



Designation: D4806 – 13

# Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel<sup>1</sup>

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## 1. Scope\*

1.1 This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume % for use as automotive spark-ignition engine fuel covered by Specification D4814. The significance of this specification is shown in Appendix X1.

1.2 The user is advised to check with the national regulatory agencies where the ethanol is denatured and used. The sulfur limit and denaturing formulas in this specification are acceptable for the U.S. market. Other countries or jurisdictions may allow or require other denaturing formulas and sulfur limits.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 The following safety hazards caveat pertains only to the method modification in 8.7 of this specification: *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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

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

- D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- D381 Test Method for Gum Content in Fuels by Jet Evaporation
- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

<sup>1</sup> This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A0.02 on Oxygenated Fuels and Components.

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<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.

- D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products
- D1688 Test Methods for Copper in Water
- D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
- D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
- 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, Petroleum Products, and Lubricants
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination
- D4814 Specification for Automotive Spark-Ignition Engine Fuel
- D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
- D5501 Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20% Ethanol by Gas Chromatography
- D5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C<sub>9</sub>, and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography
- D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
- D6423 Test Method for Determination of pH<sub>E</sub> of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)
- D6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
- D7039 Test Method for Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
- D7318 Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration

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

**TABLE 1 Performance Requirements**

Property	Limit	Method
Ethanol, volume %, min	92.1	D5501
Methanol, volume %, max	0.5	D5501
Solvent-washed gum content, mg/100 mL, max	5.0	D381
Water, volume % (mass %), max	1.0 (1.26)	E203 or E1064
Inorganic Chloride, mass ppm (mg/L), max	10. (8)	D7319 or D7328
Copper, mg/kg, max	0.1	D1688
Acidity (as acetic acid CH <sub>3</sub> COOH) mass % (mg/L), max	0.007 (56) (Note 3)	D1613 or D7795
pHe	6.5 to 9.0	D6423
Sulfur, mass ppm, max	30.	D2622, D3120, D5453, or D7039
Existent sulfate, mass ppm, max	4	D7318, D7319, or D7328

**D7319** Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol by Direct Injection Suppressed Ion Chromatography

**D7328** Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection

**D7795** Test Method for Acidity in Ethanol and Ethanol Blends by Titration

**E29** Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

**E203** Test Method for Water Using Volumetric Karl Fischer Titration

**E300** Practice for Sampling Industrial Chemicals

**E1064** Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

2.2 Other Standards:<sup>3</sup>

United States Code of Federal Regulations, Title 27, Parts 19, 20, and 21

### 3. Terminology

3.1 For general terminology, refer to Terminology **D4175**.

NOTE 1—The user is advised that the definitions used by various industries, marketers, and regulatory bodies can differ from those specific to this specification. It is the responsibility of the user to ensure that the terms used in a particular context are clearly understood.

#### 3.2 Definitions:

3.2.1 *denaturants, n*—materials added to ethanol to make it unsuitable for beverage use under a formula approved by a regulatory agency to prevent the imposition of beverage alcohol tax.

3.2.1.1 *Discussion*—Denaturants are only those materials added by the denaturer to comply with the approved formula; any materials absorbed later are not denaturants.

3.2.2 *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.

3.2.3 *ethanol, n*—ethyl alcohol, the chemical compound C<sub>2</sub>H<sub>5</sub>OH.

3.2.4 *fuel ethanol, n*—a grade of undenatured ethanol with other components common to its production (including water) that do not affect the use of the product as a component for automotive spark-ignition engine fuels.

3.2.5 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines. **D4814**

3.2.6 *gasoline-ethanol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen) of denatured fuel ethanol.

3.2.7 *oxygenate*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement. **D4814**

#### 3.3 Definitions of Terms Specific to This Standard:

3.3.1 *pHe, n*—a measure of the acid strength of denatured fuel ethanol.

### 4. Performance Requirements (Table 1)

4.1 *Denatured Fuel Ethanol*—After fuel ethanol is denatured as specified in Section 5, it shall conform to the following requirements at the time of blending with gasoline. (See Note 2.)

