Trace Analysis of Ethanol, MTBE, and Related Oxygenate Compounds in Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry

ARTICLE *in* ANALYTICAL CHEMISTRY · NOVEMBER 2000

Impact Factor: 5.64 · DOI: 10.1021/ac000462v · Source: PubMed

4 AUTHORS, INCLUDING:

David A Cassada
University of Nebraska at Lincoln
33 PUBLICATIONS **712** CITATIONS
SEE PROFILE

Daniel D Snow
University of Nebraska at Lincoln
93 PUBLICATIONS **1,614** CITATIONS
SEE PROFILE

Roy Spalding
University of Nebraska at Lincoln
68 PUBLICATIONS **1,969** CITATIONS
SEE PROFILE

Anal. Chem. **2000,** *72,* 4654−4658

Trace Analysis of Ethanol, MTBE, and Related Oxygenate Compounds in Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry

D. A. Cassada, Y. Zhang, D. D. Snow,* and R. F. Spalding

Water Sciences Laboratory, Water Center, School of Natural Resource Sciences, University of Nebraska, 103 Natural Resources Hall, Lincoln, Nebraska 68583-0844

Solid-phase microextraction (SPME) and gas chromatography/mass spectrometry have been combined for trace-level determination of very polar compounds in water, including the widely used gasoline oxygenates ethanol and methyl *tert*-butyl ether (MTBE). A relatively simple extraction method using a divinylbenzene/Carboxen/poly(dimethylsiloxane) SPME fiber was optimized for the routine analysis of ethanol and MTBE in groundwater and reagent water. A sodium chloride concentration of 25% (w/w) combined with an extraction time of 25 min provided the greatest sensitivity while maintaining analytical efficiency. Replicate analyses in fortified reagent and groundwater spiked with microgram per liter concentrations of ethanol and MTBE indicate quantitative and reproducible recovery of these and related oxygenate compounds. Method detection limits were 15 μg L^{-1} for ethanol, 1.8 μg L^{-1} for *tert*-butyl alcohol, 0.038 μg L^{-1} for *tert*-amyl methyl ether, 0.025 μg L^{-1} for ethyl-*tert*-butyl ether, and 0.008 μg L^{-1} for MTBE.

The Clean Air Act of 1990 requires the use of emissions-reducing oxygenated fuels in areas failing to meet national air quality standards. Methyl *tert*-butyl ether (MTBE) and ethanol are most commonly selected by petroleum refiners and distributors as additives for producing cleaner burning gasolines, although ethyl *tert*-butyl ether (ETBE), *tert*-amyl ethyl ether (TAME), diisopropyl ether (DIPE), *tert*-butyl alcohol (TBA), and methanol are also used. Due to increased use of MTBE since the 1980s and its environmental mobility and persistence, reported detections of MTBE in groundwater and surface water are on a dramatic upswing.[1] Recently, the USEPA Office of Ground Water and Drinking Water established an advisory panel to examine the behavior of oxygenates in the environment and the causes of groundwater contamination by oxygenated fuels.[2] The information currently available on gasoline oxygenates in groundwater and surface water has focused on the presence of ethers, primarily MTBE. To date, very little information is available regarding the occurrence of ethanol in groundwater or surface water, which could be significant given the use of gasohol (10% ethanol in unleaded gasoline) in many states. This is in part due to ethanol's low toxicity and persistence, but primarily due to the lack of a sensitive and reliable method for determining this compound in water at trace concentrations (<100 μg L^{-1}).

Ethanol concentrations in water at the milligram per liter level are relatively easy to measure using gas chromatography with direct aqueous injection (DAI) techniques and flame ionization (GC/FID) or mass-selective detection (GC/MSD). Potter[3] described a method for analysis of petroleum-contaminated groundwater using DAI-GC/FID with a detection limit for ethanol reported to be near 0.10 mg/L. Beihoffer and Ferguson[4] utilized DAI-GC/MSD for determination of alcohols and carboxylic acids in groundwater with detection limits in the low milligram per liter range. The primary limitations of the sensitivity of DAI methods are related to the following: (1) the limited volume, typically no more than 5−10 μL, that can be injected; (2) the response and selectivity of the detector; (3) the selectivity of the column in the presence of water and other polar organics; and (4) degradation of the stationary phase by water.

