

# Laboratory Method for Analysis of Small Concentrations of Methyl *tert*-Butyl Ether and Other Ether Gasoline Oxygenates in Water

*This Fact Sheet presents data for analysis of nanogram-per-liter concentrations of methyl *tert*-butyl ether (MTBE) and three other ether gasoline oxygenates, including methyl *tert*-pentyl ether (TAME), diisopropyl ether (DIPE), and ethyl *tert*-butyl ether (ETBE), by purge-and-trap capillary-column gas chromatography/mass spectrometry. Long-term method detection levels (LT-MDLs) for MTBE, TAME, DIPE, and ETBE ranged from 15 to 83 nanograms per liter (0.015 to 0.083 microgram per liter). Nanogram-per-liter-concentration detections are reported if all of the identification criteria are met, whereas previous methods censored detections at a pre-determined method reporting level. The reporting level for this method is defined as two times the LT-MDL, does not censor detections at less than this concentration, and is referred to as the nondetection value (NDV). Bias and variability data from multiple analyses, analysts, and instruments over a 60-day period show the oxygenate recoveries ranging from 100 to 109 percent, with 6 to 8 percent relative standard deviation. MTBE, TAME, DIPE, and ETBE were not detected in the analysis of 225 laboratory reagent blanks from January to December 1997. A preservation study in ground water and surface water indicates that all the oxygenates are stable at pH 2 for up to 216 days, with recoveries ranging from 94 to 115 percent on day 216, and relative standard deviations ranging from 5 to 9 percent for the duration of the study. A full description of this purge-and-trap method is available in Connor and others (1998).*

Methyl *tert*-butyl ether (MTBE) is added to gasoline seasonally in many parts of the United States to increase the octane level, to reduce vehicular carbon monoxide levels, and to reduce ozone

levels in urban air. MTBE was the second most frequently detected volatile organic compound (VOC) in shallow ground water in urban areas in a study of 8 urban and 20 agricultural areas throughout the United States in 1993 and 1994 (Squillace and others, 1996). In a study from 16 metropolitan areas across the United States, MTBE was the seventh most frequently detected VOC in urban storm water, sampled from 1991 through 1995 (Delzer and others, 1996).

The U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) routinely analyzes water samples for MTBE and for three other ether gasoline oxygenates as part of the National Water-Quality Assessment Program (NAWQA). The three additional ether gasoline oxygenates include methyl *tert*-pentyl ether, also known as methyl *tert*-amyl ether (TAME); diisopropyl ether (DIPE); and ethyl *tert*-butyl ether (ETBE). The USGS began routinely analyzing water samples for MTBE in 1991 and for TAME, DIPE, and ETBE in 1995. Generally, MTBE is the most frequently detected, followed by TAME, DIPE, and ETBE.

The purpose of this Fact Sheet is to explain briefly the analytical method implemented by the USGS for determining MTBE and other ether gasoline oxygenates at nanogram-per-liter concentrations. This Fact Sheet supersedes Raese and others (1995), the main difference being the procedure for reporting nanogram-per-liter-concentration detections at less than the reporting level. Nanogram-per-liter-concentration detections are reported if all of the identification criteria are met, whereas previous methods censored detections at a pre-determined method reporting level. The reporting level for this method is defined as two times the long-term method

detection level (LT-MDL), and is referred to as the nondetection value (NDV). Values detected at less than the NDV are reported as estimated concentrations to indicate uncertainty in the quantitation. The publication by Raese and others (1995) contains limited data for TAME and ETBE, and no data for DIPE, since these compounds were introduced to the method in 1995.

## Application

The USGS laboratory method (Connor and others, 1998) is suitable for determining MTBE and other VOCs in unfiltered samples of surface water and ground water. The method is also suitable for determining MTBE, TAME, DIPE, and ETBE in drinking-water samples. The calibrations for MTBE, TAME, DIPE, and ETBE for undiluted water samples range from 100 to 20,000 nanograms per liter (ng/L). Water samples containing concentrations greater than 20,000 ng/L are diluted.

