacement will occur.

For environmental samples collected in the field, the presence of other compounds may thus affect the detection of MTBE. The main interfering compounds are the volatile aromatic compounds, including BTEX, and TMBs, which are readily soluble components of gasoline commonly

Table 1

Amounts (%) of benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes, and MTBE in gasoline obtained from gas stations (Albany, NY, USA)

	Stewart's shops		Mobil	
	Regular	Premium	Regular	Premium
Monoaromatic				
Benzene	1.58	2.02	1.01	1.10
Toluene	11.2	13.7	12.1	13.6
Ethylbenzene	2.48	3.97	1.88	2.16
Xylenes	11.5	19.7	11.7	13.8
Trimethylbenzenes	4.10	6.46	5.48	6.30
Total BTEX/TMBs	30.9	45.9	32.2	37.0
MTBE	2.28	2.15	1.36	2.70

found in groundwater near leaking underground storage tanks. Gasolines from local gas stations were characterized against the standard; the relative amounts of MTBE and BTEX/TMBs in gasoline are shown in Table 1. Total BTEX/TMBs in local gasolines ranged from 31 to 46%. The composition of gasoline is very complex, as shown in Fig. 5a; however, the headspace SPME–GC–MS chromatogram of gasoline contains only low-molecular-mass compounds, mainly MTBE and BTEX, with minor aliphatic hydrocarbons and TMBs (Fig. 5b). The headspace SPME with a suitable fiber coating may reduce much of the interference from other organic compounds, but not BTEX/TMBs [11,21]. It seems that CAR–PDMS fiber adsorbs differentially among BTEX/TMBs in the headspace extraction; smaller compounds like benzene and toluene adsorb the most, and then the ethylbenzene and xylenes, and to a less extent the TMBs. It might be possible that molecular mass and size of analyte, boiling point and vapor pressure of analyte, and relative and total concentration of analytes could affect the competitive extraction of analytes by the CAR–PDMS fiber. To test the possibility of matrix effects on the calibration curve, we spiked gasoline (Stewart's shops, regular grade) at concentrations of 0.97 and 4.8 mg/l into MTBE solutions and analyzed these by our method. It was found that the signals of both MTBE and MTBE- $d_3$  were decreased by 70% in the presence of gasoline at the concentration of 0.97 mg/l, which indicates that the MDLs may be increased to around 20 ng/l compared to 6.6 ng/l for the gasoline-free samples. The linear concentration range of MTBE for CAR–PDMS fiber was up to 160  $\mu\text{g/l}$  in the samples containing 0.97 mg/l of the gasoline, or about 0.3 mg/l of total BTEX/TMBs, as shown in Fig. 4a ( $r^2 = 0.992$ ), which is very similar to the linear range in the gasoline-free samples. The slope of the calibration curve for the sample with 0.97 mg/l of gasoline was also very similar to that of the curve obtained without the gasoline matrix (0.16 versus 0.17). There is no linear range existent in the calibration with the presence of 4.8 mg/l gasoline (Stewart's shops, regular grade) as shown in Fig. 4. The results of this study indicate that CAR–PDMS fiber, an adsorption-type fiber,

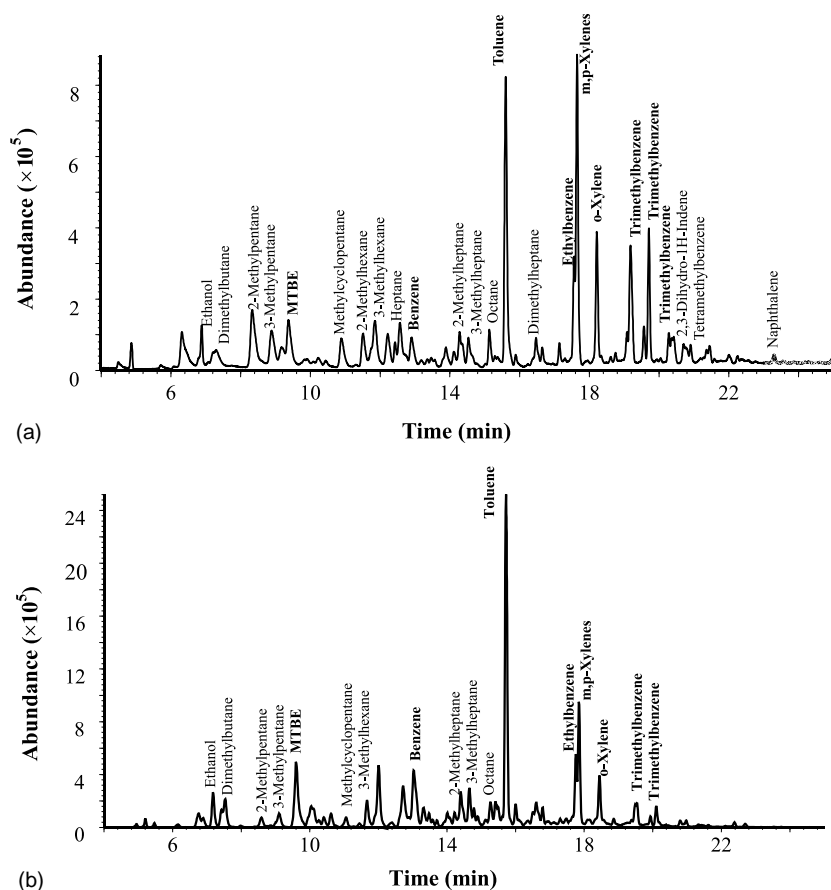


Fig. 5. Total ion chromatograms obtained by (a) direct injection of a gasoline-in-methanol solution (100 mg/l) and (b) using headspace SPME extraction of a gasoline-in-aqueous solution (1 mg/l).