Trace levels of ethers have been more successfully analyzed by DAI methods. Church et al.[5] described a DAI-GC/MSD method for the determination of MTBE and related compounds with a MTBE detection limit near 0.1 μg L^{-1} by maximizing the amount of sample injected (10 μL) and venting the water after injection. Determination of ethanol was not reported in the method; however, instrument detection limits for acetone and isopropyl alcohol were 10−100 times higher than the limits for the ethers. The reduced sensitivity may be due to greatly increased noise levels for ions with masses less than ∼100 amu as well as the difficulty of chromatographically separating the more polar and highly miscible alcohols and ketones from a water matrix. In general, both the flame ionization and mass-selective detectors require nanogram quantities of low molecular weight organics (<100 amu) to produce a reproducible signal. In comparison, DAI of 10 μL of water containing 1.0 μg L^{-1} MTBE is equivalent to injecting 10 pg of target compound.

(1) Squillace, P. J.; Zogorst, J. S.; Wilbur, W. G.; Price, C. V. *Environ. Sci. Technol.* **1996**, *31*, 1721−1730.
(2) Notice of oxygenate use in gasoline panel meeting. *Fed. Regist.* 40 CFR Part 80, 1998.
(3) Potter, T. L. *Ground Water Monit. Remed.* **1996**, *16*, 157−162.
(4) Beihoffer, J.; Ferguson C. *J. Chromatogr. Sci.* **1994**, *32*, 102−106.
(5) Church, C. D.; Isabelle L. M.; Pankow, J. F.; Rose, D. L.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, *31*, 3723−3726.

10.1021/ac000462v CCC: $19.00
Published on Web 08/24/2000

Purge-and-trap methods, including closed loop stripping,[6] have also been employed in an attempt to increase the amount of material injected into the gas chromatograph. Closed loop stripping methods coupled with GC/MSD produce a highly sensitive technique capable of detecting picogram per liter concentrations of many trace polar organics such as terpenes and phenols.[7] However, very polar and miscible low molecular weight compounds such as ethanol have low and variable recoveries that result in poor sensitivities.[5,8,9]

For more than 10 years, solid-phase extraction (SPE) has been widely used to concentrate a wide variety of compounds in water. In SPE, an aliquot of a water sample is passed through a column packed with a suitable stationary phase that selectively sorbs analytes of interest. Target compounds are then flushed from the stationary phase with organic solvents. The high polarity and miscibility of ethanol in water severely constrain the analytical chemist's choice of available stationary phases. Nonpolar bonded silica phases are unlikely to partition ethanol from water. Although activated carbon may be suitable for limited extraction of ethanol from water, it may be difficult to find a suitable solvent that would efficiently elute ethanol from the carbon phase. SPE experiments with zeolites[10] and other novel stationary phases indicate minimal retention of low molecular weight alcohols in water.

Solid-phase microextraction (SPME), a relatively new form of SPE, has been successfully utilized to rapidly concentrate a wide variety of polar and nonpolar organic compounds in aqueous matrixes.[11] SPME is a solventless extraction technique that relies on direct partitioning of analytes in either sample headspace or matrix to a small amount of stationary phase bonded to a fused-silica fiber. The sorbed analytes are thermally desorbed from the fiber in a narrow-bore GC injection port. The selectivity of SPME for different classes of compounds is highly dependent upon the composition of the stationary phase.

In the past 5 years, SPME-GC/FID has been successfully utilized to determine ppm levels of ethanol in water,[12] beverages,[13] and blood and urine.[14] Lee et al.[14] used a relatively new SPME fiber consisting of a mixture of divinylbenzene (DVB), Carboxen (a porous carbon molecular sieve), and poly(dimethylsiloxane) (PDMS) to obtain detection limits for ethanol in blood and urine significantly lower than other reported methods. This SPME sorbent is over 20 times more efficient at sorbing ethanol than the polyacrylate used by Shirley et al.[12] and Yang and Peppard.[13] The Carboxen fiber has also been successfully used for SPME headspace extraction and GC/MS analysis of picogram per liter concentrations of very polar odor-causing compounds in drinking water.[15] Gaines et al.[16] reported an SPME-GC/FID method for determination of MTBE and aromatic compounds in water with detection limits near 0.5 μg L^{-1}.