The NWQL introduced a new method of reporting detections of VOCs at less than the method reporting levels (Connor and others, 1998). All positive detections of VOCs are reported as long as all of the identification criteria are met and the quantity detected is statistically different from the quantity, if any, detected in laboratory blanks. As a result of this strategy, the term nondetection value (NDV) has been introduced and is defined as the value reported when no VOCs are determined to be present. The NDV is defined as twice the LT-MDL (Connor and others, 1998) and limits the chance of both false positives and false negatives to less than 1 percent. The LT-MDL is similar to the U.S. Environmental Protection Agency's (USEPA) definition of method detection limit



(U.S. Environmental Protection Agency, 1984). It differs from the USEPA, however, in that the LT-MDL is determined from at least 30 low-level spikes in reagent-water samples over a much longer period to ensure that method variability is measured. Analyzing multiple low-level spikes over time accounts for day-to-day variability caused by instruments, operators, and calibrations. The LT-MDL determined for this MTBE method is 83 ng/L, for TAME 32 ng/L, for DIPE 21 ng/L, and for ETBE 15 ng/L.

## Summary of Method

The method (Connor and others, 1998) uses purge-and-trap gas chromatography/mass spectrometry (GC/MS) to identify the ether gasoline oxygenates. The VOCs are purged from water samples by bubbling helium through a 25-milliliter (mL) aqueous sample. MTBE and other compounds are trapped in a tube that contains suitable sorbent materials and then thermally desorbed onto a 75-meter (m) by 0.53-millimeter (mm) inside diameter Megabore® capillary column. A gas chromatograph is temperature programmed to separate the VOCs, which are detected by a mass spectrometer. Identification of each

compound is confirmed by analyzing reference material under the same conditions as the samples and comparing retention times and mass spectra with reference material.

Purge-and-trap analyses using a mass spectrometer provide a reliable identification of MTBE, TAME, DIPE, and ETBE because the gas chromatograph retention time and mass spectrum are unique for each compound. Further confirmation of the presence of these compounds is not required for the purposes of this study.

## Analytical Method

### Instrumentation

Water samples are analyzed using the following instruments:

- Hewlett-Packard Models 5971 and 5972 mass spectrometer, electron impact ionization, full-scan mode data acquisition, 41 to 300 atomic mass units, or equivalent.
- Hewlett-Packard Models 5890 and 5990 gas chromatograph, with subambient cooling capability.
- 75-m by 0.53-mm inside diameter Megabore® capillary column (Rtx 624), with 3-micrometer (μm) film thickness, or equivalent.

- Archon Autosampler and Tekmar 3000 purge-and-trap concentrator; alternatively a Tekmar Aquatek Autosampler and Tekmar 2000 purge-and-trap concentrator have been used previously to collect some of the data presented in this Fact Sheet.
- Carboxen B/Carboxin 1000 and 1001 sorbents used in purge-and-trap concentrator (Supelco, VOCARB 3000), or equivalent.

### Sample Preservation

VOC samples are preserved in the field by adjusting to pH 2 with 1:1 hydrochloric acid and then chilling to 4 degrees Celsius (°C). The maximum holding time is 14 days for regulatory analyses, according to guidelines set by the USEPA. However, a preservation study conducted at the NWQL for 216 days at pH 2 in ground- and surface-water samples has shown that MTBE, TAME, DIPE, and ETBE are stable at pH 2 for at least 216 days (table 1). Percent recoveries range from 94 to 115 percent for the gasoline ether oxygenates in surface water and ground water on day 216, with percent relative standard deviations ranging from 5 to 9 percent over the course of the whole study.

**Table 1.** Results of preservation studies in ground water and surface water for selected ether gasoline oxygenates, preserved to pH 2 and chilled to 4 degrees Celsius

[ng/L, nanogram per liter. Each day represents the average percent recovery for five replicate injections. Compounds are listed in the order of frequency of detection.]

Compound	Spiked concentration (ng/L)	Day 1 <sup>1</sup>	Day 14	Day 28	Day 37	Day 47	Day 56	Day 112	Day 156	Day 216
<b>GROUND WATER<sup>1</sup></b>										
Methyl <i>tert</i> -butyl ether	640	100	103	94	105	106	107	106	99	94
Methyl <i>tert</i> -pentyl ether	579	100	103	92	102	103	105	109	100	96
Diisopropyl ether	609	100	99	92	102	103	112	116	102	101
Ethyl <i>tert</i> -butyl ether	580	100	103	92	103	104	107	118	100	107
<b>SURFACE WATER<sup>1</sup></b>										
Methyl <i>tert</i> -butyl ether	2,110	100	109	99	110	111	117	111	93	98
Methyl <i>tert</i> -pentyl ether	568	100	107	97	106	107	113	117	96	103
Diisopropyl ether	604	100	99	93	104	104	120	122	106	109
Ethyl <i>tert</i> -butyl ether	561	100	107	96	107	108	115	126	97	115

<sup>1</sup>The spiked sample concentration is the average of five replicates on day 1, plus the quantity present in the unspiked sample. The concentration for day 1 is normalized to 100 percent and used to calculate percent recovery for days 14, 28, 37, 47, 56, 112, 156, and 216.

