Designation: E 202 – 00

# Standard Test Methods for Analysis of Ethylene Glycols and Propylene Glycols[1]

This standard is issued under the fixed designation E 202; 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.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 These test methods cover the chemical and physical analysis of the commonly available grades of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, and dipropylene glycol. The key sections appear in the following order:

| | Sections |
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| Purity of Reagents | 4 |
| Specific Gravity | 5-7 |
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| Acidity | 11-13 |
| Water | 14-16 |
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| Color | 26-28 |
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1.2 Review the current appropriate Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

1.3 *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.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals[2]

D 1078 Test Method for Distillation Range of Volatile Organic Liquids[3]

D 1193 Specification for Reagent Water[4]

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)[3]

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[5]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[2]

E 203 Test Method for Water Using Karl Fischer Reagent[2]

E 394 Test Method for Iron in Trace Quantities Using the 1,10-Phenanthroline Method[2]

E 611 Test Methods for Low Concentrations of Diethylene Glycol in Ethylene Glycol by Gas Chromatography[2]

## 3. Significance and Use

3.1 These test methods measure certain chemical and physical properties of ethylene glycols and propylene glycols and may be used to determine compliance with specification in which limits are established for these properties. For those tests that use the procedure of another ASTM test method, that test method should be consulted for additional information on the significance and use of that test.

## 4. Purity of Reagents

4.1 *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.[6] 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 reagent water conforming to Specification D 1193, Type II or III.

## SPECIFIC GRAVITY

## 5. Procedure

5.1 Determine the specific gravity of the sample at 20/20°C

[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] *Annual Book of ASTM Standards,* Vol 15.05.

[3] *Annual Book of ASTM Standards,* Vol 06.04.

[4] *Annual Book of ASTM Standards,* Vol 11.01.

[5] *Annual Book of ASTM Standards,* Vol 03.05.

[6] *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.

**TABLE 1 Thermometers for Distillation Range**

| Glycol | Thermometer Number | Thermometer Range |
|---|---|---|
| Ethylene glycol | 104C | 173 to 227°C |
| Diethylene glycol | 106C | 223 to 277°C |
| Triethylene glycol | 107C | 248 to 302°C |
| Propylene glycol | 104C | 173 to 227°C |
| Dipropylene glycol | 106C | 223 to 277°C |

using the pycnometer test method in accordance with Test Methods D 891, except determine the water and sample weights of the pycnometer at 20.0 ± 0.1°C.

## 6. Report

6.1 Report the specific gravity at 20/20°C (in air) to the nearest 0.0001 unit.

## 7. Precision and Bias

7.1 The following criteria should be used for judging the acceptability of results (see Note 1):

7.1.1 *Repeatability* (*Single Analyst*)—The standard deviation for a single determination has been estimated to be 0.0000651 unit at 96 dF. The 95 % limit for the difference between two such runs is 0.0002 unit.

7.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0000598 units at 48 df. The 95 % limit for the difference between two such averages is 0.0002 unit.

7.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.000191 unit at 5 dF. The 95 % limit for the difference between two such averages is 0.0005 unit.

NOTE 1—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on six samples of the five glycols whose specific gravity values range from approximately 1.0233 to 1.1255. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each sample on each of two days.[7] Practice E 180 was used in developing these precision estimates.

7.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## DISTILLATION RANGE

## 8. Procedure

8.1 Determine the distillation range of the sample in accordance with Test Method D 1078. Use the conditions as specified in Test Method D 1078, and the ASTM Solvents Distillation Thermometer shown in Table 1 . (See Note 2 for certain allowable exceptions in applying this test method to triethylene glycol.)

NOTE 2—In the distillation of triethylene glycol, it may not be possible to collect the first drop of liquid within 15 min or to maintain the prescribed distillation rate of 4 to 5 mL/min with some sources of gas. In this case, up to 30 min can be allowed to collect the first drop, and a distillation rate of 2 to 3 mL/min is satisfactory. Alternatively, the flask chamber may be covered with a suitable shield so that only the upper neck and thermometer are exposed to room air to achieve the specified rates.

8.2 Use the following values of *K* in the equation for barometric correction (Test Method D 1078):

| Chemical | *K* |
|---|---|
| Ethylene glycol | 0.045 |
| Diethylene glycol | 0.050 |
| Triethylene glycol | 0.055 |
| Propylene glycol | 0.043 |
| Dipropylene glycol | 0.051 |

## 9. Report

9.1 Report the corrected temperatures to the nearest 0.1°C at each volume required by the specification for the glycol being analyzed.

## 10. Precision and Bias

10.1 The following criteria should be used for judging the acceptability of results (Note 3):

10.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value in the table.

10.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

10.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 3—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on eleven samples of the five glycols whose distillation ranges varied from 1.4 to 9.7°C. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each sample on each of two days.[7] Practice E 180 was used in developing these precision estimates.

10.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## ACIDITY

## 11. Procedure

11.1 Determine the acidity of the sample in accordance with Test Method D 1613.

## 12. Report

12.1 Report the acidity, expressed as weight percent of acetic acid, to the nearest 0.0001 %.

## 13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results (see Note 4):

[7] Details of the interlaboratory study are available as Research Report E15-0013 from ASTM Headquarters.

