Designation: D 5441 – 98 (Reapproved 2003)$^{\epsilon 1}$

Standard Test Method for
Analysis of Methyl Tert-Butyl Ether (MTBE) by Gas Chromatography[1]

This standard is issued under the fixed designation D 5441; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ϵ^1 NOTE—Warning notes were editorially moved into the standard text in August 2003.

1. Scope

1.1 This test method covers the determination of the purity of methyl tert-butyl ether (MTBE) by gas chromatography. It also provides a procedure to measure impurities in MTBE such as C_4 to C_{12} olefins, methyl, isopropyl and tert-butyl alcohols, methyl sec-butyl and methyl tert-amyl ethers, acetone, and methyl ethyl ketone. Impurities are determined to a minimum concentration of 0.02 mass %.

1.2 This test method is not applicable to the determination of MTBE in gasoline.

1.3 Water cannot be determined by this test method and must be measured by a procedure such as Test Method D 1364 and the result used to normalize the chromatographic values.

1.4 A majority of the impurities in MTBE is resolved by the test method, however, some co-elution is encountered.

1.5 This test method is inappropriate for impurities that boil at temperatures higher than 180°C or for impurities that cause poor or no response in a flame ionization detector, such as water.

1.6 The values stated in SI (metric) units of measurement are preferred and used throughout the standard. Alternate units, in common usage, are also provided to improve clarity and aid the user of this test method.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
D 1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)[2]

D 3700 Practice for Obtaining LPG Samples Using Floating Piston Cylinder[3]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]
D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[3]
D 4626 Practice for Calculation of Gas Chromatographic Response Factors[3]
E 355 Practice for Gas Chromatography Terms and Relationships[4]
E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography[4]

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E 355 and E 594.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 C_4 to C_{12} olefins—common olefin impurities in MTBE are unreacted feedstock and dimers or trimers of feed such as trimethylpentene or pentamethylheptene.

4. Summary of Test Method

4.1 A representative aliquot of the MTBE product sample is introduced into a gas chromatograph equipped with a methyl silicone bonded phase fused silica open tubular column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column.

4.2 The detector signal is processed by an electronic data acquisition system or integrating computer. Each eluting component is identified by comparing its retention time to those established by analyzing standards under identical conditions.

4.3 The concentration of each component in mass percent is determined by normalization of the peak areas after each peak area has been corrected by a detector response multiplication factor. The detector response factors are determined by analyzing prepared standards with concentrations similar to those encountered in the sample.

5. Significance and Use

5.1 The presence of impurities in MTBE product can have a deleterious effect upon the value of MTBE as a gasoline additive. Oxygenate and olefin contents are of primary concern. This test method provides a knowledge of the composition of MTBE product. This is useful in the evaluation of process operations control, in the valuation of the product, and for regulatory purposes.

5.2 Open tubular column gas chromatography with a flame ionization detector, used by the test method, is a technique that is sensitive to the contaminants commonly found in MTBE, and a technique that is widely used.

6. Interferences

6.1 Cyclopentane and 2,3-dimethylbutane have been observed to co-elute with MTBE. However, these are not commonly found impurities in MTBE.

7. Apparatus

7.1 *Gas Chromatograph*—Instrumentation capable of operating at the conditions listed in Table 1. A heated flash vaporizing injector designed to provide a linear sample split injection (that is, 200:1) is required for proper sample introduction. Carrier gas controls must be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. Pressure control devices and gages must be designed to attain the linear velocity required in the column used (for example, if a 150 m column is used, a pressure of approximately 550 kPa (80 psig) is required). A hydrogen flame ionization detector with associated gas controls and electronics, designed for optimum response with open tubular columns, is required.

