



Designation: D6919 – 17

Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography¹

This standard is issued under the fixed designation D6919; 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 is valid for the simultaneous determination of the inorganic alkali and alkaline earth cations, lithium, sodium, potassium, magnesium, and calcium, as well as the ammonium cation in reagent water, drinking water, and wastewaters by suppressed and nonsuppressed ion chromatography.

1.2 The anticipated range of the test method is 0.05–200 mg/L. The specific concentration ranges tested for this test method for each cation were as follows (measured in mg/L):

Lithium	0.4–10.0
Sodium	4.0–40.0
Ammonium	0.4–10.0
Potassium	1.2–20.0
Magnesium	2.4–20.0
Calcium	4.0–40.0

1.2.1 The upper limits may be extended by appropriate dilution or by the use of a smaller injection volume. In some cases, using a larger injection loop may extend the lower limits. It is the responsibility of the user to ensure the validity of this test method for concentrations if the range is extended.

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

1.4 It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

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 determine the applicability of regulatory limitations prior to use.* For hazards statements specific to this test method, see 8.3.

1.6 *This international standard was developed in accordance with internationally recognized principles on standard-*

ization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits
- D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
- D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)³
- D5810 Guide for Spiking into Aqueous Samples
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- D5905 Practice for the Preparation of Substitute Wastewater

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.2 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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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

4. Summary of Test Method

4.1 Inorganic cations and the ammonium cation, hereafter referred to as ammonium, are determined by ion chromatography in water and wastewater samples from a fixed sample volume, typically 10–50 μL . The cationic analytes are separated using a cation-exchange material, which is packed into guard and analytical columns. A dilute acid solution is typically used as the eluent.

4.1.1 The separated cations are detected by using conductivity detection. To achieve sensitive conductivity detection, it is essential that the background signal arising from the eluent have low baseline noise. One means to achieve low background noise is to combine the conductivity detector with a suppressor device that will reduce the conductance of the eluent, hence background noise, and also transform the separated cations into their more conductive corresponding bases.⁴

4.1.2 Detection can also be achieved without chemical suppression, whereby the difference between the equivalent ionic conductance of the eluent and analyte cation is measured directly after the analytical column. This test method will consider both suppressed and nonsuppressed detection technologies. The conductivity data is plotted to produce a chromatogram that is used to determine peak areas. A chromatographic integrator or appropriate computer-based data system is typically used for data presentation.

4.2 The cations are identified based on their retention times compared to known standards. Quantification is accomplished by measuring cation peak areas and comparing them to the areas generated from known standards. The results are calculated using a standard curve based on peak areas of known concentrations of standards in reagent water.

5. Significance and Use

5.1 This test method is applicable to the simultaneous determination of dissolved alkali and alkaline earth cations and ammonium in water and wastewaters. Alkali and alkaline earth cations are traditionally determined by using spectroscopic techniques, such as AAS or ICP; whereas ammonium can be measured by using a variety of wet chemical methods, including colorimetry, ammonia-selective electrode, and titrimetry. However, ion chromatography provides a relatively straightforward method for the simultaneous determination of cations, such as lithium, sodium, potassium, calcium, magnesium, and ammonium, in fewer than 20–30 min.

6. Interferences

6.1 No individual interferences have been established, but it is possible that some low-molecular-weight organic bases (amines) may have similar retention times to analytes of interest, particularly later-eluting solutes, such as potassium, magnesium, and calcium. Potential interferences include amines such as mono-, di-, and trimethylamines; mono-, di-, and triethylamines; and alkanolamines.

6.1.1 High concentrations of analyte cations can interfere with the determination of low concentrations of other analyte cations with similar retention times. For instance, high levels of sodium can interfere with the determination of low levels of ammonium (that is, at ratios >1000:1).