has a low MDL and limited linear range, and is therefore good for trace-level ( $<160 \mu\text{g/l}$ ) extractions of MTBE in relatively clean samples, containing less than 1 mg/l of gasoline. In contrast to the adsorbent fibers, absorbent fibers such as PDMS fiber have higher MDLs but larger linear ranges [22], which may be a better choice for higher-level MTBE extractions ( $>160 \mu\text{g/l}$ ) or for samples highly contaminated with gasoline ( $>1 \text{ ppm}$ ). Deuterated internal standards have similar physiochemical properties to MTBE and can improve the quality control and precision of the method by minimizing extraction errors and accounting for matrix effects. Therefore, the use of deuterated internal standard in the SPME method is mandatory, not only because it significantly improves the accuracy and precision, but also because the monitoring of internal-standard peak areas can indicate how the matrix affects the extraction of MTBE.

### 3.5. Application to environmental samples

Rain and snow samples were collected by placing glass bottles on the ground in the enclosed courtyard of the Wadsworth Center in Albany, NY, USA, minimally impacted from atmospheric emissions or leaky underground storage tanks, in late November and early December 2001,

Table 2

Concentration (ng/l) of MTBE in various water samples from Albany, NY, USA

Sample	Concentration <sup>a</sup>	R.S.D. (%)
Milli-Q water	ND <sup>b</sup>	
Fountain water	10.2	7.4
Tap water	14.4	6.8
Snow	33.4	5.5
Rain	167	2.7

<sup>a</sup> Mean value from three replicate analyses.

<sup>b</sup> ND: not detectable.

using the standard water-sampling technique for VOCs [23]. The samples were stored in a refrigerator at  $4^\circ\text{C}$  (snow samples were first melted to water at room temperature) and analyzed within 24 h of sampling. Tap water, fountain water, and Milli-Q water from the Wadsworth Center laboratories were also analyzed. The internal standard was added at a concentration of  $4.37 \mu\text{g/l}$  to each sample before extraction was carried out. All samples were extracted with one single CAR-PDMS fiber. The results are summarized in Table 2. As can be seen, MTBE was detected at concentrations of 10 and 14 ng/l in fountain and tap water samples, respectively, values well below federal regulatory limits. MTBE was not detected in the Milli-Q water samples. The

concentrations of MTBE were 167 and 33 ng/l in the rain and snow samples, respectively. The precision data for each of the SPME–GC–MS determinations of the four water samples ranged from 2.7 to 7.4% from triplicate analyses.

In New York State, 12 downstate counties (in and around New York City and Long Island) participate in the RFG (reformulated gasoline, containing 11–15% (v/v) of MTBE) program, with conventional gasoline used in the remaining counties [24]. Although conventional gasoline may also contain MTBE, the highest concentrations (1–8% (v/v)) are generally in premium grades, which together constitute a relatively small percentage of all gasoline sold. The transfer of MTBE from atmospheric gases to rainwater is dependent on the temperature and on the concentrations of MTBE in the air. Thus, the concentration of MTBE in precipitation can be predicted using a modified form of Henry's law, assuming MTBE is in the gaseous phase, and the concentrations in the atmosphere and in precipitation are in equilibrium. The concentration of MTBE in air can be calculated using the following equation, presented by Schwarzenbach et al. [25]:  $C_a = C_w H/RT$ , where  $C_w$  is the concentration (in mol/l) of MTBE in water;  $C_a$  is the concentration (in mol/l) of MTBE in the atmosphere;  $R$  is the gas constant,  $8.21 \times 10^{-2}$  atm l/(mol K);  $T$  is the temperature (in Kelvin); and  $H$  is Henry's law constant, in atm l/mol (1 atm = 101 325 Pa). For a winter temperature of 5 °C (close to the average temperature of 5.6 °C or 42 °F on 20 November 2001, when the rainwater was collected), the value for  $H$  for MTBE is  $1 \times 10^{-4}$  atm m<sup>3</sup>/mol [4,26]. Therefore, for a precipitation concentration of 0.167 µg/l in Albany, the equilibrium concentration of MTBE in air would be 0.72 µg/m<sup>3</sup> (0.19 ppb, v/v (ppbv)). This value is slightly less than the mean measured atmospheric concentrations of 0.25 [4,27], 0.82 [28], and 0.66 ppbv [29] sampled respectively in New Jersey and California in the USA, and in Switzerland [9]. The use of MTBE in gasoline in New Jersey (11%) is about five times higher than in the Albany (1–3%) area. The small difference of the atmospheric MTBE concentrations (0.19 ppbv MTBE in air in Albany versus 0.25 ppbv MTBE in air in New Jersey) may not simply be explained by significant variations of MTBE emissions between the two locations because atmospheric MTBE can be transported for long distances, giving its half-life of 5.5 days in the atmosphere [30]. Bruce reported concentrations of MTBE in shallow groundwater and snow samples from Denver, CO, USA of 600 and 11–88 ng/l, respectively [31], values slightly higher than the values in rainwater and snow from Albany measured in this study.

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