NOTE: Data presented in this table were collected with the Tekmar Aquatek autosampler and Tekmar 2000 purge-and-trap concentrator.



## Sample Preparation

By use of the Archon autosampler, a 25-mL aliquot of water is automatically introduced to the purge vessel via the autosampler transfer line. One microliter of an internal standard/surrogate solution is then transferred to the purge vessel automatically. The sample 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 sample is dry purged for 2 minutes to remove excess water vapor, then it is desorbed at 250°C for 4 minutes and transferred to the gas chromatograph (GC). The temperature of the GC is lowered to -20°C before the desorption step. The GC is programmed to hold for 1 minute at -20°C, increase 20°C per minute to 20°C, increase 5°C per minute to 160°C, and finally, increase to 200°C at 10°C per minute, and held for 5 minutes.

## Calibration

Five to nine calibration standard solutions that contain MTBE and other selected compounds are prepared in reagent water to produce concentrations ranging from 100 to 20,000 ng/L. These standard solutions are analyzed to establish calibration curves. One internal standard, fluorobenzene, is used for calibration and quantitation.

## Identification

MTBE, TAME, DIPE, and ETBE are identified in water samples by compar-

ing the mass ion profiles and GC retention time (fig. 1A for MTBE, fig. 1B for TAME) to the mass ion profiles and retention time of the reference 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 for MTBE, fig. 3A for TAME) with the reference mass spectrum (fig. 2B for MTBE, fig. 3B for TAME). Refer to figure 4 for a reference mass spectrum of DIPE, and figure 5 for a reference mass spectrum of ETBE. In order for MTBE, TAME, DIPE, or ETBE to be considered "detected," all three mass ion profiles must be present at greater than two times the noise level, the relative abundances of the ions in the sample should match the reference spectrum, and the peak width should be at least eight to ten scans wide. Quantitation ions, qualifying ions, and chromatographic retention times for the selected

gasoline ether oxygenates are listed in table 2.

## Quantitation

Once MTBE has been identified in a water sample, then a number needs to be assigned to the quantity detected. The MTBE is quantitated using the most abundant ion for MTBE, relative to the most abundant ion in fluorobenzene, the internal standard. If the quantity detected is within the calibration range of 100 to 20,000 ng/L, the amount is reported as is. If the quantity is greater than 20,000 ng/L, the sample is diluted and reanalyzed. If the quantity detected is less than the lowest calibration standard of 100 ng/L, then the concentration is reported as "estimated" with an "E" code qualifier in the data base. "E" implies that only the concentration detected is estimated; "E" does not imply the identification is in question.

