



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

This standard is issued under the fixed designation E 611; 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 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 E 202 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 E 2409 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:

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

1.3 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.

1.4 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions for chemicals used 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 applica-*

bility of regulatory limitations prior to use. For a specific warning statement, see 15.1.5.

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E 202 Test Methods for Analysis of Ethylene Glycols and Propylene Glycols

E 2409 Test Method for Glycol Impurities in Mono-, Di-, Tri- and Tetraethylene Glycol (Gas Chromatographic Method)

2.2 *Other Documents:* 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 E 202 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

¹ These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and are the direct responsibility of Subcommittee E15.01 on General 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.

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

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 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.³ 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 D 1193.

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.

³ *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. Pharmacopeial Convention, Inc. (USPC), 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.

8. Preparation of Chromatographic Column

8.1 Dissolve 20 g of the polyethylene glycol in approximately 200 mL of CH₂Cl₂ with gentle warming to aid solution.

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.

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 E 202.

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 concen-

tration 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 E 202. 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.

NOTE 6—The time the needle should be left in the injection port may vary from instrument to instrument. Leave the needle long enough so that maximum sized peaks are obtained for a fixed volume of sample.

10.3 Obtain a chromatogram of the sample using attenuation settings that allow for maximum peak heights for each

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.

peak without going off scale. Approximate retention times for the glycols are given in Table 2. A typical chromatogram is shown in Fig. 1.

10.4 Repeat 10.3 to obtain a duplicate chromatogram. The area percent of each glycol peak of the chromatograms should agree within approximately 0.01 area %.

10.5 Determine the area under each peak except the pressure peak due to sample injection. If the apparatus does not have an integrator, draw base lines under the peaks and measure the areas.

NOTE 7—The precision and bias statements in Section 13 were developed from data obtained using electronic integration or triangulation. The statements may not apply if other test methods of integration or peak area measurement are used.

11. Calculation

11.1 Calibration Factors:

11.1.1 When “hearts cuts” of glycols are used to prepare the standard mixture, obtain the calibration factor for diethylene glycol as follows:

$$F = \frac{W}{A_{\%}} \quad (1)$$

where:

- F = calibration factor for diethylene glycol,
- W = mass percent of diethylene glycol in standard mixture, and
- $A_{\%}$ = average area percent of diethylene glycol in standard mixture.

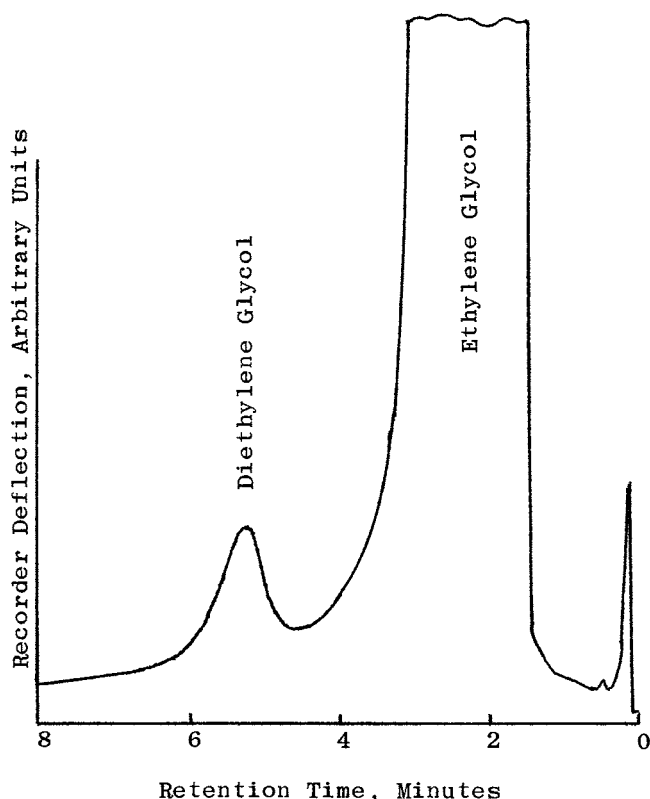


FIG. 1 Typical Chromatogram of Ethylene Glycol Containing 0.07 % Diethylene Glycol, Test Method A (Nonderivative)

