

Introduction

Methyl *tert*-butyl ether (MTBE) was found in shallow ground-water samples in a study of 8 urban and 20 agricultural areas throughout the United States in 1993 and 1994 (Squillace and others, 1995, p. 1). The compound is added to gasoline either seasonally or year round in many parts of the United States to increase the octane level and to reduce carbon monoxide and ozone levels in the air.

The U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), near Denver, uses state-of-the-art technology to analyze samples for MTBE as part of the USGS water-quality studies. In addition, the NWQL offers custom analyses to determine two other fuel oxygenates—ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME). The NWQL was not able to obtain a reference standard for *tert*-amyl ethyl ether (TAEE), another possible fuel oxygenate (Shelley and Fouhy, 1994, p. 63).

The shallow ground-water samples were collected as part of the USGS National Water-Quality Assessment Program. These samples were collected from 211 urban wells or springs and 562 agricultural wells sampled by the USGS in 1993 and 1994. The wells were keyed to specific land-use areas to assess the effects of different uses on ground-water quality (Squillace and others, 1995, p. 2). Ground-water samples were preserved on site to pH less than or equal to 2 with a solution of 1:1 hydrochloric acid. All samples were analyzed at the NWQL within 2 weeks after collection.

The purpose of this fact sheet is to explain briefly the analytical method implemented by the USGS for determining MTBE and other fuel oxygenates. The scope is necessarily limited to an overview of the analytical method (instrumentation, sample

preparation, calibration and quantitation, identification, and preservation of samples) and method performance (reagent blanks, accuracy, and precision).

Application

The USGS laboratory method is suitable for determining MTBE and other volatile organic compounds (VOCs) in whole water. The method detection limit for MTBE concentrations is 0.06 microgram per liter ($\mu\text{g/L}$), and the method reporting limit is 0.20 $\mu\text{g/L}$. The linear calibration of MTBE concentrations for undiluted water samples ranges from 0.05 to 20 $\mu\text{g/L}$. Water samples containing concentrations greater than 20 $\mu\text{g/L}$ are diluted.

Summary of Method

The method uses purge and trap gas chromatography/mass spectrometry (GC/MS) to identify the fuel oxygenates. The VOCs are purged from water samples by bubbling helium through a 25-milliliter (mL) aqueous sample (Rose and Schroeder, 1995, p. 4). MTBE and other compounds are trapped in a tube containing suitable sorbent materials and then thermally desorbed onto a 0.53-millimeter (mm) inside diameter capillary column. A gas chromatograph is temperature programmed to separate the VOCs, which are detected by a mass spectrometer. Identification of MTBE is confirmed by analyzing reference material under the same conditions as the samples and comparing retention times and mass spectra with reference material from the National Institute of Standards and Technology.

Purge and trap analyses using a mass-spectrometer detector provide a reliable identification of MTBE, because the GC retention time and mass spectra are unique for the compound. Further confirmation of the presence of this compound is not required. MTBE was

not detected in any laboratory reagent blanks (analyzed May–November 1993 and March 1994–June 1995); the accuracy and precision of MTBE analyses were within accepted limits of 80 to 120 percent with a relative standard deviation of less than 20 percent (U.S. Environmental Protection Agency, 1992, p. 20).

Analytical Method

Instrumentation

The NWQL method for determining MTBE concentration is comparable to the U.S. Environmental Protection Agency Method 524.2 (U.S. Environmental Protection Agency, 1992). Water samples are analyzed using the following instruments:

- Hewlett-Packard Models 5971 and 5972 GC/MS equipped with a Channeltron 5778 electron multiplier, 75-meter (m) by 0.53-mm inside diameter capillary column (DB-624), with 3-micrometer (μm) film thickness;
- Tekmar Aquatek Autosampler; and
- Carboxin B/Carboxin 1000 and 1001 sorbents used in purge and trap concentrator (Supelco, VOCARB 3000).

Sample Preparation

A 25-mL aliquot of water is automatically introduced to the purge vessel via the Autosampler transfer line. The sample then is purged with helium for 11 minutes at a flow rate of 40 milliliters per minute (mL/min). Compounds purged by helium are collected on the VOCARB 3000 solid sorbent trap at ambient temperature. The temperature of the gas chromatograph is lowered to -20°C prior to the desorption step. Desorb temperature is 250°C for 1 minute, followed by a bake cycle at 260°C for 10 minutes.