NOTE 2—For purposes of determining conformance with these specification limits, an observed value or a calculated value shall be rounded “to the nearest unit” in the right-most significant digit used in expressing the specification limit, in accordance with the rounding method of Practice **E29**. For a specification limit expressed as an integer, a trailing zero is significant only if the decimal point is specified. For a specified limit expressed as an integer, and the right-most digit is non-zero, the right-most digit is significant without a decimal point being specified. This convention applies to specified limits in Table 1 and will not be observed in the remainder of this specification.

NOTE 3—Denatured fuel ethanol may contain additives, such as corrosion inhibitors and detergents, that can affect the titratable acidity (acidity as acetic acid) of the finished denatured fuel ethanol. Although the base fuel ethanol may meet the acidity specification, the effect of these additives can produce an apparent high titratable acidity of the finished product. Contact the ethanol supplier if there is a question regarding the titratable acidity of the denatured fuel ethanol to verify that the base fuel ethanol meets the acidity requirements in Table 1.

4.2 *Other Properties*—Limits more restrictive than those specified above, or the specification of additional properties such as color, may be agreed upon between the supplier and the purchaser.

<sup>3</sup> A printed copy of the Code of Federal Regulations may be purchased from the U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401 or the online store at <http://bookstore.gpo.gov/>. The Code of Federal Regulations may be browsed online at <http://www.gpoaccess.gov/cfr/index.html>.

## 5. Denaturants

### 5.1 General Requirements:

5.1.1 *Allowable Denaturants*—The only denaturants allowed for the denatured fuel ethanol defined by this specification are natural gasoline, gasoline blendstocks or unleaded gasoline. Small amounts of the same or similar hydrocarbons absorbed by the denatured fuel ethanol as it moves through the distribution system is not denaturant. A jurisdiction can maintain approved formulas to denature alcohol for fuel use. This specification is specific to spark-ignition engine fuel. Denaturants that could provide satisfactory performance for other uses could cause damage to spark-ignition engines. The fuel ethanol formulas approved by the alcohol regulatory agency for fuel use could include denaturing materials which are not allowed by this ASTM specification. It is the denaturer’s responsibility to consult the regulations to ensure legal denaturing of the fuel ethanol and to ensure compliance with this specification with regard to allowed denaturants.

5.1.2 *Prohibited Denaturants*—This specification prohibits the use of hydrocarbons with an end boiling point higher than 225°C as determined by Test Method D86, although they may be permitted by TTB regulations. Some kerosines, for instance, promote piston scuff in automotive engines. Specific mention must be made of some materials that have extremely adverse effects on fuel stability, automotive engines, and fuel systems. These materials shall not be used as denaturants for fuel ethanol under any circumstances. They are as follows: methanol, pyrroles, turpentine, ketones, and tars (high-molecular weight pyrolysis products of fossil or nonfossil vegetable matter). Ketone denaturants tend to degrade fuel stability or increase the tendency of a gasoline-ethanol blend to corrode metals and attack elastomers. These effects become more serious if the concentration of a ketone such as 4-methyl pentanone (methyl isobutyl ketone) exceeds one part by volume per 100 parts by volume of fuel ethanol. There is no information available on the effects of denaturants other than those mentioned above. Therefore, the only denaturants that shall be used are those listed in 5.1.1.

5.1.3 *Denaturant Level*—A buyer may ask the denaturer to denature within a specific range (for example, 1.96 to 2.5 volume %). A buyer may also ask the denaturer to certify the range used for the denaturant addition. A buyer or distributor may commingle receipts certified within the same range and provide a certification of conformance with the product from that commingling. The blender may use this certification of conformance for the product to demonstrate compliance with the denaturant limits. If the product is shipped directly from a denaturer to a blender, the initial certification from the denaturer may be used to demonstrate compliance. Compliance with the denaturant limit cannot be determined analytically. Compliance must be based on the information from the original denaturer. The limits for the denaturant addition are shown in Table 2.

