



Designation: D6423 – 19

Standard Test Method for Determination of pHe of Denatured Fuel Ethanol and Ethanol Fuel Blends¹

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1. Scope*

1.1 This test method covers a procedure to determine a measure of the acid strength of high ethanol content fuels. These include denatured fuel ethanol and ethanol fuel blends. The test method is applicable to denatured fuel ethanol and ethanol fuel blends containing ethanol at 51 % by volume, or more.

1.2 Acid strength as measured in this test method is defined as pHe. A pHe value for alcohol solutions is not comparable to pH values of water solutions.

1.2.1 The value of pHe measured will depend somewhat on the fuel blend, the stirring rate, and the time the electrode is in the fuel.

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

1.3.1 Hydrogen ion activity in water is expressed as pH and hydrogen ion activity in ethanol is expressed as pHe.

1.4 *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

[D1193 Specification for Reagent Water](#)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.A0.02 on Oxygenated Fuels and Components.

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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.

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

[D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel](#)

[D5798 Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines](#)

3. Terminology

3.1 For general terminology, refer to Terminology [D4175](#).

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. **D4806**

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. **D4806**

3.2.3 *ethanol, n*—ethyl alcohol, the chemical compound, $\text{CH}_3\text{CH}_2\text{OH}$. **D4806**

3.2.4 *ethanol fuel blend, n*—a blend of ethanol and hydrocarbons for use in flexible-fuel automotive spark-ignition engines of which the ethanol portion is 51 % to 83 % by volume. **D5798**

3.2.5 *flexible-fuel vehicle, n*—a vehicle designed to operate on both gasoline or ethanol fuel blends and can operate on any mixture of both. **D5798**

3.2.5.1 *Discussion*—In the United States, these vehicles have U.S. EPA emissions certifications using gasoline complying with U.S. EPA requirements and ethanol fuel blends that meet the requirements of Specification [D5798](#).

3.2.5.2 *Discussion*—Flex-fuel vehicle and FFV are commonly used synonyms for flexible-fuel vehicle.

3.2.5.3 *Discussion*—The fuels may also contain anti-oxidants, corrosion inhibitors, metal deactivators, and dyes but

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

do not contain lead additives. A jurisdiction may set limits on lead content from all sources.

3.2.6 *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. **D4806**

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

3.2.7 *hydrocarbon, n*—a compound composed solely of hydrogen and carbon. **D5798**

3.2.8 *pHe, n*—a measure of the acid strength, defined by Test Method D6423, of ethanol-hydrocarbon blends.

3.2.8.1 *Discussion*—This measurement is sometimes thought to be analogous to the traditional pH measurement of hydrogen ion activity in aqueous systems, but the measurements done in Test Method D6423 are in a nearly anhydrous environment.

4. Summary of Test Method

4.1 The sample is analyzed at room temperature using a specified electrode system and a pH meter with an input impedance $>10^{12} \Omega$ (ohms). Meters designed for use with ion-specific electrodes normally meet this criteria.

4.2 Readings are taken at exactly 30 s because the meter reading will change throughout the analysis due to glass-electrode voltage drift caused by dehydration of the glass-electrode membrane. Because alcohol dehydrates the glass-electrode membrane, time spent soaking in alcohol solution should be minimized.

4.3 The electrode is soaked in water-based pH 7 buffer between readings to prepare it for the next sample. This rehydrates the glass electrode, a necessary step to preserve the electrode's response characteristics.

4.4 The electrodes are cleaned/rehydrated at least every ten samples by alternately soaking several times in 1 mol/L NaOH solution and 1 mol/L H₂SO₄ (or 1 mol/L HCl) for about 30 s each. New electrodes are treated by this procedure before first use.

5. Significance and Use

5.1 The acid strength, as measured by pHe, is a good predictor of the corrosion potential of ethanol fuels. It is preferable to total acidity because total acidity does not measure acid strength; overestimates the contribution of weak acids, such as carbonic acid; and can underestimate the corrosion potential of low concentrations of strong acids, such as sulfuric acid.

6. Apparatus

6.1 *pH meter*—As recommended for use with ion-specific electrodes, commercially available pH meters with an input of $>10^{12} \Omega$ are acceptable for this test method. Temperature compensation and readability to 0.01 pH unit are recommended.

6.2 *Electrode*—ORION Ross Sure-Flow combination electrode³ or Metrohm ETOH-Trode⁴ with a glass body shall be used. (See Note 1.) Because the measurement is (of necessity) not made at equilibrium, it is essential that this exact electrode pair be used to ensure the reproducibility of results. Critical features of this electrode include a high leak-rate sleeve-junction reference electrode and a large membrane glass measuring electrode. High leak-rate reference electrodes minimize salt-bridge junction potential drift, especially in extremely low conductivity solutions like fuel alcohols. For similar reasons, large membrane glass electrodes (measuring electrodes) were found to perform better and have longer life in alcohol fuels. Since this is a method-based parameter, other electrodes (even those of similar design) will likely give different results under some or all conditions due to the use of a different size or type of glass membrane for the pH electrode, a different type of salt bridge junction, or other small differences, which may affect their nonequilibrium response.

NOTE 1—This equipment, as listed in RR:D02-1796, was used to develop the precision statement and no statistically significant differences were found between these pieces of equipment: ORION Ross Sure-Flow combination electrode³ and Metrohm ETOH-Trode.⁴ This listing is not an endorsement or certification by ASTM International.

6.3 *Reference Electrode Filling Solution*—Although some references suggest alcoholic filling solutions for measurements in alcohol, this test method was developed using an aqueous KCl filling solution and aqueous buffer calibration solutions. The effect of alcoholic filling solution was not investigated.

6.4 *Temperature Compensator*—The thermocompensator is a temperature-sensitive resistance element immersed in the sample with the electrodes. The thermocompensator automatically corrects for the change in slope of the glass electrode response (with change in temperature) but does not correct for actual changes in sample pH with temperature. Because temperature compensation corrects only for changes in pH electrode response with temperature, the fuel sample must be at $22 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$.

6.5 *Beakers*, borosilicate glass, 100 mL, graduations are useful to determine sample size. This size beaker ensures a proper vortex with the 60 mL sample. The 100 mL beaker gives sufficient depth to submerge the electrode to the correct level.

6.6 *Magnetic Stirrer*—Any laboratory magnetic stirrer may be used, along with a TFE-fluorocarbon-coated stirring bar 19 mm to 25 mm long.

6.7 *Timer*, capable of measuring seconds.

³ The specified electrode (ORION Cat. No. 8172BNWP) is available from many laboratory supply companies, or from the manufacturer: Thermo Fisher Scientific, 22 Alpha Road, Chelmsford, MA, 01824, USA, 1-978-232-6000, Info.water@thermo.com. For Europe: <https://eu.fishersci.com/eu>. For Asia Pacific: <http://ebiz.thermofisher.com/AsiaPortal>. For Latin America: www.fishersci.com.

⁴ The specified electrode (Metrohm Part # 60269100) is available from the manufacturer: Metrohm AG, Ionenstrasse 9101 Herisau Switzerland. Metrohm USA, 6555 Pelican Creek Circle, Riverview, FL, 33578. Metrohm Pensalab Instrumentação Analítica LTDA, Rua Minerva, 167-Perdizes, São Paulo, SP, Brazil CEP 05007-030. Metrohm Singapore Pte, Ltd., 31 Toh Guan Road East, #06-08 LW Techno Centre, Singapore, 608608.