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# Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel[1]

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 (ε) 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 15 % by volume for use as automotive spark-ignition engine fuel covered by Specification D4814 as well as other fuel applications or specifications involving ethanol. The significance of this specification is shown in Appendix X1.

1.2 Jurisdictions may vary in their regulatory requirements for the allowable or prohibited types of denaturants, chemical composition of the denaturant or concentration of denaturant needed to denature the ethanol. The user is advised to check with the national and regional regulatory agencies where the ethanol is denatured and used.

1.2.1 Specific regulatory requirements for denatured fuel ethanol and acceptable denaturants from various jurisdictions are given in Appendixes for information.

1.3 The values stated in SI units are to be regarded as standard.

1.3.1 *Exception*—Values given in parentheses are provided for information only. Non-SI units are shown in the Appendix if they are in a direct quotation from government regulations. In most cases, U.S. federal regulations specify non-SI units.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels 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

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 Products, Liquid Fuels, 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 %

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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.

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

Ethanol by Gas Chromatography
D5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, $C_9$ 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 pHe of Denatured Fuel Ethanol and Ethanol Fuel Blends
D6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
D7039 Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends 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 and Butanol 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
D7347 Test Method for Determination of Olefin Content in Denatured Ethanol by Supercritical Fluid Chromatography
D7576 Test Method for Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography
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
D7923 Test Method for Water in Ethanol and Hydrocarbon Blends by Karl Fischer 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 *Government Regulations:*
United States Code of Federal Regulations, Title 27, Parts 19, 20, and 21[3]
United States Code of Federal Regulations, Title 40, Part 80
California Code of Regulations, CCR Title 13, §2260 – §2298[4]

## 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 $CH_3CH_2OH$.

3.2.4 *fuel ethanol, n*—a grade of 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.

3.2.4.1 *Discussion*—The common components do not include denaturant.

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 blendstock, n*—a liquid hydrocarbon component suitable for use in spark-ignition engine fuels.

3.2.6.1 *Discussion*—Examples of gasoline blendstock include natural gasoline, raffinate, reformate, conventional gasoline blendstock for oxygenate blending (CBOB), and reformulated gasoline blendstock for oxygenate blending (RBOB).

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

3.2.8 *oxygenate, n*—a molecule composed solely of carbon, hydrogen, and oxygen. **D4814**

3.2.8.1 *Discussion*—In this standard, the oxygenate of interest is ethanol.

3.2.9 *pHe, n*—a measure of hydrogen ion activity, defined by Test Method D6423. **D6423**

3.2.9.1 *Discussion*—The traditional pH measurement of hydrogen ion activity is in an aqueous system but the measurement done in Test Method D6423 is in a nearly anhydrous environment. **D6423**

3.3 *Abbreviations:*

3.3.1 *CCR*—California Code of Regulations

3.3.2 *CFR*—U.S. Code of Federal Regulations

3.3.3 *DFE*—Denatured Fuel Ethanol

3.3.4 *EPA*—The U.S. Environmental Protection Agency

[3] 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.

[4] California regulations are available online at http://government.westlaw.com.

**TABLE 1 Performance Requirements**

| Property | Limit | Method |
|---|---|---|
| Ethanol, % by volume, min | 92.1 | D5501 |
| Methanol, % by volume, max | 0.5 | D5501 |
| Solvent-washed gum content, mg/100 mL, max | 5 | D381 |
| Water, % by volume (% by mass), max | 1.0 (1.26) | D7923, E203, or E1064 |
| Inorganic Chloride, mg/kg (mg/L), max | 6.7 (5) | D7319 or D7328 |
| Copper, mg/kg, max | 0.1 | D1688 |
| Acidity (as acetic acid $CH_3COOH$) mg/kg, (% by mass) [mg/L], max | 70 (0.0070) [56] (Note 2) | D7795 |
| pHe | 6.5 to 9.0 | D6423 |
| Sulfur, mg/kg, max | 30. | D2622, D3120, D5453, or D7039 |
| Existent sulfate, mg/kg, max | 4 | D7318, D7319, or D7328 |

3.3.5 *IRS*—U.S. Internal Revenue Service

3.3.6 *RBOB*—reformulated blendstock for oxygenate blending

3.3.7 *RIN*—Renewable Identification Number

3.3.8 *TTB*—The Alcohol and Tobacco Tax and Trade Bureau of the U.S Department of Treasury

## 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.

NOTE 2—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.

4.3 For purposes of determining conformance with the specified limits in Table 1, an observed value or a calculated value shall be rounded "to the nearest unit" in the last righthand digit used in expressing the specification limit, in accordance with the rounding method of Practice E29, unless otherwise specified.

## 5. Denaturant and Regulatory Information

5.1 *General Requirements*—This specification provides general information for the denaturants to be used in denatured fuel ethanol and the concentration of denaturant to be added. Jurisdictions may vary in their regulatory requirements for the allowable or prohibited types of denaturants, chemical composition of the denaturant or concentration of denaturant needed to denature the ethanol.

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.

5.1.1.1 This specification is specific to denatured fuel ethanol as a blendstock in 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 The natural gasoline, gasoline blendstock, or unleaded gasoline used as denaturant should not contain materials at concentrations that can separate from solution at the expected temperatures of blending, storage, and use. If drag reducing agent (additive) (DRA) is used in the distribution system, it should not be present in the product delivered to be used as a denaturant at a concentration or shear condition that can separate from the denatured fuel ethanol under those conditions.

5.1.3 *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 some 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.

