



Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel¹

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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:²

- 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

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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.

- 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, C₉, 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_E 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 ₃ 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

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:³

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 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>.

3.2.3 *ethanol*, *n*—ethyl alcohol, the chemical compound C₂H₅OH.

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.

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 ^A	ASTM	The maximum amount of denaturant allowed by this specification.
Additional United States' Denaturant Regulations		
1.96 min ^A	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 ^{B, C}	EPA ^C	The maximum amount of denaturant the EPA allows in denatured fuel ethanol for determining volumes for RFS2 compliance purposes.

^A For purposes of determining conformance with this limit, the Absolute Method in Practice **E29** should be used.

^B For purposes of determining conformance with this limit, the Rounding Method in Practice **E29** should be used.

^C 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 (70°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. 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 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 CO₂, Test Method **D1613** is an acceptable method. If a sample is known to have dissolved CO₂ or if dissolved CO₂ 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^{e1}, **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; denatur-

ants; 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 mass % to a 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 volume % denatured fuel ethanol with a gasoline containing 14 volume % aromatics and 0.6 mass % dissolved water (about 0.5 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.

X1.1.2 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 mass ppm 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 is very soluble in ethanol, and in the presence of water it converts to carbonic acid. Test Method **D1613** has an option to use either water or alcohol as solvent. Since ethanol is completely soluble in water, water is added to the sample and the mixture is titrated with aqueous sodium hydroxide solution. Dissolved CO_2 converted to carbonic acid will be titrated as an “acid.” The presence of dissolved CO_2 will thus create a high bias in the acidity results. If there is sufficient dissolved CO_2 , Test Method **D1613** can incorrectly indicate that the sample is above the maximum allowed acidity in the specification. In the absence of any dissolved CO_2 , Test Method **D1613** is an acceptable test method. If a sample is known to have dissolved CO_2 or if dissolved CO_2 is expected to be present, Test Method **D7795** is the preferred method. In cases of differing results between the two test methods, Test Method **D7795** shall be the referee method.

X1.1.6 *pHe*—When the pHe of ethanol used as a fuel for automotive spark-ignition engines is below 6.5, fuel pumps can malfunction as a result of film forming between the brushes and commutator, fuel injectors can fail from corrosive wear, and excessive engine cylinder wear can occur. When the pHe is above 9.0, fuel pump plastic parts can fail. The adverse effects are less when ethanol is used at 10 volume % in a blend with gasoline.

X1.1.7 Appearance—Turbidity or evidence of precipitation normally indicates major contamination.

X1.1.8 Ethanol—The ethanol content is important in determining the blend ratios for adding denatured fuel ethanol into the finished gasoline. The ethanol content of denatured fuel ethanol will vary based on levels of denaturant, water and the minor components common to ethanol production.

X1.1.9 Existent Sulfate—The presence of small amounts of inorganic sulfates in denatured fuel ethanol under the right conditions can contribute to turbine meter deposits and the premature plugging of fuel dispensing pump filters in the fuel distribution system. The sulfates also have been shown to cause fuel injector sticking resulting in engine misfiring and poor driveability in automobiles.

X1.1.10 Denaturant—Section 5 discusses the denaturants that are allowed or prohibited and the denaturing levels for product meeting this specification. Denaturant is added in the specified concentration range to comply with TTB and IRS requirements. The content is set by volumetric addition during the denaturing process. Standard analytical methods do not

exist to directly or indirectly determine the denaturant content or acceptability of the denaturant beyond that point.

X1.1.11 Sulfur—The Federal Tier 2 Motor Vehicle and Emissions Standards and Gasoline Sulfur Control Requirements establish sulfur standards for refineries and importers producing reformulated gasoline, Reformulated Blendstock for Oxygenate Blending (RBOB), and conventional gasoline. EPA has established gasoline sulfur content standards for gasoline and denatured fuel ethanol blended into gasoline. Sulfur contaminates the catalytic converter necessary for reducing emissions of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx).

X1.1.12 Methanol—Small amounts of methanol can be produced in the ethanol production process. Methanol at high concentrations can be corrosive to components of the fuel system and has a greater effect on increasing vapor pressure than does ethanol. The limit is set to prevent methanol corrosion and the incremental effect on vapor pressure. The limit is also to prevent methanol from being used as a denaturant.

X2. CALIFORNIA ETHANOL REQUIREMENTS

X2.1 California Ethanol Requirements

X2.1.1 The California Air Resources Board has approved standards for denatured ethanol to be field-blended with California Reformulated Gasoline Blendstock for Oxygenate Blending (CARBOB) to make California Phase 3 Reformulated Gasoline (CaRFG3). Standards also have been specified for the denaturant. These California standards for denatured ethanol and denaturant became effective Dec. 31, 2003 and were amended on Aug. 29, 2008.

X2.1.2 The California standards for denatured ethanol set maximum limits on sulfur, benzene, olefins, and aromatics contents as shown in [Table X2.1](#), and also require the denatured ethanol to comply with the performance requirements in Specification D4806-99.

