



Designation: **E2469—08a E2469 – 16**

## Standard Test Method for Chloride in Mono-, Di- and Tri-ethylene Glycol by Ion Chromatography<sup>1</sup>

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 ( $\epsilon$ ) 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 Material Safety Data Sheets (~~MSDS~~)(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:*<sup>2</sup>

[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for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals](#) (Withdrawn 2009)<sup>3</sup>

[E300 Practice for Sampling Industrial Chemicals](#)

[ASTM E2469-16](#)

<https://standards.iteh.ai/catalog/standards/sist/988e9f64-b524-46e3-9e3d-a45bab39f816/astm-e2469-16>

### 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

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

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

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. 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- $\mu$ L 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 ( $\leq 2$  ( $< 2$   $\mu$ L) 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. Autosampler optional](#).

NOTE 2—The ion chromatography 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 ( $\leq 2$  ( $< 2$   $\mu$ L) conductivity cell, conductivity detector, PEEK tubing, PEEK injection valve with a fixed sample loop and electrolytic eluent generation module. An

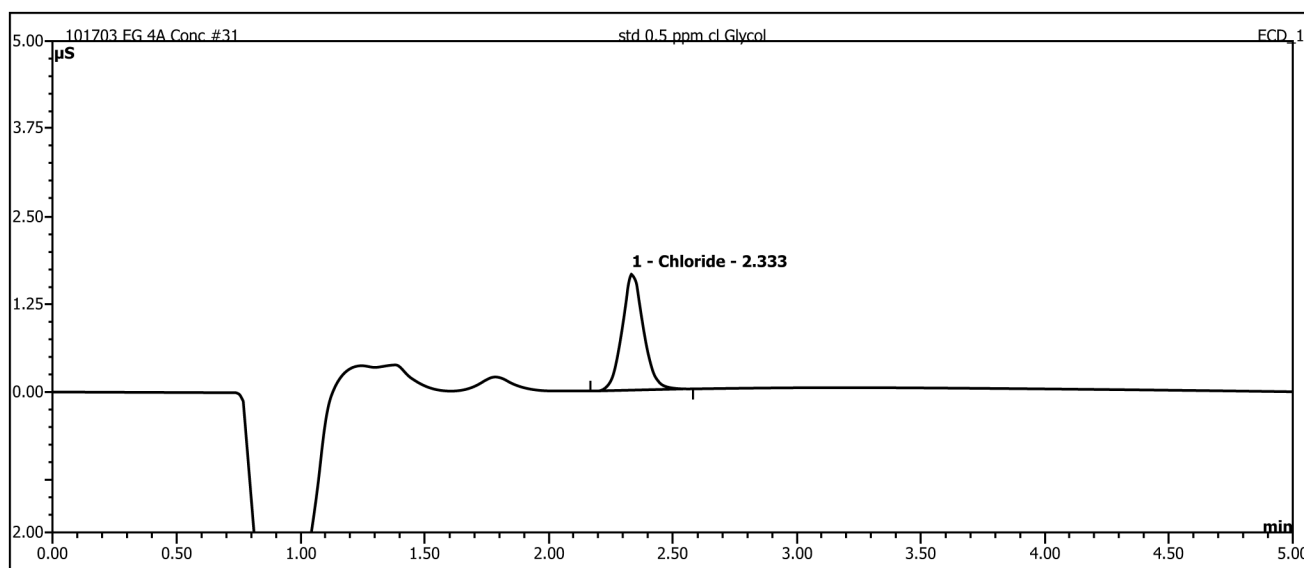


FIG. 1 Representative Sample Chromatogram Obtained Using the Conditions Outlined in 11.1 (Configuration A)

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.

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.<sup>4</sup>

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.

<sup>4</sup> The sole source of supply of the potassium hydroxide eluent generation cartridge known to the committee at this time is Dionex Corp., Thermo Fisher Scientific, 1228 Titan Way, Sunnyvale, CA 94088-3603, 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,<sup>1</sup> which you may attend.

