Designation: D7795 – 15 (Reapproved 2022)ε1

# Standard Test Method for Acidity in Ethanol and Ethanol Blends by Titration[1]

This standard is issued under the fixed designation D7795; 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.

ε[1] NOTE—Editorially updated references in Section 3 and 19.2 in May 2022.

## 1. Scope

1.1 This test method covers the determination of acidity as acetic acid (see Specification D4806) in commonly available grades of denatured ethanol, and ethanol blends with gasoline ranging from E95 to E30. 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 and ethanol blends may be analyzed directly by this test method without any sample preparation.

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

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, 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

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

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

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

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

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

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

3.2 *Abbreviations:*

3.2.1 $KHC_8H_4O_4$—KHP-Potassium Acid Phthalate

## 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 or ethanol blend 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 base

[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 D02.06 on Analysis of Liquid Fuels and Lubricants.

Current edition approved April 1, 2022. Published May 2022. Originally approved in 2012. Last previous edition approved in 2015 as D7795 – 15. DOI: 10.1520/D7795-15R22E01.

[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.

(NaOH) solution. Acid content is calculated as milligrams of acetic acid per kilogram of sample.

## 5. Significance and Use

5.1 This test method measures acidity in ethanol or ethanol blends quantitatively. Denatured fuel ethanol may contain additives such as corrosion inhibitors and detergents as well as contaminants from manufacturing that can affect the acidity of finished ethanol fuel. Very dilute aqueous solutions of low molecular mass organic acids, such as acetic acid, are highly corrosive to many metals. It is important to keep such acids at a very low level.

5.2 Acceptable levels of acidity in ethanol or ethanol blends 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 solutions will absorb carbon dioxide from the air to produce carbonate ions in the titrant 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 ethanol or ethanol blend samples to the air to avoid contamination by carbon dioxide.

## 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 Ethanol or ethanol blend products are intended for industrial use only.

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

7.3.1 *Chemical Hazard:*

7.3.1.1 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.

7.3.1.2 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 such as E30, 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 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 bars is also satisfactory.