Designation: E202 – 12

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

This standard is issued under the fixed designation E202; 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 U.S. 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:

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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 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 for apparatus descriptions.

1.4 *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:*[2]

D891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals

D1078 Test Method for Distillation Range of Volatile Organic Liquids

D1193 Specification for Reagent Water

D1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)

D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D5386 Test Method for Color of Liquids Using Tristimulus Colorimetry

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E203 Test Method for Water Using Volumetric Karl Fischer Titration

E394 Test Method for Iron in Trace Quantities Using the 1,10-Phenanthroline Method

E611 Test Methods for Low Concentrations of Diethlyene Glycol in Ethylene Glycol by Gas Chromatography

E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

E1615 Test Method for Iron in Trace Quantities Using the FerroZine Method

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

E2679 Test Method for Acidity in Mono-, Di-, Tri- and Tetraethylene Glycol byNon-Aqueous Potentiometric Titration

2.2 *ASTM Adjuncts:*

Adjunct ADJD6300 Determination of Precision and Bias for Use in Test Methods for Petroleum Products and Lubricants[4]

3. Significance and Use

3.1 These test methods measure certain chemical and physical properties of ethylene glycols and propylene glycols and

[1] These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicalsand 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.

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

[4] Available from ASTM International Headquarters.

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

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.

3.2 Alternative test methods and technology for several of the methods can be found in the Appendix. Use of these methods is optional and individuals using the alternative methods should assure themselves that the method is sufficient and appropriate for the application. Precision data presented in this standard is only for the original test methods listed.

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.[5] 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 D1193, Type II or III.

5. Quality Control

5.1 It is recommended that a control chart for the concentration of the impurities in the glycol quality control sample be established and maintained according to common guidelines.[6] Measure the control sample each time a test sample(s) is tested. If the measured value exceeds the action limit of the control chart, take appropriate action before proceeding with sample tests.

SPECIFIC GRAVITY

6. Procedure

6.1 Determine the relative density of the sample at 20/20°C using the pycnometer test method in accordance with Test Methods D891, except determine the water and sample weights of the pycnometer at 20.0 ± 0.1°C.

7. Report

7.1 Report the relative density at 20/20°C (in air) to the nearest 0.0001 unit.

8. Precision and Bias

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

8.1.1 *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.

8.1.2 *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.

8.1.3 *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 E180 was used in developing these precision estimates.

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

DISTILLATION RANGE

9. Procedure

9.1 Determine the distillation range of the sample in accordance with Test Method D1078. Use the conditions as specified in Test Method D1078, and the ASTM Solvents Distillation Thermometer shown in Table 1 of Test Method D1078. (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.

9.2 Use the following values of *K* in the equation for barometric correction (Test Method D1078):

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

10. Report

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

11. Precision and Bias

11.1 *Interlaboratory Study*: [8], [9]

[5] *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,* VWR International Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[6] ASTM Manual on Presentation of Data and Control Chart Analysis, 7th Edition, ASTM Manual Series MNL 7A (revision of Special Technical Publication (STP) 15D).

[7] Supporting data have been filed at ASTM Headquarters and my be obtained by requesting Research Report RR: RR:E15-0013.

[8] Supporting data have been filed at ASTM Headquarters and my be obtained by requesting Research Report RR: RR:E15-1114.

11.2 The precision of this test method was obtained from an interlaboratory study conducted in 2000 involving manual and automatic distillation procedures. The study involved six samples of different boiling point ranges, done in duplicate. Ten laboratories performed automatic Test Method D1078 distillation, and five laboratories performed manual Test Method D1078 distillation. It was found that the precision is dependent on the boiling point temperature. The data were statistically evaluated using ASTM D2PP software (ASTM Adjunct ADJD6300).[4]

11.3 *Repeatability*—Two results, each the mean of two runs, obtained by the same operator should be considered suspect if they differ by more than the repeatability values shown in Table 1 at a 95 % confidence level.

11.4 *Reproducibility*—Two results, each the mean of two runs, obtained by operators in different laboratories should be considered suspect if they differ by more than the reproducibility values shown in Table 1 at a 95 % confidence level.

11.5 *Bias:*

11.5.1 *Absolute Bias*—Since the temperature measuring devices specified by this test method are calibrated against the normal boiling point of toluene (99.9+ % purity), this test method has no bias with respect to pure toluene as a reference material.