This paper describes a simple and sensitive SPME-GC/MS method for the trace concentration analysis of ethanol, MTBE, ETBE, TAME, and TBA in water. The sensitivity of the analysis has been optimized for ethanol, the most difficult to detect compound, and has resulted in a highly sensitive method for the determination of other gasoline oxygenates and degradation compounds.

EXPERIMENTAL SECTION

Reagents and Materials. Ethanol (dehydrated, 200 proof) was obtained from Pharmcoproducts, Inc. (Brookfield, CT). Isopropyl alcohol (Optima grade), *n*-propyl alcohol (Certified grade), and MTBE (HPLC grade) were obtained from Fisher Scientific (Pittsburgh, PA). ETBE (99%), TAME (97%), and TBA (HPLC grade) were obtained from Aldrich Chemicals (Milwaukee, WI). Purified water was obtained by passing distilled water through a Fisher Barnstead 4-Module Nanopure cartridge system. Sodium chloride (certified A. C. S. grade) was obtained from Fisher Scientific and purified by heating overnight at 110 °C. Fused-silica capillary gas chromatography columns were obtained from J & W Scientific, Inc. (Folsom, CA). Helium (Ultrapure Carrier Grade) was obtained from Air Products and Chemicals, Inc (Allentown, PA). SPME fibers and sample vials (4 mL, clear, screw top, hole cap, PTFE/silicone septa) used in this study were obtained from Supelco, Inc. (Bellefonte, PA).

Method Calibration. Three-point calibration curves of ethanol, TBA, MTBE, ETBE, and TAME were prepared using isopropyl alcohol or *n*-propyl alcohol as an internal standard. The calibration stock solutions were prepared separately from neat solvents and diluted in purified water to convenient concentrations for preparation of calibration standards. Three calibration standards containing ethanol and TBA at concentrations of 20, 100, and 200 μg L^{-1}; MTBE, ETBE, and TAME at concentrations of 0.04, 2, and 4 μg L^{-1}; and a constant isopropyl alcohol or *n*-propyl alcohol concentration of 200 μg L^{-1} were prepared. Calibration standards were extracted and analyzed in the same manner as the samples using a sodium chloride concentration of 25% (w/v). Calibration curves were linear with coefficients (r^2) greater than 0.98.

Solid-Phase Microextraction Conditions. Carbowax/DVB, polyacrylate and DVB/Carboxen/PDMS fibers (Supelco, Inc.) were compared for suitability in extracting and detecting ethanol. The DVB/Carboxen/PDMS fiber produced a 2−3 times higher signal/noise ratio for ethanol in comparison to the other two fibers, with a correspondingly lower background signal at ethanol's retention time from coeluting compounds. The DVB/Carboxen/PDMS fiber was therefore chosen for further methods development.

The methodology included inserting a new 2-cm 50/30-μm DVB/Carboxen/PDMS fiber in a manual injection holder and preconditioning before the day's analyses by performing two blank injections at an elevated injection temperature of 260 °C. On

(6) Grob, K.; Grob, G. *J. Chromatogr.* **1974**, *90*, 303−313.
(7) *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, 1998.
(8) Kopfler, F. C.; Melton, R. G.; Lingg, R. D.; Coleman, W. E. GC/MS determination of volatiles for the National Organics Reconnaissance Survey (NORS) of drinking water. In *Identification and Analysis of Organic Pollutants in Water*; Keith, L. H., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1976; pp 87−104.
(9) Ramstad, T.; Nestrick, T. *Water Res.* **1981**, *15*, 375−381.
(10) Ogwana, I. A. Trace analysis of volatile organic compounds in water by GC and HPLC. Ph.D. Dissertation, Iowa State University, Ames, IA, 1986.
(11) Pawliszyn, J. *Solid-Phase Microextraction: Theory and Practice*; Wiley-VCH: New York, 1997.
(12) Shirley, R.; Mani, V.; Butler, M. *Supelco Rep.* **1995**, *14*, 4−5.
(13) Yang, X.; Peppard, T. *J. Agric. Food Chem.* **1995**, *42*, 1925−1930.
(14) Lee, X. P.; Kumazawa, T.; Sato, K.; Seno, H.; Ishii, A.; Suzuki, O. *Chromatographia* **1998**, *47*, 593−595.
(15) Lloyd, S. W.; Lea, J. M.; Zimba, P. V.; Grimm, C. C. *Water Res.* **1998**, *32*, 2140−2146.
(16) Gaines, R. B.; Ledford, E. B.; Stuart, J. D. *J. Microcolumn Sep.* **1998**, *10*, 597−604.

