



Designation: D5501 – 20 (Reapproved 2024)^{ε 1}

Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography¹

This standard is issued under the fixed designation D5501; 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.

ε¹ NOTE—Footnote 5 was updated editorially in December 2024.

1. Scope

1.1 This test method covers the determination of the ethanol content of hydrocarbon blends containing greater than 20 % ethanol. This method is applicable to denatured fuel ethanol, ethanol fuel blends, and mid-level ethanol blends.

1.1.1 Ethanol is determined from 20 % by mass to 100 % by mass and methanol is determined from 0.01 % by mass to 0.6 % by mass. Equations used to convert these individual alcohols from percent by mass to percent by volume are provided.

NOTE 1—Fuels containing less than 20 % ethanol may be quantified using Test Method D5599, and less than 12 % ethanol may be quantified using Test Method D4815.

1.2 This test method does not purport to identify all individual components common to ethanol production or those components that make up the denaturant or hydrocarbon constituent of the fuel.

1.3 Water cannot be determined by this test method and shall be measured by a procedure such as Test Method D7923, E203, or E1064 and the result used to correct the concentrations determined by this method.

1.4 This test method is inappropriate for impurities that boil at temperatures higher than 225 °C or for impurities that cause poor or no response in a flame ionization detector, such as water.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information purposes only.

1.6 *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.

1.7 *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
- D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)
- D4052 Test Method for Density, Relative Density, and API 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
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D4626 Practice for Calculation of Gas Chromatographic Response Factors
- D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
- D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography
- D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

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 D02.04.0L on Hydrocarbon Analysis.

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

- D5798** Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines
- D6299** Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6792** Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D7923** Test Method for Water in Ethanol and Hydrocarbon Blends by Karl Fischer Titration
- E203** Test Method for Water Using Volumetric Karl Fischer Titration
- E355** Practice for Gas Chromatography Terms and Relationships
- E594** Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
- E1064** Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration
- E1510** Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs
- E3237** Specification for Undenatured Ethanol from Biomass for Use in Industrial Applications

2.2 U.S. Federal Standards:³

- 40 CFR 80.1426** How are RINs generated and assigned to batches of renewable fuel by renewable fuel producers or importers?
- 27 CFR 30.22** Hydrometers and Thermometers
- 27 CFR 30.67** Table 7, for correction of volume of spirituous liquors to 60 °F

3. Terminology

3.1 Definitions—This test method makes reference to many common chromatographic procedures, terms, and relationships. Detailed definitions can be found in Terminology **D4175**, and Practices **E355** and **E594**.

3.2 Definitions:

3.2.1 denatured fuel ethanol, *n*—fuel ethanol made unfit for beverage use by the addition of denaturants under formula(s) approved by the applicable regulatory agency to prevent the imposition of beverage alcohol tax.

3.2.2 mass response factor (*MRF*), *n*—constant of proportionality that converts area to mass percent.

3.2.3 relative mass response factor (*RMRF*), *n*—mass response factor of a component divided by that of another component.

3.2.3.1 Discussion—In this test method, the mass response factors are relative to that of *n*-heptane.

3.2.4 tangential skimming, *n*—in gas chromatography, integration technique used when a “rider” peak elutes on the tail of a primary peak.

3.2.4.1 Discussion—Since the majority of the area beneath the rider peak belongs to the primary peak, in tangential skimming the top of the primary peak tail is used as the

baseline of the rider peak, and the triangulated area beneath the rider peak is added to the primary peak.

3.3 Abbreviations:

- 3.3.1 CFR**—U.S. Code of Federal Regulations
- 3.3.2 EPA**—The U.S. Environmental Protection Agency
- 3.3.3 *MRF***—mass response factor
- 3.3.4 *RIN***—Renewable Identification Number
- 3.3.5 *RMRF***—relative mass response factor
- 3.3.6 *TTB***—The Alcohol and Tobacco Tax and Trade Bureau of the U.S. Department of Treasury

4. Summary of Test Method

4.1 A representative aliquot of the fuel ethanol sample is introduced into a gas chromatograph equipped with a polydimethylsiloxane bonded phase capillary column. Carrier gas transports the vaporized aliquot through the column where the components are chromatographically separated in order of boiling point temperature. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The ethanol and methanol components are identified by comparing their retention times to the ones identified by analyzing standards under identical conditions. The concentrations of all components are determined in mass percent by normalization of the peak areas. After correction for water content, results may be reported in mass percent or volume percent.

5. Significance and Use

5.1 This test method provides a method of determining the percentage of ethanol in an ethanol-gasoline fuel blend over the range of 20 % by mass to 100 % by mass for compliance with fuel specifications and federal or local fuel regulations.

5.2 Ethanol content of denatured fuel ethanol for gasoline blending is required in accordance with Specification **D4806**.

5.3 Ethanol content of ethanol fuel blends for flexible-fuel automotive spark-ignition engines is required in accordance with Specification **D5798**.

5.4 This test method is acceptable for determining the percentage of ethanol for either denatured fuel ethanol or undenatured ethanol for use in industrial applications using Table 3(a) or Table 3(b).

5.4.1 Refer to local, federal, or other authorities having jurisdiction for information regarding the correct implementation of either Table 3(a) or Table 3(b).

5.4.2 Specific regulatory requirements for U.S. domestic fuel applications are given in **Appendix X5** for information.

6. Apparatus

6.1 Gas Chromatograph, capable of operating at the conditions listed in **Table 1**. A heated flash vaporizing injector designed to provide a linear sample split injection (for example, 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 and flow control devices shall be designed to attain the linear velocity required in the column

³ Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.