Designation: D6423 − 14

Standard Test Method for Determination of pHe of Denatured Fuel Ethanol and Ethanol Fuel Blends[1]

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D4175 Terminology Relating to Petroleum, Petroleum Products, 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, C_2H_5OH.

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 either unleaded gasoline or ethanol fuel blends or mixtures of both. **D5798**

3.2.6 *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. **D4806**

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

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *pHe, n*—a measure of the acid strength of ethanol-hydrocarbon blends defined by this apparatus and procedure.

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

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[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.

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

impedance >10^{12} Ω (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 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} Ω 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 electrode[3] or Metrohm ETOH-Trode[4] 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 electrode[3] 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 °C ± 2 °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.

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.

[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.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. 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.