



Designation: **E2409 – 20 E2409 – 20a**

Standard Test Method for Glycol Impurities in Mono-, Di-, Tri- and Tetraethylene Glycol and in Mono- and Dipropylene Glycol (Gas Chromatographic Method)¹

This standard is issued under the fixed designation E2409; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method describes the gas chromatographic determination of glycol impurities in Mono-, ~~Di-, Tri-,~~ Tri-, and Tetraethylene Glycol (MEG, DEG, ~~TEG and TetraEG~~), and in Mono- and Dipropylene Glycol (MPG and ~~DPG~~).

1.2 This test method is applicable to MEG, DEG, TEG, and TetraEG with impurities to 3000 mg/kg. The limit of detection (LOD) is 22 mg/kg and the limit of quantitation (LOQ) is 73 mg/kg.

NOTE 1—LOD and LOQ were calculated using the lowest level sample in the ILS.

1.3 This test method is applicable to MPG and DPG to 2.5 %.

1.4 Review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions. The following applies for the purposes of determining the conformance of the test results using this test method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section 7.

1.7 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

[D1193 Specification for Reagent Water](#)

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.14 on Alcohols & Glycols.

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

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

[D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials](#)
[E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications](#)
[E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals](#)
 (Withdrawn 2009)³
[E300 Practice for Sampling Industrial Chemicals](#)
[E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration](#)

2.2 *Other Document:*

Manufacturers' instruction manuals of gas chromatograph and digital integration system used

3. Summary of Test Method

3.1 A portion of the test sample is analyzed by temperature-programmed, capillary gas chromatography over a polyethylene glycol column, using flame ionization detection. For quantification, the External Standard Technique or the Internal Standard (Marker) Technique are applied. When applying the Internal Standard Technique, the standard addition technique is used to eliminate the effect of other impurities present in the glycols. For this purpose, a blank glycol is used, as 100 % pure glycol samples are not available.

4. Significance and Use

4.1 Knowledge of the impurities is required to establish whether the product meets the requirements of its specifications.

5. Apparatus

5.1 Autoinjectors are required for all gas chromatograph standards using an external standard to calculate results.

5.2 *Gas Chromatograph(s)*, provided with a sample splitter or on-column injection, flame ionization detector and temperature-programming facilities. Optional are pressure programming and auto sampler facilities. The instrument must be suitable for analysis according to the operating instructions given in [Table 1](#) or [Table 2](#).

5.1.1 *Columns*—The analytical column (chemically bonded cross-linked polyethylene glycol) used must completely separate. MEG, DEG, TEG, TeEG, PentaEG (Penta-ethylene Glycol) and 1,4-butanediol, or MPG, DPG, TPG, and TePG

Figs. A1.1 through A1.5 show examples of chromatograms conforming to the requirements.

5.3 *Columns*—The analytical column (chemically bonded cross-linked polyethylene glycol) used must completely separate. MEG, DEG, TEG, TetraEG, PentaEG (Penta-ethylene Glycol), and 1,4-butanediol, or MPG, DPG, TPG, and TetraPG (Tetrapropylene Glycol).

Fig. A1.1 through Fig. A1.5 show examples of chromatograms conforming to the requirements.

5.4 *Digital Integration Equipment*—Chromatographic data systems are preferred but electronic integration may be used if the user can demonstrate that the results are consistent with the precision statement.

5.5 *Analytical Balance*, readability 0.1 mg, calibrated. Re-calibrate or verify at regular intervals.

5.6 *Crimp Top Vials*, 1 mL and 5 mL.

5.7 *Crimper/De-capper*, for capping and de-capping the vials.

5.8 *Micro Syringes*, 10 µL.

5.9 *Bottles*, 50 mL, with screw cap.

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

TABLE 1 Typical Recommended Operating Parameters for the GC Analysis of Glycol Impurities in MEG, DEG, TEG or TeEGTEG, and TetraG

Column ^A	
Type	Capillary wide-bore
Material	Fused silica
Length × I.D.	15 m × 0.53 mm
Stationary Phase	Polyethylene glycol, for example, DB-Wax
Film Thickness	1 µm
Detector System	
Type	FID
Sensitivity	The ratio of the signal to the noise level must be at least 2:1 at a concentration of 5 mg/kg DEG in MEG
Temperatures	
Column Oven	0.05 min at 70°C Programmed from 70 to 230°C at 25°C/min 10 min at 230°C
Detector	250°C
Carrier Gas	Helium or Nitrogen
Carrier Gas	Helium, nitrogen, or hydrogen. <u>Warning! Helium carrier gas was used to develop this standard. Use of nitrogen or hydrogen requires different conditions. The user must conduct the necessary evaluation to determine that equivalent results are obtained.</u>
Calibration	see Section 9
Calibration	see Section 10
Injected Volume	0.2 µL (on-column injection), or 0.5 µL up to 1 µL (using split injection technique)
Split Ratio	1:10 or appropriate split ratio to allow adequate sensitivity as defined under Detector System (only if split injection technique is used)

