Designation: D7796 – 17

An American National Standard

Standard Test Method for
Analysis of Ethyl tert-Butyl Ether (ETBE) by Gas Chromatography[1]

1. Scope*

1.1 This test method covers the determination of the purity of ethyl *tert*-butyl ether (ETBE) by gas chromatography. It also provides a procedure to measure impurities in ETBE 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.

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

1.3 Water cannot be determined by this test method and shall be measured by a procedure such as Test Method D6304 and the result used to normalize the chromatographic values.

1.4 Most of the impurities in ETBE are 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 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 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 Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration

D7618 Specification for Ethyl Tertiary-Butyl Ether (ETBE) for Blending with Aviation Spark-Ignition Engine Fuel

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_4 to C_{12} *olefins, n*—common olefin impurities in ETBE including 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 ETBE product sample is introduced into a gas chromatograph equipped with a methyl silicon 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.

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*A Summary of Changes section appears at the end of this standard

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 and the water content of the sample. The detector response factors are determined by analyzing prepared standards with the concentrations similar to those encountered in the sample.

5. Significance and Use

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

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, and MTBE is typically present at very low concentrations in ETBE.

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 shall be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. Pressure control devices and gages shall 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 µL 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*[3]—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 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 shall 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 *Ethyl tert-Butyl Ether,* 99.99 % pure. (**Warning**—Flammable liquid. Harmful if inhaled.)

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

8.5 *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 µL 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 cm⁄s – 24 cm⁄s		

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[3] 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.

8.6 *Reference Standards:*

8.6.1 *tert-Amyl methyl ether.* (**Warning**—Flammable liquid. Harmful if inhaled.)

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

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

8.6.4 *sec-Butyl methyl ether.* (**Warning**—Flammable liquid. Harmful if inhaled.)

8.6.5 *4,4-Dimethyl-2-neopentyl-1-pentene.* (**Warning**—Flammable liquid. Harmful if inhaled.)

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

8.6.7 *Methanol.* (**Warning**—Toxic flammable liquid. Harmful if inhaled or ingested.)

8.6.8 *2-Methyl-2-butene.* (**Warning**—Flammable liquid. Harmful if inhaled.)

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

8.6.10 *2,2,4,6,6-Pentamethyl-3-heptene.* (**Warning**—Flammable liquid. Harmful if inhaled.)

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

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

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

8.6.14 *2,4,4-Trimethyl-1-pentene.* (**Warning**—Flammable liquid. Harmful if inhaled.)

8.6.15 *2,4,4-Trimethyl-2-pentene.* (**Warning**—Flammable liquid. Harmful if inhaled.)

8.6.16 *Dimethyl ether.* (**Warning**—Extremely flammable gas. Harmful if inhaled.)

8.6.17 *Diethyl ether.* (**Warning**—Flammable liquid. Harmful if inhaled.)

8.6.18 *2,2,4-Trimethylpentane.* (**Warning**—Flammable liquid. Harmful if inhaled.)

8.6.19 *Ethanol.* (**Warning**—Flammable liquid.)

9. Sampling

9.1 ETBE may 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 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 the 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 cm⁄s 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:*

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

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 ETBE 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 ETBE 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 shall 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,
W_A = peak width at half height of Component A, and