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Improved Analysis of MTBE, TAME, and TBA in Petroleum Fuel-Contaminated Groundwater by SPME Using Deuterated Internal Standards with GC−MS

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An improved method is described for the routine analysis of methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and *tert*-butyl alcohol (TBA) in petroleum fuel-contaminated groundwater samples using solid-phase microextraction (SPME) and deuterated internal standards combined with gas chromatography mass spectrometry (GC-MS). Factors affecting method performance (SPME fiber selection, headspace or liquid extraction, extraction time, calibration conditions, salt addition, method sensitivity, and matrix effects) are evaluated using groundwater samples from a chalk aquifer contaminated with petroleum fuel containing MTBE, TAME, and TBA. The detection sensitivity and analytical efficiency of the method was optimized for these compounds using a PDMS-Carboxen fiber, sample NaCl content of 25% (w/v), and extraction time of 30 min. Internal calibration standards (deuterated MTBE and TBA) are necessary to control extraction errors during analysis. SPME extraction efficiency and detection sensitivity for the oxygenates and TBA decreased as the background matrix concentration of benzene, toluene, ethylbenzene, and xylenes (BTEX) increased up to 300 mg/L total BTEX. However, reliable measurement of MTBE, TAME, and TBA was possible in this BTEX matrix using deuterated internal standards. The precision, accuracy, and reliability of the method were verified by analysis of certified standards. Analytical accuracy, determined from replicate ($n = 10$) analysis of spiked laboratory standards and groundwater samples, was 97%, with a precision of 1.6−2.9% for MTBE, 3.1−5.8% for TAME, and 1.6−1.7% for TBA. Method detection limits under the conditions described are 2 μg/L for TBA (by liquid sampling) and 1 μg/L for MTBE and TAME (by headspace sampling). This sensitivity can be increased for MTBE by further refinement of the method.

Introduction

Since the early 1980s unleaded petroleum fuels in many countries have contained ether oxygenate compounds, such as methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), ethyl *tert*-butyl ether (ETBE), and diisopropyl ether (DIPE), and alcohols such as *tert*-butyl alcohol (TBA), ethanol, and methanol to increase the octane level and reduce atmospheric emissions of carbon monoxide and ozone. MTBE is the most widely used compound, accounting for 85% of oxygenate usage in the United States alone (*1*). Typical United States unleaded fuels contain 11−15% v/v MTBE (*1*), but this varies between <1% to 15% in many European countries (*2*). The increased use of ether oxygenates in unleaded fuels over the last 15 years (*2*, *3*) has increased the detection of these compounds, particularly MTBE, in the atmosphere, surface waters, and groundwater supplies (*2*, *4*), raising concern over the human health risks from environmental contamination by ether oxygenates.

MTBE may naturally biodegrade very slowly under aerobic (*5*−*9*) and anaerobic conditions (*10*−*13*) to characteristic organic metabolites such as *tert*-butyl formate (TBF), *tert*-amyl alcohol (TAA), and TBA. However, TBF is frequently rapidly transformed to TBA, which is the major biodegradation product likely to accumulate in soils, surface waters, and groundwater (*5*, *6*). Assessing the environmental risk from MTBE and other oxygenate compounds requires reliable methods to detect these at low levels in environmental samples. This is critical in determining the origin of TBA in petroleum fuel-contaminated groundwater, which may arise from in situ biodegradation of MTBE or a trace impurity in MTBE added to the reformulated fuel (*1*).

MTBE and other oxygenates in groundwater are frequently measured using standard U.S. EPA approved methods (e.g. EPA 8021B, EPA 8260B, ASTM D4815) originally developed for the analysis of benzene, toluene, ethylbenzene, xylenes (BTEX), and other aromatic hydrocarbons (*14*). These methods use purge and trap or headspace sampling techniques, with gas-chromatography photoionization (GC-PID), flame ionization (GC-FID), or mass spectrometric (GC−MS) detection (*1*). However, they can produce false positive identification of MTBE and TBA in hydrocarbon mixtures due to coelution with nontarget compounds having similar retention times and decreased detection sensitivity for oxygenate compounds in the presence of high concentrations of other (e.g. BTEX) hydrocarbons. A 14-fold decrease in detection sensitivity for TBA when analyzed by U.S. EPA method 8021B in the presence of only 5 mg/L total petroleum hydrocarbons (TPH) has been reported (*14*). These artifacts occur at relatively low concentrations (∼1 mg/L) of TPH (*14*), limiting the value of these methods for the analysis of oxygenates over the concentration range of hydrocarbon mixtures typically found at petroleum spill sites. This matrix interference can be reduced by sample dilution but results in increased method detection limits (MDLs) for MTBE and TBA (*1, 14*). Methods using GC−MS detection are more reliable for MTBE analysis in hydrocarbon mixtures (*14*, *15*) and are now recommended by the U.S. EPA (*1*) and U.K. Environment Agency (*2*). However, due to high polarity and low Henry's constant TBA analysis by standard purge and trap or headspace sampling techniques is difficult. Direct aqueous injection techniques have been developed to measure TBA (*5*), but these have not been widely applied.