Calibration and Quantitation

Five to nine calibration standard solutions containing MTBE and other selected compounds are prepared in reagent water to produce concentrations ranging from 0.05 to 20 µg/L. Analysis of these standard solutions is used to establish calibration curves with THRU-PUT Systems, Inc., Target software. Two internal standards are used for calibration: fluorobenzene and 1,2-dichlorobenzene-*d*₄. The amount of each compound is quantitated using the most abundant ion, relative to the internal standard (table 1).

Identification

For a water sample, MTBE is identified by comparing the mass ion profiles and the GC retention time (fig. 1) to the retention time and mass ion profiles of the MTBE standard (not shown). The GC retention time of the sample should be within 0.1 minute of the reference standard. The identity is verified by comparing the sample's mass spectrum (fig. 2A) with the MTBE of the reference mass spectrum (fig. 2B). To confirm identification, the sample spectrum is normalized to the abundance of the quantitation ion in the MTBE reference and subtracted from the MTBE reference sample. The difference spectrum should be within 30 percent of the MTBE reference (fig. 2C). Chromatographic retention time for VOCs is listed in table 1.

Preservation

Samples of VOCs are preserved by adjusting to pH 2 or less with 1:1 hydrochloric acid and then chilling to 4°C. The maximum holding time is 14 days. Replicate reagent-water spikes (2.0 µg/L), adjusted to pH 2, were prepared and analyzed on days 1, 7, and 14. Recovery for MTBE was 97 percent after 14 days with a relative standard deviation (RSD) of 2.5 percent; for ETBE, 100 percent after 14 days, RSD 1.8 percent; and for TAME, 97 percent after 14 days, RSD 2.1 percent. Recovery and precision results for the preservation study are listed in table 2. For comparison, U.S. Environmental Protection Agency methods for VOCs in

Table 1.--Quantitation ions and secondary ions for volatile organic compounds listed by chromatographic retention times

[amu, atomic mass units; MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether]

Compound	Mass per unit charge		Chromatographic retention time (minutes)
	Quantitation ion (amu)	Secondary ion (amu)	
Internal standard			
Fluorobenzene	96	70	15.244
Selected compounds			
MTBE	73	43, 57	10.781
ETBE	59	57, 87	12.590
TAME	73	43, 55	14.934

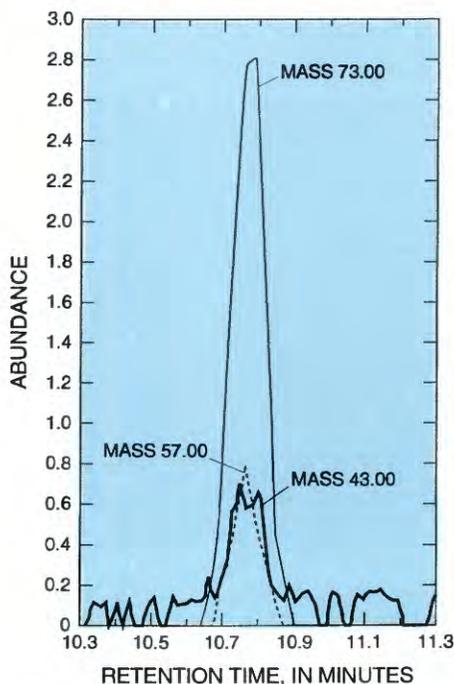


Figure 1. Mass ion profiles for methyl *tert*-butyl ether determined for a ground-water sample.

drinking water (Method 524.2) specify that mean accuracy should be 80 to 120 percent and the RSD less than 20 percent (U.S. Environmental Protection Agency, 1992).

Method Performance

Laboratory Reagent Blanks

Laboratory reagent blanks are routinely analyzed with each set of water samples using blank water prepared at the

NWQL. Reagent blank water is prepared by boiling deionized water for 1 hour, cooling, and purging with high-quality nitrogen gas until ready for use. MTBE was not detected in any of these laboratory reagent blanks.

Accuracy and Precision

Reagent water spiked with VOCs is routinely analyzed with each set of samples to measure accuracy and precision. Accuracy and precision of MTBE analyses were evaluated by analyzing spiked replicates of reagent water and ground water at concentrations ranging from 0.1 to 5 µg/L. The spiked replicates represent data collected from short-term (1 day) to long-term (1 year) time periods for MTBE, ETBE, and TAME (table 3). The data also represent measurements from three instruments by three analysts. Long-term data are not yet available for ETBE and TAME, which are being evaluated for addition to the method.