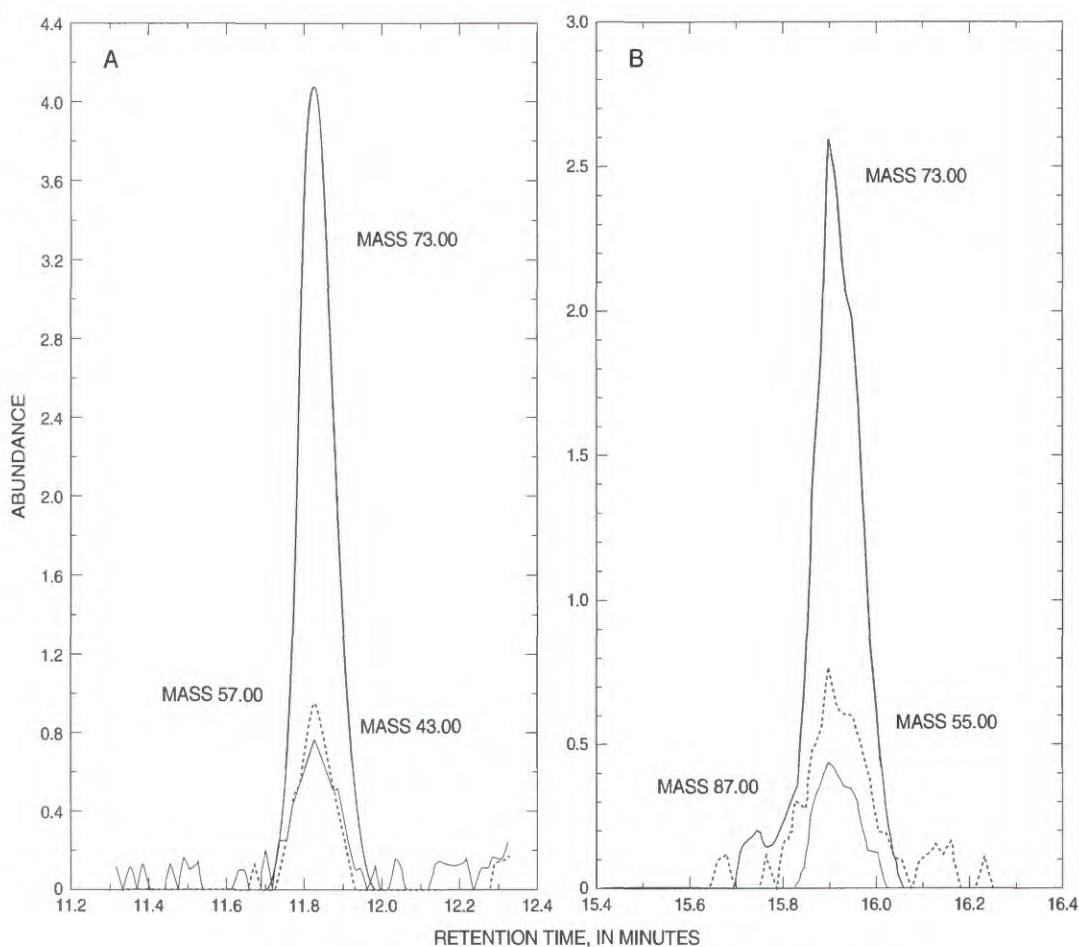
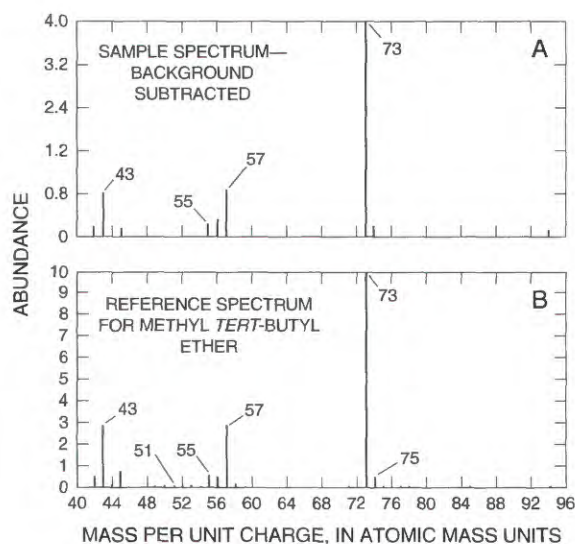
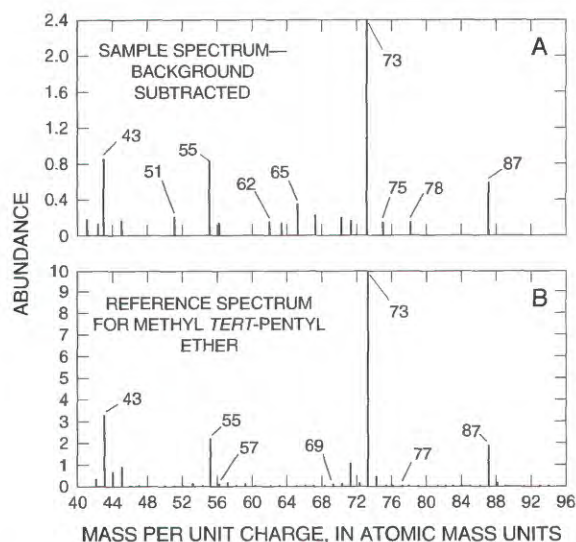