11.5.2 *Relative Bias Between Manual and Automatic D1078 Distillation*—Statistical comparison between the variances of automatic and manual D1078 distillation results did not indicate any statistically significant difference. Statistical comparison of the averages of the six samples used in the study indicated that the paired-sample, two-tailed, t-test for the initial boiling point (IBP) and 50 % distillation point showed a small relative bias that is not statistically significant. A small but statistically significant bias was indicated for the automatic and manual D1078 dry point (DP). The observed bias (if any) are only for the samples studied and may not be necessarily applicable to other samples.

NOTE 3—In cases of dispute, the parties involved may agree to designate either the manual or the automatic method to be the referee test method. If an agreement on which method to designate cannot be made, the referee test method will be the manual method.

[9] Supporting data have been filed at ASTM Headquarters and my be obtained by requesting Research Report RR: RR:E15-1123.

ACIDITY

12. Procedure

12.1 Determine the acidity of the sample in accordance with Test Method E2679.

13. Report

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

14. Precision and Bias

14.1 *Precision*—The following criteria should be used to judge the acceptability of the results (see Note 4):

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

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

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

NOTE 4—The precision statements are preliminary based on 5 analyses by one analyst on two days for samples of MEG, DEG, TEG and TTEG containing approximately 1.7 mg/kg, 1.8 mg/kg, 33.0 mg/kg and 4.7 mg/kg acidity as acetic acid respectively. An interlaboratory study is planned for 2009/2010. Practice E180 was used in developing these precision estimates.

14.2 *Bias*—The bias of this test method was determined by spiking samples of MEG with acetic acid in the 5 to 50 mg/kg range and analyzing the spiked and unspiked samples. The accuracy (recovery) was estimated to be the values given in Table 3 based on the titration curves. The bias depends upon the accuracy of the titration, weighing of the spike and the extent of any interferences.

WATER

15. Procedure

15.1 Determine the water content of the sample using any suitable Karl Fischer reagent titration method. Test Method E1064 is recommended.

TABLE 1 Guide E2409 Glycol Impurities by Gas Chromatography (GC)

Test Result, mg/kg	Sample	Average over all Laboratories	Repeatability Standard Deviation	Intermediate Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Intermediate Limit	Reproducibility Limit
DEG	MEG	374.59	7.3	7.3	34.0	20.6	20.6	95.3
MEG	DEG	1479.73	46.3	76.0	215.1	129.7	212.9	602.4
TEG	DEG	3499.69	92.8	143.2	306.5	260.0	401.0	858.3
DEG	TEG	489.32	56.8	70.9	201.7	159.1	198.5	564.9
TTEG	TEG	1020.00	96.3	96.3	244.1	269.8	269.8	683.5
DEG	TeEG	1646.25	55.4	55.4	95.4	155.1	155.1	267.1
TEG	TeEG	7908.35	221.9	221.9	1350.7	621.2	621.2	3782.0
PentaEG	TeEG	2084.93	58.7	72.9	156.3	164.5	204.1	437.5

TABLE 2 Precision for Acidity in Glycols

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

TABLE 3 Accuracy for Acidity in Glycols Acidity as Acetic Acid in MEG

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

16. Report

16.1 Report the water content to the nearest 0.001 % mass.

17. Precision and Bias

17.1 In 2007, ASTM International Committee E15 on Industrial and Specialty Chemicals conducted and completed Interlaboratory Study No. 52 to determine Precision data for six test methods used in the analysis of glycols. The precision of this test method is based on the interlaboratory study of Test Method E1064, conducted in 2007. Each of 17 laboratories were asked to test three different materials. Fourteen laboratories tested MEG, 13 laboratories tested DEG and 13 laboratories tested TEG. Every "test result" represents an individual determination. Two test results were conducted on each of two days for a total of four test results per assay. Note that in the combined study, eight laboratories used a single analyst, seven laboratories used two analysts (on different days), and two laboratories did not record this information. In the event that there were missing values for one or more laboratories, this information was noted in the results. See Table 4.

17.1.1 *Repeatability* Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

17.1.2 *Reproducibility*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; " *R*" is the interval representing the difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

17.1.3 *Intermediate Precision*—The day-to-day standard deviation within a laboratory for results produced by the same operator, determined through statistical analysis following Practice E180. Practice E180 was used to conform to this particular study design which required an estimate of intermediate precision. The statistical analysis was conducted using the SAS statistical analysis software, Version 8.0.