^A The mentioned DB-Wax column is available from Agilent Technologies, 5301 Stevens-Creek Blvd, Santa Clara, CA 95051, USA. Other column suppliers market equivalent stationary phases choice of column is based on resolution requirements. Any column may be used that is capable of resolving all significant impurities from the major component. The column and conditions described in Table 1 under trade names, therefore, it is permissible to use a different column from an alternative supplier. have been used successfully and shall be used as a referee in cases of dispute. However, the chromatogram obtained must be equivalent, with regard to separation of the glycol components and 1,4-butanediol, to those illustrated in Fig. A1.1, Fig. A1.2, Fig. A1.3, Fig. A1.4 and Fig. A1.5.

6. Reagents and Materials

6.1 *Purity of Reagents*—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.

6.2 Calibration Standards:

6.2.1 *Mono-ethylene Glycol (MEG)*, minimum purity ~~99.5 % mass (m/m)~~ 99.5 mass %.

6.2.2 *Di-ethylene Glycol (DEG)*, minimum purity ~~99.5 % mass (m/m)~~ 99.5 mass %.

⁴ ACS Reagent Chemicals, *Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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 2 Typical Operating Parameters for the GC Analysis of Glycol Impurities in MPG or DPG

Column ^A	
Type	Capillary wide-bore
Material	Fused silica
Length × I.D.	30 m × 0.32 mm
Stationary Phase	Poly ethylene glycol, for example, DB-Wax
Film Thickness	0.5 µm
Detector System	
Type	FID
Sensitivity	The ratio of the signal to the noise level must be at least 2 to 1 at a concentration of 0.01 % (m/m) DPG in MPG
Temperatures	
Column Oven	5 min at 150°C Programmed from 150 to 180°C at 5°C/min 0 min at 180°C Programmed from 180 to 240°C at 30°C/min 10 min at 240°C
Detector	300°C
Carrier Gas	Helium
Calibration	see Section 9
Calibration	see Section 10
Injected Volume	0.1 µL or 0.5 µL (using split injection technique)
Split Ratio	1 to 10 or appropriate split ratio to allow adequate sensitivity as defined under Detector System

iTech Standards
(<https://standards.itih.ai>)

Document Preview

- 6.2.3 *Tri-ethylene Glycol* (TEG), minimum purity ~~99.5 % mass (m/m)~~ 99.5 mass %.
 - 6.2.4 *Tetra-ethylene Glycol* (~~TeEG, also called TTEG~~), (TetraEG), of maximum purity available.
 - 6.2.5 *Penta-ethylene Glycol* (PentaEG), of maximum purity available, or <https://standards.itih.ai/catalog/standards/sist/5375ad38-4baa-4468-888d-169ac4d1cc4a/astm-e2409-20a>
 - 6.2.6 *Mono-propylene Glycol* (MPG), minimum purity ~~99.5 % mass (m/m)~~ 99.5 mass %.
 - 6.2.7 *Di-propylene Glycol* (DPG), minimum purity ~~99.5 % mass (m/m)~~ 99.5 mass %.
 - 6.2.8 *Tri-propylene Glycol* (TPG), of maximum purity available.
 - 6.2.9 *Tetra-propylene Glycol* (~~TePG~~), (TetraPG), of maximum purity available.
- 6.3 *Internal Standard:*
- 6.3.1 *1,4-Butanediol* minimum purity ~~97 % mass (m/m)~~ 97 mass %, for ethylene glycols, if necessary.
 - 6.3.2 *n-Octane* minimum purity ~~97 % mass (m/m)~~ 97 mass %, for propylene glycols, if necessary.
- 6.4 *Ethylene Glycol Quality Control Sample*, fiber grade MEG, DEG, TEG₂ or TeEG or *Propylene Glycol Quality Control Sample*, MPG or DPG (only required if maintaining a control chart). Store nitrogen capped at a temperature between 0 and 5°C. Warm to ambient temperature before use. See Section 15.
- 6.5 ~~*Water, Purity of Water—HPLC grade.*~~ Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to type I of Specification D1193.

6.6 *Solutions:*

6.6.1 *Internal Standard Solution*—Weigh about 0.15 g 1,4-butanediol (m_1) to the nearest 0.1 mg into a 50 mL bottle. Add ultra-pure water up to a total mass of 50 g (m_2), weighing to the nearest 0.1 mg. Calculate the concentration of this solution to the nearest 0.1 mg/kg; or

6.6.2 *External Standard Solution*, of accurately known
 MEG, DEG, TEG, TetraEG, and TeEGPentaEG content; or
 MPG, DPG, TPG, and TePGTetraPG content (see [9.4.10.4](#)).