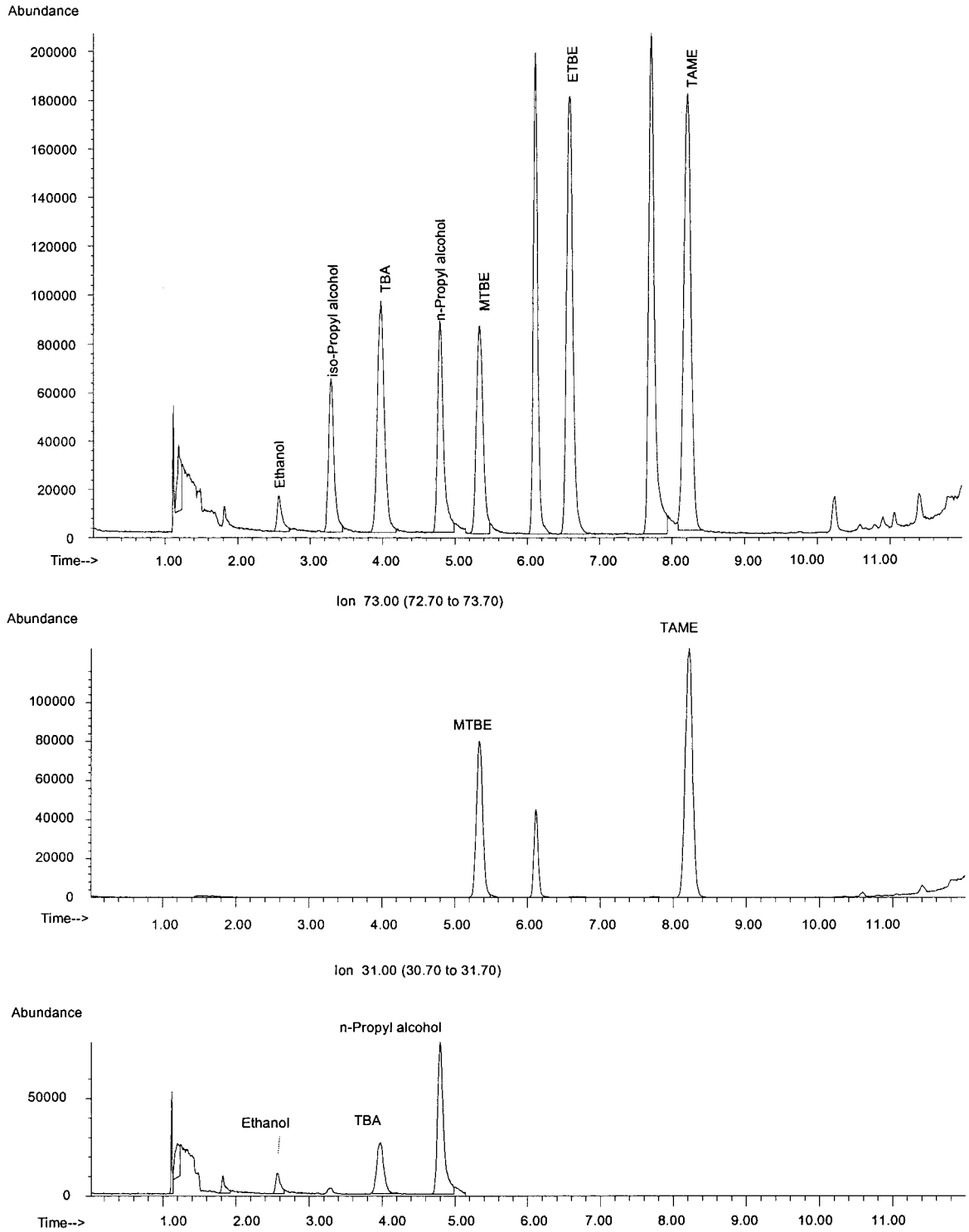

Figure 1. Total ion chromatogram and SIM chromatograms for a 100 μg L^{-1} alcohol and 2 μg L^{-1} ether standard extracted for 25 min with 25% NaCl. The retention times for analytes are given in Table 1.