**TABLE 2 Distillation Range Precision Values**

| | Ethylene Glycol Distillation Range | | Diethylene and Triethylene Glycols | Propylene and Dipropylene Glycols |
|---|---|---|---|---|
| | 0 to 5°C/qa | 5 to 15°C | | |
| *Initial boiling point,° C:* | | | | |
| Repeatability | | | | |
| Standard deviation | 0.154 (54[A]) | 0.154 (54) | 0.218 (52) | 0.148 (56) |
| 95 % limit | 0.4 | 0.4 | 0.6 | 0.4 |
| Laboratory Precision (Within Laboratory Between Days) | | | | |
| Standard deviation | 0.173 (27) | 0.173 (27) | 0.119 (23) | 0.0901(28) |
| 95 % limit | 0.5 | 0.5 | 0.4 | 0.2 |
| Reproducibility | | | | |
| Standard deviation | 0.414 (8) | 0.414 (8) | 0.489 (6) | 0.190 (6) |
| 95 % limit | 1.2 | 1.2 | 1.4 | 0.5 |
| *5 mL, °C:* | | | | |
| Repeatability | | | | |
| Standard deviation | 0.118 (54) | 0.118 (54) | ... | ... |
| 95 % limit | 0.3 | 0.3 | ... | ... |
| Laboratory Precision (Within Laboratory Between Days) | | | | |
| Standard deviation | 0.147 (27) | 0.147 (27) | ... | ... |
| 95 % limit | 0.4 | 0.4 | ... | ... |
| Reproducibility | | | | |
| Standard deviation | 0.317 (8) | 0.317 (8) | ... | ... |
| 95 % limit | 0.9 | 0.9 | ... | ... |
| 50 mL, °C: | | | | |
| Repeatability | | | | |
| Standard deviation | 0.0783 (54) | 0.0783(54) | 0.129 (52) | 0.0892(56) |
| 95 % limit | 0.2 | 0.2 | 0.4 | 0.2 |
| Laboratory Precision (Within Laboratory Between Days) | | | | |
| Standard deviation | 0.0981 (27) | 0.0981(27) | 0.0961(26) | 0.0505(28) |
| 95 % limit | 0.3 | 0.3 | 0.3 | 0.1 |
| Reproducibility | | | | |
| Standard deviation | 0.279 (8) | 0.279 (8) | 0.201 (6) | 0.133 (6) |
| 95 % limit | 0.8 | 0.8 | 0.6 | 0.4 |
| *95 mL, °C:* | | | | |
| Repeatability | | | | |
| Standard deviation | 0.0837 (54) | 0.0837(54) | ... | ... |
| 95 % limit | 0.2 | 0.2 | ... | ... |
| Laboratory Precision (Within Laboratory Between Days) | | | | |
| Standard deviation | 0.126 (27) | 0.126 (27) | ... | ... |
| 95 % limit | 0.4 | 0.4 | ... | ... |
| Reproducibility | | | | |
| Standard deviation | 0.336 (8) | 0.336 (8) | ... | ... |
| 95 % limit | 0.9 | 0.9 | ... | ... |
| *Dry point C:* | | | | |
| Repeatability | | | | |
| Standard deviation | 0.0779 (14) | 0.384 (36) | 0.272 (46) | 0.193 (56) |
| 95 % limit | 0.2 | 1.1 | 0.8 | 0.5 |
| Laboratory Precision (Within Laboratory Between Days) | | | | |
| Standard deviation | 0.122 (8) | 0.640 (18) | 0.103 (23) | 0.250 (28) |
| 95 % limit | 0.3 | 1.8 | 0.3 | 0.7 |
| Reproducibility | | | | |
| Standard deviation | 0.466 (7) | 2.77 (8) | 1.12 (5) | 0.896 (6) |
| 95 % limit | 1.3 | 7.8 | 3.1 | 2.5 |

[A]Degrees of freedom indicated by values within parentheses.

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0000918 % absolute at 92 dF. The 95 % limit for the difference between two such runs is 0.0003 % absolute.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.000116 % absolute at 46 dF. The 95 % limit for the difference between two such averages is 0.0003 % 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 0.000279 % absolute at 5 df. The 95 % limit for the difference between two such averages is 0.0008 % absolute.

NOTE 4—These precision estimates are based on an interlaboratory study performed in 1962 and 1963 on six samples of the five glycols whose acidity values ranged from 0.0008 to 0.0044 %. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each of two days.[7] Practice E 180 was used in developing these precision estimates.

13.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## WATER

### 14. Procedure

14.1 Determine the water content of the sample using any suitable Karl Fischer reagent titration method. Test Method E 203 is recommended.

### 15. Report

15.1 Report the water content to the nearest 0.01 %.

### 16. Precision and Bias

16.1 The following criteria should be used for judging the acceptability of results (see Note 5):

16.1.1 *Repeatability* (*Single Analyst*)—The standard deviation for a single determination has been estimated to be 0.000370 % absolute at 92 dF. The 95 % limit for the difference between two such runs is 0.01 % absolute.

16.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.00819 % absolute at 58 df. The 95 % limit for the difference between two such averages is 0.02 % absolute.

16.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0187 % absolute at 9 df. The 95 % limit for the difference between two such averages is 0.05 % absolute.

NOTE 5—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on seven samples of the five glycols whose water values ranged from 0.02 to 0.31 %. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each sample on each of two days. Each analyst employed the form of the Karl Fischer reagent titration method commonly used in the analyst's laboratory. The 1962 study on three samples of ethylene glycol by nine laboratories failed to show any significant differences in precision attributable to differences in the methods used.[7] Practice E 180 was used in developing these precision estimates.

16.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## IRON

### 17. Summary of Test Method

17.1 The sample is diluted with water and the iron determined photometrically at approximately 510 nm by the ortho-phenanthroline method without a preliminary ashing. The amounts and the concentrations of hydroxylamine hydrochloride and ortho-phenanthroline solutions added has been increased over that given in conventional write-ups in order to overcome the depression of the ferrous-ortho-phenanthroline complex color by the large amount of glycol present.

### 18. Significance and Use

18.1 This test method is essentially identical to Test Method E 394, which should be consulted for details on possible interferences. Both test methods assume that the amount of color developed is proportional to the amount of iron in the test solution and that the calibration curve is linear over the specified concentration range.

### 19. Apparatus

19.1 *Spectrophotometer*, capable of measuring light absorption at approximately 510 nm.

NOTE 6—A discussion of photometers and photometric practice is given in Practice E 60.

19.2 *Absorption Cells*, 5-cm light path.