Solid-phase microextraction (SPME) has been used to analyze BTEX and polyaromatic hydrocarbons (*16*, *17*), phenols (*18*), heteroaromatic compounds (*19*), solvents (*20*), and aliphatic organic acids (*21*) in surface water, industrial wastewater, and groundwater samples. Analysis of ether oxygenate compounds in water by SPME has also been evaluated (*3*, *4*, *12*, *22*). SPME analysis of groundwater is an equilibration sampling technique using a three-phase system

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comprising a gas, liquid (aqueous), and polymeric solid phase. Organic compounds are partitioned directly from the liquid or gaseous phase of a sample into the coated fused silica fiber (solid phase) for a fixed time period. The sorbed fractions are then analyzed either by GC, following thermal desorption from the fiber in the heated injection port, or by HPLC, following solvent desorption (*4*, *16*, *19*, *22*).

The mass absorbed by the fiber depends on the analyte distribution constant (*K*), sample stirring, sample volume, and volume/thickness of the fiber coating material (*16*, *18*, *19*). Values of *K* vary as a function of fiber type and thickness of coating and decrease as aqueous solubility increases (*4*, *16*, *18*). SPME offers significant advantages over other methods for the analysis of dissolved petroleum hydrocarbons. These include a substantially reduced sample volume (e.g. <5 mL), a simplified preparation method (in terms of time and equipment requirements), the combination of sampling, extraction, concentration, and sample introduction within a single step (without the use of organic solvents), decreased analyte loss during sample preparation, and better precision (*18*, *19*). SPME is cheaper as the fiber can be reused many times, and MDLs are very good for a wide range of organic pollutants (*16*). SPME can also differentiate between total and freely dissolved organic compounds in complex organic matrices (*17*).

This paper describes an improved method for the analysis of MTBE, TAME, and TBA in petroleum fuel-contaminated groundwater samples by SPME using deuterated internal standards coupled with GC−MS. Factors affecting method performance are assessed. A key emphasis was optimization of the method for TBA quantification, without compromising the analytical capability for other oxygenate compounds. The method is evaluated using groundwater samples from a petroleum spill site on the U.K. Chalk aquifer (*23*). The spilled fuel contains respectively 2.88% v/v and 1.65% v/v of MTBE and TAME. TBA is present as a trace impurity at an unknown concentration in the MTBE.

Experimental Section

Materials and Methods. Unfiltered unpreserved groundwater samples were collected from the petroleum spill site in 20-mL volatile organic analyte vials fitted with PTFE-lined silicone septum, using methods previously described (*23*). The sample vials were filled completely and chilled at 4 °C until analysis within 48 h. Organic compound standards used for calibration were prepared in deionized water from a stock solution containing 4200 mg/L MTBE (Fluka), 4200 mg/L TAME (Fluka), and 420 mg/L TBA (Fluka) in Methanol (Fisher). A mixed internal standard stock solution containing 20 mg/L deuterated TBA (TBA-d_{10}, $((CD_3)_3COD$, Aldrich Chem) and 300 mg/L deuterated MTBE (MTBE-d_3, $(CH_3)_3COD_3$, Aldrich Chem) was also prepared. Each compound was obtained in the highest available purity. A certified analytical quality control (AQC) standard containing MTBE, TAME, TBA, and BTEX compounds was custom-made by Supelco and was shipped in sealed 1-mL vials. An AQC sample containing 2348 μg/L of MTBE, 2257 μg/L of TAME, 220.5 μg/L of TBA, 1979 μg/L of benzene, 2000 μg/L of toluene, 2313 μg/L of ethylbenzene, and 2022 μg/L of xylenes was prepared and analyzed with each sample set.

