



Designation: ~~D4806~~—~~13~~ D4806 – 13a

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

This standard is issued under the fixed designation D4806; 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 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

[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<sup>13a</sup>

[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

<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.

Current edition approved ~~May 1, 2013~~ June 15, 2013. Published ~~May 2013~~ July 2013. Originally approved in 1988. Last previous edition approved in ~~2012~~ 2013 as ~~D4806-12~~ D4806-13. DOI: ~~10.1520/D4806-13~~ 10.1520/D4806-13A.

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

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

- D6423 Test Method for Determination of pHe 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
- 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
- D7757 Test Method for Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
- 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.

<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>.

#### 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

**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        |

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.

# iTeh Standards (<https://standards.iteh.ai>) Document Preview

[ASTM D4806-13a](#)

<https://standards.iteh.ai/catalog/standards/sist/e7a26d64-712e-46a5-a50f-0fa806a16f53/astm-d4806-13a>

**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.

## 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 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.

**iTeh Standards**  
**(<https://standards.iteh.ai>)**  
**Document Preview**

[ASTM D4806-13a](#)

<https://standards.iteh.ai/catalog/standards/sist/e7a26d64-712e-46a5-a50f-0fa806a16f53/astm-d4806-13a>

### 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  $21^{\circ}\text{C}$ ,  $21^{\circ}\text{C}$  ( $70^{\circ}\text{F}$ ), 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—Test Method D7757 is no ASTM approved test method—a procedure for determining silicon compounds in gasoline, gasoline-oxygenate blends, denaturants, or denatured fuel ethanol, although some laboratories are possibly using non-ASTM methods.~~ content but no specification limits have been established for this silicon.

## 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  $\text{CO}_2$ , Test Method D1613 is an acceptable method. If a sample is known to have dissolved  $\text{CO}_2$  or if dissolved  $\text{CO}_2$  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.