Designation: 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-, 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 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

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.

[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.

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

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

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.

5.3 *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 *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. Recalibrate 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.

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

[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 1 Recommended Operating Parameters for the GC Analysis of Glycol Impurities in MEG, DEG, TEG, 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, nitrogen, or hydrogen. 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.
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 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 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, and Fig. A1.3, or Fig. A1.4 and Fig. A1.5.

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 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

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 %.

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

6.2.3 *Tri-ethylene Glycol* (TEG), minimum purity 99.5 mass %.

6.2.4 *Tetra-ethylene Glycol* (TetraEG), of maximum purity available.

6.2.5 *Penta-ethylene Glycol* (PentaEG), of maximum purity available, or

6.2.6 *Mono-propylene Glycol* (MPG), minimum purity 99.5 mass %.

6.2.7 *Di-propylene Glycol* (DPG), minimum purity 99.5 mass %.

6.2.8 *Tri-propylene Glycol* (TPG), of maximum purity available.

6.2.9 *Tetra-propylene Glycol* (TetraPG), of maximum purity available.

6.3 *Internal Standard:*

6.3.1 *1,4-Butanediol* minimum purity 97 mass %, for ethylene glycols, if necessary.

6.3.2 *n-Octane* minimum purity 97 mass %, for propylene glycols, if necessary.

6.4 *Ethylene Glycol Quality Control Sample,* fiber grade MEG, DEG, TEG, 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 *Purity of Water*—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 PentaEG content; or MPG, DPG, TPG, and TetraPG content (see 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 10.