A 1-mL volume of the calibration standards and groundwater samples was placed in separate 2-mL vials, fitted with PTFE-lined silicone septa, that contained 0.25 g of sodium chloride (NaCl) (Certified AR reagent Fisher). A 10-μL volume of the mixed internal standard (MTBE-d_3 and TBA-d_{10}) was added to this solution using a gastight calibrated syringe and mixed thoroughly. SPME was performed on these solutions using a 75 μm poly(dimethylsiloxane) (PDMS)-Carboxen fiber (Supelco), which was conditioned according to the manufacturer's instructions prior to analysis. Deionized water method blanks containing the deuterated internal standards were run at the start, during and at the end of the sample analyses. Standard calibrations were linear ($r^2 = 0.99$) over 3 orders of magnitude for all measured compounds.

Instrumentation. A Combi-PAL autosampler (CTC Analytics) with SPME adaptor and fiber holder was used. The sample was extracted for 30 min, then thermally desorbed for 7 min into a Varian 1079 injector held at 280 °C in the splitless mode initially, and then opened to a 100:1 ratio after 3 min. A 0.75 mm i.d. liner (Varian Inc.) was used. Separation was achieved on a CP Select 624 column (Chrompack) in a Varian 3800 Gas Chromatograph. The initial column temperature was 30 °C, which was held for 6 min and then heated at 5 °C/min to 80 °C then a final 20 °C/min to 250 °C to clean the column. A constant flow (1 mL/min) of helium was used as carrier gas.

A Varian Saturn 2000 ion trap mass spectrometer utilizing Saturn workstation 5.55 software was used for analyte detection and integration. Temperature settings on the transfer line (170 °C), manifold (80 °C), and the ion trap (150 °C) were constant during the analysis. The mass spectrometer was tuned to optimize for TBA detection in the organic matrix analyzed. For this, the program was set to run from 9 to 12 min over a mass range of m/z 40−80 at 0.59 s/scan (10 μScans) but at 0.54 s/scan (4 μScans) in the mass range 40−200 m/z for the remainder of the run. Analytes were identified from their retention time and mass spectrum, which was qualified by the (most intense) base peak ion, as obtained from the analysis of individual pure standards (*3*). The quantification ions and retention times used for analyte detection were as follows: TBA-d_{10}: m/z 65, 10.20 min; TBA: m/z 59, 10.42 min; MTBE-d_3: m/z 76, 10.70 min; MTBE: m/z 73, 10.77 min; TAME: m/z 73, 16.00 min. Analyte concentrations were automatically calculated by the instrument software using the external calibration and ratio of internal standard to analyte signals.

Results and Discussion

SPME Fiber Selection. A comparison was made of the extraction efficiency of 65 μm Carbowax-divinylbenzene (DVB), 65 μm PDMS-DVB, and 75 μm PDMS-Carboxen SPME, fibers for a mixed calibration standard containing MTBE (1400 μg/L), TAME (1400 μg/L), and TBA (140 μg/L). Based on peak area response using a liquid sample extraction, the Carbowax-DVB and PDMS-DVB fibers extracted less analytes than the PDMS-Carboxen fiber (data not shown). This difference in extraction performance probably reflects variations in the polarity of the individual fibers and relative sorption affinity for the polar oxygenate compounds. The inferior performance of Carbowax-DVB and PDMS-DVB fibers for SPME analysis of ether oxygenates has also been found in other studies (*3*, *22*). All further work was therefore carried out using a PDMS-Carboxen fiber.