17.1.3.1 The E180 analysis considers the two test results from each day as being run under repeatability, intermediate, and reproducibility precision for each assay. The repeatability precision would be estimated from the two sets of duplicate test results within each day, and the intermediate precision would be estimated from the agreement between the two days, all pooled over laboratories. Caveat: Since two days is a short time period, the intermediate precision would probably be underestimated by the E180 analysis.

17.1.4 Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

17.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

17.3 The precision statement was determined through statistical examination of qualified results, from seventeen laboratories, on three materials. These three materials were described as the following:

Fluid 1: Monoethylene Glycol
Fluid 2: Diethylene Glycol
Fluid 3: Triethylene Glycol

17.3.1 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

IRON

18. Procedure

18.1 Determine the iron content of the sample in accordance with Test Method E1615.

19. Report

19.1 Report the iron content to the nearest 0.001 µg/g.

20. Precision and Bias

20.1 In 2007, Committee E15 on Industrial and Specialty Chemicals conducted and completed Interlaboratory Study #52 to determine precision data for six test methods used in the analysis of glycols. The precision of this test method is based on the interlaboratoy study of E1615. Each of 15 laboratories

TABLE 4 E1064 Water in Organic Liquids by Coulometric Karl Fischer Titration

Test Result % mass	Sample	Average over all Laboratories	Repeatability Standard Deviation	Intermediate Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Intermediate Unit	Reproducibility Limit
Water	MEG	0.0086	0.0009	0.0014	0.0025	0.0026	0.0038	0.0071
Water	DEG	0.0649	0.0012	0.0014	0.0049	0.0032	0.0039	0.0137
Water	TEG	0.0498	0.0019	0.0129	0.0157	0.0054	0.0361	0.0439

were asked to test three different materials. Thirteen laboratories tested MEG, 11 laboratories tested DEG, and 10 laboratories tested TEG. Every test result represents an individual determination. Two test results were conducted on each of two days for a total of four test results per assay. Note that in the combined study, 8 laboratories used a single analyst, 7 laboratories used 2 analysts (on different days) and 2 laboratories did not record this information. In the event that there were missing values for one or more laboratories, this information was noted in the results. The details of this study are given in an ASTM Research Report.[10]

20.1.1 *Repeatability*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

20.1.2 *Reproducibility*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

20.1.3 *Intermediate Precision*—The day-to-day standard deviation within a laboratory for results produced by the same operator, determined through statistical analysis following Practice E180. Practice E180 was used to conform to this particular study design which required an estimate of intermediate precision. The statistical analysis was conducted using the SAS statistical analysis software, Version 8.0.

20.1.3.1 The Practice E180 analysis considers the two test results from each day as being run under repeatability conditions and estimates the repeatability, intermediate, and reproducibilty precision for each assay. The repeatability precision would be estimated from the two sets of duplicate test results within each day, and the intermediate precision would be estimated from the agreement between the two days, all pooled over laboratories. Caveat: Since two days is a short time period, the intermediate precision would probably be underestimated by the PracticeE180 analysis.

20.1.4 Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

20.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

20.3 The precision statement was determined through statistical examination of qualified results, from fifteen laboratories, on three materials. These three materials were described as the following:

Fluid 1: Monoethylene Glycol
Fluid 2: Diethylene Glycol
Fluid 3: Triethylene Glycol

[10] Supporting data have been filed at ASTM Headquarters and my be obtained by requesting Research Report RR: RR:E15-1064.

20.3.1 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

COLOR

21. Procedure

21.1 Determine the color of the sample in accordance with Test Method D1209.

22. Report

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

23. Precision and Bias

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

23.1.1 *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.

23.1.2 *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.

23.1.3 *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 5—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 one 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 E180 was used in developing these precision estimates.

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

GAS CHROMATOGRAPHIC ANALYSIS

24. Procedure

24.1 Determine the purity of Ethylene Glycol samples in accordance with E2409. For Propylene Glycol purity analysis, refer to the Alternative Test Methods in the Appendixes.

