



Designation: ~~E202-10~~ Designation: E202 - 12

Standard Test Methods for Analysis of Ethylene Glycols and Propylene Glycols¹

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 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 |
|------------------------------|-------------|
| Purity of Reagents | 4 |
| Specific Gravity | 6-8 |
| Distillation Range | 9-11 |
| Acidity | 12-14 |
| Water | 15-17 |
| Iron | 18-20 |
| Color | 21-23 |
| Gas Chromatographic Analysis | 24-26 |
| Alternative Test Methods | Appendix X1 |

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
- 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 Diethylene 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 (Gas Chromatographic Method)
- E2679 Test Method for Acidity in Mono-, Di-, Tri- and Tetraethylene Glycol by Non-Aqueous Potentiometric Titration

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.

Current edition approved Aug/April 1, 2010-2012. Published September 2010-May 2012. Originally approved in 1962. Last previous edition approved in 2009/2010 as E202-09-E202-10. DOI: 10.1520/E0202-102.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

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

2.2 *ASTM Adjuncts:*

Adjunct ADJD6300 Determination of Precision and Bias for Use in Test Methods for Petroleum Products and Lubricants³

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.

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.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean 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.⁵ 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 $20.0 \pm 0.1^\circ\text{C}$.

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.⁶ 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.

³ 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.

⁴ Available from ASTM International Headquarters.

⁵ ASTM Manual on Presentation of Data and Control Chart Analysis, 7th Edition, ASTM Manual Series MNL 7A (revision of Special Technical Publication (STP) 15D).

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

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

⁸ ASTM Manual on Presentation of Data and Control Chart Analysis, 7th Edition, ASTM Manual Series MNL 7A (revision of Special Technical Publication (STP) 15D).

⁹ Supporting data have been filed at ASTM Headquarters and may be obtained by requesting Research Report RR: RR:E15-1064; RR:E15-0013.

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 | <i>K</i> |
|--------------------|----------|
| 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 The following criteria should be used for judging the acceptability of results (Note 3):

11.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 2 of Test Method

11.1 *Interlaboratory Study:* ^{7, 8}

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 at the indicated degrees of freedom. The 95% limit for the difference between two such runs is the value in the table.

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

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 1 at the indicated degrees of freedom. The 95% limit for the difference between two such averages is the value in the table. 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).³

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.

⁷ Supporting data have been filed at ASTM Headquarters and may be obtained by requesting Research Report RR:RR:E15-1063; RR: RR:E15-1114.

⁸ These Parameters are summarized in Table X2.1 as typical values. See Note X2.4.

⁸ Supporting data have been filed at ASTM Headquarters and may be obtained by requesting Research Report RR: RR:E15-1123.

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 |

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.

NOTE3—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.⁵ Practice E180 was used in developing these precision estimates.

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

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 1 and Table 2 at the indicated degrees of freedom. The 95 % limit of difference between two such runs is also given in Table 1 and 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 1 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.

16. Report

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

TABLE 1 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 2 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 |

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 3 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

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 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.

TABLE 3 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 |

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 interlaboratory study of E1615. Each of 15 laboratories 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.⁹

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

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 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 Practice E180 analysis. The Practice 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 Practice E180 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

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.

⁹Details of the interlaboratory study are available from ASTM Headquarters. Request E15-0028.

⁹ Supporting data have been filed at ASTM Headquarters and may be obtained by requesting Research Report RR: RR:E15-1064.