



Standard Test Methods for Low Concentrations of Diethylene Glycol in Ethylene Glycol by Gas Chromatography¹

This standard is issued under the fixed designation E611; 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—Editorial change was made in Subsection 1.3 in May 2016.

1. Scope*

1.1 These test methods are intended primarily for the analysis of mixtures of ethylene and diethylene glycols in which the diethylene glycol concentration is 0.1 % or less. Both test methods should be applicable to higher concentrations of diethylene glycol, but precision and bias estimates have been obtained only for 0.05 to 0.1 % diethylene glycol.

NOTE 1—Test Methods E202 describe another gas chromatographic test method applicable to mixtures of ethylene, diethylene, and triethylene glycols and mixtures of propylene, dipropylene, and tripropylene glycols in which one of the glycols is the principal component and the other two are present in concentrations of 0.1 to 1 % each.

NOTE 2—Test Method E2409 describes another gas chromatographic test method for the determination of glycol impurities in mono-, di-, tri- and tetraethylene glycol (MEG, DEG, TEG and TeEG) in the range of 5 to 3000 $\mu\text{g/g}$.

1.2 The two test methods are given as follows:

Test Method A—Nonderivative Method	Sections 5 to 13
Test Method B—Derivative Method	14 to 22

1.3 Review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions for chemicals used in this standard.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard with the exception of foot-pound units for apparatus descriptions.

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.* For a specific warning statement, see 15.1.5.

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

E202 Test Methods for Analysis of Ethylene Glycols and Propylene Glycols

E2409 Test Method for Glycol Impurities in Mono-, Di-, Tri- and Tetraethylene Glycol and in Mono- and Dipropylene Glycol (Gas Chromatographic Method)

2.2 Other Document:

Manufacturers' instruction manuals of gas chromatograph

3. Significance and Use

3.1 Either test method may be used to determine the concentrations of diethylene glycol in ethylene glycol. The concentrations of the components are obtained by a normalization technique, based on the assumption that all components are eluted under the conditions used. If all components should not be eluted, the calculated concentrations will be erroneously high, with the major component showing the most significant absolute error. Since water is not detected by these procedures, the results are on a water-free basis. Water may be determined in accordance with the applicable sections of Test Methods E202 and the gas chromatographic results corrected for the water concentration.

3.2 Both test methods are currently in industrial use. Test Method A is the simpler of the two test methods because it does not require the preparation of derivatives prior to gas chromatographic analysis. The results obtained by Test Method A are slightly more accurate than those obtained by Test Method B. With respect to precision there is no significant difference between the two test methods. Test Method B has been

¹ These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and are 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.

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

reported to be suitable also for the analysis of a wide variety of glycol ethers, but this use is beyond the scope of this standard.

4. Purity of Reagents

4.1 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.

4.2 Unless otherwise indicated, references to water shall be understood to mean Type II or III reagent water conforming to Specification **D1193**.

TEST METHOD A—NONDERIVATIVE METHOD

5. Summary of Test Method

5.1 The sample is injected into a gas chromatographic column. The components are separated as they pass through the column with helium carrier gas, their presence in the effluent is detected by a flame ionization detector, and recorded as a chromatogram. The areas under the peaks due to the sample components are corrected by applying appropriate calibration factors to obtain the composition of the sample on a weight percentage basis.

6. Apparatus

6.1 *Gas Chromatographic Instrument* having the following minimal characteristics (see **Table 1**).

6.1.1 *Sample Injection Port*, with heater characteristics necessary for operation at 210°C.

6.1.2 *Column Oven*, capable of isothermal operation at 168°C.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., 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. Pharmacopial Convention, Inc. (USP), Rockville, MD.

6.1.3 *Detector*, of conventional flame ionization type, capable of operating at 168°C. A conventional thermal conductivity detector can be used, but sensitivity will be reduced and water may be detected as a peak eluting with the pressure peak due to sample injection, depending upon the concentration of water. The precision and bias statements in Section **13** are for flame ionization detectors.