Liquid versus Headspace Sampling. Liquid sampling by the SPME fiber was assumed to be more suitable for TBA, due to its high polarity and relatively low Henry's constant. Extraction efficiency for liquid sampling of the oxygenate compounds was increased by the addition of NaCl to samples and calibration standards. This increases the ionic strength of water samples, with the effect of "salting out" the more volatile hydrophobic organic compounds (e.g. BTEX) in the mixture. By reducing their aqueous solubility the more volatile compounds partition further into the headspace of sample vials (*18*). The corresponding effect is an improved extraction efficiency and detection sensitivity for oxygenate compounds in the liquid phase when this phase is sampled (*3*, *4*). This is shown in Figure 1 for the detection of TBA in deionized water containing BTEX (3.5 mg/L of each compound) and TBA-d_{10}, as a function of added NaCl. The results, based on the analysis of five replicate samples for each NaCl addition,

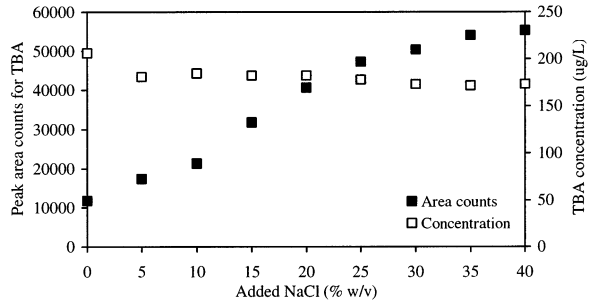

FIGURE 1. Plot of peak area counts and concentration (corrected using internal standard) for TBA measured by liquid sampling, as a function of NaCl added to sample vials.

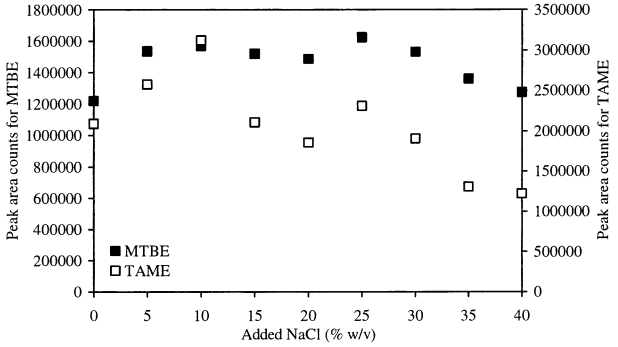

FIGURE 2. Plot of peak area counts for MTBE and TAME measured by liquid sampling, as a function of NaCl added to sample vials.

indicate that the peak area (i.e. sensitivity) for TBA detection increases with the amount of NaCl added to samples. However, the measured TBA concentration, after correction by the internal standard, is similar for all NaCl contents. The measured concentration of TBA obtained from headspace sampling of this sample was a factor of 3 lower than the TBA concentration measured by liquid sampling. The addition of NaCl, combined with liquid sampling, increases the detection sensitivity for TBA, by reducing the competition from BTEX in the hydrocarbon matrix for sorption sites on the SPME fiber. However, the detection sensitivity (peak area) for MTBE and particularly TAME is decreased above 25% w/v added NaCl due to increased partitioning of the relatively less polar MTBE and TAME into the headspace of sample vials (Figure 2) (*3*, *4*). This effect can be corrected using internal standards, as noted for TBA. All further method evaluation was therefore made using liquid sampling with 25% w/v added NaCl for optimum results.

Extraction Time. As SPME is an equilibration extraction method, the maximum amount of analyte extracted by the fiber (and hence the method sensitivity and detection limit) under a given set of conditions is determined by the time to reach adsorption equilibrium (*16*). The efficiency of analyte extraction by SPME was assessed using an extraction recovery-time curve for samples (*16*, *18*). This was obtained by comparing the detection of a known concentration of the oxygenate compounds as a function of contact time with the SPME fiber. Five replicate samples were analyzed at each extraction time. The results show that detection efficiency of the SPME fiber (expressed as peak area counts for each oxygenate compound) increases with the extraction time of liquid samples (Figure 3). The detection response for TBA levels off after 30 min extraction time. MDLs for MTBE and TAME were better than that for TBA (see below), for comparable sample extraction times. An optimum sample extraction time of 30 min was therefore chosen for routine analyses, as a balance between obtaining maximum analyte recovery and shortest sample turnaround. This extraction

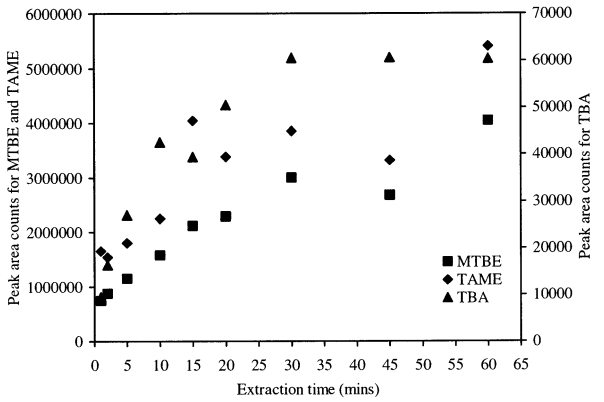

FIGURE 3. Plot of detection efficiency (expressed as peak area counts) for oxygenate compounds as a function of liquid sample extraction time by SPME fiber.