5.1.4 *Denaturant Level*—A buyer may ask the denaturer to denature within a specific range (for example, 1.96 % to 2.5 % by 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 shall be based on the information from the original denaturer. The maximum concentration of denaturant allowed in this specification is 5 % by volume.

5.2 *Regulatory Information for Denaturants and Denatured Fuel Ethanol:*

5.2.1 Users of this specification are advised to consult with the applicable regulatory agency for specific requirements for denaturants (types, composition, and amounts) and denatured fuel ethanol in their jurisdictions. The requirements can be covered by regulations specific to a jurisdiction or by multiple regulations due to overlapping jurisdictions. Appendixes have been developed to provide information for several jurisdictions describing the requirements within the designated jurisdiction:

5.2.1.1 Appendix X2, Regulatory Requirements for California.

5.2.1.2 Appendix X3, Regulatory Requirements for the United States.

## 6. Workmanship

6.1 At the point of custody transfer, the denatured fuel ethanol shall be visually free of sediment, suspended, or undissolved matter. It shall be clear and bright at the product temperature at the point of custody transfer or at a lower temperature agreed upon by the purchaser and seller.

NOTE 3—Fuel components should be resistant to phase separation or undissolved matter at the lowest temperatures to which it is likely to be subjected, dependent on the time and place of its intended use. See Specification D4814 Table X8.1 for guidance.

NOTE 4—Solubility is temperature dependent. As this fuel component cools, some high molecular weight additives can become insoluble.

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. Test Method D7757 is a procedure for determining silicon 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 5—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 D7923, E203, or E1064.

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

8.4 *Acidity*—Test Method D7795.

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$^{\varepsilon1}$, 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.

## 9. Keywords

9.1 acidity; automotive spark-ignition engine fuel; base gasoline; chloride ion; copper; corrosion inhibitors; denaturants; denatured fuel ethanol; ethanol; fuel; fuel ethanol; gasoline; gasoline-ethanol blend; oxygenate; solvent-washed gum content; sulfate ion; sulfur; water

## APPENDIXES

**(Nonmandatory Information)**

## X1. SIGNIFICANCE OF SPECIFIED PROPERTIES

### X1.1 Denatured Fuel Alcohol

X1.1.1 *Water*—Karl Fischer analysis is generally the only consistently reliable procedure for the determination of water in denatured ethanol. Test Method E203 describes the modifications required to run the test in the presence of alcohols. Relative density or specific gravity is needed to convert the Karl Fischer water determination from E203 and E1064 from a percent by mass to a percent by volume. Methods D1298 and D4052 are recommended for determination of relative density.

X1.1.1.1 Methods and tables exist to determine the water content of ethanol/water mixtures based on the specific gravity of the mixture. These methods do not work for water determination after the denaturant has been added.

X1.1.1.2 Blends of denatured fuel ethanol and gasoline or similar hydrocarbons have a limited solvency for water. This solvency will vary with the ethanol content, the temperature of the blend, and the aromatic content of the base gasoline. A fuel made by blending 10 % by volume denatured fuel ethanol with a gasoline containing 14 % by volume aromatics and 0.6 % by mass dissolved water (about 0.5 % by volume), will separate into a lower alcohol-rich aqueous phase and an upper hydrocarbon phase if cooled to about 7 °C. As normal spark-ignition engines will not run on the aqueous phase material, such a separation is likely to cause serious operating problems. The phase separation of gasoline-ethanol blends is affected by the total water content of the mixture. This includes the water content from the ethanol and gasoline hydrocarbons blended at the rack and the water adsorbed from the transportation and storage infrastructure for the blended fuel. All water sources should be identified, monitored and controlled to prevent phase separation of the blended fuel. Denatured fuel ethanol is hygroscopic and can pick up water from the atmosphere during long-term storage. Prudent precautions to reduce water exposure and monitor the product should be considered if long term storage is expected.

X1.1.1.3 Test Method D7923 may be used to measure water content in denatured fuel ethanol in concentrations 0.05 % to 5.0 % by mass.

X1.1.2 *Solvent-Washed Gum Content:*

X1.1.2.1 The test for solvent-washed gum content measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, nonvolatile material such as additives, carrier oils used with additives, and diesel fuels. Solvent-washed gum consists of heptane-insoluble gum. The fuel-insoluble portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

X1.1.2.2 Solvent-washed gum can contribute to deposits on the surfaces of carburetors, fuel injectors, and intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum from pure alcohols such as ethanol on malfunctions of modern engines is not known. The test method is used essentially to detect the presence of high boiling, heptane-insoluble impurities.

X1.1.2.3 Because the precision statements for Test Method D381 were developed using only data on hydrocarbons, they are not applicable to denatured fuel ethanol.

X1.1.3 *Chloride Ion*—Low concentrations of chloride ions are corrosive to many metals.

X1.1.4 *Copper*—Copper is a very active catalyst for the low-temperature oxidation of hydrocarbons. Experimental work has shown that copper concentrations higher than 0.012 mg/kg in commercial gasolines can significantly increase the rate of gum formation.

X1.1.5 *Acidity*—Very dilute aqueous solutions of low-molecular weight organic acids such as acetic acid ($CH_3COOH$) are highly corrosive to many metals. It is therefore necessary to keep such acids at a very low level.

X1.1.5.1 The acidity method is intended to determine the concentration of organic acids in ethanol. However, carbon dioxide gas is very soluble in ethanol, and in the presence of available water, a small portion of the gas converts to carbonic acid. In denatured fuel ethanol, the water content is very low and the ethanol molecules will combine with the water leaving very little water available for the carbon dioxide molecule. One