### 20. Reagents

20.1 *Hydroxylamine Hydrochloride Solution* (300 g/L)—Prepare fresh as needed. See the paragraph on hydroxylamine hydrochloride solution in the section on Nonstandardized Reagent Solutions and Indicator Solutions in Practice E 200.

20.2 *Iron, Standard Solution* (1 mL = 0.005 mg Fe)—Prepare the standard iron solution (1 mL = 0.01 mg Fe) in accordance with the paragraph on alternate method in the section on Standard Ion Solutions of Practice E 200. Accurately dilute the resulting solution (0.01 mg/mL) 1:1 for the 0.005-mg/mL solution required.

20.3 *Ortho-Phenanthroline Solution* (3 g/L)—Dissolve 0.9 g of 1,10-phenanthroline monohydrate in 30 mL of iron-free ethanol (Note 7) and dilute to 300 mL with water.

NOTE 7—Specially denatured alcohol conforming to Formula No. 30 of the U.S. Bureau of Internal Revenue has been found satisfactory for this purpose.

### 21. Preparation of Calibration Curve

21.1 Prepare a series of at least five standards by adding 1.0 to 12.0 mL of standard iron solution (1 mL = 0.005 mg Fe) from a buret to 100-mL glass-stoppered graduates so that the concentration range from 0.000 to 0.060 mg Fe is covered in approximately equal increments. Make up to 80 mL with water. Add 80 mL of water to another graduate as a blank. Add 5 mL of $NH_2OH{\cdot}HCl$ solution, make up to the 100-mL mark with ortho-phenanthroline solution and mix.

21.2 Obtain the absorbance of each standard, corrected for the blank, in accordance with 22.3. Prepare a calibration curve by plotting the absorbances of the standard iron solutions in 5-cm cells against the milligrams of iron per 100 mL of solution. This curve must be determined for each instrument and should be checked periodically.

### 22. Procedure

22.1 For samples containing 0 to 0.5 ppm Fe, weigh about 80 g of sample to the nearest 0.1 g into a 100-mL glass-stoppered graduate. For samples of larger iron content, use proportionally smaller samples. Dilute with water to 80 mL. Add 80 mL of water to another graduate as a blank.

22.2 Add 5 mL of $NH_2OH{\cdot}HCl$ solution to each graduate and mix. Make up to the 100-mL mark with ortho-phenanthroline solution and again mix.

22.3 Allow to stand for 5 min, fill a 5-cm absorption cell, and measure the absorbance at approximately 510 nm, corrected for the blank (Note 8). From the calibration curve, read the milligrams of iron present.

NOTE 8—Although the ferrous-ortho-phenanthroline complex is reported to have a maximum absorbance at approximately 510 nm, the measurements on both the standard iron and sample solutions should be made at or near the wavelength at which maximum absorbance is obtained with each individual instrument, as indicated by scanning in this region of the spectrum. This step will ensure that the measurements will be made with a maximum of sensitivity and will reduce wavelength calibration errors.

### 23. Calculation

23.1 Calculate the iron present, in parts per million, as follows:

$$\text{Iron, ppm} = \left(\frac{W}{S}\right) \times 1000 \quad (1)$$

where:
$W$ = iron found, mg, and
$S$ = sample used, g.

### 24. Report

24.1 Report the iron content of the sample to the nearest 0.01 ppm.

### 25. Precision and Bias

25.1 The following criteria should be used for judging the acceptability of results (see Note 9):

25.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.00744 ppm at 92 dF. The 95 % limit for the difference between two such runs is 0.02 % ppm.

25.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.00971 at 45 dF. The 95 % limit for the difference between two such averages is 0.03 % ppm.

25.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0255 ppm absolute at 8 df. The 95 % limit for the difference between two such averages is 0.07 ppm.

NOTE 9—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on a total of seven samples of ethylene glycol, propylene glycol, and dipropylene glycol whose iron values ranged from 0.06 to 0.45 ppm. A total of ten laboratories cooperated in the studies

in which each analyst performed duplicate determinations on each sample on each of two days.[7] Practice E 180 was used in developing these precision estimates.

25.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## COLOR

### 26. Procedure

26.1 Determine the color of the sample in accordance with Test Method D 1209.

### 27. Report

27.1 Estimate and report the color to the nearest one platinum-cobalt unit.

### 28. Precision and Bias

28.1 The following criteria should be used for judging the acceptability of results (see Note 10):

28.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0 unit at 40 dF. The 95 % limit for the difference between two such runs is two units.

28.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.64 unit at 46 dF. The 95 % limit for the difference between two such averages is two units.

28.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 2.47 units at 9 df. The 95 % limit for the difference between two such averages is seven units.

NOTE 10—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on a total of six samples of the five glycols whose color ranged from 2 to 21 platinum-cobalt units. Because the test results are based on visual comparison of the untreated sample with standards, duplicate determinations at low levels of color are almost always in perfect agreement. This was confirmed in the 1962 study of two samples of ethylene glycol with average colors of 2 and 21 platinum-cobalt units. The standard deviation for duplicate determinations was estimated to be 0.0 units at 40 dF. Therefore the stated 95 % limit in the repeatability statement is based on the reporting of results to the nearest 1 unit. The 1963 study omitted the duplicate determinations. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each sample on each of two days.[7] Practice E 180 was used in developing these precision estimates.

28.1.4 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## GAS CHROMATOGRAPHIC ANALYSIS

### 29. Scope

29.1 This gas chromatographic test method is intended for the analysis of mixtures of ethylene, diethylene, and triethylene glycols or 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 not more than 1 %, each. Up to 1 % tetraethylene glycol in triethylene glycol may be analyzed by this test method. The isomers of dipropylene and tripropylene glycol are not completely resolved under the conditions used. Gas chromatographic test methods for determining less than 0.1 % diethylene glycol in ethylene glycol are in accordance with Test Methods E 611.