### 5.2 United States’ Denaturant Regulations:

5.2.1 *Denaturing Formulas*—In the United States, ethanol is rendered unfit for beverage use by the addition of denaturants under formulas approved by the Alcohol and Tobacco Tax and Trade Bureau (TTB) of the U. S. Treasury Department that

TABLE 2 Denaturant Limits

Limit, volume %	Source	Requirement
5 max <sup>A</sup>	ASTM	The maximum amount of denaturant allowed by this specification.
<b>Additional United States’ Denaturant Regulations</b>		
1.96 min <sup>A</sup>	TTB	TTB Formulas require a minimum of two parts of approved denaturant to 100 parts of ethanol with a minimum of 195 proof ethanol.
2 max <sup>B, C</sup>	EPA <sup>C</sup>	The maximum amount of denaturant the EPA allows in denatured fuel ethanol for determining volumes for RFS2 compliance purposes.

<sup>A</sup> For purposes of determining conformance with this limit, the Absolute Method in Practice E29 should be used.

<sup>B</sup> For purposes of determining conformance with this limit, the Rounding Method in Practice E29 should be used.

<sup>C</sup> See Appendix X3 for additional information on the EPA limit.

allow the denatured alcohol to ship from the denaturer free of beverage excise tax and to be distributed and used as a fuel component without TTB permits. TTB regulations concerning the preparation, handling, distribution and use of denatured ethanol formulas are published in the United States Code of Federal Regulations, Title 27, Parts 19, 20, and 21. The denatured fuel ethanol allowed by this specification shall contain a minimum of 1.96 volume % denaturant. The U. S. Environmental Protection Agency regulations stipulate that denaturant added in excess of 2 volume % shall not be considered when determining volumes for the purposes of compliance with the Renewable Fuel Standard. This absolute limitation includes volumes for Renewable Identification Number (RIN) generation and volumes for retiring RINs. The limits for the denaturant addition are shown in Table 2.

5.2.2 To avoid imposition of the beverage excise tax, TTB regulations require the denaturer to add specific quantities of approved denaturants to the ethanol prior to shipping. The denaturant content is determined by the ratio of metered denaturant and ethanol volumes at the time of denaturing. The TTB regulations stipulate the record keeping requirements for the denaturer. These regulations include records of the quantities of ethanol and denaturant added in the denaturing process. The TTB periodically audits the denaturing facilities and associated records for compliance with these regulations. The regulations do not require the receiver to analytically verify that the material added was an approved denaturant or that it was added within the necessary concentration range. Approved analytical methods or calculations do not exist to permit any of the following: (1) to confirm compliance with this section of the specification after the denaturing process, (2) to determine that the denaturant used was approved by the TTB or allowed in this specification, (3) to quantify the ratio of denaturant added during the denaturing process, or (4) to distinguish between the hydrocarbons added as part of the denaturing process and those absorbed later in the distribution system. There is no ASTM approved test method for determining denaturant concentration in denatured fuel ethanol, although regulatory agencies may use non-ASTM methods for investigative purposes.

### 5.3 Requirements Outside the United States:

5.3.1 Users of this specification are advised to consult with the applicable regulatory agency for specific requirements for denaturants (composition and amounts) in their jurisdictions.

## 6. Workmanship

6.1 The denatured fuel ethanol shall be visually free of sediment and suspended matter. It shall be clear and bright at the ambient temperature or 21°C, whichever is higher.

6.2 The product shall be free of any adulterant or contaminant that can render the material unacceptable for its commonly used applications.

6.2.1 Manufacturers, importers, and others denaturing fuel ethanol shall avoid ethanol (for example, improperly recycled ethanol) or denaturants contaminated by silicon-containing materials, or both. Silicon contamination of gasoline-oxygenate blends has led to fouled vehicle components (for example, spark plugs, exhaust oxygen sensors, catalytic converters) requiring parts replacement and repairs. There is no ASTM approved test method for determining silicon compounds in gasoline, gasoline-oxygenate blends, denaturants, or denatured fuel ethanol, although some laboratories are possibly using non-ASTM methods.

## 7. Sampling, Containers, and Sample Handling

7.1 The user is strongly advised to review all intended test methods prior to sampling to understand the importance and effects of sampling technique, proper containers, and special handling required for each test method.

