Designation: E2679 – 09 (Reapproved 2016)ε1

Standard Test Method for Acidity in Mono-, Di-, Tri- and Tetraethylene Glycol by Non-Aqueous Potentiometric Titration[1]

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.

ε1 NOTE—Minor editorial changes were made in February 2016.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in the section on Hazards, Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.16 on Industrial and Specialty Product Standards.

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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.

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 II or III 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 DI Type II 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 DI Type II water. Mix thoroughly to dissolve the KHP. Record the total weight 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 (see 13.1). The KHP solution should be made fresh before use.

8.1.7 *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 should be obtained from the manufacturer.

[4] *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. (USP), Rockville, MD.

8.1.8 *Potassium Hydroxide (KOH) 0.01 mol/L*—Weigh 1.122 ± 0.02 g of 50 % KOH into a one liter volumetric flask that contains about 200 mL of Type II deionized water that has been degassed to remove dissolved CO_2. Dilute to the one-liter mark with additional deionized water. The KOH solution should be standardized using the KHP solution to determine the titer. The titrant titer should be checked periodically due to absorption of carbon dioxide with use over time. A titrant of sodium hydroxide, 0.01 mol/L NaOH, made from 50 % NaOH may be substituted for KOH.

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

9. Hazards

9.1 Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents and procedures before beginning laboratory work. Sources of information include: operation manuals, SDS, literature, and other related data. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

9.2 Ethylene glycol products are intended for industrial use only. Before handling or using these products, read the current SDS for each product (see 9.1).

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

9.3.1 *Chemical Hazard:*

9.3.1.1 A solution of 50 % potassium hydroxide or sodium hydroxide is corrosive and should be handled in a fume hood with gloves, chemical goggles, and lab coat or chemical-resistant apron. Always add the base to water when diluting 50 % KOH or NaOH.

9.3.1.2 Ethanol is a flammable and toxic solvent that is used to prepare the lithium chloride electrolyte solution for the combination electrode. Be careful when handling a flammable solvent and work in a well-ventilated area away from sources of ignition.

10. Preparation of Apparatus

10.1 Prepare the titrator in accordance with the manufacturer's instructions. Care should be taken to see that there are no air bubbles in the buret tip which might be dispensed during the titration and can lead to errors.

10.2 *Preparation of Electrodes:*

10.2.1 When the combination pH electrode contains a Ag/AgCl reference with an electrolyte which is not 1–3 mol/L LiCl in ethanol, the electrolyte must 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 the LiCl electrolyte solution and fill the reference compartment with the LiCl/ethanol electrolyte.

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 before use. The glass membrane needs to be rehydrated after titration of glycol (non-aqueous) material.

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 for any appreciable period of time between titrations. 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 7.2).

11.1.2 Verify that the electrode is filled with 1–3 mol/L LiCl in ethanol solution (see 7.2).

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 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 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.

11.1.5 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 25ºC. In practice, the electrode zero point potential should be within ±15 mV (corresponding to pH 6.75 to 7.25) and the slope should be >0.95 (>56.2 mV per pH at 25ºC). 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 you should follow the electrode manufacture's instructions for electrode maintenance or replace the electrode. The pH electrode must be calibrated at regular intervals using fresh buffer solutions.

11.1.6 The slope is automatically stored in the titrator.

11.2 *Standardization of the 0.01 mol/L KOH Titrant:*

11.2.1 Weigh 2 g of the KHP solution and record the weight to the nearest 0.0001 g (or pipette 2 mL of KHP solution using a Class A pipette) into a beaker and add approximately 50 mL of CO_2 free water. Place vessel on the magnetic stirrer and titrate the KHP standard with the 0.01 mol/L KOH. Record the volume of titrant used to neutralize the KHP. This volume of KHP solution will use approximately 2 mL of the 0.01 mol/L KOH.

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 KOH. The average of the titrant molarity determinations should agree ±0.0005 mol/L and this average is used to calculate the acidity (see 13.1).