TABLE 1 Typical Operating Conditions

Column Temperature Program			
Column length	50 m	100 m	150 m
Initial temperature	40°C	50°C	60°C
Initial hold time	13 min	13 min	13 min
Program rate	10°C/min	10°C/min	10°C/min
Final temperature	180°C	180°C	180°C
Final hold time	3 min	7 min	20 min
Injector			
Temperature	200°C		
Split ratio	200:1		
Sample size	0.1 to 0.5 µL		
Detector			
Type	flame ionization		
Temperature	250°C		
Fuel gas	hydrogen (≈30 mL/min)		
Oxidizing gas	air (≈300 mL/min)		
Make-up gas	nitrogen (≈30 mL/min)		
Carrier Gas			
Type	helium		
Average linear velocity	20–24 cm/s		

7.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 0.1 to 0.5 µL injections are suitable. It should be noted that inadequate splitter design, or poor injection technique, or both can result in poor resolution. Overloading of the column can also cause loss of resolution for some components and, since overloaded peaks are skewed, variation in retention times. Watch for any skewed peaks that indicate overloading during column evaluation. Observe the component size and where possible, avoid conditions leading to this problem during the analyses.

7.3 *Open Tubular Column*—This test method utilizes a fused silica open tubular column with non-polar methyl silicone bonded (cross-linked) phase internal coating such as one of the following:[5]

Column length	50 m	100 m	150 m
Film thickness	0.5 µm	0.5 µm	1.0 µm
Internal diameter	0.20 mm	0.25 mm	0.25 mm

Other columns with equal or greater resolving power may be used. A minimum resolution between trans-2-pentene and tert-butanol, and between cis-2-pentene and tert-butanol of 1.3 is required. The 150 m column is expected to decrease the likelihood of co–elution of impurities.

7.4 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantification of these analyses must meet or exceed these minimum requirements:

7.4.1 Capacity for at least 50 peaks per analysis,

7.4.2 Normalized area percent calculations with response factors,

7.4.3 Identification of individual components based on retention time,

7.4.4 Noise and spike rejection capability,

7.4.5 Sampling rate for fast (<1 s) peaks,

7.4.6 Positive and negative sloping baseline correction,

7.4.7 Peak detection sensitivity compensation for narrow and broad peaks, and

7.4.8 Non-resolved peaks separated by perpendicular drop or tangential skimming as needed.

8. Reagents and Materials

8.1 *Carrier Gas*, helium, 99.99 % pure. (**Warning**—Compressed gas under high pressure.)

8.2 *Fuel Gas*, hydrogen, 99.99 % pure. (**Warning**—Extremely flammable gas under pressure.)

8.3 *Oxidant*, air, oil free. (**Warning**—Compressed gas under high pressure.)

8.4 *Make-Up Gas*, nitrogen, 99.99 % pure. (**Warning**—Compressed gas under high pressure.)

8.5 *Reference Standards*:

8.5.1 *tert-Amyl methyl ether*,[6] (**Warning**—Flammable liquid. Harmful if inhaled.)

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[5] Petrocol DH series columns available from Supelco, Inc., Bellefonte, PA, USA have proven satisfactory for this test method and were used to obtain the retention data and example chromatogram shown. Also, HP-PONA columns available from Hewlett Packard Company, Wilmington, DE, have been found satisfactory.

[6] A 96 % pure sample obtained from Aldrich Chemical Company, Inc., Milwaukee, WI was the highest purity found.

8.5.2 *Butane*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.3 *tert-Butanol*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.4 *sec-Butyl methyl ether*, [7] (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.5 *4,4-Dimethyl-2-neopentyl-1-pentene*, [8] (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.6 *Isobutylene*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.7 *Methanol*, (**Warning**—See Note 1.)

NOTE 1—**Warning:** Toxic Flammable Liquid. Harmful if inhaled or ingested.

8.5.8 *2-Methyl-2-butene*, [8] (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.9 *Methyl tert-butyl ether*, 99 + % pure,[9] (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.10 *2,2,4,6,6-Pentamethyl-3-heptene*, [8] (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.11 *n-Pentane*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.12 *cis-2-Pentene*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.13 *trans-2-Pentene* (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.14 *2,4,4-Trimethyl-1-pentene*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.15 *2,4,4-Trimethyl-2-pentene*, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.16 *1 % Contaminant Standard*, [10] contains 1.0 % of some of the contaminants in MTBE, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.17 *0.1 % Contaminant Standard*, [10] contains 0.1 % of some of the contaminants in MTBE, (**Warning**—Flammable liquid. Harmful if inhaled.)

9. Sampling

9.1 MTBE can be sampled either in a floating piston cylinder or into an open container since vapor pressures less than 70 kPa (10 psi) are expected.