6.1.4 *Recorder*, 0 to 1-mV range, that 1-s full scale deflection with a chart speed of approximately 1.3 cm/min or other convenient speed that will produce a satisfactory chromatogram, and an attenuator switch to change the recorder range as required to keep the chromatogram on scale.

NOTE 3—On instruments using electronic integration the attenuation feature is not required.

6.1.5 *Column*, 50 in. long, $\frac{3}{16}$ in. in outside diameter with a wall thickness of 0.030 in. for copper or 0.020 in. for stainless steel construction; packed with 10 % polyethylene glycol on orange calcinated diatomite with dimethyldichlorosilane, DMCS, 60/80 mesh.

6.1.6 *Microsyringe*, 10- μ L capacity.

6.1.7 *Copper or Stainless Steel Tubing*, $\frac{3}{16}$ in. in outside diameter with a wall thickness of 0.030 in. for copper or 0.020 in. for stainless steel.

NOTE 4—The copper tubing should be sealed, refrigeration grade. If the seal has been broken, clean the copper tubing with an acetone wash and dry with nitrogen before filling. Stainless steel tubing should be pre-washed with successive volumes of 10 % HCl, distilled water, acetone, methylene chloride, and dried with nitrogen.

7. Reagents and Materials

7.1 *Air*, compressed.

7.2 *Orange Calcinated Diatomite with Dimethyldichlorosilane*, 60/80 mesh.

7.3 *Ethylene Glycol and Diethylene Glycol*—See Section **9** for purity requirements.

7.4 *Helium* (He).

7.5 *Hydrogen* (H₂).

7.6 *Methylene Chloride (Dichloromethane)* (CH₂Cl₂).

7.7 *Polyethylene Glycol*, 20 000 molecular weight.

TABLE 1 Instrument Parameters, Method A—Nonderivative

Instrument	Varian Aerograph, Model 204, equipped with flame ionization detectors ^A
Strip-chart recorder	0-1 mV range
Chart speed	$\frac{1}{2}$ in. (12.7 mm)/min
Column	50 in. (1270 mm) of $\frac{3}{16}$ -in. (4.8-mm) outside diameter copper or stainless steel tubing packed with 10 % polyethylene glycol, 20 000 molecular weight, on Chromosorb G, DMCS, 60/80 mesh
Column temperature	168°C
Carrier gas	helium at 100 mL/min
Hydrogen flow rate	40 mL/min
Air flow rate	400 mL/min
Injection port temperature	210°C
Detector block temperature	168°C
Sample size	2 μ L
Injection time	28 s

^A The parameters in this table apply to a Varian Aerograph, Model 204, manufactured by Varian Div., 611 Hansen Way, Palo Alto, CA 94303. Any similar instrument may be used for this method with appropriate modifications of the parameters.

8. Preparation of Chromatographic Column

8.1 Dissolve 20 g of the polyethylene glycol in approximately 200 mL of CH_2Cl_2 with gentle warming to aid solution. Add 180 g of orange calcinated diatomite with dimethyldichlorosilane, DMCS, and sufficient CH_2Cl_2 to form a slurry, and mix well, making certain that all particles are wetted. Evaporate the CH_2Cl_2 by heating gently over a steam bath in a fume hood until the mixture is dry. Frequent stirring of the slurry during the drying operation is necessary to obtain a uniform coating. The use of a vacuum rotary evaporator will shorten the time required for drying.

8.2 Screen the dried packing through a 50-mesh (300- μm screen opening) and an 80-mesh (180- μm screen opening) screen to remove any lumps and fines. Fill a 127-cm section 1.4-cm outside diameter copper or stainless steel tubing with the screened packing retained on the 80-mesh screen. Gently vibrate the tubing during packing to ensure uniform packing. Use borosilicate glass wool for plugs in the ends of the column. Columns packed using vacuum or by blowing the packing into the tubing are generally unsatisfactory.

8.3 Condition the column prior to use by placing the column in the chromatograph in accordance with 10.1, but do not connect the column to the detector. Pass helium through the column at 100 mL/min during the conditioning.