TABLE 1. Analysis of TBA in Laboratory Standard Obtained with and without the Use of an Internal Standard

analysis of five replicates containing 120 μg/L TBA	internal standard calibration	external standard calibration only
range (μg/L)	113.2−119.4	96.6−135.6
mean (μg/L)	115.6	115.7
SD (μg/L)	±2.5	±15.8

time is comparable to that used in other studies (*4*, *22*). A desorption time of 7 min was also found to be optimum, to condition the SPME fiber in preparation for the next sample extraction without decreasing the lifetime of the fiber too much.

Use of Internal Calibration Standards. The advantage of using internal calibration standards was evaluated using deuterated TBA (TBA-d_{10}) and deuterated MTBE (MTBE-d_3). These internal calibration standards have similar physiochemical properties to the oxygenate compounds and can improve the quality control and precision of the method by minimizing extraction errors and accounting for matrix effects (*16*, *18*, *19*). Results are illustrated in Table 1 for analyses of five replicate laboratory standards containing 120 μg/L of TBA, obtained using external standards for calibration but with and without the addition of the internal standards. A similar mean TBA concentration was obtained in each analysis (which may be fortuitous), but the standard deviation of analyses obtained without the internal standard was unacceptably higher.

Analytical Accuracy and Precision. Analytical accuracy was assessed from the recovery of analyte spikes added to various samples. A TBA standard was prepared and analyzed using internal standard (TBA-d_{10}) calibration, which provided an average ($n = 5$) TBA concentration of 285 μg/L. A 58 μg/L TBA standard was added to this solution and the composite sample was reanalyzed. The average ($n = 5$) concentration measured in this sample was 334.5 μg/L, compared with a true value of 343 μg/L, which represents a 97.5% recovery of the standard spike. The 285 μg/L TBA standard was also added to a groundwater sample containing 104 μg/L TBA. Replicate ($n = 5$) analysis of this composite sample gave an average TBA concentration of 378 μg/L, compared with a true value of 389 μg/L. This represents a 97% recovery of the added TBA spike from the groundwater sample, comparable with that achieved using SPME in other studies (*4*).

Analytical precision was assessed by replicate analysis of a groundwater sample containing MTBE, TAME, TBA, and 15 mg/L total BTEX. This was compared with the analytical precision obtained for a mixed laboratory standard containing

TABLE 2. Replicate Analysis of MTBE, TAME, and TBA in a Groundwater Sample Containing BTEX Compounds and a Laboratory Mixed Standard

	groundwater sample containing 15 000 μg/L total BTEX			laboratory mixed oxygenate standard		
analysis of 10 replicates	MTBE	TAME	TBA	MTBE	TAME	TBA
range (μg/L)	13117−14387	5631−6805	273.3−287.6	1651−1740	1523−1702	169.4−178.5
mean (μg/L)	13673	5890	281	1707	1636	174
SD (μg/L)	±404	±342	±4.7	±28	±51	±3.1
coeff of variation (%)	2.9	5.8	1.6	1.6	3.1	1.7

the oxygenate compounds. In both cases, the analysis was undertaken using internal standard calibration and addition of 25% w/v NaCl. The results for 10 replicate analyses of the groundwater sample and laboratory standard are presented in Table 2. These show that the method provides a precision (coefficient of variation) of 1.6% for MTBE, 3.1% for TAME, and 1.7% for TBA in the laboratory mixed oxygenate standard. Comparable analytical precision is obtained for MTBE, TAME, and TBA in the groundwater sample, indicating that the high BTEX background matrix has no significant affect on the method performance.

