



Designation: E3334 – 22

# Standard Test Method for Acidity in Ethanol and Ethanol Solutions<sup>1</sup>

This standard is issued under the fixed designation E3334; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of acidity as acetic acid in ethanol and ethanol solutions. This test method may be applied to ethanol samples containing very little water (dehydrated alcohols) to solutions with significant water (low proof ethanol samples). The solutions include denatured alcohols such as the U.S. denatured ethanol formulas defined in 27.CFR.Part 21. This test method is used for determining low levels of acidity, below 200 mg/kg (ppm mass), with the exclusion of carbon dioxide.

1.1.1 *Procedure A*—Developed specifically for measurement of acidity by potentiometric titration. This is the referee method.

1.1.2 *Procedure B*—Developed specifically for measurement of acidity by color end point titration.

1.2 The ethanol may be analyzed directly by this test method with minimal sample preparation.

1.3 Review the current and appropriate Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions and proper personal protective equipment.

1.4 *Units*—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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Some specific hazards statements are given in Section 7 on Hazards.*

1.6 *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.*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E48 on Bioenergy and Industrial Chemicals from Biomass and is the direct responsibility of Subcommittee E48.A0 on Product Specifications.

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## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

D770 Specification for Isopropyl Alcohol

D1193 Specification for Reagent Water

D7795 Test Method for Acidity in Ethanol and Ethanol Blends by Titration

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

2.2 *U.S. Federal Standards*:

United States Code of Federal Regulations, Title 27, Part 21 Formulas for Denatured Alcohol and Rum<sup>3</sup>

United States Pharmacopeia General Chapters Alcohol Determination<sup>4</sup>

## 3. Terminology

3.1 *Definitions*:

3.1.1 *acidity, n*—the quality, state, or degree of being acid.

3.1.1.1 *Discussion*—The amount of acid titrated with a strong base (NaOH or KOH) in a sample, calculated as acetic acid in mg/kg (ppm mass).

3.1.2 *ethanol, n*—ethyl alcohol, the chemical compound C<sub>2</sub>H<sub>5</sub>OH.

3.2 *Abbreviations*:

3.2.1 *KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>*—KHP—Potassium Hydrogen Phthalate

3.2.2 *NaOH*—Sodium Hydroxide

3.2.3 *KOH*—Potassium Hydroxide

## 4. Summary of Test Method

4.1 Samples are purged with nitrogen prior to and during titration for the elimination of carbon dioxide and then a known amount of ethanol sample is analyzed potentiometrically either using a monotonic or dynamic end point titrant addition, as specified in Procedure A, or by color end point titration, as specified in Procedure B, using a strong base (NaOH or KOH) solution. Acid content is calculated as milligrams of acetic acid per kilogram of sample.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from <https://www.ecfr.gov/>.

<sup>4</sup> Available from USP, <https://www.usp.org/>.

## 5. Significance and Use

5.1 This test method measures acidity quantitatively. Very dilute aqueous solutions of low molecular mass organic acids, such as acetic acid, are highly corrosive to many metals.

5.2 Acceptable levels of acidity in ethanol can vary with different specifications, but in general, it is below 200 mg/kg (ppm). Knowledge of the acidity can be required to establish whether the product quality meets specification.

## 6. Interferences

6.1 Basic titrants can absorb carbon dioxide from the air to produce carbonate ions and change the concentration of the titrant. Care should be taken to minimize exposure of basic titrants to the air as much as possible. Verify the concentration of the titrant (standardize the titrant) frequently enough to detect concentration changes of 0.0005 mol/L (M), and especially if prolonged exposure to the air occurs.

6.2 Minimize exposure of the samples to the air during storage to avoid contamination by carbon dioxide. Carbon dioxide is highly soluble in ethanol. As a sample is titrated with a base, the dissolved carbon dioxide can convert to carbonate ions and provide incorrect acidity analysis. The samples are purged with nitrogen prior to and during the analysis to avoid this interference.

## PROCEDURE A—POTENTIOMETRIC TITRATION

## 8. Apparatus

8.1 *Potentiometric Titrator*—Automatic titration systems capable of adding fixed increments of titrant at fixed time intervals (monotonic) or variable titrant increments with electrode stability between increment additions (dynamic) with endpoint seeking capabilities as prescribed in the method. At the very least, the automatic titration system shall meet the performance and specification requirements as warranted by the manufacturer.