### 30. Summary of Test Method

30.1 The sample is injected 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. Two modes of operating the gas chromatograph are described: linear programmed temperature and isothermal. Linear programmed temperature operation tends to give sharper peaks, and is, therefore, preferred when it is desired to detect very low concentrations of impurities.

### 31. Significance and Use

31.1 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 components showing the most significant error on an absolute basis. Although water is detected under the conditions used, the best accuracy is obtained by calculating the gas chromatographic results on a water-free basis and correcting these results for the water content of the sample in accordance with Sections 14-16.

### 32. Apparatus

32.1 *Gas Chromatographic Instruments*, having the minimal following characteristics.[8]

32.1.1 *Sample Injection Port*, with heater characteristics necessary for operations at 215 and 235°C.

32.1.2 *Column Oven*, capable of isothermal operation at 170 to 200°C, or linear programmed temperature operation between 150 and 225°C at approximately 5°C/min.

32.1.3 *Detector* of the conventional dual-pass thermal conductivity type, capable of operation at 270°C.

32.1.4 *Recorder*, 0 to 1-mV range, 1-s full-scale deflection with a chart speed of approximately ½in./min (12.7 mm/min) or other convenient speed that will produce a satisfactory chromatogram, and an attenuator switch to change the recorder range as required.

32.1.5 *Column*, 4 ft (122 cm) long, ¼ in. (6.35 mm) in outside diameter with a wall thickness of 0.032 in. (0.813 mm) for aluminum or 0.065 in. (1.65 mm) for stainless steel construction; packed with 7 % polyethylene glycol on tetrafluoroethylene polymer.

32.2 *Microsyringe*, 50-µL capacity.[9]

[8] These parameters are summarized in Table 3 as typical values. See Note 13.

[9] Hamilton Microsyringe No. 705 has been found satisfactory and is available from supply houses.

32.3 *Planimeter*—The use of a planimeter to measure peak areas is recommended unless the recorder used with the chromatograph is equipped with an integrator.

32.4 *Aluminum or Stainless Steel Tubing*, 0.25 in. (6.35 mm) in outside diameter, with wall thickness of 0.032 in. (0.813 mm) for aluminum and 0.065 in. (1.65 mm) for stainless steel.

## 33. Reagents and Materials

33.1 *Polyethylene Glycol,*[10] 20 000 molecular weight.

33.2 *Tetrafluoroethylene Polymer.*[11]

33.3 *Methylene Chloride* ($CH_2Cl_2$).

33.4 *Helium* (He).

33.5 *Ethylene, Diethylene, Triethylene, Tetraethylene, Propylene, Dipropylene, and Tripropylene Glycols*— See Section 35 for purity requirements.

## 34. Preparation of Chromatographic Column

34.1 Dissolve 14 g of the polyethylene glycol in approximately 200 mL of $CH_2Cl_2$ with gentle warming to aid solution. Add 186 g of tetrafluoroethylene polymer and sufficient $CH_2Cl_2$ to form a slurry, and mix well, making certain that all particles are wetted. Evaporate $CH_2Cl_2$ 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 greatly shorten the time required for drying.

34.2 Screen the dried packing through a No. 30 mesh sieve to remove lumps. Fill a 4-ft (122-cm) section of ¼-in. (6-mm) outside diameter aluminum or stainless-steel tubing with the screened packing (Note 11). Gently vibrate or tap the column during the filling to ensure uniform packing, but exercise care not to pack too tightly. Approximately 25 mL, or 14.1 g, of packing is required to fill the aluminum tubing. Plug the ends of the tubing with glass wool, and shape the tubing so it may be mounted conveniently in the oven of the chromatograph.

NOTE 11—Chilling the packing in a refrigerator has been reported to facilitate the handling of the packing during the filling of the tube.

34.3 Condition the column prior to use by placing the column in the chromatograph in accordance with 36.2, except heat the column to 225°C and maintain at that temperature for at least 4 h. Pass helium through the column at the specified rate.

## 35. Calibration Factors

35.1 In order to obtain the composition of the sample in terms of weight percent, the areas associated with each component must be multiplied 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, glycols obtained from "hearts cuts" should be used. The calibration factors should be checked periodically or whenever there is evidence of a change in the column or instrument.

35.2 *Test Method A*:

35.2.1 Purify the commercial grade of each glycol needed by careful fractional distillation in glass at reduced pressure, discarding the first 30 % and retaining the next 30 % as the "hearts cuts". These fractions should be analyzed in accordance with 36.2 or 36.3 to be sure they are free from other homologues of the glycol.

35.2.2 Prepare a standard mixture of these glycols whose composition approximates that of the glycols to be analyzed. The composition of this standard should be known to the nearest 0.01 %. Correct the composition for any water present as determined in accordance with 14.1, using the equation in 37.2.4.

35.2.3 Obtain at least two chromatograms of the standard mixture in accordance with 36.2 or 36.3 and calculate the average area percent for each of the glycols present in accordance with 37.2.1 (Note 12). Do not include any areas associated with air and water in calculating the area percentages. Using the weight percent in the standard mixture and the average area percent, calculate the factor for each glycol in accordance with 37.1.1.

NOTE 12—The same mode of operation of the chromatograph must be used in analyzing the standard mixture as will be used to analyze samples. Different calibration factors may be obtained for linear programmed temperature and for isothermal operation.

35.3 *Test Method B*:

35.3.1 For routine analyses, commercial grades of each glycol may be used if the gas chromatographic analysis in accordance with 36.2 or 36.3 indicates that the other glycols present do not exceed 1 area %, each.

35.3.2 Prepare a standard mixture of the glycols whose composition approximates that of the glycol to be analyzed. The composition of the standard should be known to the nearest 0.01 %. Correct the composition for any water present as determined in accordance with 14.1, using the equation in 37.2.4. If the concentrations of the minor components in the glycols added to the principal component in the standard mixture do not exceed 1 area %, the concentrations of these impurities in the mixture are insignificant at the concentration levels included in the scope of this test method.