6.1.2 High levels of sample acidity, that is, low pH, can also interfere with this analysis by overloading the column, leading to poor peak shape and loss of resolution. The pH at which the chromatographic separation begins to exhibit poor peak shape depends upon the ion-exchange capacity of the column. It is recommended that columns used for analysis of acidic samples in conjunction with the suppressed conductivity version of this test method be able to tolerate acid concentrations up to 50 mM H^+ (pH 1.3), such as the IonPac⁵ CS16 column. The columns used with nonsuppressed conductivity detection typically have lower capacity and can tolerate acid concentrations up to 10 mM H^+ (pH 2.0), such as the IC-Pak C/MD column.

6.2 A slight decrease or increase in eluent strength often allows interferences to elute after or before the peak of concern.

6.3 Sodium is a common contaminant from many sources such as fingers, water, detergents, glassware, and other incidental sources. As a precaution, the user of this test method is advised to wear plastic gloves and use plasticware for all solutions, standards, and prepared samples. In addition, method blanks should be monitored for background sodium contamination.

7. Apparatus

7.1 *Ion Chromatography Apparatus*, analytical system complete with all required accessories, including eluent pump, injector, syringes, columns, suppressor (if used), conductivity detector, data system, and compressed gasses (if required).

7.1.1 *Eluent Pump*, capable of delivering 0.25–5 mL/min of eluent at a pressure of up to 4000 psi.

7.1.2 *Injection Valve*, a low dead-volume switching valve that allows the loading of a sample into a sample loop and subsequent injection of the loop contents into the eluent stream.

7.1.3 *Guard Column*, cation-exchange column typically packed with the same material used in the analytical column. The purpose of this column is to protect the analytical column from particulate matter and irreversibly retained material.

7.1.4 *Analytical Column*, separator column, packed with a weak acid functionalized cation-exchange material, capable of separating the ions of interest from each other, and from other ions that commonly occur in the sample matrix. The chosen column must give separations equivalent to those shown in **Figs. 1 and 2**.

7.1.5 *Suppressor Device*—If using the suppressed conductivity detection mode, the suppressor must provide peak-to-peak noise of <2 nS per minute of monitored baseline.

7.1.6 *Conductivity Detector*, a low-volume, flow-through, temperature-controlled (typically at 35°C) conductivity cell equipped with a meter capable of reading 0–1000 $\mu\text{S}/\text{cm}$ on a linear scale.

⁴ International Standard ISO 14911, Water quality — Determination of dissolved Li+, Na+, NH₄+, K+, Mn²⁺, Ca²⁺, Mg²⁺, Sr²⁺ and Ba²⁺ using ion chromatography — Method for water and waste water.

⁵ IonPac is a trademark of Dionex Corporation, Sunnyvale, CA, 94088.