subsequent days using the same fiber, two blank injections were performed at 220 °C to clean and recondition the fiber before analysis. The analytes were extracted by submerging the preconditioned fiber into a water sample (3.6 mL) in a 4 mL vial that had been pretreated to contain ~25% NaCl (w/w). The water sample was magnetically stirred during the room-temperature extraction. The optimal extraction time was 25 min. Fibers can be reused for a number of injections and usually lasted for 20−30 samples. Because the SPME extraction was by direct immersion in a concentrated salt solution, the fibers tended to become fragile more quickly than by headspace extraction. Breakage was minimized by retracting the fiber slowly before removing from the vial and injection port.

Gas Chromatographic Conditions. Chromatographic separation was accomplished with a fused-silica capillary column (J & W Scientific, DB-1, 30 m by 0.32 mm i.d., 5-μm film thickness). The GC temperature was maintained at 50 °C for 4 min and then temperature programmed at 20 °C/min to 90 °C, which was held

Table 1. Quantitation, Confirming, and Reference Ions and Retention Times of Analytes and Internal Standards

analyte	quantitation ion (m/z)	confirming ion (m/z)	retention times (min)
ethanol	31.0 $(M - CH_3)^+$	45.0 $(M - H)^+$	2.57
TBA	59.0 $(M - CH_3)^+$	31.0 $(M - C_3H_7)^+$	3.98
MTBE	73.0 $(M - CH_3)^+$	45.0 $(M - CH_3)^+$	5.34
ETBE	59.0 $(M - C_3H_7)^+$	87.0 $(M - CH_3)^+$	6.59
TAME	73.0 $(M - C_2H_5)^+$	87.0 $(M - CH_3)^+$	8.22

internal standard	reference ion (m/z)	retention times (min)
isopropyl alcohol	45.0 $(M - CH_3)^+$	3.29
n-propyl alcohol	31.0 $(M - C_2H_5)^+$	4.80

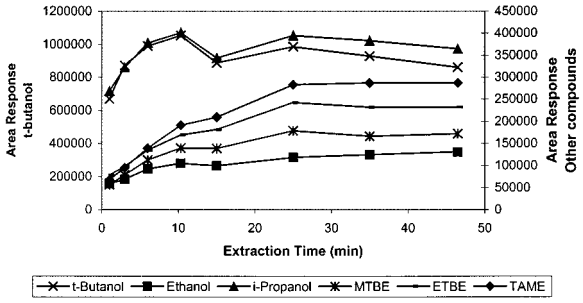

Figure 2. Effect of extraction time on the response of ethanol, isopropyl alcohol, *tert*-butyl alcohol, MTBE, ETBE, and TAME. NaCl concentration, 25% (w/w).

for 3 min and then raised to 200 °C at 40 °C/min. The GC was held at that temperature for 11.25 min to allow for elution of less volatile compounds. The total time of analysis was 23 min.

The injection port was equipped with a Merlin Microseal septum (Hewlett-Packard, Avondale, PA) and a 0.75-mm-i.d. injection liner (Supelco, Inc.) 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 0.4 min after injection. The injection port temperature was 220 °C with a helium head pressure maintained at 34.5 kPa (5.0 psi). The SPME fiber was conditioned for the next analysis in the hot injection liner for 2 min after injection.

Mass Spectrometric Conditions. The analytes were detected with an HP 5970 mass spectrometer detector (MSD, Hewlett-Packard), which uses electron impact ionization for fragmentation. For increased sensitivity and specificity, the MSD was operated in the selected ion monitoring (SIM) mode with ion dwell times of 100 ms. A typical chromatogram is shown in Figure 1. The quantitation ions of interest and ion designations for the oxygenated analytes as well as the reference ions for the internal standards are given in Table 1. Although the extraction and analysis may easily be adapted to flame ionization detection (FID) for simple matrixes, the risk of interferences from coeluting compounds will very likely limit method sensitivity.

