Designation: D7795 – 15

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.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D770 Specification for Isopropyl Alcohol

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

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 *acidity, n*—the quality, state, or degree of being acid. **D4175**

3.1.1.1 *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 (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.

[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.

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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**

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 propellertype 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.

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.[3] Other grades may be

[3] *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.

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_2 free water by sparging 1 L of water (9.2) with nitrogen (9.8) for no less than 3 min.

9.3 *Potassium Acid Phthalate ($KHC_8H_4O_4$), primary standard, dried*—Place 4 g to 5 g of primary standard potassium acid phthalate $KHC_8H_4O_4$ 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 Standardization of Solutions, Precision and Bias, Preparation of 50 % of NaOH Solutions and standardizations section 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, refined,* 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 (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).

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 ±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 ±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 ± 5 mL of CO_2 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 ±0.0005 mol/L (M).

12. Procedure—Potentiometric Titration

12.1 Weigh 60 g ± 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 ± 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,* 10 mL, graduated in 0.05 mL subdivisions.

13.2 *Erlenmeyer Flask,* 250 mL capacity.

13.3 *Sparging System,* a gas delivery system suitable to deliver inert 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.[3] 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_2 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 Acid Phthalate ($KHC_8H_4O_4$), primary standard, dried*—Place 4 g to 5 g of primary standard potassium acid phthalate ($KHC_8H_4O_4$) 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 ±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 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.

14.1.6 *Sodium Hydroxide, Standard Solution (0.01* N)—Prepare and standardize a 0.01 *N* sodium hydroxide (NaOH) solution (Note 3) in accordance with the Preparation and Standardization of Solutions, Precision and Bias, Preparation of 50 % of NaOH Solutions and standardizations section of Practice E200.

NOTE 2—Alternatively, KOH (0.01 *N*) in isopropyl alcohol solution may be used instead of (0.01 *N*) NaOH.

14.1.7 *Alcohols, Refined, Ethyl or Isopropyl.*

NOTE 3—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 (or equivalent regulations in other jurisdictions) is suitable for use as the solvent. The use of methyl alcohol is not recommended.

14.1.8 *Phenolphthalein Indicator Solution, (*10 g/L*)*—Dissolve 1 g of phenolphthalein in ethyl or isopropyl alcohol and dilute to 100 mL with alcohol.

14.1.9 *Nitrogen,* 99.9 % *pure.*

15. Standardization

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

15.1.1 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 pipet) into a beaker and add 50 mL ± 5 mL of CO_2 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 using phenolphthalein as end point. This volume of KHP solution may use approximately 2 mL of the 0.01 mol/L (M) NaOH.

15.1.2 Prepare two additional KHP solutions and standardize the titrant as above in 15.1.1.

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

16. Procedure—Color End Point Titration

16.1 Weigh 60 g ± 5 g to the nearest 0.001 g of Ethanol or Ethanol blend into a titration beaker and record the mass.

16.2 Add 1 mL of Phenolphthalein Indicator Solution.

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

16.4 Record the volume of titrant used to reach the first stable pink color, which lasts at least 15 s.

17. Calculation or Interpretation of Results for Procedure A and Procedure B

17.1 Calculation of the KHP concentration and NaOH molarity (mol/L).

17.1.1 *Calculation by Volume:*

$$\text{KHP solution concentration, mol/L} = \frac{\text{mass of KHP, g}}{(204.23) \times (\text{total volume of KHP solution, L})}$$

$$\text{NaOH molarity (mol/L)} = \frac{(\text{2.00 mL KHP solution}) \times (\text{Molarity KHP solution, mol/L})}{\text{NaOH, mL}}$$

17.1.2 *Calculation by Mass:*

$$\text{KHP solution concentration, mg/g} = \frac{(\text{mass of KHP, g}) \times 1000}{(\text{total mass of solution, g})}$$

$$\text{NaOH molarity (mol/L)} = \frac{(\text{mass of KHP, g}) \times (\text{concentration KHP solution, mg/g})}{(204.23) \times \text{NaOH, mL}}$$

17.1.3 *Calculation of Acidity:*

$$\text{Acidity as Acetic Acid in mg/kg (ppm)} = \frac{\text{titrant, mL} \times \text{Molarity of titrant} \times 60050}{\text{Sample mass, g}}$$

where:

Acetic Acid	=	the acidity of the sample as mg/kg (µg/g) acetic acid,
Molarity of Titrant	=	NaOH molarity (mol/L) titrant (approximately 0.01 mol/L (M),
Titrant, mL	=	volume (mL) of titrant used to reach the end point,
Sample Mass	=	Sample size, g, and
60050	=	60.05 g/mol acetic acid ×1000 mg/g.