7. Hazards

7.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

8. Sampling, Test Specimens, and Test Units

8.1 Follow the relevant instructions for sampling as given in Practice [E300](#).

9. Preparation of Apparatus

9.1 *Gas Chromatograph(s) and Column(s)*—Check the performance of the gas chromatograph and column as described in Section [9.10](#).

10. Calibration and Standardization

10.1 Two methods of quantification may be employed: the Internal Standard (Marker) Technique or the External Standard Technique.

10.2 *Internal Standard Technique for Ethylene Glycols:*

10.2.1 Prepare calibration solutions, containing approximately 500, 1000, and 2000 mg/kg of each of the glycol components to be determined, by adding the relevant calibration standard (see [6.2](#)) to a blank sample of the glycol being analyzed. Calculate the exact concentration of each glycol component (c_1) in the calibration solutions.

10.2.2 Weigh 0.5 g of each calibration solution (m_3) to the nearest 0.1 mg, into separate 5-mL vials. Add, also weighed to the nearest 0.1 mg, 0.5 g internal standard solution (see [6.6.1](#); m_4) and add HPLC-grade water up to a total mass of approximately 5 g. Cap the vials and mix thoroughly.

10.2.3 Prepare a blank calibration solution by weighing 0.5 g blank sample of the glycol being analyzed (m_5), weighed to the nearest 0.1 mg, into a 5-mL vial. Add 0.5 g internal standard solution (see [6.6.1](#); m_6), also weighed to the nearest 0.1 mg, and add HPLC grade water up to a total mass of approximately 5 g. Cap the vial and mix thoroughly.

10.2.4 Calibrate separately for each impurity in MEG, DEG, TEG, or TeEG by using the Internal Standard (Marker) Technique.

10.2.5 Fill a 1-mL sample vial with the calibration solution from the 5-mL vial (see [9.2.2.10.2.2](#) and [9.2.3.10.2.3](#)). Close the vial by means of an aluminum crimp cap.

10.2.6 Analyze each calibration solution and the blank solution using the operating parameters given in [Table 1](#). Inject each solution at least twice and calculate the average peak areas for each of the calibration solutions. Apply digital integration equipment for measuring the peak areas.

10.2.7 For each chromatogram, calculate the system response factor (f) of each of the components as described in [9.2.8.10.2.8](#) through [9.2.10.2.10](#).

10.2.8 Calculate the amount of internal standard (1,4-butanediol) added to the calibration solution:

$$\text{Mass of Internal Standard } (m_7), \text{ g} = \frac{m_4 \times m_1}{m_2} \quad (1)$$

where:

- m_1 = mass of 1,4-butanediol in internal standard solution (6.6.1), g,
- m_2 = total mass of internal standard solution (6.6.1), g, and
- m_4 = mass of internal standard solution added, g.

10.2.9 Calculate the amount of internal standard (1,4-butanediol) added to the blank solution:

$$\text{Mass of Internal Standard } (m_6), \text{ g} = \frac{m_6 \times m_1}{m_2} \quad (2)$$

where:

~~m_6 = mass of internal standard solution added (9.2.3), g.~~

m_6 = mass of internal standard solution added (10.2.3), g.

10.2.10 Calculate the response factor of each component of interest in the calibration solutions by means of the following equation:

$$f = \frac{c_1 \times 10^{-6}}{\left(\frac{m_7 \times A_1}{m_3 \times A_2} \right) - \left(\frac{m_8 \times A_3}{m_5 \times A_4} \right)} \quad (3)$$

where:

~~c_1 = added concentration of glycol compound in the calibration solution, (9.2.1), mg/kg,~~

~~c_1 = added concentration of glycol compound in the calibration solution, (10.2.1), mg/kg,~~

~~A_1 = peak area of component in calibration solution, arbitrary units,~~

~~A_2 = peak area of internal standard in calibration solution, same arbitrary units,~~

~~A_3 = peak area of component in blank solution, same arbitrary units,~~

~~A_4 = peak area of internal standard in blank solution, same arbitrary units,~~

~~m_3 = mass of calibration solution (9.2.2), g,~~

~~m_3 = mass of calibration solution (10.2.2), g,~~

~~m_5 = mass of blank solution (9.2.3), g,~~

~~m_5 = mass of blank solution (10.2.3), g,~~

~~m_7 = mass of internal standard in calibration solution, as obtained in 9.2.8, g, and~~

~~m_7 = mass of internal standard in calibration solution, as obtained in 10.2.8, g, and~~

~~m_8 = mass of internal standard in blank solution, as obtained in 9.2.9, g.~~

~~m_8 = mass of internal standard in blank solution, as obtained in 10.2.9, g.~~

10.2.11 Calculate the mean of the response factors. If the individual factors differ by more than 5 % from the mean response factor, repeat the measurement of the respective calibration solution.