9.1.1 *Cylinder Sampling*—Refer to Practice D 3700 for instructions on transferring a representative sample from a source into a floating piston cylinder. Add inert gas to the ballast side of the piston to achieve a pressure of 310 kPa (45 psi) above the vapor pressure of the sample.

9.1.2 *Open Container Sampling*—Refer to Practice D 4057 for instructions on manual sampling from bulk storage into open containers. Stopper container immediately after drawing sample.

9.2 Preserve the sample by cooling to approximately 4°C and by maintaining that temperature until immediately prior to analysis.

9.3 Transfer an aliquot of the cooled sample into a precooled septum vial, then seal appropriately. Obtain the test specimen for analysis directly from the sealed septum vial, for either manual or automatic syringe injection.

10. Preparation of Apparatus

10.1 Install and condition column in accordance with manufacturer's or supplier's instructions. After conditioning, attach column outlet to flame ionization detector inlet and check for leaks throughout the system. When leaks are found, tighten or replace fittings before proceeding.

10.2 Adjust the carrier gas flow rate so that an average linear velocity at the starting temperature of the run is between 21 and 24 cm/s, as determined in Eq 1. Flow rate adjustment is made by raising or lowering the carrier gas pressure (head pressure) to the injector. The following starting point pressures can be useful to adjust the carrier gas flow:

Column length	50 m	100 m	150 m
Starting point pressure, kPa (psig)	262 (38)	275 (40)	552 (80)

10.2.1 *Average Linear Gas Velocity*:

$$u_{ave} = L/t_m \tag{1}$$

where:
L = the length of the column in cm, and
t_m = the retention time in seconds of methane.

10.3 Adjust the operating conditions of the gas chromatograph to conform to the list in Table 1. Turn on the detector, ignite the flame, and allow the system to equilibrate.

10.4 When the method is first set up, ensure that the FID is not saturated. Plot the peak area versus MTBE concentration for prepared standards in the concentration range of interest. If the plot is not linear, increase the split ratio, or use a less sensitive detector range, or both.

11. Column Evaluation and Optimization

11.1 In order to establish that the column/temperature program will perform the required separation, the resolution between cis-2-pentene and tert-butanol and between trans-2-pentene and tert-butanol must be determined. The retention of tert-butanol relative to cis- and trans-2-pentene is very temperature dependent. The order of elution of cis-2-pentene and tert-butanol reverses at subambient temperature. A column which does not resolve these components after adjusting operating conditions is unsuitable.

11.2 Analyze a standard mixture that contains approximately 1 % each of *tert*-butanol, *cis*-2-pentene, and *trans*-2-pentene in MTBE by the procedure in Section 13. Calculate resolution (*R*) between *tert*-butanol and *cis*-2-pentene and between *trans*-2-pentene and *tert*-butanol using Eq 2. Both resolutions must be at least 1.3.

$$R = \frac{2(t_B - t_A)}{1.699(W_A + W_B)} \tag{2}$$

where:
R = resolution,
t_A = retention time Component A,
t_B = retention time Component B,

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[7] Available from Farcham Laboratories, Gainesville, FL

[8] Available from Wiley Organics, Coshocton, OH.

[9] HPLC grade MTBE from Aldrich Chemical Company, Inc., Milwaukee, WI has been found to be satisfactory.

[10] These reference samples, that contain only contaminants boiling above ambient, are available from Supelco, Inc., Bellefonte, PA.

W_A = peak width at half height of Component A, and
W_B = peak width at half height of Component B and $t_B > t_A$

12. Calibration and Standardization

12.1 Component peaks from a sample analysis are identified by matching their retention time with the retention time of reference compounds analyzed under identical conditions. Typical retention times of most common contaminants in MTBE products are listed in Table 2. Analyze mixtures containing these compounds to verify their retention times. Mixtures used for determining retention times can be blended from pure compounds or purchased.[8] Retention times of other suspected contaminants can be established by analyzing mixtures containing these materials under identical conditions. A typical chromatogram of a MTBE product sample, analyzed on the 150 meter column, is shown in Fig. 1. The peaks are indexed to Table 2.

12.2 Typical mass relative response factors are found in Table 2. These response factors must be verified by analyzing a prepared standard[8] with concentrations similar to those encountered in a MTBE product sample and comparing the measured results with the prepared composition. If the measured composition does not agree with the prepared composition, the response factors should be experimentally determined according to Practice D 4626 by measuring the response factors of certified blends that have been purchased or blends prepared according to Practice D 4307.