25. Report

25.1 Report the concentrations of DEG in MEG and MEG in DEG to the nearest mg/kg and all other impurities to the nearest 10 mg/kg. Report the purity of the sample to the nearest 0.01 % mass (m/m).

26. Precision and Bias

26.1 In 2007, Committee E15 on Industrial and Specialty Chemicals conducted and completed Interlaboratory Study #52 to determine precision data for six test methods used in the analysis of glycols. The precision of this test method is based on the interlaboratory study of E2409. Each of 17 laboratories were asked to test four different materials. Fourteen laboratories tested MEG in DEG, 16 laboratories tested DEG in MEG, 9 laboratories tested DEG in TEG, 5 laboratories tested DEG in TeEG, 13 laboratories tested TEG in DEG, 5 laboratories tested TEG in TeEG, 10 laboratories tested TTEG in TEG, 4 laboratories tested PentaEG in TeEG. Every test result represents an individual determination. Two test results were conducted on each of two days for a total of four test results per assay. Note that in the combined study, 8 laboratories used a single analyst, 7 laboratories used 2 analysts (on different days) and 2 laboratories did not record this information. In the event that there were missing values for one or more laboratories, this information was noted in the results. The details of this study are given in an ASTM Research Report.[11] (See Table 1.)

26.1.1 *Repeatability*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

26.1.2 *Reproducibility*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; " *R*" is the interval representing the difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

26.1.3 *Intermediate Precision*—The day-to-day standard deviation within a laboratory for results produced by the same operator, determined through statistical analysis following Practice E180. Practice E180 was used to conform to this particular study design which required an estimate of intermediate precision. The statistical analysis was conducted using the SAS statistical analysis software, Version 8.0.

26.1.3.1 The E180 analysis considers the two test results from each day as being run under repeatability conditions and estimates the repeatability, intermediate, and reproducibility precision for each assay. The repeatability precision would be estimated from the two sets of duplicate test results within each day, and the intermediate precision would be estimated from the agreement between the two days, all pooled over laboratories. Caveat: Since two days is a short time period, the intermediate precision would probably be underestimated by the E180 analysis.

26.1.4 Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

26.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

26.3 The precision statement was determined through statistical examination of qualified results from seventeen laboratories, on four materials. These four materials were described as the following:

Fluid 1: Monoethylene Glycol
Fluid 2: Diethylene Glycol
Fluid 3: Triethylene Glycol
Fluid 4: Tetraethylene Glycol

26.3.1 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

27. Keywords

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

[11] Supporting data have been filed at ASTM Headquarters and my be obtained by requesting Research Report RR: RR:E15-1063.

APPENDIXES

X1. ALTERNATIVE TEST METHODS

X1.1 *Scope*—Listed in Table X1.1 are alternative test methods and technology for several of the test methods. Use of these methods is optional and individuals using the alternative methods should assure themselves that the method is sufficient and appropriate for the application. Precision data presented in this standard is only for the original test methods listed.

TABLE X1.1 Alternative Test Methods

Analysis	Listed Test Method	Alternative Test Method
Relative Density	D891	D4052
Distillation Range	D1078	none
Acidity	E2679	D1613
Water	E1064	E203
Iron	E1615	E394
Color	D1209	D5386
Gas Chromatographic Analysis	E2409	E611 or method in Appendix X2.

X2. ALTERNATIVE GC METHOD

GAS CHROMATOGRAPHIC ANALYSIS

X2.1 Scope

X2.1.1 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 E611.

NOTE X2.1—A new gas chromatographic method for glycols, Test Method E2409, has been developed by Committee E15.

X2.2 Summary of Test Method

X2.2.1 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.

X2.3 Significance and Use

X2.3.1 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 15 – 17.

X2.4 Apparatus

X2.4.1 *Gas Chromatographic Instruments*, having the minimal following characteristics.[12]

X2.4.1.1 *Sample Injection Port*, with heater characteristics necessary for operations at 215 and 235°C.

X2.4.1.2 *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.

[12] These Parameters are summarized in Table X2.1 as typical values. See Note X2.4.

TABLE X2.1 Typical instrument Parameters

Instrument	programmed temperature gas chromatograph[A]
Strip-chart Recorder	0 to 1-mV range
Chart Speed	½ in./min
Column	4 ft of ¼-in. OD aluminum or stainless steel tubing packed with polyethylene glycol on tetrafluoroethylene polymer
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 X2.8.3.1), 190°C for propylene glycols
Carrier Gas	Helium at 75 mL/min
Detector Current	190 mA
Injection Port Temperature	235°C for ethylene glycols 215°C for propylene glycols
Detector Block Temperature	270°C
Sample Volume	10 µ

[A] See Note X2.4.