10.3 *Internal Standard Technique for Propylene Glycols*—Calibrate by determining the calibration factor for each component of interest relative to the internal standard on the basis of peak area versus mass as follows:

10.3.1 Prepare a calibration solution by accurately weighing 0.5 g of each of the components of interest and of the internal standard, to the nearest 0.1 mg into a previously tarred, 50 mL bottle. Fill the bottle with a suitable solvent (for example, acetone/cyclohexane), close, and reweigh to the nearest 0.1 mg. Homogenize the calibration solution.

10.3.2 Analyze the calibration solution following the operating parameters given in Table 2. Introduce the calibration solution at least twice. Determine the area of the components of interest and the reference component.

10.3.3 Calculate the mean peak area of the components of interest for the calibration solution. If the two single peak areas differ by more than 3 % relative, repeat the analysis. If no satisfactory results can be obtained, stabilize the conditions and repeat 9.3-10.3.1 and 9.3-210.3.2.

10.3.4 Calculate the calibration factor (f_1) for all individual compounds, relative to the internal standard, by means of the following equation:

TABLE 3 External Standard Recommended Weights

Standard #	Target Weight of Glycol Component, ± 0.0001 g	Target Weight of High Purity Blank Glycol, ± 0.1 g
200 mg/kg	0.010	50
500 mg/kg	0.025	50
1000 mg/kg	0.050	50

$$f_i = \frac{m_i \times A_m}{m_m \times A_i} \quad (4)$$

where:

m_i = mass of component i in calibration solution (9.3.1), g;
 m_m = mass of internal standard in calibration solution (9.3.1), g;
 A_i = peak area of component i (9.3.3), arbitrary units;
 A_m = peak area of internal standard (9.3.3), same arbitrary units.

m_i = mass of component i in calibration solution (10.3.1), g;
 m_m = mass of internal standard in calibration solution (10.3.1), g;
 A_i = peak area of component i (10.3.3), arbitrary units;
 A_m = peak area of internal standard (10.3.3), same arbitrary units.

NOTE 2—An alternative for the empirical calibration factors as described in 9.210.2 and 9.310.3 is the use of theoretical factors, based on the molecular structure of the compounds of interest. Theoretical factors calculated are as follows: For MPG 3.045, for all DPG isomers 2.512, for all TPG isomers 2.244, all relative to octane. See Footnote 5-6.⁵

10.4 External Standard Technique Ethylene Glycols, similar for Propylene Glycols:

10.4.1 Prepare at least three calibration solutions, for example, containing 200, 500, and 1000 mg/kg of each of the glycol components to be determined, by adding the relevant calibration standard (see 6.2) to a blank sample of the glycol being analyzed and mix thoroughly. Weigh each glycol component to the nearest 0.1 mg and the blank glycol to the nearest 0.1 g. (See Table 3 for recommended weights.)

10.4.1.1 Calculate the exact concentration of each glycol component (C_i) in the calibration solutions. The calibration range can be adjusted if needed.

$$C_i = \frac{W_{(Comp;i)}}{W_{(Comp;i)} + W_{(Blank;i)}} \times \frac{10^6 \mu\text{g}}{\text{g}} \quad (5)$$

where:

C_i = the concentration of each glycol component in the calibration standard of interest,
 i = glycol component standard of interest,
 $W_{(Comp;i)}$ = mass (g) of glycol component added to the calibration standard of interest, and
 $W_{(Blank;i)}$ = mass (g) of blank glycol added to the calibration standard of interest.

10.4.2 Analyze each calibration solution and the blank solution using the operating parameters given in Table 1 or Table 2. Inject each solution at least twice.

10.4.2.1 Prepare a plot of area counts of the glycol component (y-axis) versus the concentration of the glycol component (mg/kg) added to the standard of interest (x-axis). Using a computer program, determine the best-fit line through the data using linear regression analysis. The relationship between concentration and peak area will be linear. Record the intercept value (concentration; mg/kg) where the resulting line crosses the x-axis ($y = 0$). Apply digital integration equipment for measuring the peak areas.

10.4.2.2 Calculate the corrected concentration (mg/kg) of the glycol component in each calibration standard as follows:

$$\text{Corrected } C_i = C_i + Y \quad (6)$$

⁵ Sternberg, J.C. *Gas Chromatography*, Academic Press, New York, 1962; pp. 231-267.