



Designation: D6423 – 20a

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

This standard is issued under the fixed designation D6423; 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 test method covers a procedure to determine a measure of the hydrogen ion activity 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 Hydrogen ion activity 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

D4814 Specification for 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 *conventional-fuel vehicle, n*—a vehicle designed to operate on spark-ignition engine fuel that complies with Specification D4814. **D5798**

3.2.2 *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**

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

3.2.3 *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**

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

3.2.5 *ethanol fuel blend, n*—an automotive spark-ignition engine fuel composed of hydrocarbon and ethanol blendstocks for flexible-fuel vehicles with ethanol concentrations greater than those used for conventional-fuel vehicles. **D5798**

3.2.5.1 *Discussion*—Ethanol fuel blends are often referred to as Ethanol Flex Fuel or EXX, where XX represents the nominal percentage by volume of denatured fuel ethanol in the finished fuel. **D5798**

3.2.6 *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**

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

3.2.6.1 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**.

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

3.2.6.3 Discussion—The fuels may also contain anti-oxidants, corrosion inhibitors, metal deactivators, and dyes but do not contain lead additives. A jurisdiction may set limits on lead content from all sources.

3.2.7 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**

3.2.7.1 Discussion—The common components do not include denaturant.

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

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

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 H_2SO_4 (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 hydrogen ion activity, 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 activity of the hydrogen ions; 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 $22^\circ\text{C} \pm 2^\circ\text{C}$.

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.

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.

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.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Commercially prepared solutions are acceptable for use.

7.2 *Buffer Solutions*—Commercially available, water-based buffer solutions (pH=4.00 and pH=7.00) are acceptable for the standardization.

7.3 *1 mol/L Hydrochloric Acid (HCl)*—Mix one volume of concentrated (12 mol/L) HCl with eleven volumes of distilled water.

7.4 *3 mol/L Potassium Chloride (KCl)*—The electrode is shipped with this filling solution already prepared.

7.5 *1 mol/L Sodium Hydroxide (NaOH)*—Dissolve 4 g of NaOH pellets in 100 mL of distilled water.

7.6 *1 mol/L Sulfuric Acid (H₂SO₄)*—Mix one volume of concentrated (18 mol/L) H₂SO₄ with 17 volumes of distilled water.

7.7 *Purity of Water*—Unless otherwise indicated, reference to water or distilled water shall be understood to mean reagent water that meets the requirements of either Type I, II, or III of Specification **D1193**.

8. Sample Containers

8.1 Care must be used in sample container selection to avoid reactions that change the pH_e of the sample. Do not use steel, plated steel, or epoxy-coated steel containers or PVC-coated glass bottles for samples. Avoid closures with a paper seal. Fluorinated high-density polyethylene and spun aluminum sample containers with polyethylene or TFE-fluorocarbon closures are acceptable. Glass bottles without an external PVC coating and utilizing TFE-fluorocarbon or polyethylene cap seals are also acceptable.

8.2 Rinse the container with a portion of the ethanol-hydrocarbon blend to be sampled before taking the sample.

9. Standardization of Assembly

9.1 Turn on the pH meter and allow it to warm up thoroughly in accordance with the manufacturer's instructions.

Note the temperature of the sample to be tested. If temperature compensation is to be manual, adjust the temperature dial of the meter to correspond to the temperature of the sample to be tested and allow time for all buffers, solutions, and the electrode to equilibrate thermally.

9.2 Clean/rehydrate the electrode after every ten samples and new electrodes before first use by alternately soaking four times in 1 mol/L NaOH solution and 1 mol/L H₂SO₄ (or 1 mol/L HCl) for about 30 s each. Remove the electrode and rinse it with distilled water into a waste container.

9.3 Calibrate the pH meter to pH=7.00 with a water-based pH=7.00 buffer solution. Remove the electrode and rinse it with distilled water into a waste container.

9.4 Calibrate the pH meter to pH=4.00 with a water-based pH=4.00 buffer solution, using the *slope* adjustment. The slope shall be in the 95 % to 100 % range, or the electrode will have to be cleaned or replaced. Remove the electrode and rinse it with distilled water into a waste container. Return the electrode to the pH=7.00 buffer, and if the measured pH is not between 6.90 and 7.10 then return to subsection **9.2**.

10. Procedure

10.1 Make sure sample is at 22 °C ± 2 °C.

10.2 Fill the electrode as needed with 3 mol/L aqueous KCl solution, supplied with the electrode.

10.3 Standardize the assembly with two reference buffer solutions, as described in **9.3** and **9.4**.

10.4 Start with a new aliquot (fresh portion) of ethanol-hydrocarbon blend sample for each measurement. Since many ethanol-hydrocarbon blend samples are poorly buffered and have low ionic strength, it is important to use a new aliquot for each measurement for best accuracy.