X2.4.1.3 *Detector* of the conventional dual-pass thermal conductivity type, capable of operation at 270°C.

X2.4.1.4 *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.

X2.4.1.5 *Column*, 4 ft long, ¼ in. in outside diameter with a wall thickness of 0.032 in. for aluminum or 0.065 in. for stainless steel construction; packed with 7 % polyethylene glycol on tetrafluoroethylene polymer.

X2.4.1.6 *Microsyringe*, 50-µL capacity.

X2.4.1.7 *Planimeter*—The use of a planimeter to measure peak areas is recommended unless the recorder used with the chromatograph is equipped with an integrator.

X2.4.1.8 *Aluminum or Stainless Steel Tubing*, 0.25 in. in outside diameter, with wall thickness of 0.032 in. for aluminum and 0.065 in. for stainless steel.

X2.5 Reagents and Materials

X2.5.1 *Polyethylene Glycol*, 20 000 molecular weight.

X2.5.2 *Tetrafluoroethylene Polymer.*

X2.5.3 *Methylene Chloride* (CH_2Cl_2).

X2.5.4 *Helium* (He).

X2.5.5 *Ethylene, Diethylene, Triethylene, Tretraethylene, Propylene, Dipropylene, and Tripropylene Glycols*—See Section X2.7 for purity requirements.

X2.6 Preparation of Chromatographic Column

X2.6.1 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.

X2.6.2 Screen the dried packing through a No. 30 mesh sieve to remove lumps. Fill a 4-ft section of ¼-in. outside diameter aluminum or stainless-steel tubing with the screened packing (Note X2.2). 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 15.1 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 X2.2—Chilling the packing in a refrigerator has been reported to facilitate the handling of the packing during the filling of the tube.

X2.6.3 Condition the column prior to use by placing the column in the chromatograph in accordance with X2.8.2, 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.

X2.7 Calibration Factors

X2.7.1 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.

X2.7.2 *Test Method A:*

X2.7.2.1 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 X2.8.2 or X2.8.3 to be sure they are free from other homologues of the glycol.

X2.7.2.2 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 15.1, using the equation in X2.9.2.4.

X2.7.2.3 Obtain at least two chromatograms of the standard mixture in accordance with X2.8.2 or X2.8.3 and calculate the average area percent for each of the glycols present in accordance with X2.9.2.1 (Note X2.3). 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 X2.9.1.1.

NOTE X2.3—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.

X2.7.3 *Test Method B:*

X2.7.3.1 For routine analyses, commercial grades of each glycol may be used if the gas chromatographic analysis in accordance with X2.8.2 or X2.7.3 indicates that the other glycols present do not exceed one area %, each.

X2.7.3.2 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 15.1, using the equation in X2.9.2.4. If the concentrations of the minor components in the glycols added to the principal component in the standard mixture do not exceed one area %, the concentrations of these impurities in the mixture are insignificant at the concentration levels included in the scope of this test method.

X2.7.3.3 Obtain at least two chromatograms of the standard mixture and of the principal glycol in accordance with X2.8.2 or X2.8.3 and calculate the average area percent for each of the glycols present in accordance with X2.9.2.1 (Note X2.3). 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 X2.9.1.2. Assume a calibration factor of unity for the principal glycol in the standard mixture.

X2.8 Procedure

X2.8.1 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.

X2.8.2 *Linear Programmed Temperature Operation:*

X2.8.2.1 Mount the column in the chromatograph and adjust the operating conditions in accordance with the parameters given in Table X2.1 (Note X2.4). 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 X2.4—The instrument parameters given in Table X2.1 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 X2.2 and Table X2.3. The parameters should be adjusted so that the peaks obtained are reasonable symmetrical, sharp, and exhibit satisfactory resolution.

X2.8.2.2 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 X2.5). Approximate retention times for the glycols are given in Table X2.2 and Table X2.3. Typical chromatograms for diethylene glycol and dipropylene glycol are shown in Fig. X2.1 and Fig. X2.2.