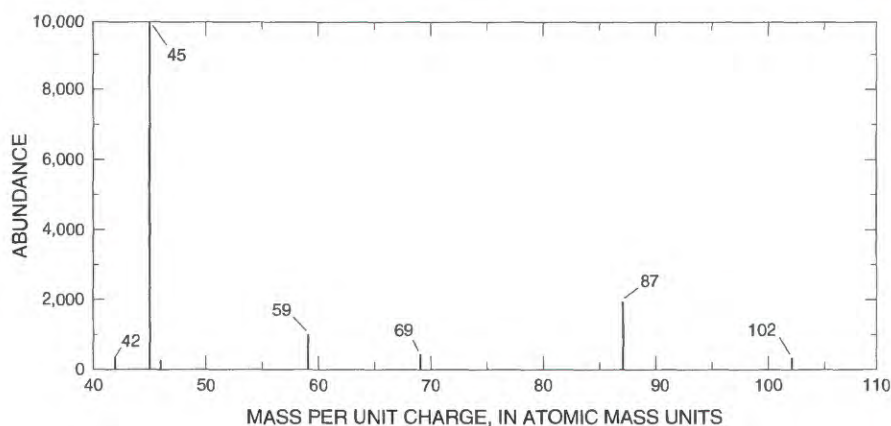
Figure 1. Mass ion profiles for (A) methyl *tert*-butyl ether, and (B) methyl *tert*-pentyl ether determined for a surface-water sample at 100 and 70 ng/L, respectively.



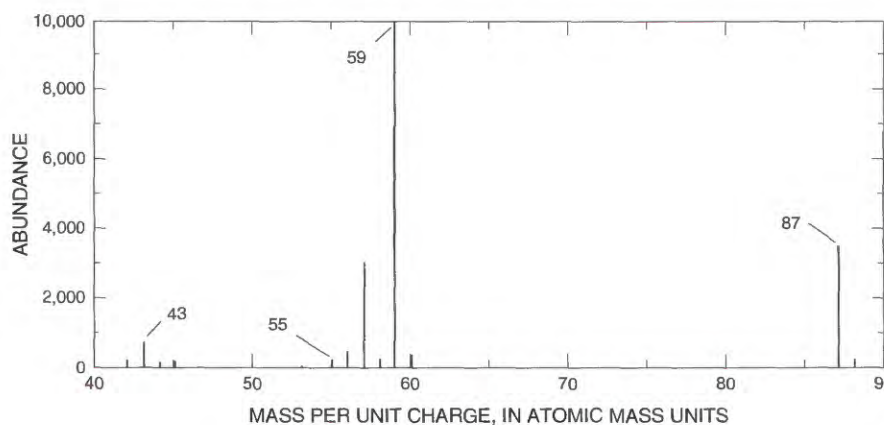
**Figure 2.** (A) Sample mass spectrum with background subtracted for methyl *tert*-butyl ether determined for a surface-water sample at 100 ng/L, and (B) reference mass spectrum for methyl *tert*-butyl ether.



**Figure 3.** (A) Sample mass spectrum with background subtracted for methyl *tert*-pentyl ether determined for a surface-water sample at 70 ng/L, and (B) reference mass spectrum for methyl *tert*-pentyl ether.



**Figure 4.** Reference mass spectrum for diisopropyl ether.



**Figure 5.** Reference mass spectrum for ethyl *tert*-butyl ether.

## Method Performance

### Laboratory Reagent Blanks

Laboratory reagent blanks are routinely analyzed with each set of water samples using reagent 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 for a minimum of 1 hour. MTBE, TAME, DIPE, and ETBE were not detected in any of 225 laboratory reagent blanks that were analyzed from January through December 1997. Previous data (1991–96) collected for laboratory reagent blanks do not show any detections for MTBE. TAME, DIPE, and ETBE were added to the VOC compound list in 1995 and historically have not shown any detections in laboratory reagent blanks.