Long-term performance of this analytical method was verified by the analysis of MTBE in 77 reagent-water spikes at 5.0 µg/L throughout a 6-month period, with a mean recovery of 98 percent and a relative standard deviation of 8 percent (fig. 3). This result is well within quality-control criteria for comparable U.S. Environmental Protection Agency methods that relative standard deviations should be less than 20 percent (U.S. Environmental Protection Agency,

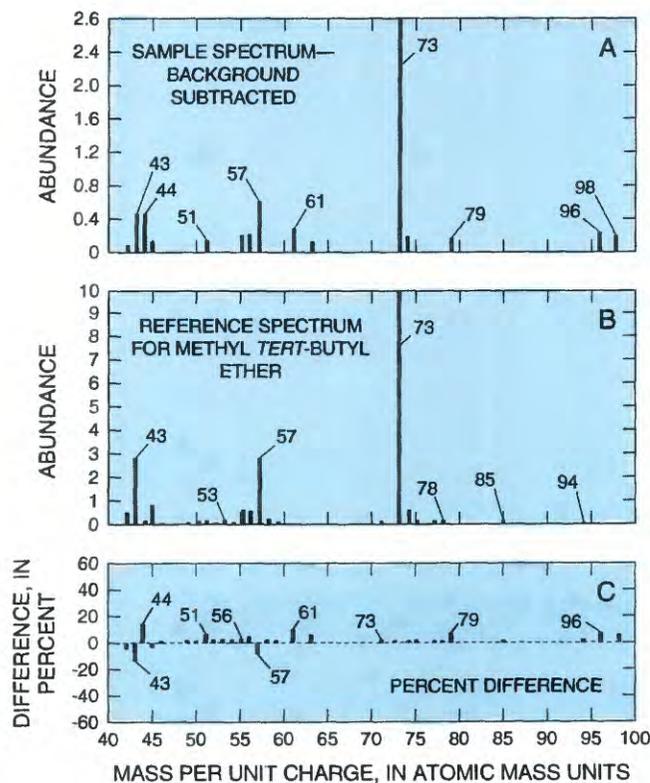


Figure 2. (A) Sample mass spectrum with background subtracted, (B) reference mass spectrum, and (C) percent difference between reference spectrum and sample spectrum normalized to quantitation-ion abundance of reference spectrum for methyl *tert*-butyl ether.

Table 2.--Recovery and precision results of a 14-day preservation study at pH 2 of reformulated fuel oxygenates

[MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether; RSD, relative standard deviation]

Compound ¹	RSD (percent)	Recovery (percent)
MTBE	2.5	97
ETBE	1.8	100
TAME	2.1	97

¹ All three compounds were analyzed May 1995 in a reagent-water matrix; spike concentration was 2.0 micrograms per liter for seven samples of each compound. A Hewlett-Packard 5971 Mass Selective Detector was used to measure results.

1992). Analysis of 80 low-level standard solutions at 0.1 and 0.2 µg/L MTBE throughout 12 months shows average recoveries of 97 to 98 percent with a relative standard deviation of 11 to 13 percent. Box plots of the MTBE

concentration in reagent water spiked at low concentrations are shown in figure 4. (Method performance is within quality-control criteria even at these low concentrations.)

References Cited

- Rose, D.L., and Schroeder, M.P., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of volatile organic compounds in water by purge and trap capillary gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 94-708, 26 p.
- Shelley, Suzanne, and Fouhy, Ken, 1994, The drive for cleaner-burning fuel: Chemical Engineering, v. 101, no. 1, January 1994, p. 61 and 63.
- Squillace, P.J., Pope, D.A., and Price, C.V., 1995, Occurrence of the gasoline additive MTBE in shallow ground water in urban and agricultural areas: U.S. Geological Survey Fact Sheet 114-95, 4 p.
- U.S. Environmental Protection Agency, 1992, Measurement of purgeable organic compounds in water by capillary-column gas chromatography/mass spectrometry, method 524.2, revision 4.0: Cincinnati, Ohio, Environmental Monitoring Systems Laboratory, August 1992, 50 p.
- Jon W. Raese, Donna L. Rose, and Mark W. Sandstrom
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- Use of brand, firm, and trade names in this publication is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 3.-- Accuracy and precision of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, and *tert*-amyl methyl ether analyses in reagent-water and ground-water samples using U.S. Geological Survey methods at the National Water Quality Laboratory

[MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether; RW, reagent water; GW, ground water; $\mu\text{g/L}$, microgram per liter; RSD, relative standard deviation; MDL, method detection limit; --, not calculated. Instrument number: 1, Hewlett-Packard (HP) 5971 Mass Selective Detector (MSD); 2, HP 5972 MSD; 3, HP 5996A MSD]