11.1.2 When commercial grades of glycols are used to prepare the standard mixture, obtain the calibration factor for diethylene glycol as follows:

$$F = \frac{B}{(A_s - A_b)} \quad (2)$$

where:

- F = calibration factor for diethylene glycol,
- B = mass percent of diethylene glycol added to the standard mixture,
- A_s = average area percent of diethylene glycol in standard mixture, and
- A_b = average area percent of diethylene glycol in the ethylene glycol used to prepare the standard mixture.

The calibration factor for ethylene glycol is assumed to be unity.

11.2 Sample Composition:

11.2.1 Calculate the area percentage of each glycol component as follows:

$$A_{\%i} = \frac{A_i T_i \times 100}{(A_1 T_1) + (A_2 T_2) + (A_m T_m) + \dots} \quad (3)$$

where:

- $A_{\%i}$ = area percent for glycol i ,
- A_1 = area for ethylene glycol,
- A_2 = area for diethylene glycol,
- A_i = area for glycol i ,
- A_m = area for any other impurity,
- T_i = attenuation for glycol i ,
- T_1 = attenuation for ethylene glycol,
- T_2 = attenuation for diethylene glycol, and
- T_m = attenuation for any other impurity.

11.2.2 Calculate the corrected area of each glycol as follows:

$$A_{ci} = A_{\%i} \times F_i \quad (4)$$

where:

- A_{ci} = corrected area for glycol i , and
- F_i = calibration factor for glycol i .

11.2.3 Calculate the mass percent of each glycol on an anhydrous basis as follows:

$$C_i = \frac{A_{ci} \times 100}{A_{c1} + A_{c2} + A_{cm} + \dots} \quad (5)$$

where:

- C_i = mass percent of glycol i , expressed on an anhydrous basis,
- A_{ci} = corrected area for glycol i ,
- A_{c1} = corrected area for ethylene glycol,
- A_{c2} = corrected area for diethylene glycol, and
- A_{cm} = corrected area for any other impurity.

11.2.4 Correct the weight percent of each glycol for water content of the sample as follows:

$$G_i = \frac{C_i (100 - D)}{100} \quad (6)$$

where:

- G_i = mass percent of glycol i , corrected for water content of sample,

- C_i = mass percent of glycol i , expressed on an anhydrous basis, and
- D = mass percent water in the sample as determined by Karl Fischer reagent.

12. Report

12.1 Report the mass percent of each glycol in the sample to the nearest 0.001 %.

13. Precision and Bias

13.1 *Precision*—The following criteria should be used for judging the acceptability of the results (Note 8):

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0028 % absolute at 40 DF. The 95 % limit for the difference between two such runs is 0.008 % absolute.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0029 % absolute at 20 DF. The 95 % limit for the difference between two such averages is 0.008 % absolute.

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0034 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 0.010 % absolute.

13.2 *Bias*—The average recovery obtained for standard samples containing 0.0523, 0.0802, and 0.1003 % diethylene glycol was 99.7 %.

NOTE 8—The precision and bias estimates are based on an interlaboratory study performed in 1975-76 in which three samples of ethylene glycol containing 0.0523, 0.0802, and 0.1003 mass % diethylene glycol were analyzed. Seven laboratories analyzed each sample in duplicate on each of 2 days. The calibration factors for converting area to masspercent were obtained from samples of known composition prepared by each laboratory. Practice E 180 was used in developing these precision estimates.

TEST METHOD B—DERIVATIVE METHOD

14. Summary of Test Method

14.1 The sample is reacted with a silylating reagent to convert the glycols to their corresponding more stable and less

polar trimethylsilyl ethers prior to injection into a gas chromatographic column. The components are separated as they pass through the column with helium carrier gas, and their presence in the effluent is detected and recorded as a chromatogram. The composition of the sample is determined by measuring the areas under the peaks of the chromatogram due to the glycol derivatives. The areas are corrected by applying appropriate calibration factors to obtain the composition of the sample on a weight percentage basis.

15. Apparatus

15.1 *Gas Chromatographic Instrument*, having the following minimal characteristics (see Table 3).

15.1.1 *Sample Injection Port*, with heater characteristics necessary for operation at 250°C.

15.1.2 *Column Oven*, capable of programmed temperature operation between 70 and 300°C at approximately 6°C/min.

15.1.3 *Detector*, of the conventional dual-pass thermal conductivity type, capable of operation at 300°C.

15.1.4 *Recorder*, 0 to 1-mV range, 1-s full scale deflection with a chart speed of approximately ½-in./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 (see Note 3).

15.1.5 *Column*, 3-m long, ⅛ in. in outside diameter with a wall thickness of 0.030 in. for aluminum or 0.020 in. for stainless steel construction; packed with 14.25 % OV-101 and 0.75 % OV-17 on Chromosorb 750, 80/100 mesh. (Warning—Drain, and rinse with water and acetone, drain, and dry with cylinder nitrogen or oil-free air. Nitric acid can cause severe burns; avoid contact with skin and clothing.)

NOTE 9—The use of stainless steel is recommended for a more permanent and leak-free column. If stainless steel tubing is used, it should be cleaned prior to packing. Carefully rinse the tubing with 15 mL of concentrated nitric acid.

15.1.6 *Microsyringes*, 10-μL and 100-μL capacity.

15.1.7 *Syringe*, 1-mL capacity.

15.1.8 *Aluminum or Stainless Steel Tubing*, 0.125 in. in outside diameter, with wall thickness of 0.030 in. (0.76 mm) for aluminum and 0.020 in. (0.51 mm) for stainless steel.

15.1.9 *Glass Vials*, 2-mL capacity, with neoprene closures.

TABLE 3 Instrument Parameters, Method B—Derivative

Instrument	programmed temperature gas chromatograph ^A
Strip-chart recorder	0-1 mV range
Chart speed	½ in. (12.7 mm)/min
Column	3 m of ⅛-in. (3.18 mm) outside diameter aluminum or stainless steel tubing packed with 14.25 % Silicone OV-101 and 0.75 % Silicone OV-17 on Chromosorb 750, 80 to 100 mesh
Column temperature	programmed from 70°C to 300°C at 6°C/min
Carrier gas	helium at 20 mL/min
Detector current	200 ma
Injection port temperature	250°C
Transfer capillary temperature	280°C
Detector block temperature	300°C
Sample volume	3 μL

^A The parameters in this table apply to a Bendix Model 2300 gas chromatograph, manufactured by Bendix Corp., Process Instruments Div., P.O. Drawer 477, Roncverte, W. VA 24970. Any similar instrument may be used for this method with appropriate modifications of the parameters.

16. Reagents and Materials

16.1 *Bis(trimethylsilyl) Trifluoroacetamide (BSTFA)*, silylation reagent.

16.2 *Orange Calcinated Diatomite Support*, 80 to 100 mesh.

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

16.4 *Helium (He)*.

NOTE 10—The suitability of each lot of silylation reagent should be verified by analyzing a standard sample to be sure the reagent will react completely with the glycols under the conditions specified in this method.

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

16.6 *Silicone UV-17*, stationary phase.

16.7 *Silicone UV-101*, stationary phase.

17. Preparation of Chromatographic Column

17.1 Weigh together 14.25 g of the Silicone OV-101 and 0.75 g of the Silicone OV-17. Dissolve this mixture in approximately 100 mL of methylene chloride. Add this solution to 85 g of orange calcinated diatomite support and mix well, making certain that all particles are wetted. If necessary, add additional methylene chloride to obtain a slurry. Evaporate the solvent in a hood under a heat lamp with occasional light stirring. The use of a vacuum rotary evaporator revolving at about 10 rpm is preferred for thorough mixing and more rapid drying.

17.2 Fill a 3-m section of 0.32-cm outside diameter aluminum or stainless steel tubing with packing. Use borosilicate glass wool for plugs in the ends of the tubing. During packing, vibrate the tubing to ensure uniform packing. Approximately 14 mL of the packing should be required to fill the tubing. Columns packed using vacuum or by blowing the packing into the tubing are generally unsatisfactory.

17.3 Condition the column prior to use by placing it in the chromatograph in accordance with 19.2, but do not connect the column to the detector and do not apply current to the filaments. Program the column from ambient temperature to 250°C at approximately 6°C/min and hold for 2 h. Raise the temperature to 300°C and hold overnight. Pass helium through the column at 20 mL/min during the conditioning.

18. Calibration Factors

18.1 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 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.

18.2 Calibration Method 1:

18.2.1 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 19 to be sure they are free from other homologues of the glycol.

18.2.2 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 Eq 6. Determine the water content as described in the applicable section of Test Methods E 202.

18.2.3 Obtain at least two chromatograms of the standard mixture as described in Section 19. Do not include any areas associated with air or the silylating reagent in calculating the area percentages. Using the mass percentages in the standard mixture and the average area percentages, calculate the factor for each glycol as described in Section 20.

18.3 Calibration Method 2:

18.3.1 For routine analyses, high-purity commercial grades of each glycol may be used. If the gas chromatographic analysis as described in Section 19 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 method. The base ethylene glycol should contain less than 0.05 area % diethylene glycol.

18.3.2 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 Eq 6. Determine the water content as described in the applicable section of Test Methods E 202.

18.3.3 Obtain at least two chromatograms of the standard mixture and of the ethylene glycol in accordance with Section 19 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 air or the silylation reagent 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 a calibration factor of unity for the ethylene glycol in the standard mixture.

19. Procedure

19.1 Inject 0.5 mL of BSTFA (silylation reagent) and 60 µL of the sample into a 2-mL vial sealed with a septum, using appropriate syringes. Shake the vial for at least 30 min using a mechanical shaker.

NOTE 11—The formation of a gel in the vial is indicative of an incorrect ratio of sample to BSTFA.

19.2 Mount the column in the chromatograph, and adjust the operating conditions in accordance with the parameters given in Table 3 (see Note 12). 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 12—The instrument parameters given in Table 3 were developed for the indicated instrument. The use of other instruments will probably require some adjustment of column temperature, programming rate, helium flow rate, etc., to achieve retention times similar to those in Table

4. Adjust the parameters so that symmetrical, sharp peaks with satisfactory resolution are obtained.

19.3 Inject 3 μL of the contents of the vial (see 19.1) into the chromatograph by means of a microsyringe, and obtain a chromatogram of the sample using attenuation settings that allow for maximum peak heights for each peak without going off scale. Approximate retention times for the glycols are given in Table 4. A typical chromatogram is shown in Fig. 2.

19.4 Repeat 19.3 to obtain a duplicate chromatogram. The area percent of the diethylene glycol peak of the chromatograms should agree within approximately 0.01 area %.

19.5 Determine the area under each peak except the pressure peak due to sample injection and those due to the silylation reagent. If the apparatus is not equipped with an integrator, draw base lines under the peaks and measure the areas.

NOTE 13—The precision and bias statements in Section 22 were developed from data obtained from six laboratories using electronic integrators and one laboratory using triangulation. The statements may not apply if other methods of integration or peak area measurement are used.