X2.1.3 California specifies that compliance with the sulfur standard shall be determined by testing the denatured ethanol using Test Method [D5453-93](#). California specifies that compliance with the standards for benzene, olefins, and aromatics contents shall be determined by testing a sample of the denaturant using the test methods specified for CARB gasoline, and then calculating the content of those compounds in the

denatured ethanol, multiplying the test value by 0.0500. However, where it is demonstrated that the denatured ethanol contains less than 5.00 % denaturant, then the test results are multiplied by the decimal fraction representing the percent denaturant.

X2.1.4 California allows an exception to the limits shown in [Table X2.1](#) where the denatured ethanol supplier takes reasonably prudent precautions to ensure the denatured ethanol that exceeds these limits will only be added to a specially designed CARBOB which has been designated to be blended with such denatured ethanol. Documentation is required to support the transfer of denatured ethanol. All CaRFG3 requirements for the final blend shall be met.

X2.1.5 California specifies the standards for the denaturant used in denatured ethanol as shown in [Table X2.2](#). Also shown are the test methods required to determine compliance.

X2.1.6 California standards allow higher amounts of benzene, olefins, and aromatics in the denaturant if the supplier takes necessary precautions to ensure that when added to the ethanol, the level is less than 5.00 volume % and the limits in [Table X2.1](#) are met.

TABLE X2.1 California Denatured Ethanol Standards (In Addition to the Performance Requirements in ASTM D4806-99)

Property	Specification Limit	Test Method
Sulfur, mass ppm, max	10	D5453-93
Benzene, vol % max	0.06	D5580-00 test results of a sample of the denaturant multiplied by 0.0500 (see X2.1.3 for exceptions)
Olefins, vol % max	0.5	D6550-00 (modified) test results of a sample of the denaturant multiplied by 0.0500 (see X2.1.3 for exceptions)
Aromatics, vol % max	1.7	D5580-00 test results of a sample of the denaturant multiplied by 0.0500 (see X2.1.3 for exceptions)

TABLE X2.2 California Denaturant Standards

Property	Specification Limit	Test Method
Benzene, vol % max	1.10	D5580-00
Olefins, vol % max	10.0	D6550-00 (modified)
Aromatics, vol % max	35.0	D5580-00

X3. U. S. EPA REGULATIONS IMPACTING THE DENATURANT CONTENT IN DENATURED FUEL ETHANOL

X3.1 There are two EPA regulations impacting the denaturant concentration in denatured fuel ethanol. In the definition for *Renewable Fuel* (40 CFR § 80.1401) the EPA states “(2) Ethanol covered by this definition shall be denatured as required and defined in 27 CFR parts 19 through 21. Any volume of denaturant added to the undenatured ethanol by a producer or importer in excess of 2 volume percent shall not be included in the volume of ethanol for purposes of determining compliance with the requirements under this subpart.”

X3.2 The EPA also has a procedure to follow when determining compliance with this regulation. Regulation 40 CFR § 80.9, “Rounding a test result for determining conformance with a fuels standard,” states “for purposes of determining compliance with the fuel standards of 40 CFR Part 80, a test result will be rounded to the nearest unit of significant digits specified in the applicable fuel standard in accordance with the rounding method described in the ASTM standard practice, ASTM E29–02^{e1}, entitled, “Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications”. The denaturant concentration in the denatured fuel ethanol is not determined by an analytical test method but is calculated from the metered volumes by the denaturer.

X3.3 The following portions of Practice E29 address the EPA denaturant limit.

6.4 Rounding Procedure—The actual rounding procedure shall be as follows:

6.4.1 When the digit next beyond the last place to be retained is less than 5, retain unchanged the digit in the last place retained.

6.4.2 When the digit next beyond the last place to be retained is greater than 5, increase by 1 the digit in the last place retained.

6.4.3 When the digit next beyond the last place to be retained is 5, and there are no digits beyond this 5, or only zeros, increase by 1 the digit in the last place retained if it is odd, leave the digit unchanged if it is even. Increase by 1 the digit in the last place retained, if there are non-zero digits beyond this 5.

X3.4 For example if the records from the denaturant addition system indicate the denaturant concentration is between 2.5 to 3.4 volume %, then using the rounding method in Practice E29–02^{e1}, the denatured fuel ethanol is deemed to contain 3 volume % denaturant.

SUMMARY OF CHANGES

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D4806 – 13) that may impact the use of this standard. (Approved June 15, 2013.)

(1) Added Test Method D7757 to 2.1 and 6.2.1.

(2) Revised 6.1.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D4806 – 12) that may impact the use of this standard. (Approved May 1, 2013.)

(1) Revised Section 5, including Table 2.

(2) Revised Appendix X3.

has identified the location of selected changes to this standard since the last issue (D4806–11a) that may impact the use of this standard. (Approved Nov. 1, 2012.)

(1) Added Test Method D7795 to Referenced Documents and standard text.

(2) Added 8.4.1 and X1.1.5.1 to describe the interference caused by CO₂ in the measurement of acidity and that Test

Method D7795 is the preferred test method because it overcomes the CO₂ interference.

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