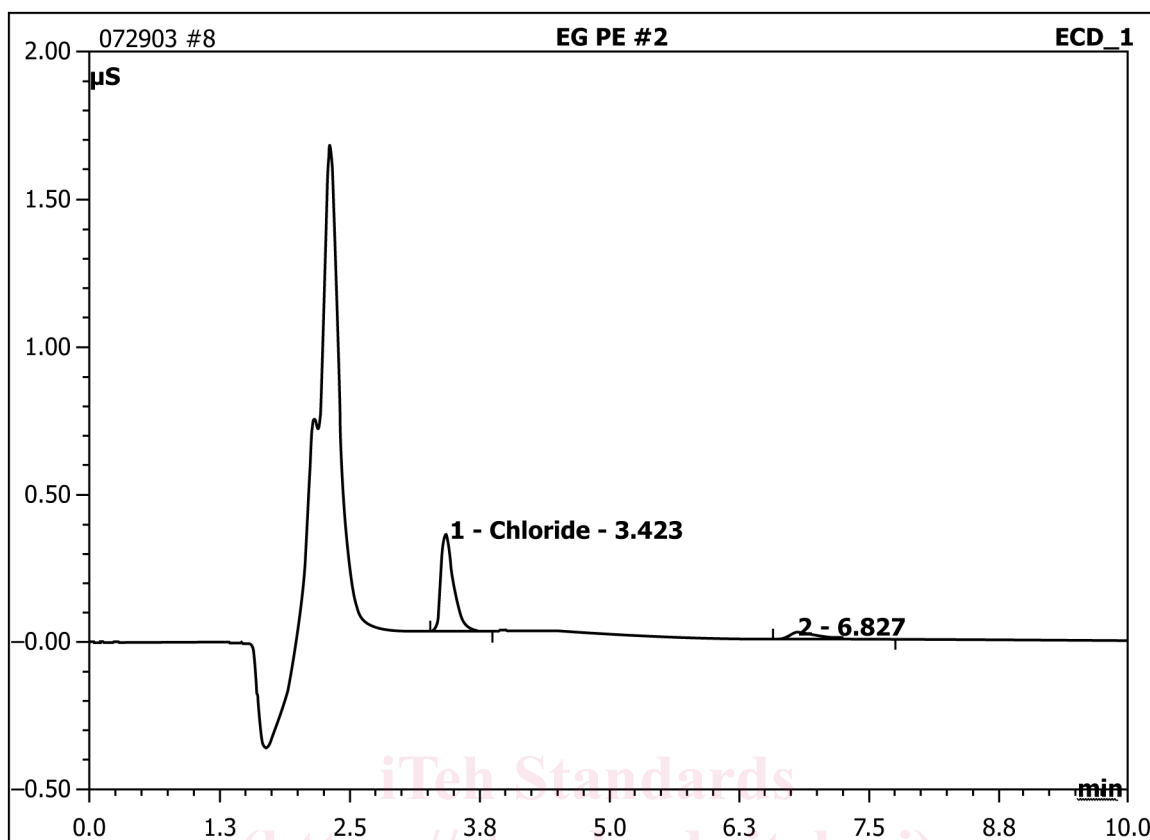


FIG. 2 Representative Sample Chromatogram Obtained Using the Conditions Outlined in 11.2 (Configuration B)

## 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.<sup>5</sup> 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- $\mu\text{m}$  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  $\mu\text{g}/\text{mL}$  chloride standard (not made from sodium chloride in 7.3.7.3), 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)*, 0.5–0.5 M sodium carbonate, commercially available.

7.8 *Sodium Bicarbonate Concentrate (Configuration A)*, 0.5–0.5 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 %).

<sup>5</sup> *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)(USP), Rockville, MD.

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)  $0.1649 \pm 0.0010$  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:

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

*where:*

*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  $10 \text{ mg/kg}$  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:*

*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

**TABLE 1 Chloride Working Standard**

Chloride Working Standard #	Nominal Concentration mg/kg	Weight of 10 mg/kg Chloride Calibration Solution (to add) g ( $\pm 0.0001$ g)	Final Weight of Chloride Working Standard (MEG DEG or TEG added) g ( $\pm 0.001$ 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

bottle. Minimize the number of times and length of time the working standards are exposed to air. Cap securely after each use.

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:*

*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)–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  $0.1250 \pm 0.0010$  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  $0.0625 \pm 0.0010$  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)–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~~ 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).