10.5 Place about 60 mL of sample in a 100 mL beaker containing an appropriately sized magnetic stirring bar and either a thermometer or an ATC probe to ensure the sample is at 22 °C ± 2 °C.

10.6 Remove the electrode from the pH=7.00 buffer, and rinse the electrode with distilled water into a waste container.

10.7 Blot the electrode to remove excess water.

10.8 Insert the electrode into the stirred ethanol-hydrocarbon blend sample at the proper depth to ensure an accurate reading (some probes have an etch line that shall be submerged in the sample), start the timer, and measure the pH_e at exactly 30 s ± 1 s. Stirring shall be rapid enough to cause a small to moderate vortex 6 mm to 8 mm deep. Note that the reading will still be changing slowly at 30 s due to dehydration of the glass pH electrode, which causes a shift in its output. If the reading is not rising at the 30 s point for low pH_e ethanol-hydrocarbon blend (pH_e<5), or gives poor repeatability in some solutions (those with low buffering capacity), the electrode probably needs to be cleaned or replaced.

10.9 Remove the electrode from the sample and rinse it with distilled water into a waste container. Return the electrode to the pH=7.00 buffer to rehydrate the glass pH electrode.

⁵ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

10.10 Soak the electrode in the buffer for 30 s, or more if required, to get the reading to fall between 6.90 and 7.10. Recalibrate to pH=7.00 if the pH is outside of the range of 6.90 to 7.10 after 5 min (return to 9.2).

10.11 Clean/rehydrate the electrode as described in 9.2 after ten alcohol samples have been measured. The electrode can give poor repeatability or high results (in alcohols) if not periodically cleaned/rehydrated in acid and base before use.

10.12 Start with 10.4 for the next sample.

11. Report

11.1 Report the pHe to the nearest 0.1 pHe for the sample, and reference this test method.

12. Precision and Bias

12.1 *Precision*—The precision of this test method as determined by statistical examination of the interlaboratory test results.⁶

NOTE 2—The ILS was conducted in the spring of 2014. It used 16 laboratories drawn from several industries. It looked at the effects of 50 %, 65 %, 80 %, and 98 % by volume ethanol, the effects of two different electrodes, and three levels of acidity; neutral, treated with H₂SO₄ and treated with NaOH. There were two blind replicates for each sample for a total of 384 samples. The ethanol was commercial denatured ethanol containing 2 % by volume natural gasoline and 1 % by volume water. The gasoline was commercial E0 with a TopTier additive treatment. The precision function is derived using samples with averages ranging from 6.4 to 9.5.

12.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1796. Contact ASTM Customer Service at service@astm.org.

apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed the following value in only one case in twenty:

$$\text{Repeatability} = 0.3963 (10.2301 - X)^{0.1584} \text{ pHe}$$

where:

X = the pHe value determined by following this test method.

For example, at a pHe level of 6.5, repeatability is $0.3963 (10.2301 - 6.5)^{0.1584} = 0.5$.

12.1.2 *Reproducibility*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed the following value in only one case in twenty:

$$\text{Reproducibility} = 0.9078 (10.2301 - X)^{0.1584} \text{ pHe}$$

where:

X = the pHe value determined by following this test method.

For example, at a pHe level of 6.5, repeatability is $0.9078 (10.2301 - 6.5)^{0.1584} = 1.1$.

12.2 *Bias*—Since there is no material having an accepted reference value for pHe, bias cannot be determined.

13. Keywords

13.1 automotive spark ignition engine fuel; corrosion potential; denatured fuel ethanol; ethanol; ethanol fuel blends; ethanol-hydrocarbon blends; fuel ethanol; hydrogen ion activity; pHe

SUMMARY OF CHANGES

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D6423 – 20) that may impact the use of this standard. (Approved July 1, 2020.)

(1) Revised definition for ethanol fuel blend and added discussion in subsection 3.2.5.

(2) Added definition for conventional-fuel vehicle in subsection 3.2.1.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D6423 – 19) that may impact the use of this standard. (Approved May 1, 2020.)

(1) Revised subsections 1.1, 1.2, 5.1, and 13.

(2) Revised definition of pHe in 3.2.9.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D6423 – 18) that may impact the use of this standard. (Approved July 1, 2019.)

(1) Revised subsection 3.2.9, moving it from *Definitions Specific to This Standard* to *Definitions*.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D6423 – 14) that may impact the use of this standard. (Approved Dec. 1, 2018.)

(1) Revised subsections **3.2.4**, **3.2.6**, and **3.2.7**.

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