35.3.3 Obtain at least two chromatograms of the standard mixture and of the principal glycol in accordance with 36.2 or 36.3 and calculate the average area percent for each of the glycols present in accordance with 37.2.1 (Note 12). Do not include any areas associated with air and water in calculating the area percentages. Using the weight percent for each glycol added to the principal glycol component and the average area percents for each of these glycols, calculate the calibration factor for each minor component in the standard mixture in accordance with 37.1.2. Assume a calibration factor of unity for the principal glycol in the standard mixture.

[10] Carbowax polyethylene glycol compound 20M, which is available from supply houses, has been found satisfactory. Other polyethylene glycols having a molecular weight of 20 000 may not perform in a satisfactory manner, and their stability and ability to separate the glycols when used in column packing should be checked by the use of standard mixtures.

[11] Haloport F, available from Alltech Assoc., 2051 Waulkegen Rd., Deerfield, IL, has been found satisfactory. Other fluorocarbons may be used if satisfactory performance is obtained.

## 36. Procedure

36.1 In analyzing the sample, either of two modes may be used in operating the gas chromatograph: linear programmed temperature or isothermal. Except for the column temperatures, the procedure is the same for either mode, but other parameters will change depending on whether ethylene or propylene glycols are being analyzed. The procedure using linear programmed temperature will be described first.

36.2 *Linear Programmed Temperature Operation*:

36.2.1 Mount the column in the chromatograph, and adjust the operating conditions in accordance with the parameters given in Table 3 (Note 13). 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 13—The instrument parameters given in Table 3 may be considered to be typical values. For any specific instrument some adjustment of column temperature, programming rate, helium flow rate, etc. will probably be required to achieve retention times similar to those in Table 4 and Table 5. The parameters should be adjusted so that the peaks obtained are reasonably symmetrical, sharp, and exhibit satisfactory resolution.

36.2.2 Inject 10 µL of the sample into the chromatograph by means of a microsyringe, and obtain a chromatogram of the sample using attenuation settings which allow for maximum peak heights for each peak without going off scale (Note 14). Approximate retention times for the glycols are given in Table 4 and Table 5. Typical chromatograms for diethylene glycol and dipropylene glycol are shown in Fig. 1 and Fig. 2.

NOTE 14—Direct "on-column" injection of the sample has been reported to result in better-shaped peaks and to eliminate, or greatly reduce, the buildup of carbon in the injection port. If this method of sample injection is used, the temperature of the injection port should be the same as that of the column.

36.2.3 Repeat 36.2.2 to obtain a duplicate chromatogram. The area percent of each peak of the chromatograms should agree within approximately 0.1 area % for duplicate chromatograms. If they do not agree this closely, obtain replicate chromatograms until agreement is achieved.

**TABLE 3 Typical Instrument Parameters**

| | |
|---|---|
| Instrument | programmed temperature gas chromatograph[A] |
| Strip-chart recorder | 0 to 1-mV range |
| Chart speed | ½ in. (12.7 mm)/min |
| Column | 4 ft of ¼-in. (122 mm of 6-mm) OD aluminum or stainless steel tubing packed with polyethylene glycol[11] on tetrafluoroethylene polymer[12] |
| Column temperature | |
| (*a*) Programmed temperature operation | 150 to 225°C at 5.6°C/min |
| (*b*) Isothermal operation | 170 or 200°C for ethylene glycols (refer to 36.3.1)<br>190°C for propylene glycols |
| Carrier gas | helium at 75 mL/min |
| Detector current | 190 mA |
| Injection port temperature | 235°C for ethylene glycols<br>215°C for propylene glycols |
| Detector block temperature | 270°C |
| Sample volume | 10 µ |

[A] See Note Note 13.

**TABLE 4 Retention Time Data [A]**

| Compound | Retention Time, min | | |
|---|---|---|---|
| | Programmed Temperature Operation | Isothermal Operation | |
| | | 170°C | 200°C |
| Air and water | 0.4 | 0.3 | 0.3 |
| Ethylene glycol | 2.2 | 1.3 | 0.8 |
| Diethylene glycol | 7.0 | 4.2 | 2.3 |
| Triethylene glycol | 11.9 | 14.0 | 5.8 |
| Tetraethylene glycol | 19.3 | ... | 16.3 |

[A] Retention times vary with component concentration and from instrument to instrument. Thus, the times listed, measured from the point of sample injection to the peak maximum, are approximate.

**TABLE 5 Retention Time Data[A]**

| Compound | Retention Time, min | |
|---|---|---|
| | Programmed Temperature Operation | Isothermal Operation at 190°C |
| Air and water | 0.5 | 0.3 |
| Propylene-glycol | 4.0 | 1.3 |
| Dipropylene glycol, 3 unresolved isomers | 8.1 | 3.3 |
| | 9.3 | 3.9 |
| | 10.3 | 4.8 |
| Tripropylene glycol[B] | 12.4 | 7.9 |

[A] Retention times vary with component concentrations and from instrument to instrument. Thus, the times listed, measured from the point of sample injection to the peak maximum, are approximate.

[B] Several isomers are usually indicated by the shape of the peak, but they are not sufficiently resolved to list separate retention times.

NOTE 15—Generally, three chromatograms may be required to obtain agreement. The first injection of the sample seems to condition the column.

NOTE 16—Frequent, rigorous cleaning of the injection port with hot water and acetone may be required to avoid a buildup of carbonaceous material in the injection port which will cause erroneous answers. Frequent septum changes help prevent extraneous peaks.

36.2.4 Draw base lines under each glycol peak and measure the area of each peak with a planimeter, unless the recorder is equipped with an integrator.