8.2 A monotonic or dynamic mode of titrant addition shall be used. During the titration, the speed and volume of the addition may vary depending on the rate of change of the system. The recommended minimum volume increment is 0.05 mL for low acidity samples, and the recommended maximum volume increment is 0.1 mL. A signal drift of 10 mV/min and endpoint recognition set to last is recommended to ensure endpoint detection. When using a monotonic titrant addition, the waiting time between increment additions shall be sufficient to allow for mixing and a stable electrode response. Wait at least 10 s between additions.

8.3 *Buret*, 5 mL capacity, capable of delivering titrant in 0.02 mL or larger increments. The buret tip shall deliver titrant directly into the titration vessel without exposure to the surrounding air. The buret used for base solutions shall have a guard tube containing carbon dioxide absorbent.

8.4 *Titration Stand*, suitable for supporting the electrode, stirrer, and buret tip.

## 7. Hazards

7.1 Each analyst shall be acquainted with the potential hazards of the equipment, reagents, products, solvents, and procedures before beginning laboratory work. Sources of information include: instrument manuals, MSDS, various literature, and other related sources. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents shall comply with all the laws and regulations from all applicable governmental agencies.

7.2 The following hazards are associated with the application of this test method and the use of an automatic titrator.

### 7.2.1 Chemical Hazard:

7.2.1.1 A solution of potassium hydroxide or sodium hydroxide is corrosive and shall be handled with the appropriate personal protective equipment such as gloves, chemical goggles, and lab coat or chemical-resistant apron. Always add the base to water when diluting 50 % NaOH or KOH.

7.2.1.2 Ethanol is a flammable and toxic solvent that is used to prepare the lithium chloride electrolyte solution for the reference electrode. When handling a flammable solvent, work in a well-ventilated area away from all sources of ignition.

8.5 *Sensing Electrode*, standard pH, suitable for non-aqueous titrations.

8.6 *Reference Electrode*—Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1M-3M LiCl in ethanol.

8.7 *Combination pH Electrodes*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. A combination pH electrode designed for nonaqueous titrations of organic solvents is needed for titration of ethanol and ethanol blends. The combination pH electrode shall have a sleeve junction on the reference compartment and shall use an inert ethanol electrolyte, 1 mol/L to 3 mol/L (M) LiCl in ethanol. Combination pH electrodes shall have the same or better response than a dual electrode system. They shall have a movable sleeve for easy rinsing and addition of electrolyte.

8.8 *Titration Beaker*, borosilicate glass or plastic beaker of suitable size for the titration.

8.9 *Sparging System*, a nitrogen gas delivery system suitable to deliver directly into the liquid sample, with an external pressure of 69 kPa (10 psi).

8.10 *Variable-Speed Mechanical Stirrer*, a suitable type, equipped with a propeller-type stirring paddle. The rate of stirring shall be sufficient to produce vigorous agitation without spattering and without stirring air into the solution. A propeller

with blades 6 mm in radius and set at a pitch of 30 to 45° is satisfactory. A magnetic stirrer and stirring bar is also satisfactory.

8.10.1 If an electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in the instrument reading during the course of the titration.

## 9. Reagents and Materials

9.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> Other grades may be used, provided it is pure enough to be used without lessening the accuracy of the determination.

9.1.1 Commercially available solutions may be used in place of laboratory preparations provided the solutions have been certified as being equivalent.

9.1.2 Alternate volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

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

9.2.1 Prepare CO<sub>2</sub> free water by sparging 1 L of water (9.2) with nitrogen (9.8) for no less than 3 min.

9.3 *Potassium Hydrogen Phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), primary standard, dried*—Place 4 g to 5 g of primary standard potassium hydrogen phthalate KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub> of 100 mesh fineness, in a weighing bottle at 120 °C for 2 h. Stopper the container and cool it in a desiccator.