Compound	Date of analysis	Matrix ¹	Spike concentration ($\mu\text{g/L}$)	Mean recovery (percent)	RSD (percent)	MDL ² ($\mu\text{g/L}$)	Number of samples	Instrument number
MTBE	3/94-3/95	RW	0.2	97	11.4	0.06	64	1
MTBE	12/94-3/95	RW	.1	98	13.2	.04	17	2
MTBE	4/94-10/94	RW	5.0	98	8.0	--	77	1,2,3
MTBE	8/94	RW	2.0	98	4.1	--	7	1
MTBE	12/94	RW	4.0	102	4.3	--	7	2
MTBE	12/94	RW	.2	98	12.2	.07	7	2
MTBE	12/94	RW	1.0	102	2.9	--	7	2
MTBE	12/94-3/95	RW	.1	103	11.7	.038	6	1
MTBE	3/95-4/95	GW	5.0	83	3.3	--	7	1
MTBE	3/95-4/95	RW	.1	96	9.4	.025	9	1
MTBE	3/95-4/95	GW	.1	84	3.6	.009	7	1
MTBE	5/95	RW	2.0	99	2.0	--	7	1
ETBE	3/95-4/95	GW	5.0	86	3.4	--	7	1
ETBE	3/95-4/95	RW	.1	96	7.3	.020	9	1
ETBE	3/95-4/95	GW	.1	84	1.2	.004	7	1
ETBE	5/95	RW	2.0	103	1.6	--	7	1
TAME	3/95-4/95	GW	5.0	83	3.3	--	7	1
TAME	3/95-4/95	RW	.1	96	7.3	.021	9	1
TAME	3/95-4/95	GW	.1	83	4.8	.013	7	1
TAME	5/95	RW	2.0	100	1.9	--	7	1

¹ Ground-water samples were selected from extra vials received at the National Water Quality Laboratory.

² MDLs were measured over the course of 2 to 5 days except for the first entry for MTBE.

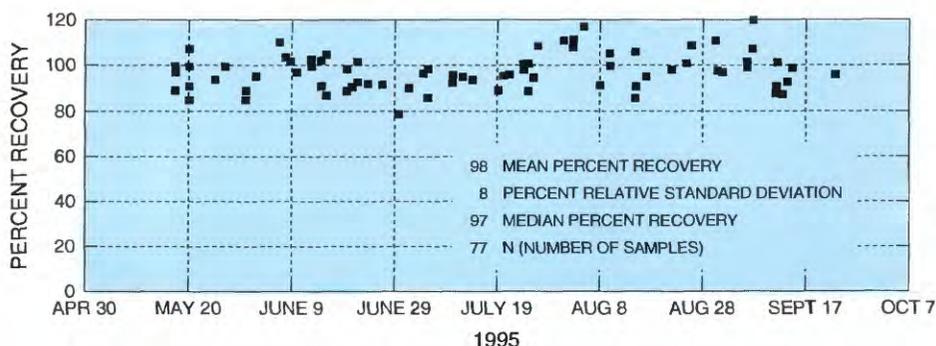


Figure 3. Percent recovery of methyl *tert*-butyl ether from reagent-water spikes (B.R. Damel, U.S. Geological Survey, written commun., 1995).

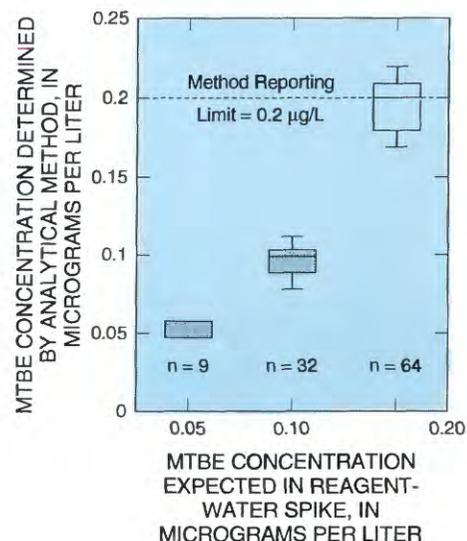


Figure 4. Concentration of methyl *tert*-butyl ether (MTBE) spiked at low levels in reagent water from March 1994 to March 1995 (n=number of samples; shading indicates that spike is less than method reporting limit; $\mu\text{g/L}$, micrograms per liter).