



Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)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 ethanol, denatured fuel ethanol, and fuel ethanol (Ed75-Ed85). The test method is applicable to fuels containing nominally 70 volume % ethanol, or higher, as described in Specifications **D4806** and **D5798**.

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. For example, a 1.5×10^{-5} M (18 ppm) solution of H_2SO_4 gives a pH of about 5.5 in water solution, but, depending on buffering strength, a pHe as low as 1 to 2 in unadditized alcohol fuel.

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

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

1.5 *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

D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel

D5798 Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A0.01 on Gasoline and Gasoline-Oxygenate Blends.

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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.

3. Terminology

3.1 Definitions:

3.1.1 *denaturants, n*—natural gasoline, gasoline components, unleaded gasoline, or toxic or noxious materials added to fuel ethanol to make it unsuitable for beverage use but not unsuitable for automotive fuel use.

3.1.2 *denatured fuel ethanol, n*—fuel ethanol made unfit for beverage use by the addition of denaturants.

3.1.3 *ethanol, n*—ethyl alcohol, the chemical compound, C_2H_5OH .

3.1.4 *fuel ethanol (Ed75-Ed85), n*—a blend of ethanol and hydrocarbons of which the ethanol portion is nominally 75 to 85 volume % denatured ethanol.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *pHe, n*—a measure of the acid strength of alcohol fuels 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 impedance $>10^{12}$ 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 M NaOH solution and 1 M H_2SO_4 (or 1 M 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

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

measure acid strength; overestimates the contribution of weak acids, such as carbonic acid; and may 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 $>10^{12}$ ohms 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 with a glass body shall be used. 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.

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 $22 \pm 2^\circ\text{C}$.

6.5 *Beakers*, borosilicate glass, 100 mL.

6.6 *Magnetic Stirrer*—Any laboratory magnetic stirrer can be used, along with a TFE-fluorocarbon-coated stirring bar approximately 19 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.⁴ 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.

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 M Hydrochloric Acid (HCl)*—Mix one volume of concentrated (12 M) HCl with eleven volumes of distilled water.

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

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

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

8. Sample Containers

8.1 Care must be used in sample container selection to avoid reactions that change the pH 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 fuel 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 several times in 1 M NaOH solution and 1 M H₂SO₄ (or 1 M HCl) for about 30 s each. Remove the electrode and rinse it well 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 must 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.

³ The specified electrode (ORION Cat. No. 8172BN) is available from many laboratory supply companies or from the manufacturer: Orion Research Incorporated, Laboratory Products Group, The Schrafft Center, 529 Main Street, Boston, MA 02129.

⁴ *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.

10. Procedure

10.1 Fill the electrode as needed with 3M aqueous KCl solution, supplied with the electrode.

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

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

10.4 Place about 50 mL of sample in a 100-mL beaker containing a magnetic stirring bar and either a thermometer or an ATC probe to ensure the sample is at $22 \pm 2^\circ\text{C}$.

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

10.6 Blot the electrode to remove excess water.

10.7 Insert the electrode into the room-temperature stirred ethanol sample, start the timer, and measure the pHe at exactly 30 ± 1 s. Stirring must be rapid enough to cause a small to moderate vortex about 6 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 pHe fuels ($\text{pHe} < 5$), or gives poor repeatability in some solutions (those with low buffering capacity), the electrode probably needs to be cleaned or replaced.

10.8 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.

10.9 Soak the electrode in the buffer until the reading falls below 7.05, but soak for at least 20 s. Recalibrate to pH=7.00 if the pH is still above 7.05 after 5 min.

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

10.11 Start with 10.3 for the next sample.

11. Precision and Bias

11.1 *Precision*—The precision of this test method as determined by statistical examination of the interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same 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 0.29 pHe in only one case in twenty.

11.1.2 *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 0.52 pHe in only one case in twenty.

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

12. Keywords

12.1 acid strength; automotive spark ignition engine fuel; corrosion potential; denatured fuel ethanol; ethanol; fuel ethanol; pHe

SUMMARY OF CHANGES

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D6423–99(2004)) that may impact the use of this standard.

(1) Revised to add an example showing the difference between pHe and PH.

(2) Revised to clarify instructions.

(3) Revised to provide background for procedural details.

(4) Revised to better describe electrode and meter requirements.

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