Effect of Matrix Interference. The analysis of aqueous samples by SPME is not considered to be influenced by matrix interference (*4*, *19*) but Black and Fine (*22*) found that aromatic hydrocarbons above a total concentration of 1 mg/L significantly impaired the analysis of ether oxygenates by SPME. Dilution of samples was necessary in their study to remove the analytical interference of the BTEX matrix but with a consequent significant (150-fold) reduction in the MDLs for MTBE and TBA. This effect probably results from a decrease in the extraction efficiency of the SPME fiber for the polar oxygenate compounds in the background matrix of less polar compounds. Groundwater samples analyzed in this study contain MTBE, TAME, and TBA in a matrix of other aromatic hydrocarbons, including BTEX, at a total concentration up to 200 mg/L, with a consequent possible reduction in analyte extraction and detection capability for the oxygenate compounds. An initial evaluation of matrix effects was made by comparing the analysis of MTBE and TBA in laboratory standards after the addition of 3.5 mg/L of each BTEX compound (21 mg/L total concentration), the latter representing mean BTEX concentration in groundwater samples from the field site. This showed that peak area counts for MTBE and TBA were significantly lower in a BTEX-amended standard compared with an unamended standard, confirming a BTEX matrix effect on oxygenate detection. This interference could be reduced by matrix-matching calibration standards with samples but is impractical for most routine applications.

The effect of increasing amounts of each BTEX species, MTBE, and TAME on the detection of TBA (~160 μg/L) in a laboratory standard is shown (Figure 4). TBA peak area counts are reduced as the background matrix concentration of other aromatic compounds increases, as expected. However, an accurate measurement of TBA concentration, correcting for this matrix effect, can be obtained in the presence of up to ~35 mg/L of each of the other aromatic compounds (~280 mg/L total concentration), provided the internal deuterated TBA standard is used. A similar depression of peak area counts occurs for MTBE detection in a laboratory standard containing increasing amounts of each BTEX species (Figure 5, insert). In this case, accurate measurement of MTBE can be obtained in a background matrix containing up to 50 mg/L (300 mg/L total concentration) of the BTEX species (Figure 5), provided the internal deuterated MTBE standard is used in the analysis. Figure 5 also shows that the BTEX matrix had no significant effect on the measured concentration of MTBE in different (0.3 mg/L and 3.1 mg/L) laboratory standards.

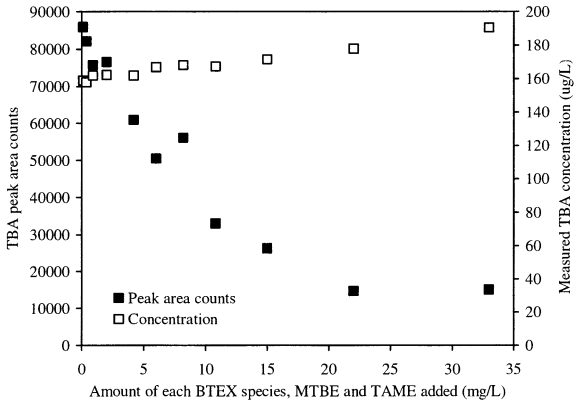

FIGURE 4. Plot of peak area counts and measured concentration corrected by internal standard for TBA laboratory standard (160 μg/L), as a function of matrix BTEX, MTBE, and TAME concentration.

This extension of accurate oxygenate detection up to a background BTEX matrix concentration of 300 mg/L is a significant improvement in the performance of the method compared with that previously achieved (*22*). It demonstrates the utility and versatility of the method, under the conditions described herein, for the analysis of trace levels of oxygenates in groundwater across the range of contaminant concentrations expected in samples from petroleum spill sites.

MDLs and Additional Verification of Method Performance. Additional confirmation of the accuracy and precision of the method was obtained by monitoring the concentration of the independent, certified, AQC standard, which includes a matrix of MTBE, TAME, TBA, and the BTEX compounds at approximately 12 mg/L total concentration. This was assessed by comparing the measured concentration of the oxygenate compounds in the AQC standard when this was routinely analyzed with groundwater samples at seven intervals over a 6-month period (192 days). The analysis was done using the internal standard calibration, and this period included two changes of the SPME fiber. The precision of the analysis (coefficient of variation) over this period was within 1% and 3% for MTBE and TBA, respectively. A lower precision was obtained for TAME (12%) and could reflect a lower sensitivity of the SPME fiber for this compound. The accuracy of the analysis, as assessed by the deviation of the mean measured concentration from the certified concentration over this period, was 1.1%, 0.8%, and 9% for MTBE, TBA, and TAME, respectively. This comparison takes into account potential analytical errors arising from renewal of the SPME fiber, instrument variability, sample matrix, sample preparation, and method calibration. It indicates that the analytical method is robust and provides consistently accurate results with an acceptable degree of precision in a representative organic matrix of background hydrocarbons.