TABLE X2.2 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 X2.3 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 X2.5—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.

X2.8.2.3 Repeat X2.8.2.2 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.

NOTE X2.6—Generally, three chromatograms may be required to obtain agreement. The first injection of the sample seems to condition the column.

NOTE X2.7—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.

X2.8.2.4 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.

X2.8.3 *Isothermal Operation:*

X2.8.3.1 Follow the procedure in accordance with X2.8.2, 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 X2.4 and Note X2.8). Approximate retention times for the glycols are given in Table X2.2 and Table X2.3. Typical chromatograms for a sample of ethylene and of diethylene glycol at temperatures of 170 and 200°C respectively, are shown in Fig. X2.3 and Fig. X2.4. A typical chromatogram of dipropylene glycol is shown in Fig. X2.5.

NOTE X2.8—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.

X2.9 Calculation

X2.9.1 *Calibration Factors:*

X2.9.1.1 When "hearts cuts" of glycols are used to prepare the standard mixture, obtain the calibration factor for each glycol as follows:

$$F_i = \frac{W_i}{A_{\%i}} \tag{X2.1}$$

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.

X2.9.1.2 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:

$$F_i = \frac{B_i}{A_{si} - A_{bi}} \tag{X2.2}$$

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.

X2.9.2 *Sample Composition:*

X2.9.2.1 Calculate the area percentage of each component as follows:

$$A_{\%i} = \frac{A_i T_i \times 100}{(A_1 T_1) + (A_2 T_2) + (A_3 T_3) + (A_4 T_4)} \tag{X2.3}$$

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.

X2.9.2.2 Calculate the corrected area of each glycol as follows:

$$A_{ci} = A_{\%i} \times F_i \tag{X2.4}$$

where:

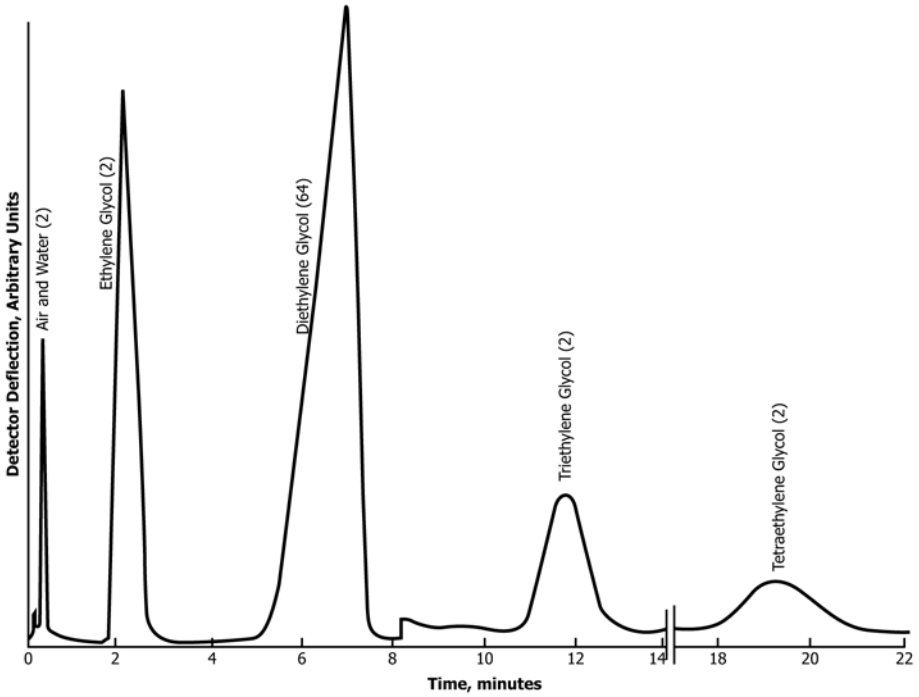

FIG. X2.1 Chromatogram of Diethylene Glycol Linear Programmed Temperature Operation (Recorder Attenuation in Parentheses)