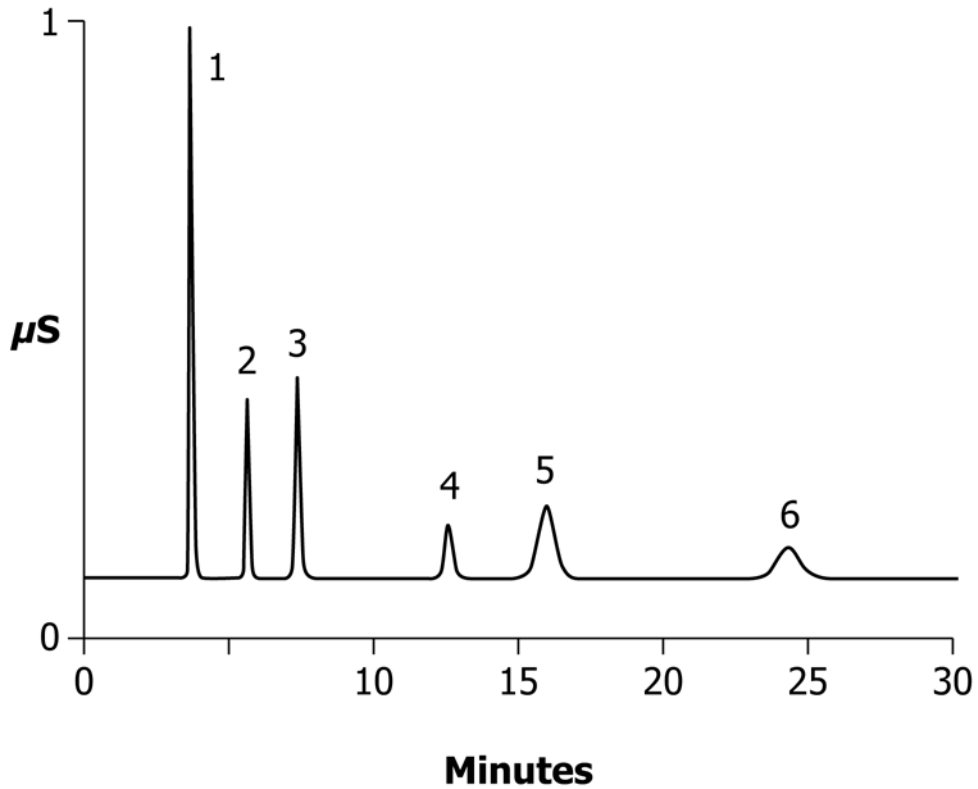


FIG. 1 Example Chromatogram of Dissolved Alkali and Alkaline Earth Cations, and Ammonium by Ion Chromatography Using Suppressed Conductivity Detection

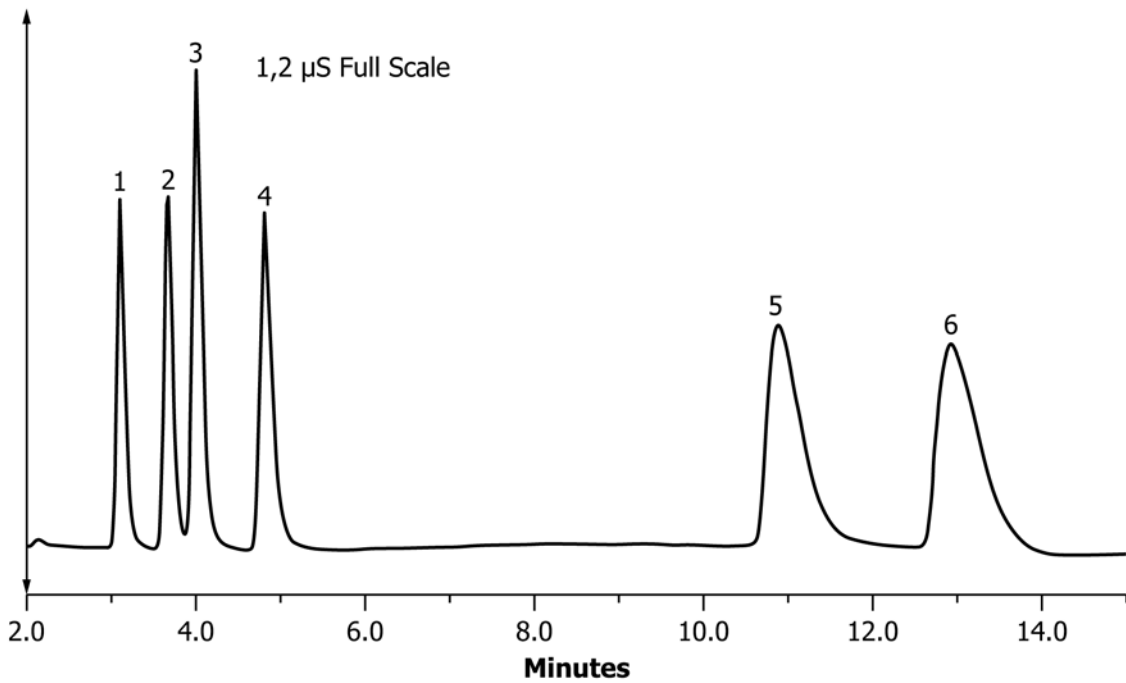


FIG. 2 Example QC Standard Chromatogram of Dissolved Alkali and Alkaline Earth Cations, and Ammonium by Ion Chromatography Using Nonchemically Suppressed Conductivity Detection (Single-Column Indirect Conductivity Detection)

7.1.7 *Data System*, a chromatographic integrator or computer-based data system capable of graphically presenting

the detector output signal versus time, as well as presenting the integrated peak areas.