RESULTS AND DISCUSSION

Optimum extraction time was determined by varying the contact time between the fiber and a standard aqueous solution (0−46 min). A graph of extraction time versus response (Figure 2) for all analytes shows that there is only a small increase in response after the initial 10 min and that after 25 min the response has remained constant or slightly decreased. To maximize sample throughput, an extraction time of 25 min was chosen since the time the fiber spends in the sample (25 min) and injection port (2 min) is approximately equal to the 27-min GC analysis cycle time (analysis + cool).

The addition of NaCl to the sample increases the efficiency of the extraction for all analytes and internal standards (Figure 3).

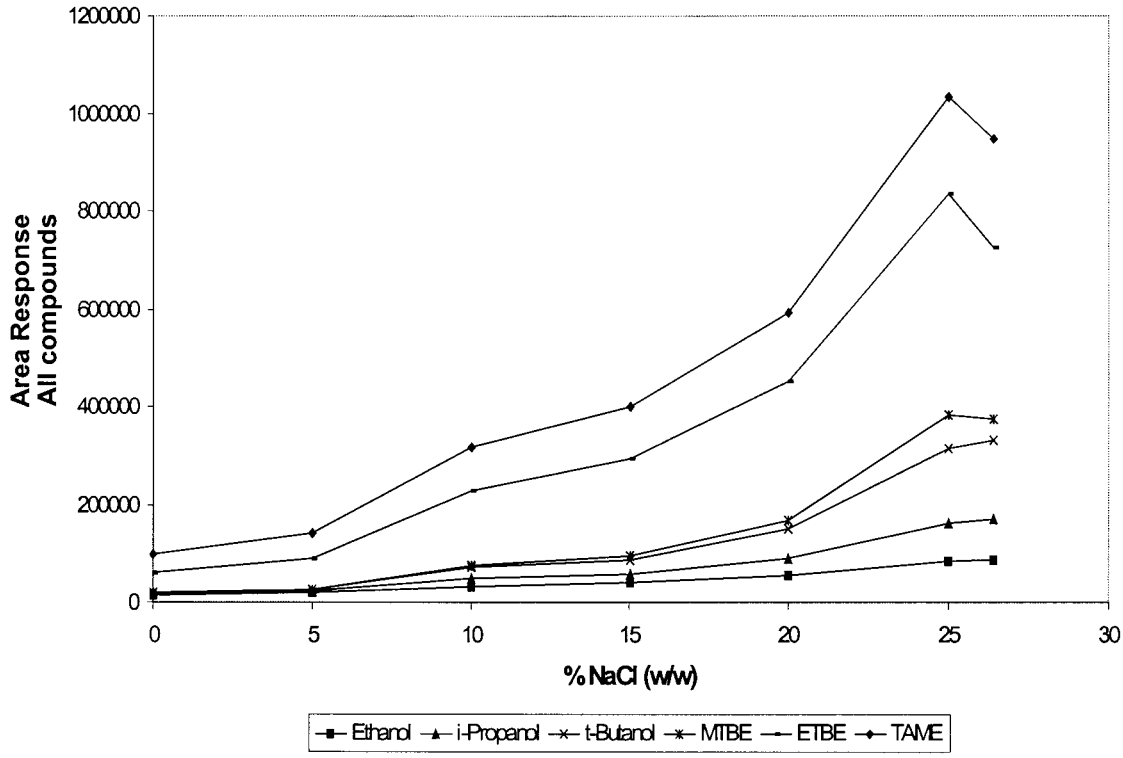

Figure 3. Effect of NaCl concentration on the response of ethanol, isopropyl alcohol, *tert*-butyl alcohol, MTBE, ETBE, and TAME. Extraction time, 25 min.

