Designation: E3334 – 22

Standard Test Method for Acidity in Ethanol and Ethanol Solutions[1]

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 (ε) 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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[3]

United States Pharmacopeia General Chapters Alcohol Determination[4]

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_2H_5OH.

3.2 *Abbreviations:*

3.2.1 *$KHC_8H_4O_4$*—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.

[1] 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] 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] Available from https://www.ecfr.gov/.

[4] 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.

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.

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.

8.5 *Sensing Electrode,* standard pH, suitable for nonaqueous 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