



Designation: D4815 – 22

Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography¹

This standard is issued under the fixed designation D4815; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of ethers and alcohols in gasolines by gas chromatography. Specific compounds determined are methyl *tert*-butylether (MTBE), ethyl *tert*-butylether (ETBE), *tert*-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, *n*-propanol, isobutanol, *tert*-butanol, *sec*-butanol, *n*-butanol, and *tert*-pentanol (*tert*-amylalcohol).

1.2 Individual ethers are determined from 0.20 % to 20.0 % by mass. Individual alcohols are determined from 0.20 % to 12.0 % by mass. Equations used to convert to mass percent oxygen and to volume percent of individual compounds are provided. At concentrations <0.20 % by mass, it is possible that hydrocarbons may interfere with several ethers and alcohols. The reporting limit of 0.20 % by mass was tested for gasolines containing a maximum of 10 % by volume olefins. It may be possible that for gasolines containing >10 % by volume olefins, the interference may be >0.20 % by mass. **Annex A1** gives a chromatogram showing the interference observed with a gasoline containing 10 % by volume olefins.

1.3 This test method includes a relative bias correlation for ethanol in spark-ignition engine fuels for the U.S. EPA regulations reporting based on Practice **D6708** accuracy assessment between Test Method D4815 and Test Method **D5599** as a possible Test Method D4815 alternative to Test Method **D5599**. The Practice **D6708** derived correlation equation is only applicable for ethanol in fuels in the concentration range from 2.28 % to 14.42 % by mass as measured by Test Method D4815. The applicable Test Method **D5599** range for ethanol is from 2.16 % to 14.39 % by mass as reported by Test Method **D5599**.

1.4 Alcohol-based fuels, such as M-85 and E-85, MTBE product, ethanol product, and denatured alcohol, are specifi-

cally excluded from this test method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

1.5 Benzene, while detected, cannot be quantified using this test method and shall be analyzed by alternate methodology (see Test Method **D3606**).

1.6 The values stated in SI units are to be regarded as standard. Alternate units, in common usage, are also provided to increase clarity and aid the users 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

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D1744 Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent (Withdrawn 2016)³

D3606 Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography

D4052 Test Method for Density, Relative Density, and API

¹ 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 **D02.04.01** on Gas Chromatography Methods.

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² 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.

³ The last approved version of this historical standard is referenced on www.astm.org.

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

Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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

D4420 Test Method for Determination of Aromatics in Finished Gasoline by Gas Chromatography (Withdrawn 2004)³

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

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

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

E203 Test Method for Water Using Volumetric Karl Fischer Titration

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *low volume connector*—a special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Sometimes this is referred to as zero dead volume union.

3.2.2 *oxygenate*—any oxygen-containing organic compound that can be used as a fuel or fuel supplement, for example, various alcohols and ethers.

3.2.3 *split ratio*—in capillary gas chromatography, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column, expressed by

$$\text{split ratio} = (S + C)/C \quad (1)$$

where:

S = flow rate at the splitter vent, and

C = flow rate at the column outlet.

3.2.4 *tert-amyl alcohol*—*tert*-pentanol.

3.3 Acronyms:

3.3.1 *DIPE*—diisopropylether.

3.3.2 *ETBE*—ethyl *tert*-butylether.

3.3.3 *MTBE*—methyl *tert*-butylether.

3.3.4 *TAME*—*tert*-amyl methylether.

3.3.5 *TCEP*—1,2,3-tris-2-cyanoethoxypropane—a gas chromatographic liquid phase.

3.3.6 *WCOT*—a type of capillary gas chromatographic column prepared by coating the inside of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 An appropriate internal standard, such as 1,2-dimethoxyethane (ethylene glycol dimethyl ether), is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar TCEP column, which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

4.2 After methylcyclopentane, but before DIPE and MTBE elute from the polar column, the valve is switched to backflush the oxygenates onto a WCOT nonpolar column. The alcohols and ethers elute from the nonpolar column in boiling point order, before elution of any major hydrocarbon constituents.

4.3 After benzene and TAME elute from the nonpolar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons.

4.4 The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of each component is calculated with reference to the internal standard.

5. Significance and Use

5.1 Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust, and evaporative emissions are some of the concerns associated with oxygenated fuels.

5.2 This test method is applicable to both quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination.

6. Apparatus

6.1 *Chromatograph*—While any gas chromatographic system, which is capable of adequately resolving the individual ethers and alcohols that are presented in Table 1, can be used for these analyses, a gas chromatographic instrument, which can be operated at the conditions given in Table 2 and has a column switching and backflushing system equivalent to Fig. 1, has been found acceptable. Carrier gas flow controllers shall be capable of precise control where the required flow rates are low (see Table 2). Pressure control devices and gages shall be capable of precise control for the typical pressures required.

6.1.1 *Detector*—A thermal conductivity detector or flame ionization detector can be used. The system shall have sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1 for 0.005 % by volume concentration of an oxygenate.

6.1.2 *Switching and Backflushing Valve*—A valve, to be located within the gas chromatographic column oven, capable of performing the functions described in Section 11 and illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.