The MDLs for the oxygenate compounds were determined using laboratory standards and an analyte signal-to-noise ratio of 5:1. An MDL of 2 μg/L was obtained for TBA, which is comparable to or better than that achieved by SPME in other studies (*4*, *22*) and significantly better than that reported

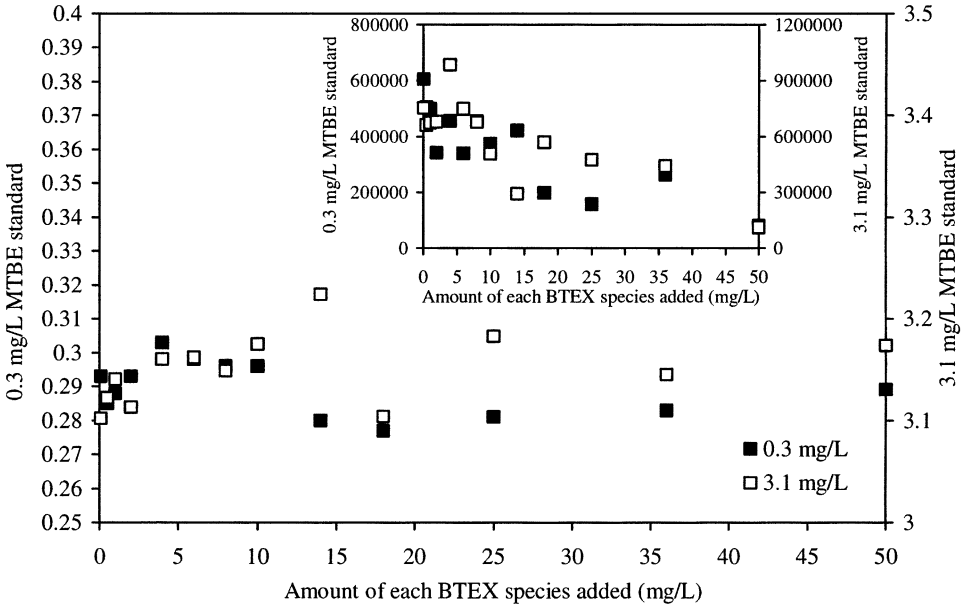

FIGURE 5. Plot of peak area counts (insert figure) and measured concentration for different MTBE reagent standards (corrected using internal standard) as a function of matrix BTEX concentration.

for purge and trap analysis of TBA (*14*). An MDL of 1 μg/L was obtained for MTBE and TAME using headspace SPME analysis of samples containing 25% (w/v) NaCl and an increased sample volume of 15 mL (in a 20 mL headspace vial). An MDL of 0.5 μg/L can be obtained for MTBE using the method and calibrating in the 0−2 μg/L range. These MDLs are comparable to those reported for SPME of MTBE and TAME in other studies (*22*).

Application of the Method. The SPME-GCMS method presented is a reliable, accurate, practical, and cost-effective procedure for the routine analysis of MTBE, TAME, and TBA at trace levels in petroleum fuel-contaminated groundwater samples. The method is optimized for TBA analysis by liquid sampling but can be used for the simultaneous analysis of MTBE and TAME by headspace sampling of the same samples, with comparable precision and accuracy. High background concentrations of BTEX hydrocarbons in samples will reduce SPME extraction efficiency and detection sensitivity for oxygenates and TBA, but this can be corrected using appropriate internal standards during the analysis. The use of deuterated internal standards in this SPME analysis permits the detection of total oxygenate concentration in the presence of competing BTEX species, which would otherwise be impossible with external calibration alone (*17*). Significantly, this allows the accurate measurement of MTBE, TAME, and TBA across the range of BTEX matrix concentrations expected in groundwater samples from petroleum spill sites. The method is a significant improvement on the performance of other methods commonly used for the analysis of these oxygenates, particularly TBA, and is a robust, versatile, and powerful technique for monitoring the environmental fate of ether oxygenates in contaminant mixtures.