12. Procedure

12.1 Weigh 85 ± 5 g to the nearest 0.001 g of glycol into a titration beaker and record the weight.

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

12.3 Record the volume of titrant used to reach the end point (inflection point) of the sample.

13. Calculation or Interpretation of Results

13.1 *Calculation of the KHP concentration and KOH molarity (mol/L):*

NOTE 1—Formula weight (FW) of KHP is 204.23 g/mol.

13.1.1 *Calculation by Volume:*

$$\text{Molarity (mol/L) of KHP solution} = \frac{(\text{grams of KHP})}{(204.23\ \text{g/mol FW KHP}) \times (\text{volume of KHP solution in liters})} \quad (1)$$

$$\text{Molarity (mol/L) of KOH} = \frac{(2.00\ \text{mL KHP}) \times (\text{Molarity KHP solution})}{(\text{milliliters KOH})} \quad (2)$$

13.1.2 *Calculation by Weight:*

$$\text{Concentration of KHP solution in mg/g} = \frac{(\text{gram KHP}) \times (1000\ \text{mg/g})}{(\text{grams total solution weight})} \quad (3)$$

$$\text{Molarity (mol/L) of KOH} = \frac{(\text{grams KHP solution}) \times (\text{concentration KHP mg/g})}{(204.23\ \text{g/mol FW KHP}) \times (\text{milliliters KOH})} \quad (4)$$

13.2 *Calculation of Acidity:*

$$\text{Acidity as Acetic Acid in mg/kg} = \frac{(\text{mL of titrant}) \times (\text{Molarity of titrant}) \times (60{,}000)}{(\text{Sample weight in grams})} \quad (5)$$

where:

acidity of acetic acid	=	the acidity of the sample as mg/kg acetic acid,
molarity of titrant	=	the molarity (mol/L) of the potassium hydroxide titrant (nominally 0.01 mol/L,
mL of titrant	=	volume (mL) of titrant used to reach the end point of the sample titration,
sample weight	=	grams of sample titrated, and
60,000	=	60.0 g/mol formula weight of acetic acid × 1000 mg/g.

14. Report

14.1 Report the following information:

14.1.1 Report the acidity as acetic acid to the nearest 0.1 mg/kg for the sample.

TABLE 1 Precision for Acidity in Glycols

Glycol ID	Grand Avg (mg/kg)	Standard Deviation (mg/kg)	Degrees of Freedom	95 % Range mg/kg absolute
MEG	1.66	0.100	5	0.280
DEG	1.75	0.114	5	0.319
TEG	33.0	1.370	5	3.836
TTEG	4.71	0.277	5	0.777

15. Quality Control

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

NOTE 2—The KHP solution or other suitable material may be used as a check sample.

15.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.[5]

15.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the testing process.[5] 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.

15.4 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 the Precision and Bias Section of this method to ensure data quality.

15.5 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.

16. Precision and Bias[6]

16.1 *Precision*—The following criteria should be used to judge the acceptability of the results (see Note 3):

16.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value given in Table 1 at the indicated degrees of freedom. The 95 % limit of difference between two such runs is also given in Table 1.

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

[6] It is recommended that the precision and accuracy of the test method be verified if another set of equipment is to be used or the test method is to be used at another location.

16.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The precision of the procedure for measuring acidity is being determined.

16.1.3 *Reproducibility (Multilaboratory)*—The precision of the procedure for measuring acidity is being determined.

