



Designation: E2679 – 22

Standard Test Method for Acidity in Mono-, Di-, Tri- and Tetraethylene Glycol by Non-Aqueous Potentiometric Titration¹

This standard is issued under the fixed designation E2679; 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 total acidity as acetic acid in commonly available grades of monoethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol using a non-aqueous potentiometric titration. This test method is useful for determining low levels of acidity, below 200 mg/kg.

1.2 The mono-, di-, tri- and tetraethylene glycols can be analyzed directly by this test method without any sample preparation.

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

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.* Specific hazards statements are given in the section on Hazards, Section 9.

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

D1193 Specification for Reagent Water

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³

3. Terminology

3.1 *Definitions:*

3.1.1 *acidity*—the amount of total acid titrated with an aqueous base (KOH or NaOH) in a sample of ethylene glycol. The acidity is calculated as acetic acid in mg/kg.

4. Summary of Test Method

4.1 An aliquot of a mono-, di-, tri- or tetraethylene glycol sample is weighed and titrated potentiometrically with a monotonic or dynamic mode of titrant addition using an aqueous base (NaOH or KOH) solution to determine the acid content in milligrams of acid as acetic acid per kilogram of sample. An ethylene glycol sample can be analyzed directly by this test method without any sample preparation using a combination pH electrode with an inert ethanol electrolyte designed for non-aqueous titrations. The potentiometric titration readings in millivolts are plotted automatically against the respective volumes of the titrating solution and the end point is identified by a well-defined inflection in the resulting curve.

5. Significance and Use

5.1 This test method provides for the quantitative determination of total acidity in ethylene glycols by non-aqueous potentiometric titration. The run time for titration of ethylene glycol samples ranges from 5 to 10 min with no sample preparation required. The length of time for a titration depends

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.14 on Alcohols & Glycols.

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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 The last approved version of this historical standard is referenced on www.astm.org.

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

on the amount of acidity in the sample and the acidity generally increases from monoethylene glycol to the higher glycols like tetraethylene glycol.

5.2 Acceptable levels of acidity in ethylene glycols vary with the manufacturer's specifications but are normally below 200 mg/kg. Knowledge of the acidity in ethylene glycols is required to establish whether the product quality meets specification requirements.

6. Interferences

6.1 Aqueous base solutions, such as the 0.01 mol/L KOH or NaOH titrant, may 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. Verify the concentration of the titrant (standardize the titrant) if prolonged exposure to the air occurs.

6.2 Minimize exposure of the ethylene glycol samples to the air to avoid contamination.

7. Apparatus

7.1 *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. As a minimum, the automatic titration system shall meet the performance and specification requirements as warranted by the manufacturer.

7.1.1 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 0.02 mL for low acidity samples such as polyester grade monoethylene glycol and the recommended maximum volume increment is 0.05 mL. A signal drift of 10 mV/min and endpoint recognition set to greatest is also recommended to ensure endpoint detection. When using a monotonic titrant addition the waiting time between increment additions needs to be sufficient to allow for mixing and electrode response. It is recommended to wait at least 10 s between additions.

7.1.2 *Buret*, 5 mL capacity, capable of delivering titrant in 0.02 mL or larger increments. The buret tip should be able to deliver titrant directly into the titration vessel without exposure to the surrounding air. It is recommended that the buret used for aqueous base solutions should have a guard tube containing a carbon dioxide absorbing substance.

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

7.2 *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 non-aqueous titrations of organic solvents is needed for titration of glycols. The combination pH electrode should have a sleeve junction on the reference compartment and should use an inert ethanol electrolyte, 1–3 mol/L LiCl in ethanol. Combination pH electrodes should have the same or

better response than a dual electrode system. They should have a movable sleeve for easy rinsing and addition of electrolyte.

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

7.4 *Stirrer*, 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.

7.4.1 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.

8. Reagents and Materials

8.1 *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.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.

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

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

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

8.1.4 50 % Potassium Hydroxide, carbonate free (Warning—Causes severe burns.)

8.1.5 50 % Sodium Hydroxide, carbonate free (Warning—Causes severe burns.)

8.1.6 *Potassium Hydrogen Phthalate (KHP) Solution*—Dry 4 to 5 g of KHP at 110 °C in an oven for 2 h. Allow the dried KHP to cool to room temperature in a desiccator before weighing. Weigh approximately 1.0 g of dried KHP and record the weight to the nearest ± 0.0001 g and make up to the mark with water in a 500 mL Class A volumetric flask. Mix thoroughly to dissolve the KHP. Express the concentration of KHP in solution as Molarity in moles of KHP per liter of solution (see 13.1). 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 water. Mix thoroughly to dissolve the KHP. Record the total weight of

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.