9.4 *Potassium Hydrogen Phthalate (KHP) Solution*—Accurately weigh approximately 1.0 g of dried KHP and record the mass to the nearest ± 0.0001 g and transfer it to a 500 mL Class A volumetric flask swept free of carbon dioxide. Add 200 mL of Type II DI water that is free of carbon dioxide, stopper and swirl gently until it is dissolved. Dilute to 500 mL and mix thoroughly. Express the concentration of KHP in solution as Molarity in moles of KHP per litre of solution. The use of a volumetric flask can be avoided by weighing 1.0 g of dried KHP to the nearest 0.0001 g into a beaker and adding 500 g of Type II carbon dioxide free DI water. Record the total mass of water and KHP to the nearest ±0.01 g and express the concentration of KHP in the solution as mg KHP per gram of solution. Mix thoroughly to dissolve the KHP and store it in a closed container.

9.5 *Sodium Hydroxide, Standard Solution (0.01 N)*—Prepare and standardize a 0.01 N sodium hydroxide (NaOH) solution in accordance with the *Preparation and Standardiza-*

*tion of Solutions, Precision and Bias, and Preparation of 50 % NaOH Solution and of Standard Solutions* sections of Practice E200.

9.5.1 Alternatively, KOH (0.01 N) in isopropyl alcohol solution may be used instead of 0.01 N NaOH.

9.6 *Alcohols*, ethyl or isopropyl.

NOTE 1—Isopropyl alcohol (99 % grade) conforming to Specification D770, or 190 proof ethyl alcohol conforming to formula No. 3A of the U.S. Bureau of Alcohol, Tobacco, and Firearms as defined in Title 27, Code of Federal Regulations Part 21 (or equivalent regulations in other jurisdictions) is suitable for use as the solvent. The use of methyl alcohol is not recommended.

9.7 *Lithium Chloride Electrolyte*—Prepare a 1 mol/L to 3 mol/L (M) solution of lithium chloride (LiCl) in ethanol per the electrode manufacturer's recommendation.

9.8 *Nitrogen*, 99.9 % pure.

9.9 *Commercial Aqueous pH 4 and pH 7 Buffer Solutions*—These solutions shall be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability is provided by the manufacturer.

## 10. Preparation of Apparatus

10.1 Prepare the titrator in accordance with the manufacturer's instructions. Any visible air bubbles in the buret tip shall be eliminated prior to titration since this can lead to errors.

10.2 *Preparation of Electrodes*—When the combination pH electrode contains Ag/AgCl reference with an electrolyte which is not 1 mol/L to 3 mol/L (M) LiCl in ethanol, the electrolyte shall be replaced. Drain the electrolyte from the electrode (vacuum suction), wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve, ensure that there will be a free flow of electrolyte into the system.

10.3 *Maintenance and Storage of Electrodes:*

10.3.1 Follow the manufacturer's instructions for storage and use of the electrode.

10.3.2 Prior to each titration, soak the prepared electrode in water for at least 2 min. Rinse the electrode with deionized water immediately prior to use. The glass membrane needs to be rehydrated after titration of non-aqueous solutions.

10.3.3 When not in use, immerse the lower half of the combination electrode in LiCl electrolyte. Do not allow electrodes to remain immersed in a titrated sample solution for any longer than it is necessary. While the electrodes are not extremely fragile, handle them carefully at all times.

## 11. Calibration and Standardization

11.1 *Calibration of Electrode:*

11.1.1 Select the correct electrode for the analysis (see 10.2).

11.1.2 Verify that the electrode is filled with 1 mol/L to 3 mol/L (M) LiCl in ethanol solution (see 10.2)

<sup>5</sup> Reagent Chemicals, American Chemical Society Specifications, 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.

11.1.3 Prepare the two buffer solutions, pH 7.0 and pH 4.0, by placing approximately 50 mL of each solution in individual 125 mL disposable beakers.

11.1.4 Calibrate the electrode using the two buffer solutions according to the manufacturer's instructions. Immerse the electrode in each buffer solution, adjust the stirring speed so that adequate mixing occurs without forming a vortex and wait for the instrument reading. When the reading is complete, rinse the electrode in high purity water, wipe gently, and repeat the measurements with the other buffer solution. Record the pH value with an accuracy of 0.01 and the temperature with an accuracy of 0.1 °C. The measured pH values should be within  $\pm 0.05$  pH units of the buffer's certified value.