36.3 *Isothermal Operation*:

36.3.1 Follow the procedure in accordance with 36.2, except use a constant column temperature of 170 °C for the analysis of mixtures of ethylene, diethylene, and triethylene glycols. A temperature of 200°C is used for mixtures containing tetraethylene glycol (Note 13 and Note 17). Approximate retention times for the glycols are given in Table 4 and Table 5. Typical chromatograms for a sample of ethylene and of diethylene glycol at temperatures of 170 and 200°C respectively, are shown in Fig. 3 and Fig. 4. A typical chromatogram of dipropylene glycol is shown in Fig. 5.

NOTE 17—The higher temperature is used to obtain a reasonably short retention time for tetraethylene glycol. Complete resolution of the ethylene and diethylene glycol peaks may not be achieved at this higher temperature if the sample contains more than approximately 1 % ethylene glycol in the presence of high concentrations of diethylene glycol.

## 37. Calculation

37.1 *Calibration Factors*:

37.1.1 When "hearts cuts" of glycols are used to prepare the standard mixture, obtain the calibration factor for each glycol as follows:

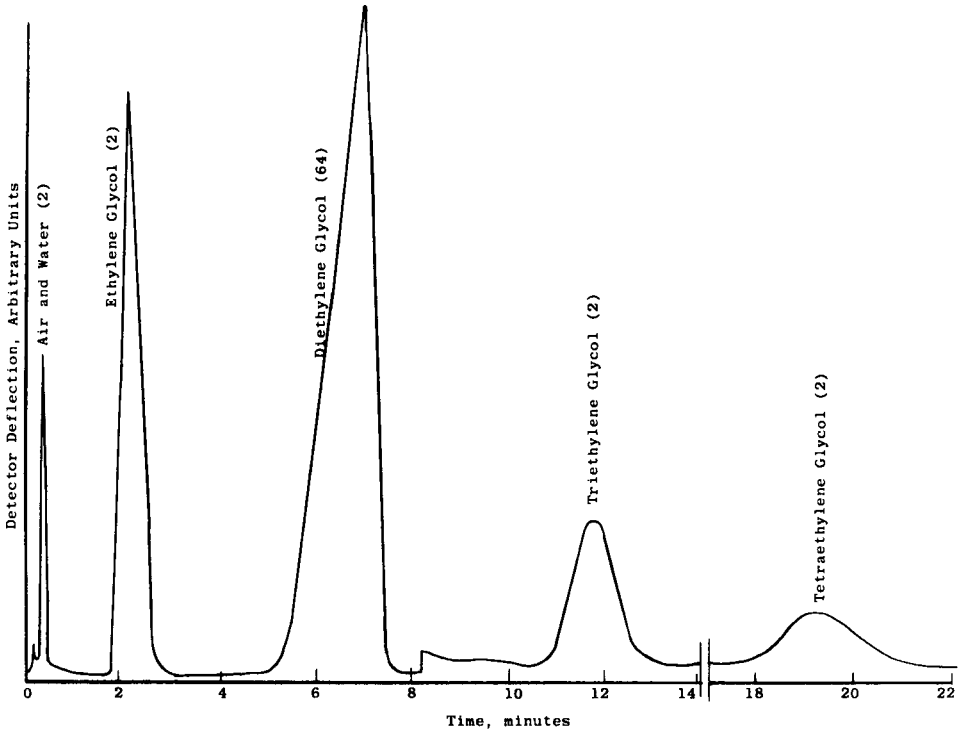


**FIG. 1 Chromatogram of Diethylene Glycol Linear Programmed Temperature Operation (Recorder Attenuation in Parentheses)**

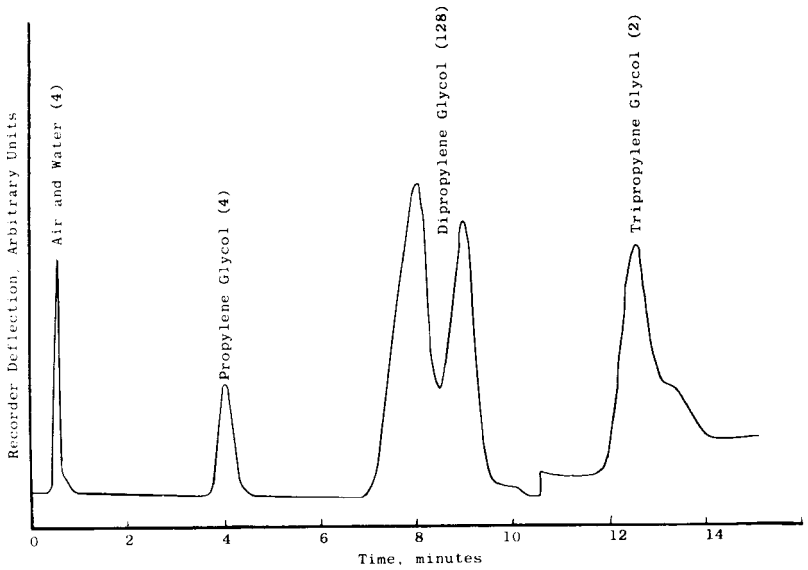


**FIG. 2 Chromatogram of Dipropylene Glycol Linear Programmed Temperature Operation (Recorder Attenuation in Parentheses)**

$$F_i = \frac{W_i}{A_{\%i}} \tag{2}$$

where:

$F_i$ = calibration factor for component $i$,
$W_i$ = weight percent of component $i$ in standard mixture, and
$A_{\%i}$ = average area percent of component $i$ in standard mixture.

37.1.2 When commercial grades of glycols are used to prepare the standard mixture, obtain the calibration factor for each glycol present in minor concentration as follows:

$$F_i = \frac{B_i}{A_{si} - A_{bi}} \tag{3}$$

where:

$F_i$ = calibration factor for component $i$,
$B_i$ = weight percent of minor component $i$ added to principal glycol in preparing the standard mixture,
$A_{si}$ = average area percent of minor component $i$ in standard mixture, and
$A_{bi}$ = average area percent of minor component $i$ in principal component.