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Literature Cited

(1) Rhodes, I. A. L.; Verstuyft, A. W. *Environ. Testing Anal.* ***2001,*** *Mar/Apr*, 6.

(2) U.K. Environment Agency. *A Review of Current MTBE Usage and Occurrence in Groundwater in England and Wales*; R&D Publication 97, HM Stationery Office: 2000.

(3) Achten, C.; Püttmann, W. *Environ. Sci. Technol.* **2000**, *34*, 1359−1364.

(4) Cassada, D. A.; Zhang, Y.; Snow, D. D.; Spalding, R. F. *Anal. Chem.* **2000**, 4654−4658.

(5) Church, C. D.; Isabelle, L. M.; Pankow, J. F.; Rose, D.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, *31*, 3723−3726.

(6) Church, C. D.; Tratnyek, P. G.; Pankow, J. F.; Landmeyer, J. E.; Baehr, A. L.; Thomas, M. A.; Schirmer, M. *U.S. Geol. Survey, Water Resour. Invest.* **1999**, *No. 99-4018C*, 93−101.

(7) Hanson, J. R.; Ackerman, C. E.; Skow, K. M. *Appl. Environ. Microbiol.* **1999**, *65*, 4788−4792.

(8) Salanitro, J.; Spinnler, G. E.; Neaville, C. C.; Maner, P. M.; Stearns, S. M.; Johnson, P. C.; Bruce, C. *Proceedings of the 5th International Symposium on In situ and On-site Bioremediation*, San Diego, CA, Batelle Press: 1999; pp 37−46.

(9) Landmeyer, J. E.; Chapelle, F. H.; Herlong, H. H.; Bradley, P. M. *Environ. Sci. Technol.* **2001**, *35*, 1118−1126.

(10) Landmeyer, J. E.; Chapelle, F. H.; Bradley, P. M.; Pankow, J. F.; Church, C. D.; Tratnyek, P. G. *Ground Water Monit. Rem.* **1998**, *18*, 93−102.

(11) Wilson, J. T.; Cho, J. S. *Proceedings of the 2nd International Conference on the Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, Batelle Press: 2000; pp 1−8.

(12) Wilson J. T.; Cho, J. S.; Vardy, J. A. *Natural attenuation of MTBE in the subsurface under methanogenic conditions*; EPA/600/R-00/006; U.S. EPA Office of Research and Development: 2000; p 49.

(13) Bradley, P. M.; Chapelle, F. H.; Landmeyer, J. E. *Appl. Environ. Microbiol.* **2001**, *67*, 1975−1978.

(14) Halden, R. U.; Happel, A. M.; Schoen, S. R. *Environ. Sci. Technol.* **2001**, *35*, 1469−1474.

(15) Rose, D. L.; Brooke, C. F.; Abney, S. R.; Raese, J. W. *Laboratory Method for Analysis of Small Concentrations of Methy tert-Butyl Ether and Other Ether Gasoline Oxygenates in Water*; U.S. Geological Survey, USGS Fact Sheet 086-98; U.S. GPO: Washington, DC, 1998.

(16) Langenfeld, J. J.; Hawthorne, S. B.; Miller, D. J. *Anal. Chem.* **1996**, *68*, 144−155.

(17) Poerschmann, J.; Zhang, Z. Y.; Kopinke, F. D.; Pawliszyn, J. *Anal. Chem.* **1997**, *69*, 597−600.

(18) Alpendurada, M.; de Fátima *J. Chromatogr.* **2000**, *A889*, 3−14.
(19) Johansen, S. S.; Arvin, E.; Mosbæk, H.; Hansen, A. B. *Toxicol. Environ. Chem.* **1998**, *66*, 195−228.
(20) Minicola, D. P.; Seed, L. P.; Pritzker, M. D.; Legge, R. L. *Adv. Environ Res.* **2001**, *5*, 81−90.
(21) Pan, L.; Pawliszyn, J. *Anal. Chem.* **1997**, *69*, 196−205.
(22) Black, L.; Fine, D. *Environ. Sci. Technol.* **2001**, *35*, 3190−3192.
(23) Wealthall, G. P.; Thornton, S. F.; Lerner, D. N. *Proceedings of the 6th International Symposium on In Situ and On-site Bioremediation*, San Diego, CA, Batelle Press: 2001; pp 59−66.

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