11.1.4.1 Verify that the calibration slope is between 0.95 and 1.02. An ideal pH glass electrode has a slope of 1.00 (100 % of the Nernst slope) and an electrode zero point of 0 mV for pH 7 at 25 °C. In practice, the electrode zero point potential shall be within  $\pm 15$  mV (corresponding to pH 6.75 to 7.25) and the slope shall be  $>0.95$  ( $>56.2$  mV per pH at 25 °C). The electrode zero point and the electrode slope may change as a result of the aging of the glass membrane or contamination of the diaphragm. If the electrode slope falls below 0.95, follow the electrode manufacturer's instructions for electrode maintenance or replace the electrode. The pH electrode shall be calibrated at regular intervals using fresh buffer solutions.

11.1.5 The slope is automatically stored in the titrator.

11.1.6 The slope is not used for sample analysis, but rather, it provides information on the responsiveness of the electrode. An electrode not meeting the stated criteria is not suitable to perform this method.

11.2 *Standardization of the 0.01 mol/L (M) NaOH Titrant:*

11.2.1 Weigh 2 g of the KHP solution and record the mass to the nearest 0.0001 g (or pipet 2 mL of KHP solution using a Class A pipette) into a beaker and add 50 mL  $\pm$  5 mL of CO<sub>2</sub> free water. Place vessel on the magnetic stirrer and titrate the KHP standard with the 0.01 mol/L (M) NaOH. Record the volume of titrant used to neutralize the KHP at the inflection point. This volume of KHP solution may use approximately 2 mL of the 0.01 mol/L (M) NaOH.

11.2.2 Prepare two additional KHP solutions and standardize the titrant as in 11.2.1.

11.2.3 Use the three determinations to calculate the average concentration (molarity) of the NaOH. The average of the titrant molarity determinations shall agree within  $\pm 0.0005$  mol/L (M).

## 12. Procedure—Potentiometric Titration

12.1 Weigh 60 g  $\pm$  5 g to the nearest 0.001 g of ethanol or ethanol blend into a titration beaker and record the mass.

12.2 Prepare the titrator in accordance with the manufacturer's instructions. Immerse the electrode, sparging tip, and buret tip into the sample, taking care such that the reference junction is immersed in the sample. Adjust the stirring speed so that adequate mixing occurs without forming a vortex.

12.3 Sparge the sample with nitrogen at a flow rate of 400 mL/min  $\pm$  20 mL/min for 120 s prior to titration, and continue to sparge throughout the entire analysis

12.4 Record the volume of titrant used to reach the last well defined end point (inflection point).

## PROCEDURE B—COLOR END POINT TITRATION

### 13. Apparatus

13.1 *Buret*, graduated in 0.05 mL subdivisions.

13.2 *Erlenmeyer Flask*, 250 mL capacity.

13.3 *Sparging System*, a nitrogen gas delivery system suitable to deliver the gas directly into the liquid sample, with an external pressure of 69 kPa (10 psi).

### 14. Reagents and Materials

14.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is pure enough to be used without lessening the accuracy of the determination.

14.1.1 Commercially available solutions may be used in place of laboratory preparations, provided the solutions have been certified as being equivalent.

14.1.2 Alternate volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

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

14.1.3.1 Prepare CO<sub>2</sub> free water by sparging 1 L of water (14.1.3) and with nitrogen (14.1.9) for no less than 3 min.

14.1.4 *Potassium Hydrogen Phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), Primary Standard, Dried*—Place 4 g to 5 g of primary standard potassium hydrogen phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) of 100 mesh fineness, in a weighing bottle at 120 °C for 2 h. Stopper the container and cool it in a desiccator.

14.1.5 *Potassium Hydrogen Phthalate (KHP) Solution*—For a volumetric standard, weigh approximately 1.0 g of dried KHP and record the weight to the nearest  $\pm 0.0001$  g and transfer it to a 500 mL Class A volumetric flask swept free of carbon dioxide. Add 200 mL of Type II DI water that is free of carbon dioxide, stopper, and swirl gently until it is dissolved. Dilute to 500 mL and mix thoroughly. Express the concentration of KHP in solution as Molarity in moles of KHP per liter of solution. The use of a volumetric flask can be avoided by