37.2 *Sample Composition*:

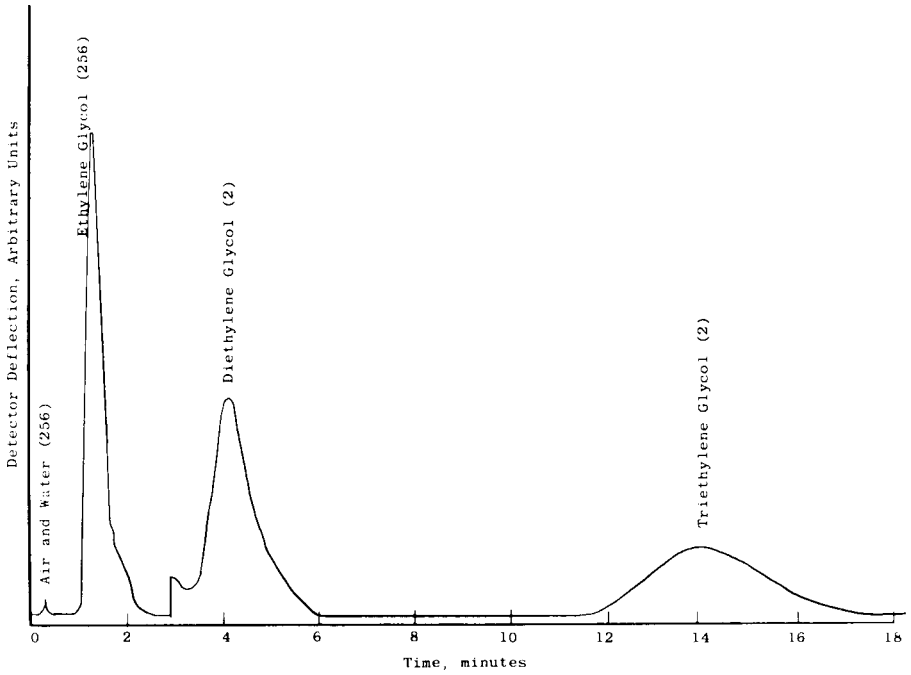


**FIG. 3 Chromatogram of Ethylene Glycol Isothermal Operation at 170°C (Recorder Attenuation in Parentheses)**

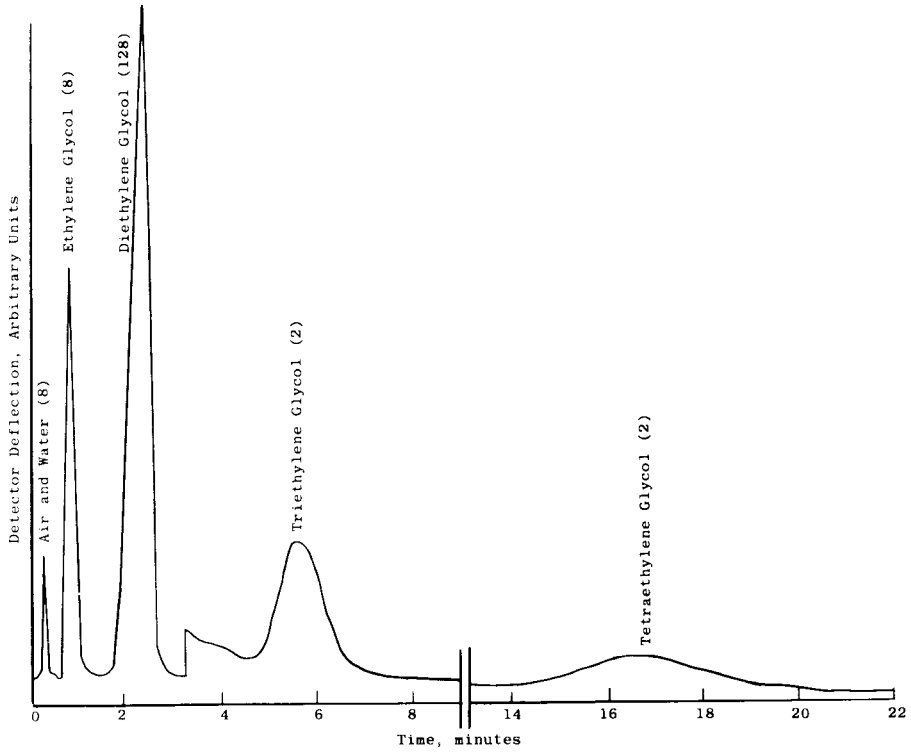


**FIG. 4 Chromatogram of Diethylene Glycol Isothermal Operation at 200°C (Recorder Attenuation in Parentheses)**

37.2.1 Calculate the area percentage of each component as follows:

$$A_{\%i} = \frac{A_i T_i \times 100}{(A_1 T_1) + (A_2 T_2) + (A_3 T_3) + (A_4 T_4)} \quad (4)$$

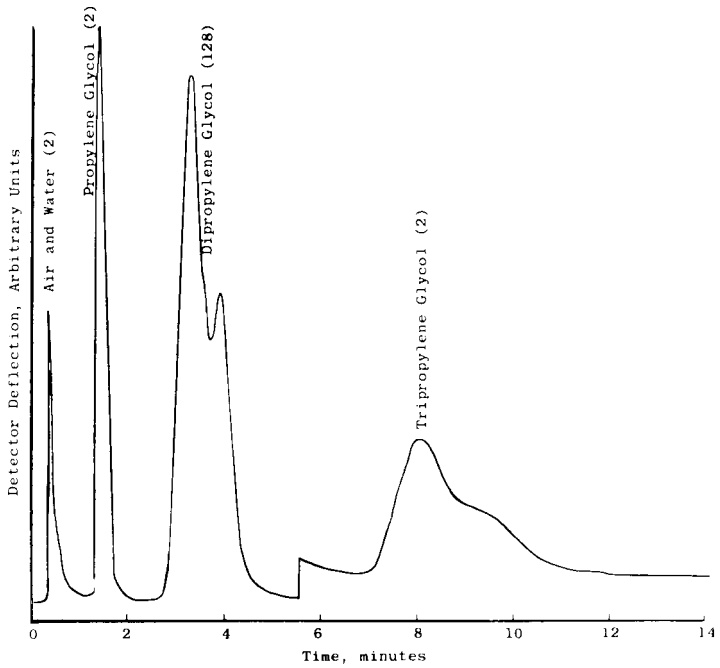


**FIG. 5 Chromatogram of Dipropylene Glycol Isothermal Operation at 190°C (Recorder Attenuation in Parentheses)**

where:

$A_{\%\ i}$ = area percent for glycol *i*,
$A_i$ = area for glycol *i*,
$T_i$ = recorder attenuation for area of glycol *i*,
$A_1, A_2, A_3, A_4$ = areas for mono, di, tri, and tetraalkyl glycols, respectively, and
$T_1, T_2, T_3, T_4$ = recorder attenuation for areas for mono, di, tri, and tetraalkyl glycols, respectively.

37.2.2 Calculate the corrected area of each glycol as follows:

$$A_{ci} = A_{\%i} \times F_i \tag{5}$$

where:

$A_{c\ i}$ = corrected area for glycol *i*,
$A_{\%i}$ = area percent for glycol *i*, and
$F_i$ = factor for glycol *i*.

37.2.3 Calculate the weight percent of each glycol on an anhydrous basis as follows:

$$C_i = \frac{A_{ci}}{A_{c1} + A_{c2} + A_{c3} + A_{c4}} \times 100 \tag{6}$$

where:

$C_i$ = weight percent of glycol *i*, expressed on an anhydrous basis,
$A_{ci}$ = corrected area for glycol *i*, and
$A_{c1}, A_{c2}, A_{c3}, A_{c4}$ = corrected areas for mono, di, tri, and tetraalkyl glycols, respectively.

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

$$G_i = \frac{C_i(100 - D)}{100} \tag{7}$$

where:

$G_i$ = weight percent of glycol *i*, corrected for water content of sample,
$C_i$ = weight percent of glycol *i*, expressed on an anhydrous basis, and
$D$ = weight percent of water in the sample as determined by Karl Fischer Reagent.

## 38. Report

38.1 Report the weight percent of each component to the nearest 0.01 %.

## 39. Precision and Bias

39.1 The following criteria should be used for judging the acceptability of results (see Note 18):

39.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 6 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value in the table.

39.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 6 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

39.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value in Table 6 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE 18—The precision estimates for the ethylene glycols are based on a 1964–1965 interlaboratory study in which three samples of the glycols were analyzed. The concentrations of the minor glycol components ranged from 0.48 to 1.00 weight %. Seven laboratories cooperated in the study in

**TABLE 6 Gas Chromatographic Precision Values**

| Standard Deviation, absolute % | Ethylene Glycols | | Propylene Glycols | |
|---|---|---|---|---|
| | Major Component[A] | Minor Component[B] | Major Component[A] | Minor Component[B] |
| *Programmed Temperature, Weight %:* | | | | |
| Repeatability | | | | |
| Standard deviation | 0.0477 (42[C]) | 0.0272 (12) | 0.0224 (64) | 0.0172 (92) |
| 95 % limit | 0.13 | 0.076 | 0.063 | 0.048 |
| Laboratory Precision (Within-Laboratory Between-Days) | | | | |
| Standard deviation | 0.0700 (21) | 0.0363 (56) | 0.0366 (32) | 0.0260 (46) |
| 95 % limit | 0.20 | 0.10 | 0.10 | 0.073 |
| Reproducibility | | | | |
| Standard deviation | 0.1024 (6) | 0.0527 (6) | 0.0615 (7) | 0.0499 (7) |
| 95 % limit | 0.29 | 0.15 | 0.17 | 0.14 |
| *Isothermal Temperature, Weight %* | | | | |
| Repeatability | | | | |
| Standard deviation | 0.0516 (42) | 0.0277 (112) | 0.0265 (70) | 0.0197 (94) |
| 95 % limit | 0.14 | 0.078 | 0.074 | 0.055 |
| Laboratory Precision (Within-Laboratory Between-Days) | | | | |
| Standard deviation | 0.0498 (21) | 0.0282 (56) | 0.0515 (35) | 0.0494 (47) |
| 95 % limit | 0.14 | 0.079 | 0.14 | 0.14 |
| Reproducibility | | | | |
| Standard deviation | 0.1033 (6) | 0.0528 (6) | 0.0633 (8) | 0.0536 (7) |
| 95 % limit | 0.29 | 0.15 | 0.18 | 0.15 |

[A] Concentration range from 97 to 100 %.
[B] Concentration range of less than 1 %.
[C] Degrees of freedom indicated by values within parentheses.

which each analyst performed duplicate determinations by each mode of instrument operation on each of two days, using seven different makes or models of instruments.[12] The calibration factors for converting area to weight percent were obtained using standard samples which, unknown to the participants, had the same composition as the test samples.[12]

The precision estimates for the propylene glycol samples are based on a 1966 interlaboratory study in which four samples of the glycols were analyzed. The concentrations of the minor components ranged from 0.25 to 0.79 weight %. Nine laboratories cooperated in the study in which each analyst performed duplicate determinations by each mode of instrument operation on each of two days, using eight different makes or models of instruments.[12] The calibration factors for converting area to weight percent were obtained using samples of known composition prepared by each analyst.[12] Practice E 180 was used in developing these precision estimates.

39.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## 40. Keywords

40.1 acidity; color; distillation range; ethylene glycols; gas chromatography; iron; propylene glycols; specific gravity; water

[12] Details of the interlaboratory study are available from ASTM Headquarters. Request RR: E15-0028.