20. Calculation

20.1 Calibration Factors—See 11.1.

20.2 Sample Composition—See 11.2.

21. Report

21.1 Report the mass percent of each glycol in the sample to the nearest 0.001 % mass (m/m).

22. Precision and Bias

22.1 Precision—The following criteria should be used for judging the acceptability of the results (Note 14):

22.1.1 Repeatability (Single Analyst)—The standard deviation for a single determination has been estimated to be 0.0031 % absolute at 42 DF. The 95 % limit for the difference between two such runs is 0.009 % absolute.

22.1.2 Laboratory Precision (Within-Laboratory, Between-Days Variability)—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0034 % absolute at 21 DF. The 95 % limit for the difference between two such averages is 0.010 % absolute.

TABLE 4 Retention Time Data,^a Method B—Derivative

Compound	Retention Time, min
Ethylene glycol	9.2
Diethylene glycol	15.2

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

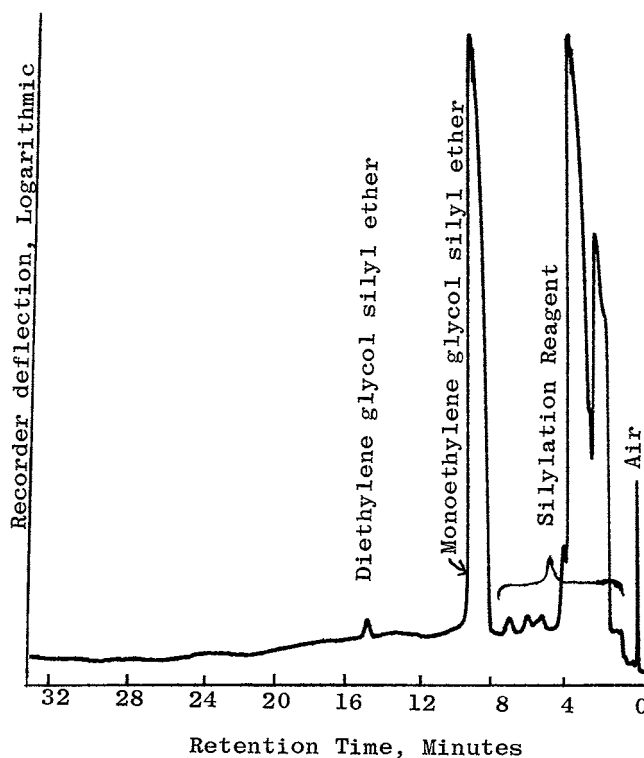


FIG. 2 Typical Chromatogram of Ethylene Glycol Containing 0.05 % Diethylene Glycol, Test Method B (Derivative)

22.1.3 Reproducibility (Multilaboratory)—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0047 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 0.013 % absolute.

22.2 Bias—The average recovery obtained for standard samples containing 0.0523, 0.0802, and 0.1003 % diethylene glycol was 103.0 %.

NOTE 14—The precision and bias estimates are based on an interlaboratory study performed in 1975-76 in which three samples of ethylene glycol containing 0.0523, 0.0802, and 0.1003 % diethylene glycol were analyzed. Seven laboratories analyzed each sample in duplicate on each of 2 days.⁴ The calibration factors for converting area to weight percent were obtained from samples of known composition prepared by each laboratory. Practice E 180 was used in developing these precision estimates.

23. Keywords

23.1 diethylene glycol; ethylene glycol; gas chromatograph

⁴ Supporting data are available from ASTM Headquarters. Request RR: E15-1026.

SUMMARY OF CHANGES

Subcommittee E15.02 has identified the location of selected changes to this standard since the last issue (E 611-03) that may impact the use of this standard.

(1) Updated units of measure to comply with the International System of Units (SI).

(2) Added to Section 1, Scope:

Note 2 and renumbered subsequent notes.

Added numbered paragraph stating that the SI units are to considered standard with the exception of apparatus descrip-

tions.

Added numbered paragraph on review of MSDS.

(3) Added to Section 2, Referenced Documents: E 2409 and Manufacturers' Instruction manuals.

(4) Added Summary of Changes section.

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