Table 2. Method Detection Limits and Recovery for Each Analyte in Fortified Blanks and Matrix Samples

analyte	SPME method detectn limit ($n = 8$) (μg L^{-1})	method detectn limit concn (μg L^{-1})	fortified blank rec ($n = 8$) (% $\pm\sigma$)	fortified blank concn (μg L^{-1})	fortified matrix rec ($n = 8$) (% $\pm\sigma$)	fortified matrix concn (μg L^{-1})
ethanol	15.0	42.6	98 ± 12	42.6	109 ± 6	106
TBA	1.8	20.7	107 ± 2	41.5	105 ± 7	104
MTBE	0.008	0.042	104 ± 5	0.84	102 ± 7	2.09
ETBE	0.025	0.039	104 ± 8	0.79	105 ± 7	1.97
TAME	0.038	0.040	106 ± 6	0.83	106 ± 5	2.07

Sensitivity also increases as the amount of salt increases until the NaCl saturation point (26.3% (w/w)) at 25 °C[17] is reached. At a salt concentration of >25% (w/w), the responses for ETBE and TAME are somewhat diminished, while the responses of the other analytes are nearly constant (Figure 3). This decrease may result when salt crystals suspended in the sample interfere with the extraction process. A NaCl concentration of 25% (w/w) was thus chosen to ensure that saturation would not be exceeded and high analyte responses would be maintained.

Detection Limit Determination and Sample Analysis. Method detection limits and recoveries for each analyte were determined by the accepted procedure of the U.S. Environmental Protection Agency.[18] A series of eight replicate samples at 40 μg L^{-1} ethanol, 20 μg L^{-1} TBA, and ether concentrations near 0.04 μg L^{-1} were analyzed and the detection limit determined from the variability of the results (Table 2). Analyte recovery in fortified reagent water at ~20% of the calibration range, which was 40 and 0.8 μg L^{-1} for the alcohols and ethers, respectively, indicates that all analytes are quantitatively recovered with recoveries ranging from 98 to 107%.

Thirty groundwater samples from multilevel samplers in the rural Clear Creek watershed in Polk County, NE, were analyzed for ethanol, MTBE, and other gasoline oxygenates. This site is many kilometers from major roadways and should be minimally impacted from atmospheric emissions or leaky underground storage tanks. None of the gasoline oxygenates or degradation products were detected. Nebraska subsidizes the manufacture and use of ethanol as a gasoline additive. The lack of detectable levels of gasoline oxygenates in the groundwater from this agricultural area probably reflects the absence of a nearby source of oxygenated gasoline. To test the possibility of matrix effects in this method, several of these groundwater samples were fortified at 50% of the calibration range. Recoveries from these fortified samples were quantitative between 102 and 109% (Table 2). Future research will be directed toward determining the occurrence and persistence of ethanol in groundwater and surface water in a variety of hydrogeologic settings.

(17) *Merck Index*, 11th ed.; Merck & Co., Inc.: Rahway, NJ, 1989; p 1359.
(18) U.S. Environmental Protection Agency, Pt. 136, App. B, 40 CFR Ch I, 7−1−89 ed., U. S. GPO: Washington, DC, 1989; p 525.

CONCLUSIONS

The analysis of ethanol, MTBE, and related compounds in water at low microgram per liter levels has been accomplished by SPME extraction and GC/MS detection. The amount of salt (NaCl) added to the water sample and the length of extraction time influence the extraction efficiency of ethanol. The sensitivity and selectivity of GC/MS detection enables accurate quantification of ethanol and TBA at low microgram per liter concentrations and MTBE, ETBE, and TAME at mid nanogram per liter concentrations.

Other factors influencing extraction efficiency including the effects of sample temperature, pH, and fiber composition may merit further investigation. Added salt can cause problems due to salt crystallization on the fiber after a hot injection and occasionally contributes to premature breakage of the fiber when the fiber is retracted back into the fiber holder. Nevertheless, the enhanced sensitivity obtained by salt addition is necessary for trace analysis of these compounds, especially for the very polar and difficult to determine ethanol.

ACKNOWLEDGMENT

We acknowledge support for this research from the California MTBE Research Partnership, the National Water Research Institute, the Nebraska Ethanol Board, and the Nebraska Research Initiative. This article has been assigned Journal Series Number 12979, Agricultural Research Division, University of Nebraska.

Received for review April 26, 2000. Accepted July 13, 2000.

AC000462V