13. Procedure

13.1 Set the instrument operating variables to the values specified in Table 1 or to a temperature determined to be suitable by the evaluation in Section 11.

13.2 When the gas chromatograph has been inoperative for more than 24 h, raise the column temperature to the maximum temperature used in the method and hold for 20 min to remove contaminants from the column. Lower the temperature to the initial method temperature.

TABLE 2 Typical Retention Times on Three Columns, Relative Mass Response Factors[A] and Densities[B,C] for Common MTBE Product Components

No. Component	Retention Time m, min			Typical Response Factor	Density at approximately 20°C g/mL
	50	100	150		
1 Methanol[D]	3.72	7.84	12.89	3.20	0.7914
2 Isobutylene[E]	3.85	8.00	13.39	1.18	0.5942
3 Butane	3.92	8.08	13.59	1.17	0.5788
4 Trans-2-butene	3.99	8.16	13.77	1.13	0.6042
5 Cis-2-butene	4.10	8.29	14.11	1.10	0.6213
6 3-methyl-1-butene	4.41	8.67	14.95	1.05	0.6272
7 Acetone	4.61	8.91	15.29	1.85	0.7899
8 Isopentane	4.66	8.93	15.51	1.04	0.6201
9 2-propanol	4.77	9.06	15.69	1.88	0.7855
10 1-pentene	4.82	9.15	15.95	1.05	0.6405
11 2-methyl-1-butene	4.95	9.31	16.15	1.00	0.6504
12 Pentane	5.00	9.37	16.37	1.05	0.6262
13 Trans-2-pentene	5.12	9.49	16.61	1.05	0.6482
14 Tert-butanol	5.20	9.57	16.70	1.30	0.7887
15 Cis-2-pentene	5.26	9.67	16.94	1.05	0.6556
16 2-methyl-2-butene	5.37	9.78	17.13	1.00	0.6623
17 Cyclopentene	6.17	10.72	18.84	1.00	0.7457
18 Methyl tert-butyl ether	6.51	11.11	19.15	1.53	0.7405
19 2,3-dimethyl-1-butene	6.55	11.17	19.25	1.00	0.6803
20 4-methyl-cis-2-pentene	6.57	11.21	19.36	1.00	0.669
21 2-methylpentane	6.63	11.28	19.39	1.00	0.6532
22 Methyl ethyl ketone	6.86	11.48	19.65	1.51	0.8054
23 3-methylpentane	7.09	11.80	20.17	1.00	0.6645
24 Sec-butyl methyl ether	7.22	11.93	20.23	1.53	0.7415
25 Ethyl tert-butyl ether	8.54	13.36	21.85	1.50	0.7519
26 Tert-amyl methyl ether	11.93	16.27	25.19	1.41	0.7703
27 3,5-dimethyl-1-hexene	14.85	18.23	27.39	0.90	0.708
28 2,4,4-trimethyl-1-pentene	15.03	18.40	27.65	0.90	0.715
29 2,4,4-trimethyl-2-pentene	16.17	19.27	28.47	0.90	0.7218
30 3,4,4-trimethyl-trans-2-pentene	17.86	20.86	30.19	0.90	0.739
31 2,3,4-trimethyl-2-pentene	19.02	22.00	31.28	0.90	0.7434
32 4,4-dimethyl-2-neopentyl-1-pentene	26.26	30.67	41.33	0.90	0.759
33 2,2,4,6,6-pentamethyl-3-heptene	26.46	30.92	41.64	0.90	0.759

