



Standard Test Method for Chloride in Mono-, Di- and Tri-ethylene Glycol by Ion Chromatography¹

This standard is issued under the fixed designation E 2469; 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.

1.4 Review the current Material Safety Data Sheets (MSDS) 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

[D 1193 Specification for Reagent Water](#)

[E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals](#)

[E 300 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 chromatography

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.

graph 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. 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.

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

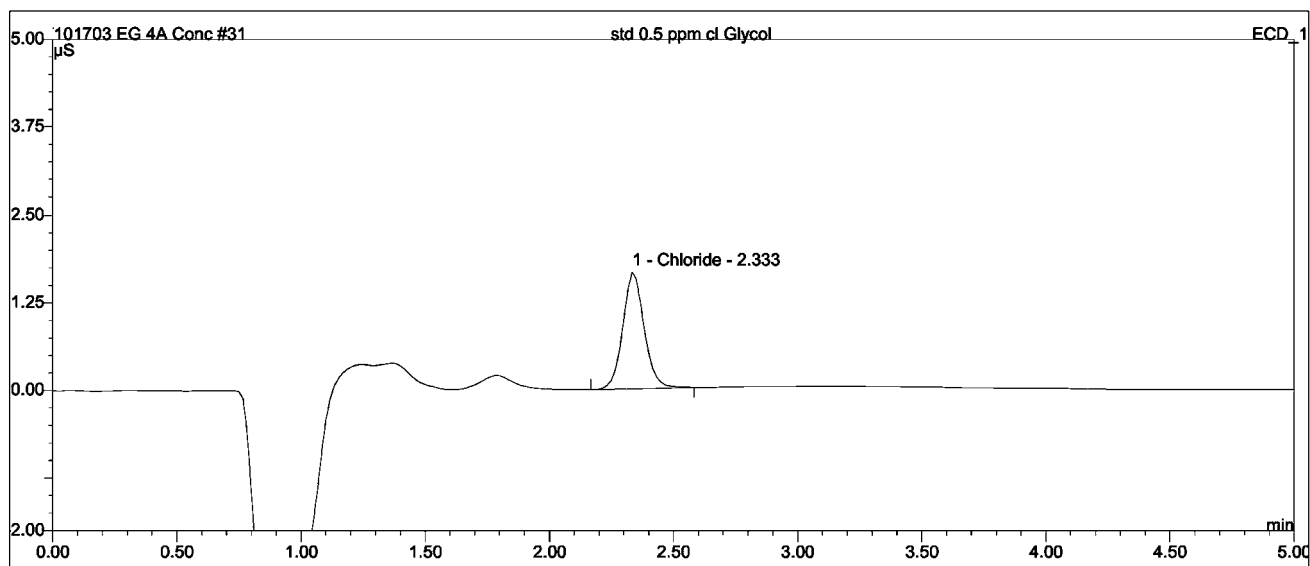


FIG. 1 Representative Sample Chromatogram Obtained Using the Conditions Outlined in 11.1 (Configuration A)

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 counter-current 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- μ 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 (< 2 μ 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. The instrument must be suitable for analysis according to the operating conditions given in [11.1](#). Autosampler optional.

NOTE 2—The ion chromatography (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](#).

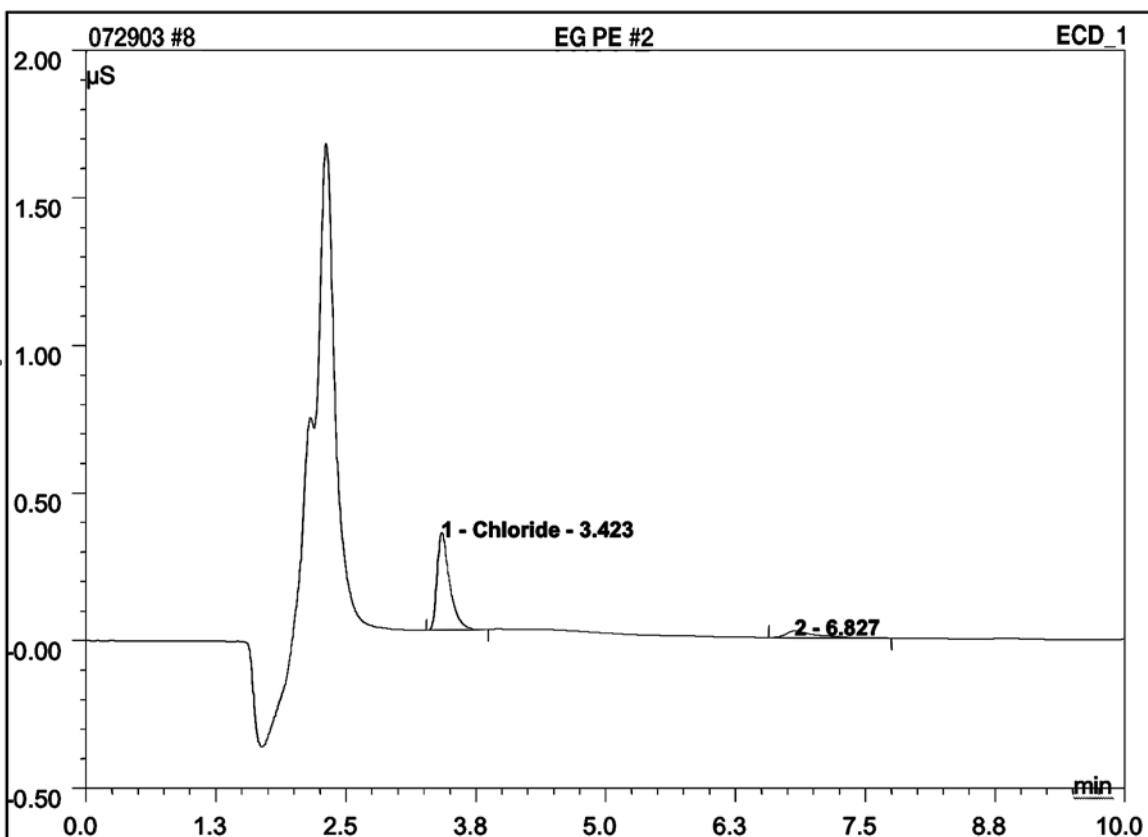


FIG. 2 Representative Sample Chromatogram Obtained Using the Conditions Outlined in 11.2 (Configuration B)

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. 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.