9. Calibration Factors

9.1 In order to obtain the composition of the sample in terms of mass percent, multiply the areas associated with the components by an appropriate calibration factor. These factors are obtained from mixtures of known composition, and should be determined for each apparatus. The calibration factors may be obtained using standards prepared from “hearts cuts” from the distillation of each of the glycols, or from commercial grades of each glycol as described in the following test methods. For highest accuracy, use glycols obtained from “hearts cuts.” Check the calibration factors periodically or whenever there is evidence of a change in the column or instrument.

9.2 Calibration Method 1:

9.2.1 Purify the commercial grade of each glycol needed by careful fractionation in glass at reduced pressure, discarding the first 30 % and retaining the next 30 % as the “hearts cuts.” Analyze these fractions as described in Section 10 to be sure they are free of other homologues of the glycol.

9.2.2 Prepare a standard mixture of these glycols whose composition approximates that of the glycol to be analyzed. The composition of the standard should be known to the nearest 0.001 %. Correct the composition for any water present using the equation in 11.2.4. Determine the water content as described in the applicable section of Test Methods E202.

9.2.3 Obtain at least two chromatograms of the standard mixture as described in Section 10 and calculate the average area percent for each of the glycols present in accordance with 11.2.1. Do not include any areas associated with the pressure peak in calculating the area percentages. Using the weight percentages in the standard mixture and the average area percentages, calculate the factor for diethylene glycol as

described in 11.1.1. Assume a calibration factor of unity for the ethylene glycol in the base ethylene glycol standard mixture.

9.3 Calibration Method 2:

9.3.1 For routine analyses, high-purity, commercial grades of each glycol may be used. If the gas chromatographic analysis as described in Section 10 indicates that the concentration of the ethylene glycol in the diethylene glycol to be added to the base ethylene glycol in the standard mixture does not exceed 0.2 area %, the concentration of the impurity is insignificant at the concentration levels included in the scope of this test method. The base ethylene glycol should contain less than 0.05 area % diethylene glycol.

9.3.2 Prepare a standard mixture of the glycols whose composition approximates that of the glycol to be analyzed. The composition of the standard mixture should be known to the nearest 0.001 %. Correct the composition for any water present using the equation in 11.2.4. Determine the water content as described in the applicable section of Test Methods E202. If the concentrations of the ethylene glycol in the diethylene glycol added to the base ethylene glycol in the standard mixture does not exceed 0.2 area %, the concentration of the impurity is insignificant at the concentration levels included in the scope of this method. The base ethylene glycol should contain less than 0.1 area % diethylene glycol.

9.3.3 Obtain at least two chromatograms of the standard mixture and of the base ethylene glycol in accordance with 10.2 and calculate the average area percent for each of the glycols present in accordance with 11.2.1. Do not include any areas associated with the pressure peak in calculating the area percentages. Using the mass percent of diethylene glycol added to the ethylene glycol and the average area percentages for the glycols calculate the calibration factor for the diethylene glycol in accordance with 11.1.2. Assume the calibration factor of unity for the ethylene glycol in the base ethylene glycol and the standard mixture.

10. Procedure

10.1 Mount the column in the chromatograph, and adjust the operating conditions in accordance with the parameters given in Table 1 (see Note 5). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable base line on the chart at the maximum sensitivity setting to be used.

Note 5—The instrument parameters given in Table 1 were developed for the indicated instrument. The use of other instruments will probably require some adjustment of column temperature, helium flow rate, etc., to achieve retention times similar to those in Table 2. Adjust the parameters so that symmetrical, sharp peaks with satisfactory resolution are obtained. Adjust the hydrogen and air flow rates so that the flame response is sensitive but constant for concentration changes over the 0 to 0.1 % range of diethylene glycol.

10.2 Inject 2 μL of the sample into the injection port of the instrument and leave the needle in the port for at least 28 s.

TABLE 2 Retention Time Data,^A Method A—Nonderivative

Compound	Retention Time, min
Ethylene glycol	2
Diethylene glycol	5

^A Retention times vary from instrument to instrument. Thus, the times listed, measured from the point of injection to the peak maximum, are approximate.