[A] Response factors are relative to heptane = 1.00.
[B] See Driesbach.[13]
[C] See Weast.[12]
[D] Methanol coelutes with isobutane on the 50 and 100 m columns but is separated on the 150 m column. Subambient temperature conditions will separate these compounds.
[E] Isobutylene and 1-butene co–elute on all three columns at the typical temperature conditions. These components are known to separate using subambient temperature.
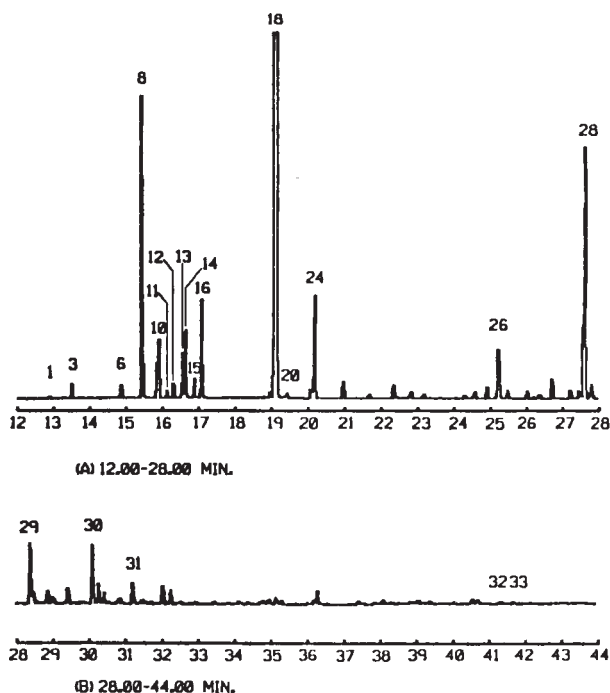
NOTE—Numbers correspond to components in Table 2.
FIG. 1 Typical Chromatogram of a MTBE Sample Analyzed on the 150 M Column

13.3 Set the recorder or integration device, or both, for accurate presentation of the data. Set instrumental sensitivity such that any component of at least 0.02 % mass will be detected, integrated, and reported.

13.4 Inject 0.1 to 0.5 μL of sample into the injection port and start the analysis. Sample size must follow guidelines discussed in 7.2. Obtain a chromatogram and peak integration report.

14. Calculation

14.1 Identify each peak by matching retention times with known reference standards or sample components as discussed in 12.1. If a computing integrator is used, examine the report to ensure that peaks are properly identified and integrated. *It is very important that all oxygenate peaks be separated from hydrocarbon peaks and correctly identified since oxygenates have very different response factors than hydrocarbons and normalization is used for quantification.*

14.2 Obtain the integrated areas of each component peak. Multiply each area by its appropriate response factor as determined in 12.2 to obtain peak areas corrected for response differences. Use a response factor of 1.00 for unknown contaminants.

14.3 Obtain the concentration of water in the sample as determined by Test Method D 1364, or equivalent.

14.4 Determine the mass % of each component using Eq 3:

$$\text{mass \% component} = \frac{\text{corrected peak area} \times (100 - \text{\% water})}{\text{total corrected peak area}} \quad (3)$$

14.5 Report the mass % of each component to two decimal places.

TABLE 3 Repeatability and Reproducibility for Selected MTBE Components

Component	Range, Weight %	Repeatability	Reproducibility
Methanol	0.0113 to 0.3719	$0.0181 * X^{0.25}$	$0.0994 * X^{0.25}$
Isobutylene/ 1-butene	0.0168 to 0.1356	0.0998 $(X + 0.0049)$	$0.3199 (X + 0.0049)$
Isopentane	0.0561 to 1.9290	$0.0390 * X^{0.6667}$	$0.1646 * X^{0.6667}$
Trans-2-pentene	0.0128 to 0.5003	$0.0084 * X^{-0.0036}$	$0.0630 * X^{0.2678}$
Tert-butanol	0.4741 to 0.8763	0.016	0.132
Cis-2-pentene	0.0970 to 0.5089	$0.0401 * X^{0.5}$	$0.1092 * X^{0.5}$
2-methyl-2-butene	0.0144 to 0.4391	$0.0122 * X^{0.0994}$	$0.0799 * X^{0.3818}$
Methyl tert-butyl ether	93.23 to 97.87	$0.0448 (X/100)^{-18}$	$0.2932 (X/100)^{-18}$
Sec-butyl methyl ether	0.0200 to 0.4821	$0.0065 * X^{0.0123}$	$0.1606 * X^{0.4424}$
Tert-amyl methyl ether	0.4961 to 0.7072	0.019	0.124
2,4,4-trimethyl- 1-pentene	0.0852 to 1.0150	0.0388 $(X + 0.0415)$	$0.2523 (X + 0.0415)$

14.6 If the volumetric concentration of each oxygenate is desired, calculate the volumetric concentration of each oxygenate using Eq 4 as follows:

$$V_i = \frac{W_i \times D_s}{D_i} \quad (4)$$

where:
V_i = volume % of Component i,
W_i = mass % of Component i from Eq 3,
D_i = density at 20°C of Component i as found in Table 2, and
D_s = density at 20°C of sample under study.