### Long-term Method Detection Levels and Nondetection Values

Long-term method detection levels (LT-MDLs) were determined by analyzing 50 low-level reagent-water spikes over 6 months by using multiple instruments, calibrations, and analysts. One low-level reagent-water spike was included per sample batch of 50 injections. The LT-MDL was calculated by



**Table 2.** Quantitation ions and qualifying ions for selected gasoline ether oxygenates

[amu, atomic mass units]

Compound	Quantitation ion (amu)	Secondary qualifying ion (amu)	Tertiary qualifying ion (amu)	Retention time (minutes)
<b>Internal standard</b>				
Fluorobenzene	96	70	50	17.00
<b>Selected compounds</b>				
Methyl <i>tert</i> -butyl ether	73	57	43	12.13
Methyl <i>tert</i> -pentyl ether	73	55	87	16.52
Diisopropyl ether	59	87	45	13.22
Ethyl <i>tert</i> -butyl ether	59	57	87	14.04

**Table 3.** Long-term method detection levels and nondetection values for selected ether gasoline oxygenates

[LT-MDL, long-term method detection level; NDV, nondetection value; ng/L, nanogram per liter; n, number of reagent-water spiked samples]

Compound	Spike concentration used for determining		NDV (ng/L)
	LT-MDL (ng/L)	LT-MDL (ng/L) n=50	
Methyl <i>tert</i> -butyl ether	110	83	166
Methyl <i>tert</i> -pentyl ether	110	32	64
Diisopropyl ether	100	21	42
Ethyl <i>tert</i> -butyl ether	50	15	30

**Table 4.** Bias and variability of selected ether gasoline oxygenates in reagent water, collected over 60 days with multiple instruments, calibrations, and operators

[ng/L, nanogram per liter; %, percent; Rec., recovery; RSD, relative standard deviation; n, number of reagent-water spiked samples]

Compound	Spiked sample concentration (ng/L)	Mean n=19 % Rec.	% RSD
Methyl <i>tert</i> -butyl ether	1,100	100	7
Methyl <i>tert</i> -pentyl ether	1,100	102	6
Diisopropyl ether	1,000	100	8
Ethyl <i>tert</i> -butyl ether	500	109	7

multiplying the standard deviation of the 50 replicates by the Student's *t*-value at the 99-percent confidence level. Nondetection values (NDV) were set at two times the LT-MDL. The NDV is used as the reporting level for this method. Refer to table 3 for LT-MDLs and NDVs for MTBE, TAME, DIPE, and ETBE.

### Bias and Variability

Bias and variability of ether gasoline oxygenates were evaluated by analyzing 19 spiked replicates of reagent water over 60 days, ranging from 500 to 1,100 ng/L in concentration. One spike was included per sample batch. The data represent multiple instruments, calibrations, and operators. Bias and variability data for all the ether gasoline oxygenates are listed in table 4. All of the oxygenates were recovered with averages ranging from 100 to 109 percent, and relative standard deviations ranging from 6 to 8 percent. The results are well within the quality-control criteria for comparable USEPA methods specifying that relative standard deviations should be less than 20 percent (Munch, 1995).

### References Cited

- Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97-829.
- Delzer, G.C., Zogorski, J.S., Lopes, T.J., and Bosshart, R.L., 1996, Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95: U.S. Geological Survey Water-Resources Investigations Report 96-4145, 6 p.

Munch, J.W., 1995, Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry, method 524.2, revision 4.1: Cincinnati, Ohio, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, 48 p.

Raese, J.W., Rose, D.L., and Sandstrom, M.W., 1995, U.S. Geological Survey laboratory method for methyl *tert*-butyl ether and other fuel oxygenates: U.S. Geological Survey Fact Sheet FS-219-95, 4 p.

Squillace, P.J., Zogorski, J.S., Wilber, W.G., and Price, C.V., 1996, Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993–1994: Environmental Science & Technology, v. 30, no. 5, p. 1721–1730.

U.S. Environmental Protection Agency, 1984, Method 6241—Purgeables, rules and regulations: Federal Register, v. 49, no. 209, October 26, p. 198–199, 43373–43384.

## INFORMATION

For information on technical reports and hydrologic data related to the National Water-Quality Assessment Program (NAWQA), contact as follows:

NAWQA VOC National Synthesis  
U.S. Geological Survey  
1608 Mount View Road  
Rapid City, SD 57702

Visit the following Web sites for more information on MTBE and other VOCs:

<http://www.sd.cr.usgs.gov/nawqa/vocns>  
<http://www.rvares.er.usgs.gov/nawqa>  
<http://water.usgs.gov>

<http://www.epa.gov/OMSWWW/fuels.htm>

For additional information on this analytical method, write to:

U.S. Geological Survey  
Chief, National Water Quality Laboratory  
Box 25046, Mail Stop 407  
Federal Center  
Denver, CO 80225

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