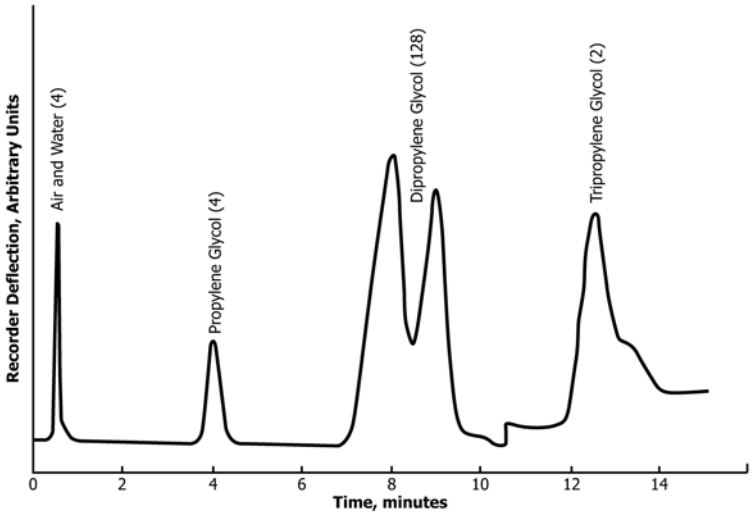

FIG. X2.2 Chromatogram of Dipropylene Glycol Linear Programmed Temperature Operation (Recorder Attenuation in Parentheses)

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

X2.9.2.3 Calculate the weight percent of each glycol on an anhydrous basis as follows:

$$C_i = \frac{A_{ci}}{A_{c1}+A_{c2}+A_{c3}+A_{c4}} \times 100 \qquad \text{(X2.5)}$$

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_{c4}, A_{c4} = corrected areas for mono, di, tri, and tetraalkyl glycols, respectively.

X2.9.2.4 Correct the weight percent of each glycol for the water content of the sample as follows:

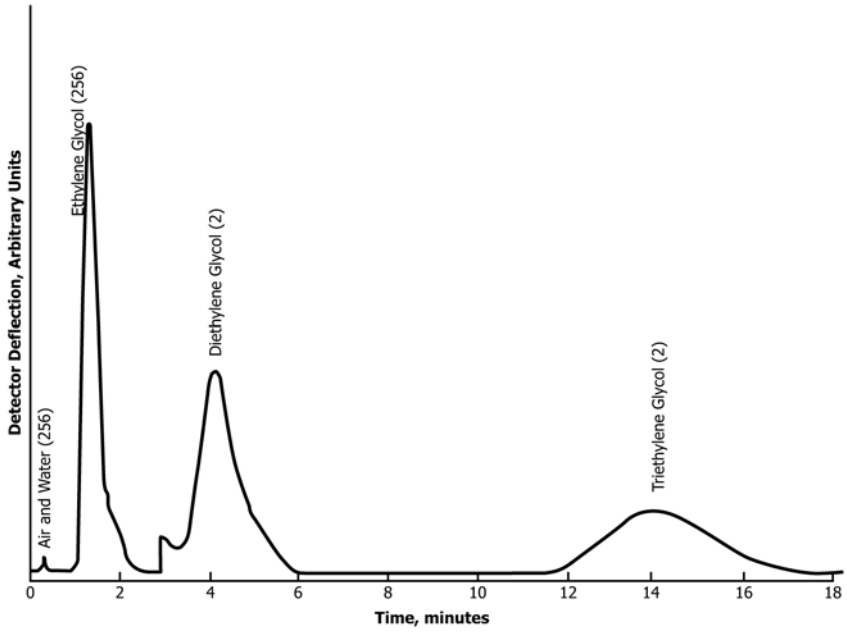

FIG. X2.3 Chromatogram of Ethylene Glycol Isothermal Operation at 170°C (Recorder Attenuation in Parentheses)