14.7 Report the volume % of each component to two decimal places.

15. Precision and Bias [11]

15.1 *Precision*—The precision of any individual measurement resulting from the application of this test method is expected to be dependent upon several factors including volatility of the component, its concentration and the degree to which it is resolved from other closely eluting components. Since it is not practical to determine the precision for measurement of every component separated by this method, Table 3 lists repeatability and reproducibility for selected representative components.[12,13]

15.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the method, exceed the values calculated from the equations listed in Table 3 only in one case in twenty. Table 4 lists typical values for repeatability over the concentration ranges of interest calculated from the equations in Table 3.

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1306.
[12] Weast, R. C., *Chemical Rubber Company Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH, 1979.
[13] Driesbach, R. R., "Physical Properties of Chemical Compounds," *Advances in Chemistry Series No. 22*, American Chemical Society, Washington, DC 1959.

TABLE 4 Typical Values for Repeatability and Reproducibility of Selected MTBE Components at Various Concentrations

Approximate Concentration	Repeatability, Mass %					
	0.1	0.2	0.5	1.0	1.5	2.0
Methanol	0.01	0.01	0.02	0.02	0.02	0.02
Isobutylene/1-butene	0.01	0.02	0.05	0.10	0.15	0.20
Isopentane	0.01	0.01	0.02	0.04	0.05	0.06
Trans-2-pentene	0.01	0.01	0.01	0.01	0.01	0.01
Tert-butanol	0.02	0.02	0.02	0.02	0.02	0.02
Cis-2-pentene	0.01	0.02	0.03	0.04	0.05	0.06
2-methyl-2-butene	0.01	0.11	0.12	0.13	0.13	
Methyl sec-butyl ether	0.01	0.01	0.01	0.01	0.01	0.01
Tert-amyl methyl ether	0.02	0.02	0.02	0.02	0.02	0.02
2,4,4-trimethyl-1-pentene	0.01	0.01	0.02	0.04	0.06	0.08
Approximate Concentration	93.00	94.00	95.00	96.00	97.00	98.00
Methyl tert-butyl ether	0.17	0.14	0.11	0.09	0.08	0.06
Approximate Concentration	Reproducibility, Mass %					
	0.1	0.2	0.5	1.0	1.5	2.0
Methanol	0.06	0.07	0.08	0.10	0.11	0.12
Isobutylene/1-butene	0.03	0.07	0.16	0.32	0.48	0.64
Isopentane	0.04	0.06	0.10	0.16	0.22	0.26
Trans-2-pentene	0.03	0.04	0.05	0.06	0.07	0.08
Tert-butanol	0.13	0.13	0.13	0.13	0.13	0.13
Cis-2-pentene	0.03	0.05	0.08	0.11	0.13	0.15
2-methyl-2-butene	0.03	0.04	0.06	0.08	0.09	0.10
Methyl sec-butyl ether	0.06	0.08	0.12	0.16	0.19	0.22
Tert-amyl methyl ether	0.12	0.12	0.12	0.12	0.12	0.12
2,4,4-trimethyl-1-pentene	0.04	0.06	0.14	0.26	0.39	0.52
Approximate Concentration	93.00	94.00	95.00	96.00	97.00	98.00
Methyl tert-butyl ether	1.08	0.89	0.74	0.61	0.51	0.42

15.1.2 *Reproducibility*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values calculated from the equations listed in Table 3 only in one case in twenty. Table 4 lists typical values for repeatability over the concentration ranges of interest calculated from the equations in Table 3.

15.2 *Bias*—Bias in the measurements resulting from the application of this test was calculated for selected compounds since it is not practical to determine bias for all compounds separated by this method. The calculations were made using the interlaboratory study results for a gravimetrically prepared blend of all of the compounds in Table 3 except for isobutylene. The calculations were accomplished using RR:D02-1007. No significant bias was observed.

16. Keywords

16.1 methyl tert-butyl ether; MTBE; open tubular column gas chromatography