7.2 Correct sampling procedures are critical to obtain a sample representative of the lot intended to be tested. Use appropriate procedures in Practice **D4057** or Practice **E300** for manual method sampling and in Practice **D4177** for automatic method sampling, as applicable.

7.3 The correct sample volume and appropriate container selection are important decisions that can impact test results. Refer to Practice **D4306** for aviation fuel container selection for tests sensitive to trace contamination. Refer to Practice **D5854** for procedures on container selection and sample mixing and handling. All sampling and storage containers should be evaluated for durability, compatibility, and contamination of denatured fuel ethanol prior to use. If samples must be collected in metal containers, do not use soldered metal containers. Soldering flux in the containers and the lead in the solder can contaminate the sample.

7.4 *Sample Size*—A minimum of about 1 L is recommended. If specific gravity is to be determined by a hydrometer method, additional volume may be required. This depends on the size of the hydrometer.

7.5 *Lot Size*—A lot shall normally consist of the amount contained in a tanker compartment or other bulk container in which it is delivered. If this definition does not apply, the definition of a lot must be agreed upon between the supplier and purchaser.

NOTE 4—See Sections 5, 6, and 7 on Significance, Safety, and Statistical Considerations, respectively, of Practice **E300** for a detailed discussion of the statistics of sampling.

## 8. Test Methods

8.1 The scope of some of the test methods listed below do not include denatured fuel ethanol. The precisions of those test methods can differ from the reported precisions when testing denatured fuel ethanol.

8.2 *Water*—Test Methods **E203** or **E1064**.

8.3 *Solvent-Washed Gum Content*—Test Method **D381**, air jet apparatus.

8.4 *Acidity*—Test Method **D1613** or **D7795**.

8.4.1 Dissolved carbon dioxide is a known interference and can cause a false high reading when using Test Method **D1613**. In the absence of dissolved CO<sub>2</sub>, Test Method **D1613** is an acceptable method. If a sample is known to have dissolved CO<sub>2</sub> or if dissolved CO<sub>2</sub> can be present, Test Method **D7795** is the preferred method. In cases of differing results between the two test methods, **D7795** shall be the referee method.

8.5 *pHe*—Test Method **D6423**.

8.6 *Inorganic Chloride*—Test Methods **D7319** or **D7328**.

8.7 *Copper*—Modification of Test Methods **D1688**, Test Method A.

8.7.1 The modifications of Test Methods **D1688**, Test Method A (atomic absorption, direct) consists of mixing reagent-grade ethanol (which can be denatured in accordance with TTB Formula 3A or 30) in place of water as the solvent or diluent for the preparation of reagents and standard solutions. However, this must not be done to prepare the stock copper solution described in the section on Copper Solution, Stock in Test Method **D1688**. Because a violent reaction can occur between the acid and the ethanol, use water, as specified, in the acid solution part of the procedure to prepare the stock copper solution. Use ethanol for the rinse and final dilution only.

8.7.2 The precision of this modified method has not been determined, but it is expected to be similar to the precision of Test Method **D1688**, Test Method A.

8.8 *Ethanol and Methanol*—Test Method **D5501**.

8.9 *Sulfur*—Test Methods **D2622**, **D3120**, **D5453**, or **D7039**. California specifies that compliance with the California sulfur standard for denatured ethanol shall be determined using Test Method **D5453-93**. EPA allows Test Methods **D3120-06<sup>e1</sup>**, **D5453-08a**, or **D7039-07** for measuring sulfur in gasoline as long as these alternative test method results are correlated to the EPA designated Test Method **D2622-05** when determining compliance with Federal EPA sulfur standards.

8.10 *Existent Sulfate*—Test Methods **D7318**, **D7319**, or **D7328**.

8.11 *Denaturant*—The denaturant content is determined by the ratio of (metered denaturant) to (metered denaturant and ethanol volumes) at the time of denaturing. There is no standardized test procedure or calculation to directly or indirectly determine the denaturant content in denatured fuel ethanol.