Designation: E2409 – 13

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 TeEG) in the range of 5 to 3000 mg/kg, and in Mono- and Dipropylene Glycol (MPG and DPG) in the range 0.01 to 2.5 % (m/m).

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

1.3 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

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]

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

5.2 *Digital Integration Equipment.*

5.3 *Analytical Balance,* readability 0.1 mg, calibrated. Recalibrate or verify at regular intervals.

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

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

5.6 *Micro Syringes,* 10 µL.

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

[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.02 on Product 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.

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

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TABLE 1 Typical Operating Parameters for the GC Analysis of Glycol Impurities in MEG, DEG, TEG or TeEG

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
Calibration	see Section 9
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 under trade names, therefore, it is permissible to use a different column from an alternative supplier. However, the chromatogram obtained must be identical, with regard to separation of the glycol components and 1,4-butanediol, to those illustrated in Figs. A1.1, A1.2, and A1.3, or A1.4 and 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 9
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

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).

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

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

6.2.4 *Tetra-ethylene Glycol* (TeEG), 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 (m/m).

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

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

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

6.3 *Internal Standard:*

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

6.3.2 n-Octane, minimum purity 97 % mass (m/m), 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, see 10.5). Store nitrogen capped at a temperature between 0 and 5°C. Warm to ambient temperature before use.

6.5 *Water,* HPLC grade.

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, and TeEG content, or
MPG, DPG, TPG, and TePG content,
to be used as external standard (see 9.4).

[4] *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 *Annual 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.

7. Sampling, Test Specimens, and Test Units

7.1 Follow the relevant instructions for sampling as given in Practice E300.

8. Preparation of Apparatus

8.1 *Gas Chromatograph(s) and Column(s)*—Check the performance of the gas chromatograph and column as described in Section 9.

9. Calibration and Standardization

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

9.2 *Internal Standard Technique for Ethylene Glycols:*

9.2.1 Prepare calibration solutions, containing 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.

9.2.2 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.

9.2.3 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.

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

9.2.5 Fill a 1-mL sample vial with the calibration solution from the 5-mL vial (see 9.2.2 and 9.2.3). Close the vial by means of an aluminum crimp cap.

9.2.6 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.

9.2.7 For each chromatogram, calculate the system response factor (f) of each of the components as described in 9.2.8 through 9.2.10.

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

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

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.

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

$$\text{Mass of Internal Standard } (m_8),\ \text{g} = \frac{m_6 \times m_1}{m_2} \tag{2}$$

where:

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

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

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

where:

c_1 = added concentration of glycol compound in the calibration solution, (9.2.1), 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_5 = mass of blank solution (9.2.3), g,
m_7 = mass of internal standard in calibration solution, as obtained in 9.2.8, g, and
m_8 = mass of internal standard in blank solution, as obtained in 9.2.9, g.

9.2.11 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.

9.3 *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:

9.3.1 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.

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

9.3.3 Calculate the mean peak areas 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 9.3.1 and 9.3.2.

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

$$f_i = \frac{m_i \times A_m}{m_m \times A_i} \tag{4}$$

where: