Designation: E2469 – 16

Standard Test Method for Chloride in Mono-, Di- and Tri-ethylene Glycol by Ion Chromatography[1]

This standard is issued under the fixed designation E2469; 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 covers the determination of inorganic chloride (chloride ion) in monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) in the range of 0.01 to 1.0 mg/kg by ion chromatography (IC).

1.2 Ethylene glycol can be analyzed directly by this test method without any sample preparation or diluted with high quality deionized water if an autosampler is used and dilution is necessary (that is, 50:50 or other suitable ratio).

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

1.3.1 The exception is the additional information of (psi) in 9.3.3, 11.1.1, and 11.2.1.

1.4 Review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first-aid procedures and safety precautions.

1.5 *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 to determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

3. Summary of Test Method

3.1 An aliquot of the glycol sample is injected directly (manually) or diluted (via autosampler) into an ion chromatograph consisting of an injector with a fixed sample loop, two anion exchange columns (guard and separator column), an anion suppressor and a conductivity detector. Ions are separated based on their affinity for the ion exchange sites of the resin with respect to the resin's affinity for the eluent. The suppressor increases the sensitivity of the test method by both increasing the conductivity of the analytes and decreasing the conductivity of the eluent. The suppressor converts the eluent and the analytes to the corresponding hydrogen form acids. The chloride is detected by conductivity detection and identified by retention time. Quantitation is by peak area using an external standard calibration curve. Instructions are provided for two equivalent IC systems.

4. Significance and Use

4.1 This test method provides for the quantitative determination of inorganic chloride (chloride ion) in monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) using ion chromatography with conductivity detection. The analysis time is less than 5 min with little or no sample preparation required. Conductivity detection is a universal detection mode and is linear over the range of the method. Acceptable levels of chloride in polyester-grade and low-conductivity-grade MEG vary with the manufacturer's specifications but are normally in the low mg/kg range. Knowledge of the chloride content in polyester-grade and low-conductivity-grade MEG is required to establish whether the MEG product meets specification requirements.

4.2 Glycols have high viscosities and a dilution with high quality deionized water may be required depending on the capability of the autosampler, if used, to deliver the injection.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.16 on Industrial and Specialty 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**

All standards and samples, whether diluted or not should be treated in the same manner.

5. Interferences

5.1 The identification of chloride is based on retention time. Interferences can be caused by ionic substances with retention times similar to that of chloride. If the eluent conditions are changed or the column capacity changes, it is possible that other anions may coelute with chloride and cause an interference.

5.2 Any anion that elutes after chloride under the analysis conditions used in the test method may cause an interference if the run time of the method isn't long enough to include that anion. When the run time of a method is too short, a late eluting anion from one analysis may be detected during the next analysis and cause an interference if it elutes at the same time as chloride. Carbonate, if present in a sample, may cause an interference in IC systems using hydroxide eluent (like Configuration B) if the run time of the analysis is not long enough to include the carbonate peak. The elution time of carbonate under the analysis conditions used in this test method is directly related to the amount of carbonate in the sample. The higher the concentration of carbonate in a sample, the faster the carbonate elutes from the column.

5.3 Method interferences can be caused by the contamination of glassware, eluent and reagents with chloride. Care must be taken to ensure glassware and apparatus are free of chloride. The use of latex gloves is recommended to prevent chloride contamination while handling samples and reagents.

5.4 In an IC system with an electrolytic membrane based suppressor operated in the recycle mode, the eluent is recycled back through the suppressor after it exits the conductivity cell to provide a source of water for electrolytic generation of hydronium ions for the regenerant. Using this system configuration, there is an interference caused by the glycol sample as it passes back through the suppressor. This interference appears as a large broad peak that upsets the baseline during the time chloride elutes from the column. Accurate quantitation of chloride is very difficult if not impossible with this interference present. To avoid this interference, an external supply of reagent water is used as the source of hydronium ions for the regenerant. In the external water mode, water flows countercurrent to the eluent through the suppressor. The water can be pressurized or pumped through the suppressor to achieve the required flow rate.

5.5 No other direct interferences have been observed in the use of this test method. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate test method.

6. Apparatus

6.1 *Analytical Balance,* capable of weighing 200 g to the nearest 0.0001 g. (See Note 1.)

6.2 *Pipettes,* capable of measuring from 100-µL to 10-mL. (See Note 1.)

NOTE 1—The accuracy of balances and pipettes should be confirmed on a regular basis and documentation of the check should be kept.

6.3 *Ion Chromatograph, Configuration A (Bottled Eluent System - Carbonate-Based) (see Note 2)*—Analytical instrument with all the required accessories including an eluent pump, temperature-controlled low volume (< 2 µL) conductivity cell, conductivity detector, PEEK tubing, and a PEEK injection valve with a fixed sample loop. An auxiliary regenerant pump or pressurized 4-L reagent bottle is required for external regenerant delivery. Autosampler (optional). The instrument must be suitable for analysis according to the operating conditions given in 11.1.

NOTE 2—The ion chromatograph (Configuration A) uses a carbonate based eluent system in which the eluent is prepared by the analyst from analytical grade reagents or commercially available concentrated carbonate solutions. There is more variability in the retention time of chloride with this type of system as a result of variations in the concentration of the eluent prepared by analysts. This is the oldest and most commonly used IC system.

6.3.1 *Anion Exchange Guard Column (for Carbonate-Based Eluent),* for protection of the analytical column from strongly retained components and organics. Better separations are obtained with the additional plates of the guard column.

6.3.2 *Anion Exchange Separator Column (for Carbonate-Based Eluent),* capable of producing separation of the chloride equivalent to or better than that shown in Fig. 1.

6.3.3 *Anion Suppressor,* an electrolytic self-regenerating membrane suppressor, micromembrane suppressor or equivalent suppressor capable of lowering the background conductance of the eluant to a level that allows the method detection limit to be achieved.

6.3.4 *Chromatography Data System,* for data acquisition and data processing.

6.4 *Ion Chromatograph, Configuration B (Eluent Generation System - Hydroxide Eluent) (see Note 3)*—Analytical instrument with all the required accessories including an eluent pump, temperature controlled low volume (< 2 µL) conductivity cell, conductivity detector, PEEK tubing, PEEK injection valve with a fixed sample loop and electrolytic eluent generation module. An auxiliary regenerant pump or pressurized 4-L reagent bottle is required for external regenerant delivery. Autosampler (optional). The instrument must be suitable for analysis according to the operating conditions given in 11.2.

NOTE 3—The IC system (Configuration B) uses on-line electrolytic eluent generation to produce a hydroxide eluent. The hydroxide eluent is generated from reagent water using an eluent generator cartridge. The concentration of hydroxide eluent is very reproducible, so the retention time for chloride is less variable than with a carbonate eluent. This newer technology for eluent generation eliminates the variability of eluent preparation by an analyst. It also eliminates the problems with eluent aging (weakening) and contamination.

NOTE 4—The IC system in Configuration B uses on-line electrolytic eluent generation to produce the eluent. The type of eluent produced depends on the eluent generator cartridge used with the IC system. There are four types of eluent generator cartridges including potassium hydroxide, carbonate-bicarbonate, lithium hydroxide and sodium hydroxide. For this test method the potassium hydroxide eluent cartridge is recommended for use with hydroxide selective columns. The carbonate-bicarbonate eluent cartridge and eluent pH modifier can be used with carbonate selective columns (6.3.1 and 6.3.2) if the analyst prefers on-line carbonate-bicarbonate eluent generation.

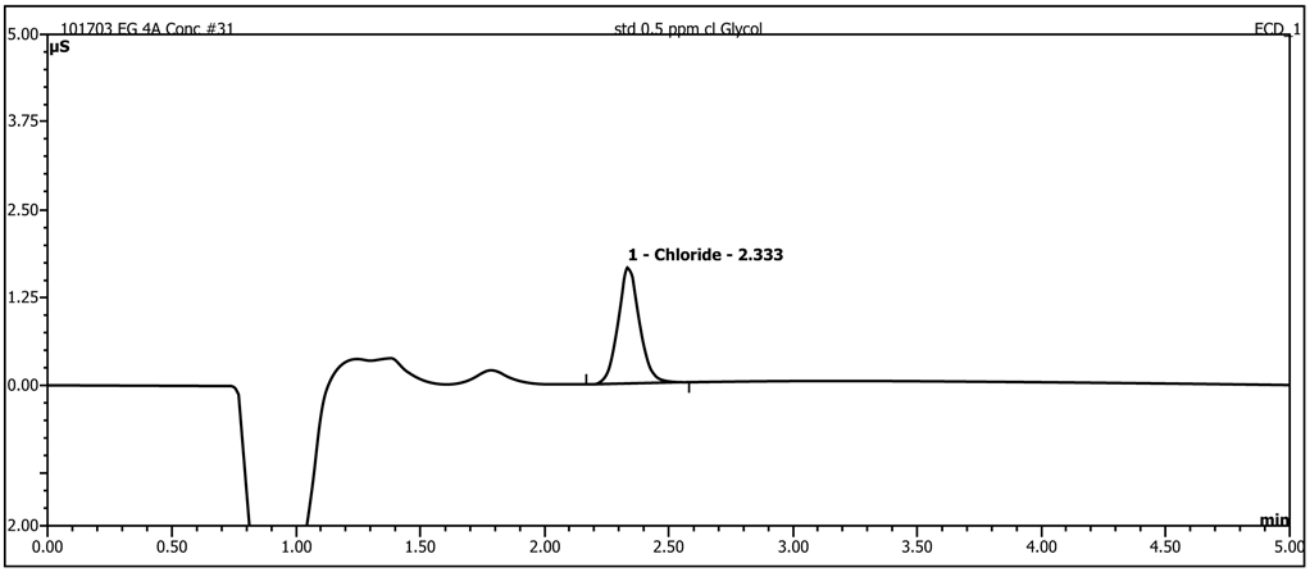

FIG. 1 Representative Sample Chromatogram Obtained Using the Conditions Outlined in 11.1 (Configuration A)

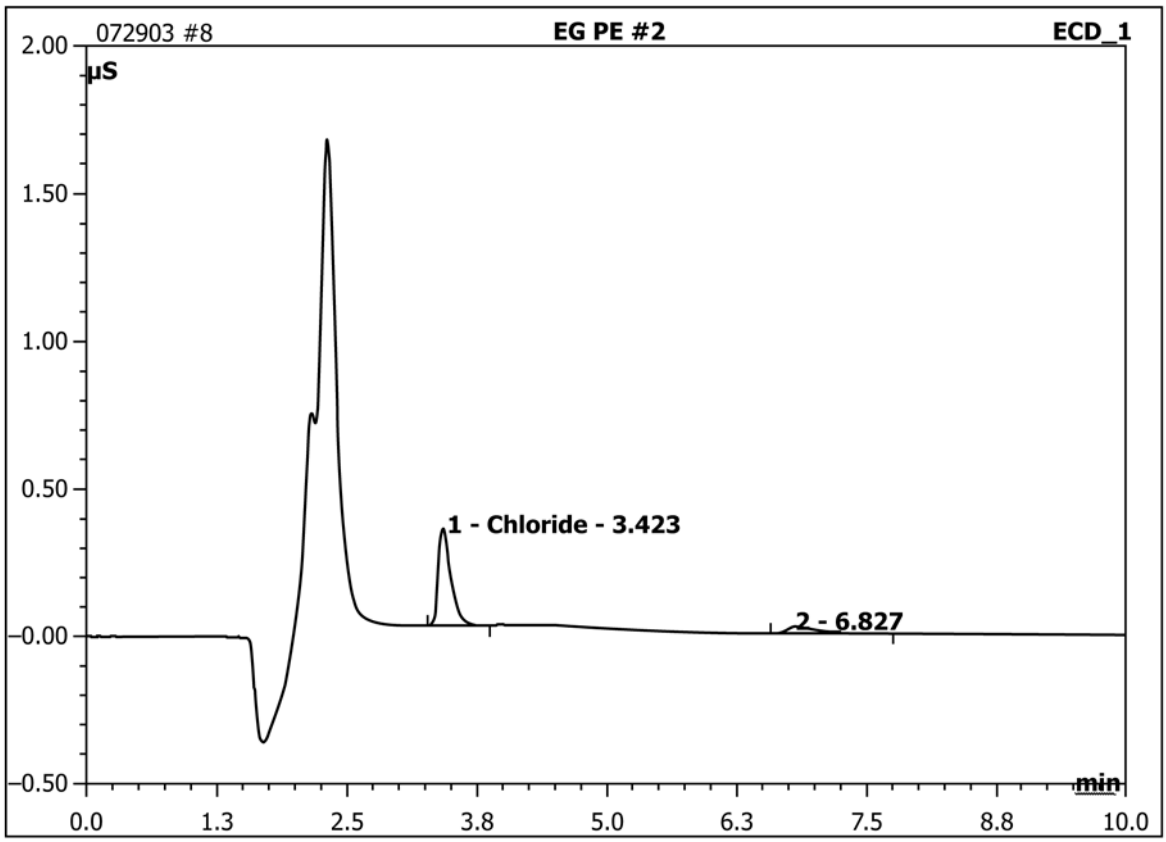

FIG. 2 Representative Sample Chromatogram Obtained Using the Conditions Outlined in 11.2 (Configuration B)

6.4.1 *Anion Exchange Guard Column (for Hydroxide Eluent),* for protection of the analytical column from strongly retained components and organics. Better separations are obtained with the additional plates of the guard column.

6.4.2 *Anion Exchange Separator Column (for Hydroxide Eluent),* capable of producing separation of chloride equivalent to or better than that shown in Fig. 2.

6.4.3 *Anion Exchange Trap Column (for Hydroxide Eluent),* electrolytic continuously regenerated trap column or equivalent trap column capable of removing anionic impurities from reagent water used with the eluent generation cartridge.

6.4.4 *Anion Suppressor,* an electrolytic self-regenerating membrane suppressor, micromembrane suppressor or equivalent suppressor capable of lowering the background conductance of the eluant to a level that allows the method detection limit to be achieved.

6.4.5 *Eluent Generator Cartridge,* capable of producing carbonate-free potassium hydroxide.[4]

6.4.6 *Chromatography Data System,* for data acquisition and data processing.

6.4.7 *Chromatography Operating System,* capable of controlling the current required for eluent generation and trap column regeneration.

6.5 *Volumetric Glassware,* 100-mL, 1-L, and 2-L volumetric flask. (See Note 5.)

6.6 *Plastic Cups with Lids,* 120 mL. (See Note 5.)

6.7 *Weigh Dish,* small disposable polystyrene. (See Note 5.)

6.8 *Bottles with Caps,* 125-mL Nalgene low density polyethylene (LDPE) narrow mouth. (See Note 5.)

6.9 *Plastic Syringe,* 10-mL with Luer-Lok Tip. (See Note 5.)

NOTE 5—Care should be taken to ensure glassware, reagents and apparatus are free of chloride contamination.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) 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.

7.2 *High-Purity Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193. It is recommended that all water be filtered through a 0.2-µm filter. For eluent preparation, it is recommended to degas the water by sparging with helium or vacuum degassing and sonication.

7.3 *Sodium Chloride,* ACS reagent grade.

7.4 *Chloride Quality Assurance Check Standard,* an independent, certified 10 µg/mL chloride standard (not made from sodium chloride in 7.3), may be purchased commercially.

7.5 *Sodium Carbonate (Configuration A),* ACS reagent grade.

7.6 *Sodium Bicarbonate (Configuration A),* ACS reagent grade.

7.7 *Sodium Carbonate Concentrate (Configuration A),* 0.5 *M* sodium carbonate, commercially available.

7.8 *Sodium Bicarbonate Concentrate (Configuration A),* 0.5 *M* sodium bicarbonate, commercially available.

7.9 *Monoethylene Glycol (MEG) (High Purity),* with low concentrations of impurities.

7.10 *Diethylene Glycol (DEG) (High Purity),* with low concentrations of impurities.

7.11 *Triethylene Glycol (TEG) (High Purity),* with low concentrations of impurities.

NOTE 6— Impurities in high-purity MEG, DEG or TEG used for preparation of the chloride working standards or for sample dilution should not exceed 0.01 mg/kg. This information should be provided by the supplier or determined by the analyst before use.

7.12 *Sulfuric Acid (for use with anion micromembrane suppressor),* concentrated sulfuric acid (95 to 98 %).

7.13 *Anion Regenerant Concentrate (for use with anion micromembrane suppressor),* 1 M sulfuric acid, commercially available.

7.14 *Isopropyl Alcohol (2-Propanol),* ACS reagent grade.

7.15 *Methyl Alcohol (Methanol, alternate for Isopropyl Alcohol),* ACS reagent grade.

7.16 *Monoethylene Glycol Quality Control Sample,* polyester grade MEG.

7.17 *Diethylene Glycol Quality Control Sample.*

7.18 *Triethylene Glycol Quality Control Sample.*

8. Reagent Solutions

8.1 *Chloride Stock Solution (1000 mg/kg Chloride in Water):*

NOTE 7—As an alternative, a 1000 µg/mL chloride standard may be purchased commercially.

NOTE 8—The density of the commercial chloride stock solution is assumed to be 1.0 g/mL at room temperature for wt/wt calculations in mg/kg.

8.1.1 Place a 125-mL Nalgene LDPE narrow mouth bottle on the balance and tare.

8.1.2 Weigh (and record to the nearest 0.0001 g) 0.1649 ± 0.0010 g of sodium chloride (7.3) into the 125-mL bottle.

8.1.3 Dilute to 100 g (and record to the nearest 0.001 g) with reagent water (7.2) and mix well. Prepare this calibration solution once a year.

8.1.4 Calculate the concentration of chloride in the chloride stock solution as follows:

$$C_{CSS} = \frac{W_{NaCl} \times 10^6\ mg \times FW_{Cl}}{W_{STD} \times 1\ kg \times FW_{NaCl}} \quad (1)$$

[4] The sole source of supply of the potassium hydroxide eluent generation cartridge known to the committee at this time is Thermo Fisher Scientific, 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA, 94088-3603, http://www.dionex.com. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USP), Rockville, MD.

where:

C_{CSS} = the concentration (mg/kg) of chloride in the chloride stock solution,
W_{NaCl} = weight (g) of sodium chloride added to the chloride stock solution (8.1.2),
W_{STD} = total weight (g) of the prepared chloride stock solution (8.1.3, nominally 100 g),
FW_{Cl} = formula weight of chloride (35.457 g/mol), and
FW_{NaCl} = formula weight of sodium chloride (58.44 g/mol).

8.2 *Chloride Calibration Solution (10 mg/kg Chloride in Water):*

NOTE 9—Pipettes are used to dispense the estimated amount of chloride stock solution (1000 mg/kg).

8.2.1 Place a 100-mL volumetric flask on the balance and tare. Pipette (and record the weight to the nearest 0.0001 g) 1000 µL of 1000 mg/kg chloride stock solution (8.1) into the 100-mL volumetric flask.

8.2.2 Dilute to 100 mL (and record the weight to the nearest 0.001 g) with reagent water (7.2) and mix well. Store the 10 mg/kg chloride calibration solution in a 125-mL Nalgene LDPE narrow mouth bottle. Prepare this calibration solution once a year.

8.2.3 Determine the concentration (mg/kg) of chloride in the chloride calibration solution as follows:

$$C_{CS} = \frac{C_{CSS} \times W_{CSS}}{W_{CS}} \quad (2)$$

where:

C_{CS} = the concentration (mg/kg) of chloride in the chloride calibration solution,
C_{CSS} = the concentration (mg/kg) of chloride in the chloride stock solution (8.1),
W_{CSS} = weight (g) of chloride stock solution added to chloride calibration solution (8.2.1), and
W_{CS} = final weight (g) of the prepared chloride calibration solution (8.2.2, nominally 100 g).

8.3 Chloride Working Standards (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 mg/kg in MEG, DEG, or TEG).

NOTE 10—Pipettes are used to dispense the estimated amount of chloride calibration solution (10 mg/kg).

8.3.1 Prepare at least five chloride working standard solutions (8.3) covering the expected range for the glycol being analyzed. Choose the dilutions such that the resulting concentrations are equally distributed over the range of interest. For each of the chloride working standards, place a 120-mL plastic cup on the balance and tare. Using Table 1 for guidance, add the appropriate amount of 10 mg/kg chloride calibration solution (8.2) and record the weight to the nearest 0.0001 g.

8.3.2 Add the high purity MEG, DEG or TEG (7.9, 7.10 or 7.11) to obtain the final weight of 100 g. Mix well to ensure a homogeneous solution. Record the final weight of the chloride working standard to the nearest 0.001 g.

NOTE 11—Chloride working standards should be prepared a minimum of every three months (monthly preparation is recommended). To avoid contamination of the standard, always pour the working standard out of the bottle for use and never put anything (pipette and so forth) into the bottle. Minimize the number of times and length of time the working standards are exposed to air. Cap securely after each use.

TABLE 1 Chloride Working Standard

Chloride Working Standard #	Nominal Concentration	Weight of 10 mg/kg Chloride Calibration Solution (to add)	Final Weight of Chloride Working Standard (MEG DEG or TEG added)
	mg/kg	g (± 0.0001 g)	g (± 0.001 g)
1	0	0	100
2	0.01	0.1	100
3	0.02	0.2	100
4	0.05	0.5	100
5	0.1	1.0	100
6	0.2	2.0	100
7	0.5	5.0	100
8	1.0	10.0	100

8.3.3 Determine the concentration (mg/kg) of chloride in each of the chloride working standards as follows:

$$C_{WS(i)} = \frac{C_{CS} \times W_{CS(i)}}{W_{WS(i)}} \quad (3)$$

where:

$C_{WS(i)}$ = the concentration (mg/kg) of chloride in chloride working standard, *i*,
C_{CS} = the concentration (mg/kg) of chloride in the chloride calibration solution (8.2),
$W_{CS(i)}$ = weight (g) of chloride calibration solution added to chloride working standard, *i* (8.3.1), and
$W_{WS(i)}$ = final weight (g) of the prepared chloride working standard, *i* (8.3.2, nominally 100 g).

8.3.4 If utilizing an autosampler and dilution is required, it is recommended to dilute standards with high purity deionized water prior to calibration. Dilution of the standards should be the same as dilution used for samples. Application of the same dilution parameter to the standards and samples will eliminate further calculations. Mix well to ensure a homogeneous solution. Record the final weight of the chloride working standard to the nearest 0.001 g.

8.4 *Anion Regenerant Solution (12.5 mM Sulfuric Acid) (for Use with Anion Micromembrane Suppressor):*

NOTE 12—Consult instrument suppressor manufacturer for preparation of the suppressor regenerate solution.

8.4.1 Add approximately 1 L of reagent water to a 2-L volumetric flask. Slowly add 1.4 mL (or 2.6 g) of concentrated sulfuric acid (7.12) to the flask taking care to avoid splashing and overheating. Bring to volume with reagent water and mix well. Prepare fresh regenerant solution at least once per month.

8.4.2 *Alternative Preparation with Anion Regenerant Concentrate*—Add 1 part of the anion regenerant concentrate (1 M sulfuric acid) (7.13) to 80 parts reagent water (for example, add 25 mL of anion regenerant concentrate to a 2-L volumetric flask. Bring to volume with reagent water and mix well). Prepare fresh regenerant solution at least once per month.

8.5 *Carbonate/Bicarbonate Eluent Solution (0.6 mM/0.4 mM) Prepared from Carbonate/Bicarbonate Salts (for use with Configuration A):*

NOTE 13—Consult with the anion analytical column manufacturer for recommended mobile phase concentration and preparation of the separation (8.5 and 8.6).

8.5.1 Place a small plastic weigh dish on the balance and tare. Add 0.1250 ± 0.0010 g of sodium carbonate (7.5) to weigh dish. Transfer the sodium carbonate in the weigh dish to a 2-L volumetric flask. Rinse the weigh dish into the volumetric flask using a small amount of reagent water.

8.5.2 Place a second small plastic weigh dish on the balance and tare. Add 0.0625 ± 0.0010 g of sodium bicarbonate (7.6) to the weigh dish. Transfer the sodium bicarbonate in the weigh dish to the 2-L volumetric flask used in 8.5.1. Rinse the weigh dish into the volumetric flask using a small amount of reagent water.

8.5.3 Add reagent water to the 2-L volumetric flask to bring it to volume and mix well. Prepare fresh eluent solution at least once every two weeks.

8.6 *Carbonate/Bicarbonate Eluent Solution (0.6 mM/0.4 mM) Prepared from Carbonate/Bicarbonate Concentrates (for Use with Configuration A)*—Add 2.4 mL of sodium carbonate concentrate (7.7) and 1.6 mL of sodium bicarbonate concentrate (7.8) to a 2-L volumetric flask. Bring to volume with reagent water and mix well. Prepare fresh eluent solution at least once every two weeks.

8.7 *Potassium Hydroxide Solution (Configuration B)*—5 mM carbonate-free potassium hydroxide made electrolytically on-line by the eluent generator module using reagent water and a potassium hydroxide cartridge which is part of the IC system (6.4).

9. Hazards

9.1 Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents and procedures before beginning laboratory work. Sources of information include: operation manuals, MSDS, literature, and other related data. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

9.2 MEG, DEG and TEG products are intended for industrial use only. Before handling or using these products, read the current MSDS for each product (9.1).

9.3 The following hazards are associated with the application of this test method and the use of an ion chromatograph.

9.3.1 *Chemical Hazard:*

9.3.1.1 **Warning—**Concentrated sulfuric acid is corrosive and should be handled in a fume hood with gloves, chemical goggles, and lab coat or chemical-resistant apron. When diluting concentrated sulfuric acid, always add acid to water.

9.3.1.2 **Warning—**Methanol and isopropyl alcohol are flammable and toxic solvents that are used to prime the pump in an IC. Be careful when handling a flammable solvent and work in a well-ventilated area away from sources of ignition.

9.3.1.3 Excessive force on the injection syringe (manual injection) can cause glycol to spray on the analyst. Wear gloves, chemical goggles, and lab coat or chemical-resistant apron when injecting a sample. Use Luer-Lok syringes to load the sample into the injection port. Turn face away from the injection port while depressing the syringe plunger. Depress syringe plunger slowly to avoid high back pressure as a result of the viscosity of the glycol sample.

9.3.2 *Electrical/Shock Hazard:*

9.3.2.1 Ion chromatographs (pump modules and conductivity detectors) contain printed circuit boards and components operating at dangerous voltages. The circuit boards and components are covered with protective panels that are identified by warning labels. Contact with these circuits boards and components can cause serious injury or painful electrical shock. Turn off the system power and unplug the line cord before removing the protective panels. After removing the protective panel in the pump or detector, wait 30 to 60 s before touching any printed circuit boards to guarantee the discharge of the capacitors.

9.3.2.2 To prevent damage to the pump circuitry and components, always wait at least 15 s after powering down before turning the power on again.

9.3.2.3 The three-conductor power cord provides a protective earth ground connection when plugged into a properly wired receptacle. Proper receptacle grounding must be verified.

9.3.3 *Pressure Hazard:*

9.3.3.1 **Warning—**Compressed gas cylinders (filtered, dry, and oil free) are initially pressurized at 15 169 to 17 237 kPa (2200 to 2500 psi). Use a regulator to reduce the delivered pressure (air cylinder) to 552 to 689 kPa (80 to 100 psi) for IC systems with air actuated solenoid valves.

9.3.3.2 Use an additional regulator to reduce the pressure (helium cylinder) to a maximum of 48 ± 14 kPa (7 ± 2 psi) for pressurizing eluent reservoirs and degassing eluent. The pressure applied to a reservoir should never exceed 69 kPa (10 psi).

9.3.3.3 Use thick-walled plastic bottles designed for use at pressures greater than 69 kPa (10 psi) as eluent reservoirs.

9.3.4 *Flammable/Explosion Hazard:* **Warning—**Hydrogen is flammable and explosive when confined in an enclosed space. The anion self-regenerating membrane suppressor used to suppress the eluent generates a small amount of hydrogen gas during the electrolytic generation of hydronium ion. The small amount of hydrogen gas is not dangerous unless the gas is trapped in a closed container and allowed to concentrate. The gas separator waste tube is an integral part of the self-regenerating membrane suppressor system. Its function is to ensure the separation of any hydrogen gas generated by the suppressor and is used to avoid concentrating the gas in the waste container. The gas separator waste tube must be open to the atmosphere and not in a confined space to operate properly. It should be positioned to extend above the top of the waste reservoir or drain. A gas separator waste tube is required on the waste line coming from an self-regenerating membrane suppressor.

10. Calibration

10.1 Turn on the IC system and all components. Allow the eluent to pump through the columns and the anion suppressor to equilibrate the IC system using the conditions in Section 11 until the baseline and background conductance are stable. This

usually requires 30-min to 1-h equilibration time depending on how recently the system was operated.

10.2 Use a Luer-Lok syringe or autosampler to fill the injection loop with reagent water (7.2) for a system water blank. Inject a volume that will not overload the column or detector (10 to 70-µL) aliquot into the IC and separate the components according to the conditions outlined in Section 11. Injected volume should be enough to handle the high standards and give enough response on the detector for the low standards. If a chloride peak is detected in the water blank, repeat the injection of reagent water until the chloride peak is no longer detected.

10.3 Use a clean Luer-Lok syringe to fill the injection loop with each of the chloride working standards in order of increasing concentration (8.3.1). Inject the same volume as the water blank (10.2) into the IC and separate the components according to the conditions outlined in Section 11. It is recommended that each standard be analyzed in duplicate. Determine the retention time for the chloride peak.

10.4 Calibrate the system according to the instrument manufacturer's operating instructions for an external standard calibration based on peak areas and a linear fit for the calibration curve not forced through zero. It is recommended to perform standard addition on the glycol used for the calibration standards preparation. This will determine the presence or absence of chloride. If chloride is present, the initial concentration can be determined by means of a programmed spreadsheet or equivalent. The initial concentration of chloride should then be added to all standards concentrations in the calibration curve, or, if chloride is present in the initial glycol and if the IC software allows, pure glycol run can be subtracted electronically from all the standards and no modification to calculated concentration of the standards will be required.

NOTE 14—If no chloride is detected in chloride working standard #1, then it is not necessary to include this standard in the calibration.

10.5 A calibration curve can be prepared by plotting the peak area obtained for each of the calibration standards of interest (10.3; *y*-axis) versus the amount (mg/kg) of chloride in each standard (8.3.2; *x*-axis) using a software program such as Excel or a linear best fit program on a calculator. Perform a least-squares linear regression analysis on the data to calculate the slope and the intercept of the calibration curve.

$$y_{(i)} = mx_{(i)} + b \tag{4}$$

where:

$y_{(i)}$ = the peak area of the calibration standard of interest (9.3),
$x_{(i)}$ = the concentration of the calibration standard of interest (8.3.3),
m = the slope of the linear regression line,
b = the intercept of the linear regression line, and
i = the calibration standard of interest.

NOTE 15—Many IC systems (software) have the ability to calculate a calibration graph automatically after measuring the calibration solutions and subsequently show the amount/concentration of the analyte being measured directly on a display or printed report. In such cases, no calibration graph need be constructed and the calculation can be started with Section 13. It is, however, recommended that the calculation procedure of the instrument be verified and that the characteristics of the calibration graph be established according to suitable regression analysis software.

10.6 Evaluate the linearity of the calibration function obtained either by calculating the correlation coefficient r (a correlation of ±1.0000 indicates a perfect fit, a typical value is r ≥ ±0.9900) and/or by calculating the so-called "y-residuals" of the calibration function, plotting the y-residuals versus the known concentrations, and visually evaluate the result. The graph should show a random scatter around an average of zero.

10.7 It is recommended that a quality assurance check standard for chloride be analyzed to verify the accuracy of the calibration curve. The concentration of the check standard analyzed should be near the sales specification limit for the ethylene glycol analyzed (for example, 0.1 to 0.2 mg/kg chloride). A glycol sample with a known concentration of chloride can be used or a working check standard can be prepared from the 10 µg/mL certified quality assurance check standard for chloride (7.4, Note 7), which is independent of the chloride stock solution used to prepare the calibration standards as follows:

10.7.1 Place a 100-mL volumetric flask on the balance and tare. Pipette (and record the weight to the nearest 0.0001 g) 1000 µL of 10 µg/mL chloride (7.4) into a 100-mL volumetric flask.

10.7.2 Dilute to 100 mL (and record to the nearest 0.001 g) with high-purity MEG, DEG or TEG (7.9, 7.10 or 7.11) and mix well.

10.8 Analyze the diluted check standard as described in 10.3.

10.9 Calculate the concentration of chloride in the diluted check standard from the calibration curve (10.4). For a working check standard (diluted solution in 10.7.2), multiply the concentration of chloride calculated from the calibration curve by the dilution factor for the check standard as shown below:

$$C_{(i)} = \frac{D_{(i)} \times W_{Diluted\ Solution(i)}}{W_{CS(i)}} \tag{5}$$

where:

$C_{(i)}$ = the concentration (mg/kg) of chloride in the check standard (i),
$D_{(i)}$ = the concentration (mg/kg) of chloride in the diluted check standard determined from the calibration curve, (i) (10.4),
$W_{Diluted\ Solution(i)}$ = total weight (g) of the diluted check standard (10.7.2), and
$W_{CS(i)}$ = the weight (g) of check standard (10.7.1) used to prepare the quality assurance check standard.

10.10 Compare the results to the certified or known value for the check standard. The result for the check standard should be within three standard deviations of the known value (mean). If the result for the check standard is outside of the acceptable limits, repeat the preparation of the working standards in 8.3 and the calibration in 10.3 and 10.4.

NOTE 16—Once a suitable linear calibration function has been established, the stability of the analytical measurement system can be

monitored via quality control procedures (see Section 14). From an accuracy perspective, it is recommended to choose the property level of the quality control sample well within the calibration range, for example, between 25 to 75 % of the calibration range, or at the product specification level. As long as the measurement system remains unchanged and is stable as indicated by the in-control state of SQC, the calibration function can be applied confidently without a need for recalibration.

11. Conditioning and Sampling

NOTE 17—The parameters summarized in 11.1 and 11.2 are provided as guidelines for setting up the test method. Pressures, flow rates, and integration parameters will depend on each chromatographic system and may vary from those stated in 11.1 and 11.2.

11.1 *IC System, Configuration A (Bottled Eluent System - Carbonate Based)*

11.1.1 *Operating Conditions:*

Analytical Columns	Carbonate selective anion exchange guard column, 4 × 50-mm and separator column, 4 × 250-mm
Column Temperature[A]	Room temperature (~25°C) or optimal temperature
Injector	6-port PEEK injection valve
Detector	Conductivity cell at 35°C or same as column oven temperature if used
Suppressor[B] / Settings	Chemical or electrolytic anion suppressor at 50 mA
Suppressor Mode[C]	Deionized or external water regenerant at 4 mL/min
Eluent[D]	0.6 mM Na_2CO_3/0.4 mM $NaHCO^3$
Eluent Flow Rate[A]	2 mL/min
Sample Loop	70 µL
System Pressure[B]	1425 psig or optimal pressure
Run Time	5 min or optimal run time
Background Conductance	10 µS
System Equilibration	Equilibrate IC system for at least 30 min prior to sample analysis; if system has been off for a week or longer equilibrate for at least 1 h
Retention Time	Approximately 2.3 min for chloride

[A] A chemical suppressor with 100 mM sulfuric acid or an anion micromembrane suppressor with 12.5 mM sulfuric acid as regenerant can be used.
[B] Consult column manufacturer for optimal temperature, system pressure and run time. A column heater may be used to achieve desired separation.
[C] For chemical suppressor, rinse with DI water and for electrolytic anion suppressor use external water regenerate.
[D] Consult column manufacturer for appropriate concentration and preparation.

11.1.2 A representative chromatogram is illustrated in Fig. 1.

11.2 *System, Configuration B (Eluent Generation System - Hydroxide Based)*

11.2.1 *Operating Conditions:*

Analytical Columns	Hydroxide selective anion exchange guard column, 4 × 50-mm and separator column, 4 × 250-mm
Trap Column	Continuously regenerated anion trap column for hydroxide eluent
Injector	6-port PEEK injection valve
Detector	Conductivity cell at 35°C
Column Temperature	Column Heater at 30°C
Suppressor[A] / Settings	Electrolytic anion suppressor at 20 mA
Suppressor Mode	External water regenerant at 4 mL/min
Eluent Generator Cartridge	Potassium hydroxide cartridge
Mobile Phases	100 % reagent water
Eluant	5 mM KOH (carbonate-free)
Eluent Flow Rate	1 mL/min
Sample Loop	70 µL
System Pressure	2265 psig
Run Time	10 min
Background Conductance	<1 µS
System Equilibration	Equilibrate IC system for at least 30 min at 15 mM KOH prior to sample analysis; if system has been off for a week or longer equilibrate for at least 1 h at 15 mM KOH
Retention Time	Approximately 3.4 min for chloride

[A] An anion micromembrane suppressor with 12.5 mM sulfuric acid as regenerant can be used.

11.2.2 A representative chromatogram is illustrated in Fig. 2.

11.3 *Sampling:*

11.3.1 Collect the sample in a scrupulously clean glass bottle in accordance with Practice E300. Care should be taken to minimize exposure to air to avoid chloride contamination.

12. Procedure

12.1 Turn on the IC system and all components. Allow the eluent to pump through the columns and the anion suppressor to equilibrate the IC system using the conditions in Section 11 until the baseline and background conductance are stable. This usually requires from 30-min to 1-h equilibration time depending on how recently the system was operated.

12.2 Use a Luer-Lok syringe or autosampler to fill the injection loop with reagent water (7.2) for a system water blank. Inject a volume that will not overload the column or detector (10 to 70-µL) aliquot into the IC and separate the components according to the conditions outlined in Section 11. If a chloride peak is detected in the water blank, repeat the injection of reagent water until the chloride peak is no longer detected.

12.3 Use a clean Luer-Lok syringe or autosampler to fill the injection loop with each sample. Inject a volume that will not overload the column or detector (10 to 70-µL) aliquot into the chromatograph and separate the components according to the chromatographic conditions outlined in Section 11. Identify chloride by its retention time. It is recommended that each sample be analyzed in duplicate and the average result reported. Sample dilution with high-purity mono-, di- or triethylene glycol (7.9, 7.10 or 7.11) may be necessary if the chloride is beyond the calibration range of the test method.

12.4 If performing ten or more analyses in sequence, reanalyze the quality assurance check standard or one of the chloride working standards after every ten sample injections. If the results are not within three standard deviations of the certified or known value, recalibrate and reanalyze samples that were run after the last acceptable value of the quality assurance check standard or chloride working standard.

13. Calculation

13.1 Calculations to determine the concentration of chloride in ethylene glycol samples are performed using data acquisition and integration software (6.3.4 or 6.4.6). Calculations are based on a linear fit for the calibration curve, not forced through zero, and the chloride peak area.

13.2 If manual calculations are used, calculate the concentration of chloride in ethylene glycol samples as follows:

TABLE 2 E2469 Chloride in MEG by IC

Test Result mg/kg	Sample	Average Over All Laboratories	Repeatability Standard Deviation	Intermediate Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Intermediate Limit	Reproducibility Limit
Chloride	MEG	0.1135	0.0078	0.0084	0.0332	0.0220	0.0235	0.0929

$$C_s = \frac{(A_s - b)}{m} \quad (6)$$

where:

C_s = the concentration of chloride in the sample,
A_s = the peak area of chloride in the sample (12.3),
m = the slope of the linear regression line (10.5), and
b = the intercept of the linear regression line (10.5).

14. Quality Control

14.1 Although the procedure in Section 12 is described such that only one test result is obtained, it is recommended to either:

14.1.1 Perform a second (duplicate) determination, to enable comparison of the duplicate results with the listed repeatability in Table 2. Choose this option if this test method is performed on an infrequent basis.

14.1.2 Use statistical quality control (SQC) principles in order to monitor its state of in-control, of which a summary is given below. For more detailed guidance, refer to Practice D6299. Choose this option if this test method is performed on a regular basis.

14.1.2.1 Analyze the QC sample under intermediate precision conditions and construct a control chart for chloride content.

14.1.2.2 While testing regular samples, gather new SQC data. Maintain the control chart and evaluate the data according to the rules supplied. In short, if the measured value is within the control chart action limits and part of a random data pattern, the system can be considered in statistical control. If the measured value exceeds an action limit or belongs to a non-random data pattern, this is an indication of the system being out of statistical control. In that case, investigate for the root cause and take remedial action(s) to eliminate this. Next, reanalyze the QC sample to verify the system is in statistical control again, before proceeding with sample tests.

14.1.2.3 Continue to analyze the QC sample on a regular basis. The frequency depends on the criticality of the test.

14.1.2.4 From SQC data obtained under statistical control, calculate the intermediate precision. Compare this value with the intermediate precision as included in Table 2.

15. Report

15.1 Report the following information:

15.1.1 Report the concentration of chloride in MEG to the nearest 0.01 mg/kg.

15.1.2 Report the concentration of chloride in DEG to the nearest 0.1 mg/kg.

15.1.3 Report the concentration of chloride in TEG to the nearest 0.1 mg/kg.

16. Precision and Bias[6]

16.1 There is no information to date on Precision and Bias for DEG or TEG or diluted MEG, DEG or TEG. An interlaboratory study is planned for 2008–2009.

16.2 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 E2469, Standard Test Method for Chloride in Monoethylene Glycol by Ion Chromatography. Each of seven laboratories tested MEG. 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 labs used a single analyst, seven labs used two analysts (on different days) and two labs did not record this information. In the event that there were missing values for one or more labs, this information was noted in the results. The details of this study are given in ASTM Research Report RR:E15-1067.

16.2.1 *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.

16.2.2 *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.

16.2.3 *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.

16.2.3.1 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

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1067.

period, the intermediate precision would probably be underestimated by the Practice E180 analysis.

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

16.3 *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.

16.4 The precision statement was determined through statistical examination of qualified results, from eight laboratories, on one material. The material was described as the following: Fluid 1: Mono-ethylene glycol. To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

17. Linearity[7]

17.1 Peak area response for chloride was found to be linear for both the IC system with Bottled Carbonate Eluent (Configuration A) and the IC system Eluent Generation of Hydroxide Eluent (Configuration B) over the range of 0.01 to 1.0 mg/kg.

[7] It is recommended that the precision, accuracy, linearity, limit of detection, and limit of quantitation of the test method be verified if another set of equipment is to be used or the test method is to be used at another location.

18. Limit of Detection/Limit of Quantitation[7]

18.1 *IC System with Bottled Carbonate Eluent (Configuration A):*

18.1.1 The limit of detection for chloride, defined as three times the signal-to-noise ratio, was determined to be 0.004 mg/kg chloride in polyester-grade MEG.

18.1.2 The limit of quantitation for chloride, defined as ten times the signal-to-noise ratio, was determined to be 0.012 mg/kg chloride in polyester-grade MEG.

18.2 *IC System with Eluent Generation – Hydroxide (Configuration B):*

18.2.1 The limit of detection for chloride, defined as three times the signal-to-noise ratio, was determined to be 0.002 mg/kg chloride in polyester-grade MEG.

18.2.2 The limit of quantitation for chloride, defined as ten times the signal-to-noise ratio, was determined to be 0.006 mg/kg chloride in polyester-grade MEG.

19. Keywords

19.1 chloride; DEG; diethylene glycol; IC; ion chromatography; MEG; monoethylene glycol; TEG; triethylene glycol

SUMMARY OF CHANGES

Committee E15 has identified the location of selected changes to this standard since the last issue (E2469 – 08a) that may impact the use of this standard. (Approved Jan. 1, 2016.)

(1) Revisions were made in the following sections: 1.3.1, 6.3, 6.4, 8.3, 8.3.1, 10.5, 10.7, 10.10, 12.4, and 14.1.

(2) The following sections were added: Note 16, 14.1.1, and 14.1.2 – 14.1.2.4.