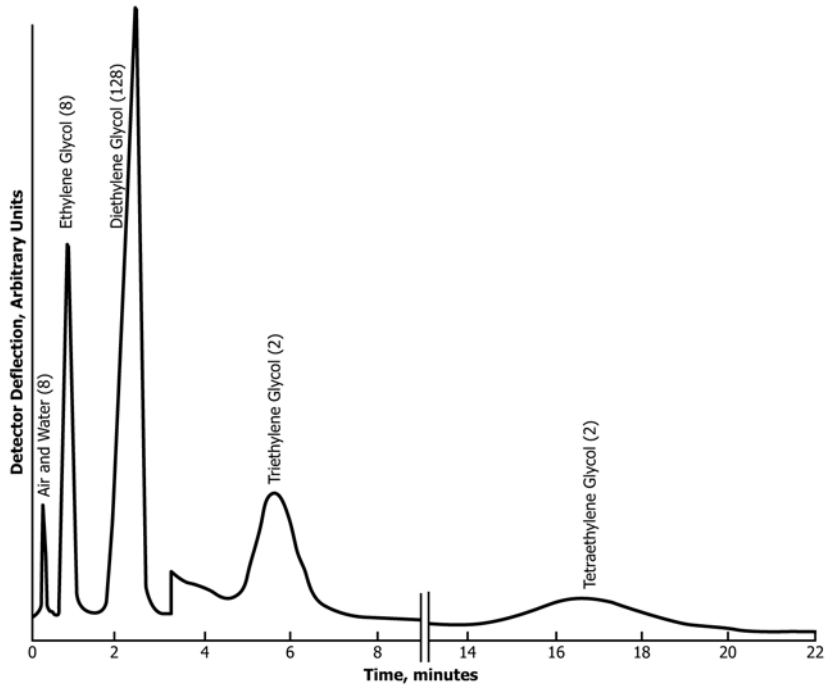

FIG. X2.4 Chromatogram of Diethylene Glycol Isothermal Operation at 200°C (Recorder Attenuation in Parentheses)

$$G_i = \frac{C_i(100 - D)}{100} \quad \text{(X2.6)}$$

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.

X2.10 Report

X2.10.1 Report the weight percent of each component to the nearest 0.01 %.

X2.11 Precision and Bias

X2.11.1 The following criteria should be used for judging the acceptability of results (see Note X2.9):

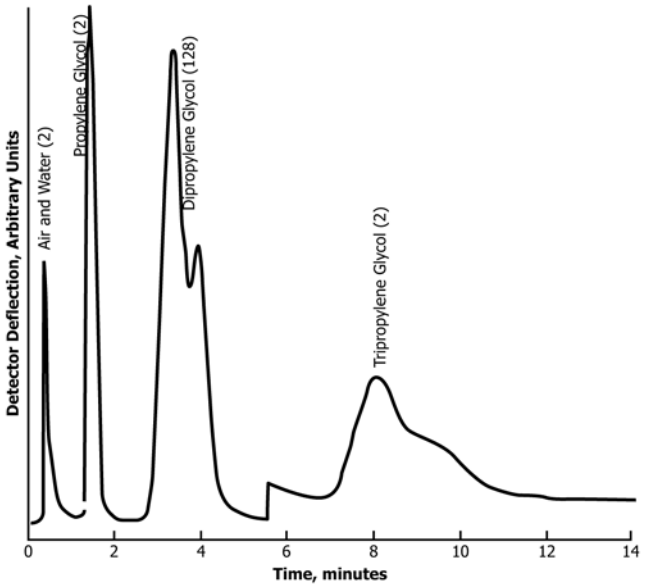

FIG. X2.5 Chromatogram of Dipropylene Glycol Isothermal Operation at 190°C (Recorder Attenuation in Parentheses)

X2.11.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table X2.4 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value in the table.

X2.11.1.2 *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 X2.4 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

X2.11.1.3 *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 X2.4 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

NOTE X2.9—The precision estimates for the ethylene glycols are based on a 1964 to 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 which each analyst performed duplicate determinations by

TABLE X2.4 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
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.

each mode of instrument operation on each of two days, using seven different makes or models of instruments.[13] 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.[13]

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.[13] The calibration factors for converting area to weight percent were obtained using samples of known composition prepared by each analyst.[13] Practice E180 was used in developing these precision estimates.

X2.11.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

[13] Details of the interlaboratory study are available from ASTM Headquarters. Request E15–0028.

X2.12 Keywords

X2.12.1 acidity; color; distillation range; ethylene glycols; gas chromatography; iron; propylene glycols; specific gravity; water

SUMMARY OF CHANGES

Subcommittee E15.01 has identified the location of selected changes to this standard since the last issue (E202-10) that may impact the use of this standard. (Approved April 1, 2012)

(1) Distillation—The precision and bias section became incorrect when a new interlaboratory study was done in 2000. The verbiage in Test Methods E202 is now consistent with the verbiage in the original standard Test Method D1078.

(2) Glycol Impurities—The precision and bias table for *r* and *R* values was missing from original standard Test Method E2409.