NOTE 3—The precision statements are preliminary based on five analyses by one analyst on two days for samples of MEG, DEG, TEG and TTEG containing approximately 1.7 mg/kg, 1.8 mg/kg, 33.0 mg/kg and 4.7 mg/kg acidity as acetic acid respectively. An interlaboratory study is planned for 2009/2010. Practice E180 was used in developing these precision estimates.[7]

TABLE 2 Accuracy for Acidity in Glycols Acidity as Acetic Acid in MEG

Actual Concentration (mg/kg)	Found Concentration (mg/kg)	Average Recovery (%)
6.62	6.04	91.2
11.91	10.90	91.5
27.30	25.67	94.0
51.51	48.72	94.6

16.2 *Bias:*

16.2.1 The bias of this test method was determined by spiking samples of MEG with acetic acid in the 5 to 50 mg/kg range and analyzing the spiked and unspiked samples. The accuracy (recovery) was estimated to be the values given in Table 2 based on the titration curves. The bias depends upon the accuracy of the titration, weighing of the spike and the extent of any interferences.

17. Keywords

17.1 acetic acid; acidity; diethylene glycol; monoethylene glycol; non-aqueous titration; potentiometric; tetraethylene glycol; titration; triethylene glycol

[7] Supporting data have been filed at ASTM Headquarters and may be obtained by requesting Research Report RR:E15-1070.

ANNEX

(Mandatory Information)

A1. TITRATION CURVES

A1.1 *Titration Curves for MEG, DEG, TEG and TTEG*:

