



Designation: D5441 – 98 (Reapproved 2017)

# Standard Test Method for Analysis of Methyl Tert-Butyl Ether (MTBE) by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D5441; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 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<sub>4</sub> to C<sub>12</sub> 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 D1364 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.

1.6.1 *Exception*—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 establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recom-*

*mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4626 Practice for Calculation of Gas Chromatographic Response Factors

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

## 3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355 and E594.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *C<sub>4</sub> to C<sub>12</sub> 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.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

Current edition approved Oct. 1, 2017. Published November 2017. Originally approved in 1993. Last previous edition approved in 2013 as D5441–98(2013). DOI: 10.1520/D5441-98R17.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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 gauges 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.

7.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 0.1  $\mu\text{L}$  to 0.5  $\mu\text{L}$  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*<sup>3</sup>—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:

Column length	50 m	100 m	150 m
Film thickness	0.5 $\mu\text{m}$	0.5 $\mu\text{m}$	1.0 $\mu\text{m}$
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.)

**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 $\mu\text{L}$		
Detector			
Type	flame ionization		
Temperature	250 °C		
Fuel gas	hydrogen ( $\approx$ 30 mL/min)		
Oxidizing gas	air ( $\approx$ 300 mL/min)		
Make-up gas	nitrogen ( $\approx$ 30 mL/min)		
Carrier Gas			
Type	helium		
Average linear velocity	20 cm/s to 24 cm/s		

<sup>3</sup> Petrocol DH series columns from Supelco, Inc., Bellefonte, PA were used to obtain the retention data and example chromatogram shown in this standard. Other suitable columns are available commercially.

### 8.5 Reference Standards:

8.5.1 *tert*-Amyl methyl ether, <sup>4,5</sup> (**Warning**—Flammable liquid. Harmful if inhaled.)

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, <sup>6,5</sup> (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.5 *4,4*-Dimethyl-2-neopentyl-1-pentene, <sup>7,5</sup> (**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, <sup>7,5</sup> (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.9 *Methyl tert*-butyl ether, 99 + % pure, <sup>8,5</sup> (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.10 *2,2,4,6,6*-Pentamethyl-3-heptene, <sup>7,5</sup> (**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, <sup>9,5</sup> contains 1.0 % of some of the contaminants in MTBE, (**Warning**—Flammable liquid. Harmful if inhaled.)

8.5.17 0.1 % Contaminant Standard, <sup>9,5</sup> 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.

<sup>4</sup> The sole source of supply of the apparatus known to the committee at this time is Aldrich Chemical Company, Inc., Milwaukee, WI. A 96 % pure sample obtained from Aldrich was the highest purity found.

<sup>5</sup> If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>6</sup> The sole source of supply of the apparatus known to the committee at this time is Farcham Laboratories, Gainesville, FL.

<sup>7</sup> The sole source of supply of the apparatus known to the committee at this time is Organic Technologies (formerly Wiley Organics), P.O. Box 640, 1245 S. 6th St., Coshocton, OH 43812.

<sup>8</sup> The sole source of supply of the apparatus, HPLC grade MTBE, known to the committee at this time is from Aldrich Chemical Company, Inc., Milwaukee, WI.

<sup>9</sup> The sole source of supply of the apparatus, reference samples that contain only contaminants boiling above ambient, known to the committee at this time is Supelco, Inc., Bellefonte, PA.

9.1.1 *Cylinder Sampling*—Refer to Practice **D3700** 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 **D4057** 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 pre-cooled 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:

$$u_{ave} = L/t_m \quad (1)$$

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.