18. Report

18.1 Report the acidity as acetic acid to the nearest 0.1 mg/kg for the sample, and reference this test method including specifying whether Procedure A or Procedure B was used.

19. Quality Control

19.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is representative of the samples typically analyzed, if possible.

19.1.1 The KHP solution or other suitable material may be used as a check sample. No data is available for the shelf life of the KHP solution.

19.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.[4]

19.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the testing process. Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration or standardization.

19.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC precision should be periodically checked against the precision listed in Precision and Bias, Section 20, of this test method to ensure data quality.

19.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. Because the acidity can vary while the QC sample is in storage, when an out-of-control situation arises, the stability of the QC sample can be a source of the error.

20. Precision and Bias[5]

20.1 The precision of this test method was determined by the statistical evaluation of the interlaboratory test results. The interlaboratory test results evaluated both Procedure A (Potentiometric Titration) and Procedure B (Color End Point Titration; both sets of precision equations are provided, with calculated values in Table 1.

[4] ASTM MNL 7A, *Manual on Presentation of Data Control Chart Analysis*, 7th edition, ASTM International, W. Conshohocken, PA.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1822. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Acidity (mg/kg)

NOTE 1—Where X is the average of two test results. X units = mg/kg Acidity.

Procedure	Repeatability Limit (r)	Reproducibility (R)
Potentiometric Titration	$0.1965 \cdot X^{0.67}$	$0.4796 \cdot X^{0.67}$
Color End Point Titration	$2.5127 \cdot X^{0.4189}$	$3.4181 \cdot X^{0.4189}$

20.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

20.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

20.1.1.2 Repeatability limits are listed in Table 1.

20.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

20.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions that is accepted as plausible due to random causes under normal and correct operation of the test method.

20.1.2.2 Reproducibility limits are listed in Table 1.

20.2 *Bias*—The bias between the two procedures (A and B) was determined in accordance with Practice D6708 and found to be as follows: Procedure B gives results approximately 10 ppm larger than Procedure A on average.

20.3 The precision statement was determined through statistical examination of nine materials with blind duplicates from seven laboratories for each procedure (A and B). The materials consisted of three blends of gasoline with ethanol, E30, E60, and denatured ethanol. These blends were measured pure, and with an addition of a known acetic acid spike of 100 mg/kg (ppm) and 200 mg/kg (ppm).

20.4 Levels of acidity tested ranged from 8.5 mg/kg to 268 mg/kg for potentiometric titration and 10.5 mg/kg to 265 mg/kg for manual titration.

21. Keywords

21.1 acidity; denatured fuel ethanol; E30, E60 acetic acid; E95; ethanol; ethanol blends; potentiometric; titration

APPENDIX

(Nonmandatory Information)

X1. CHECK FOR ELECTRODE PERFORMANCE

X1.1 The kinetic electrode test measures the kinetic response of the electrode. Electrodes can calibrate with acceptable slope and intercept values yet still not have a good enough response for titration. The speed of response and subsequent stability is important for a titration electrode. A manual check is described in the Appendix that can be carried out with a titrator set to read millivolts continuously. The essence of this check is to challenge the electrode coming from rest in a water solution with buffers and measure the potential after 30 s and 60 s. A fast electrode reaches a stable point in less than 30 s and changes little from 30 s to 60 s. Use buffers pH 4 and pH 7 for this check, as needed.

X1.2 Procedure

X1.2.1 Set the titrator to read millivolts continuously. Have provision for stirring the buffer solution at the same speed used for titrations.

X1.2.2 Allow the electrode to stabilize for 1 min in distilled or equivalent deionized water.

X1.2.3 Remove the electrode from the water, and place it in the pH 4 buffer. Start a stopwatch at about the moment when the buffer solution touches the electrode.

X1.2.4 After 30 s, note the potential. After an additional 30 s, note the potential again. The difference between the two potentials is termed the drift.

X1.2.5 Repeat the procedure for pH 7 buffer.

X1.3 Calculate the drift for each of the buffers. The electrode response may be judged as follows:

drift < 1 excellent
1 < drift < 2 good
2 < drift < 3 acceptable
3 < drift < 4 questionable
4 < drift unacceptable

X1.4 The difference between the 60 s potentials for pH 4 buffer and pH 7 buffer should be greater than 162 mV, or 54 mV per pH number. Electrodes with a slope less than 54 mV per pH number are not reliable for titration.

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D7795 – 12) that may impact the use of this standard. (Approved Dec. 15, 2015.)

(1) Revised subsections 11.2.3, 12.3, 15.1.3, and 16.3 with new purge conditions.

(2) Revised Section 20, including updating Table 1.