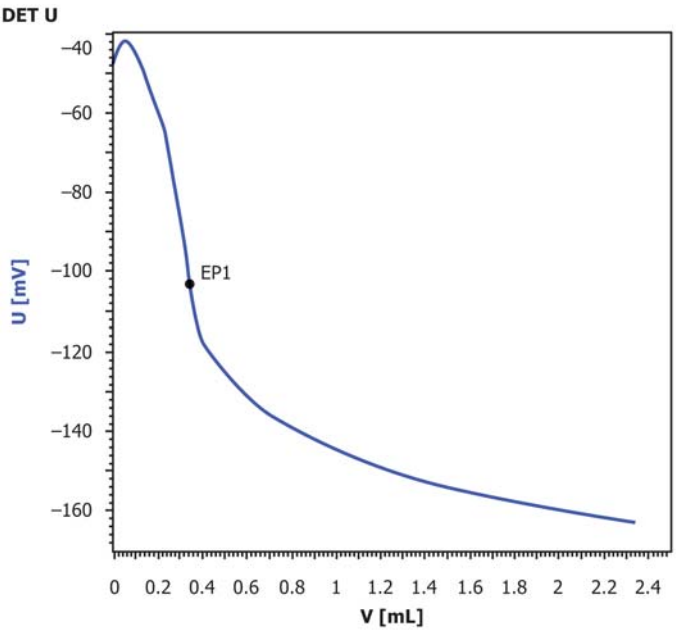

FIG. A1.1 Titration Curve for MEG

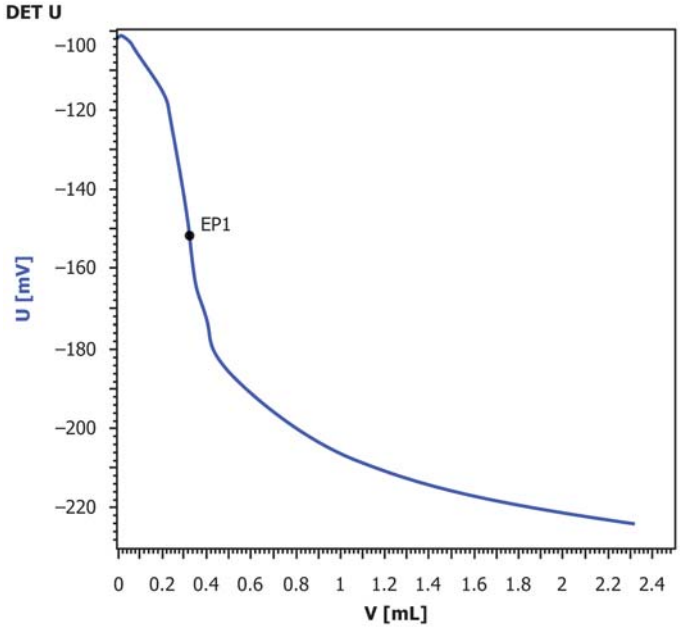

FIG. A1.2 Titration Curve for DEG

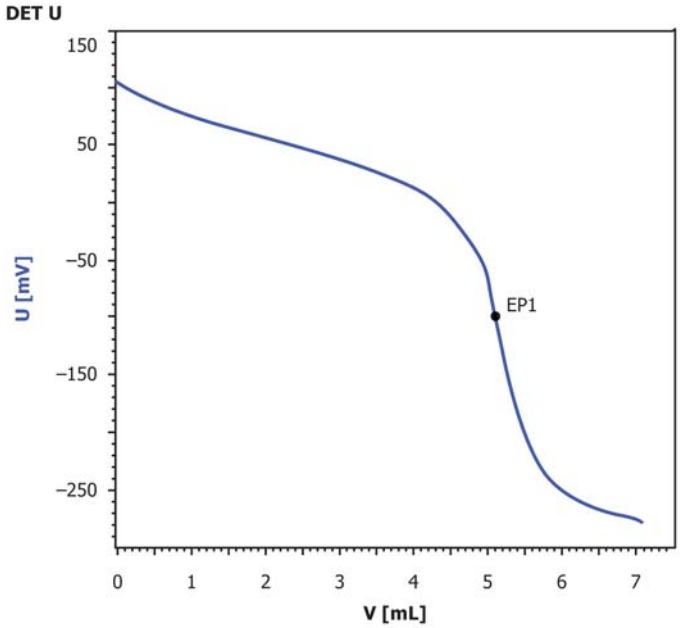

FIG. A1.3 Titration Curve for TEG

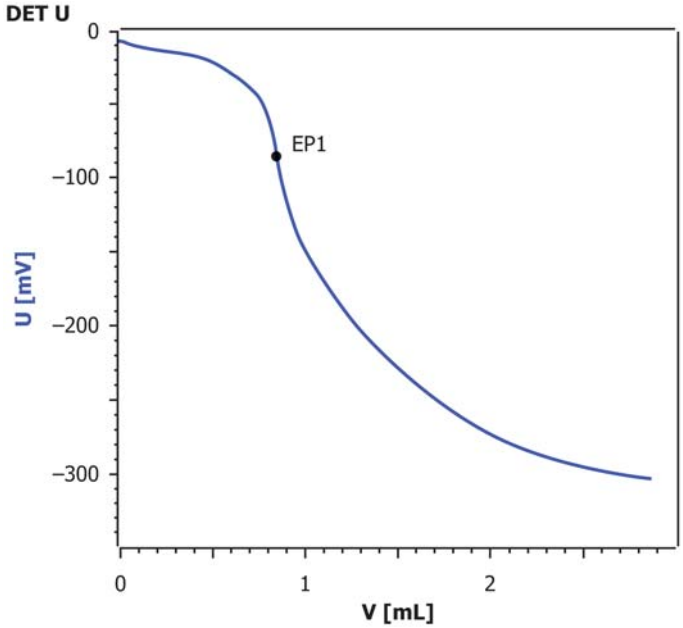

FIG. A1.4 Titration Curve for TTEG

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 response good enough 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.

X1.2 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 and 60 s. A fast electrode reaches a stable point in less than 30 s and changes little from 30 to 60 s. Use buffers pH 4 and pH 7 for this check, as needed.

X1.3 *Procedure*:

X1.3.1 Set the titrator to read millivolts continuously. Have provision for stirring the buffer solution at the same speed used for titrations.

X1.3.2 Allow the electrode to stabilize for 1 min in distilled or equivalent deionized water.

X1.3.3 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.

X1.3.4 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.

X1.3.5 Repeat the procedure for pH 7 buffer.

X1.4 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

X1.5 The difference between the 60 s potentials for pH 4 buffer and pH 7 buffer should be greater than 162 mV, or 54 mV/pH number. Electrodes with a slope less than 54 mV/pH number are not reliable for titration.