



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.

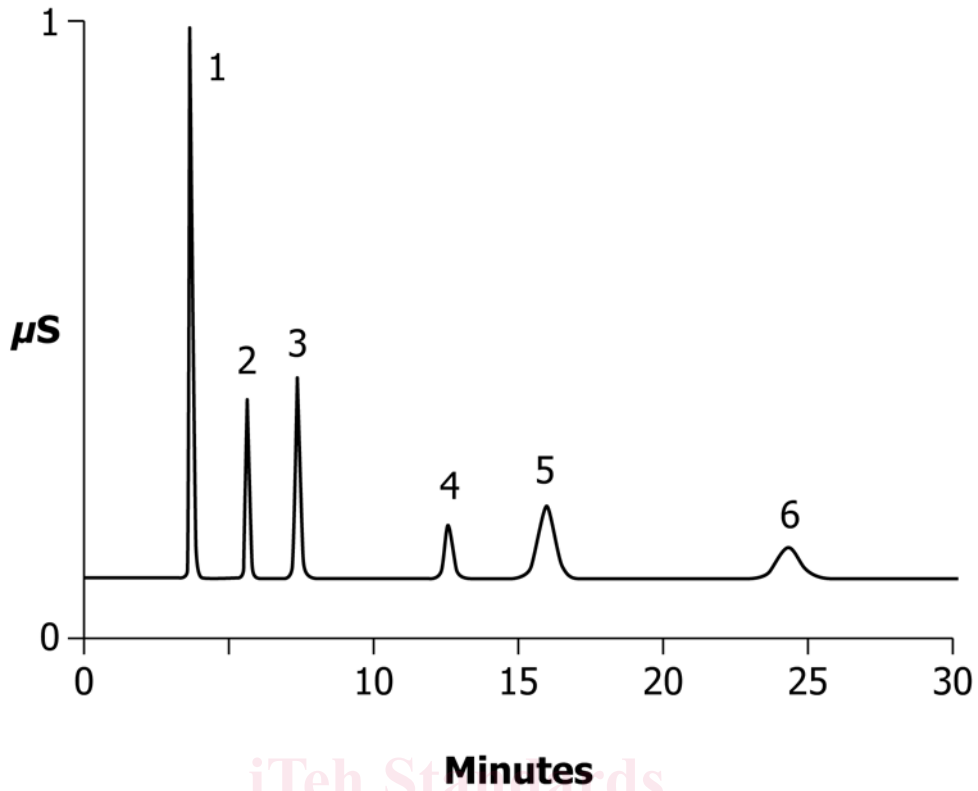


FIG. 1 Example Chromatogram of Dissolved Alkali and Alkaline Earth Cations, and Ammonium by Ion Chromatography Using Suppressed Conductivity Detection

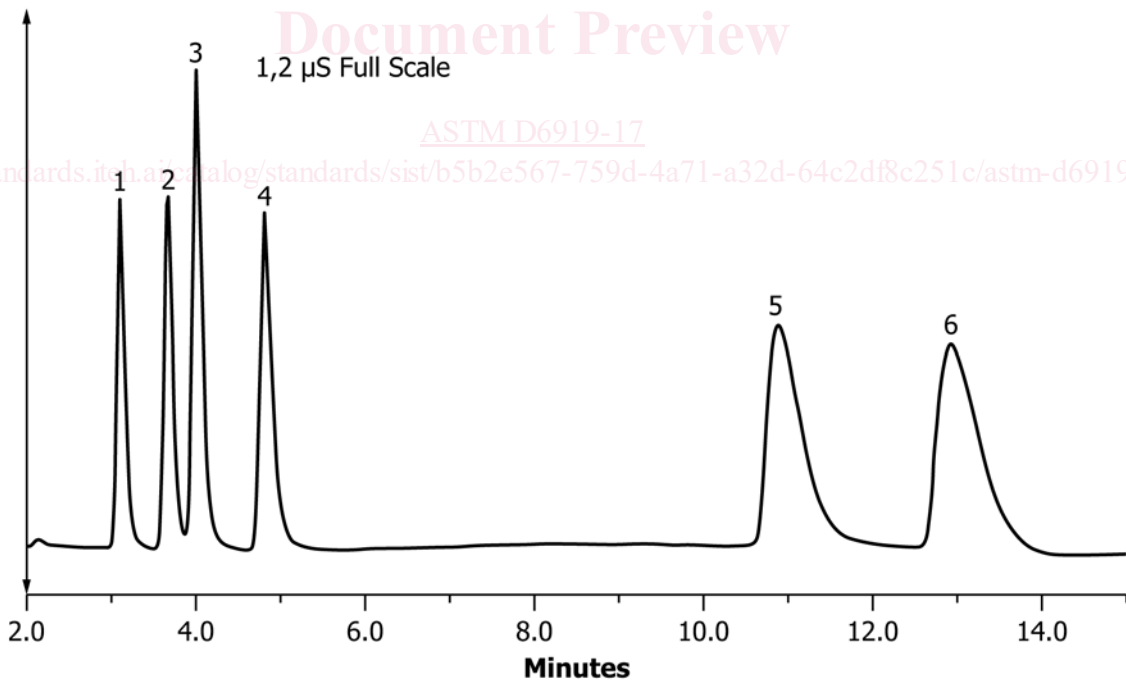


FIG. 2 Example QC Standard Chromatogram of Dissolved Alkali and Alkaline Earth Cations, and Ammonium by Ion Chromatography Using Nonchemically Suppressed Conductivity Detection (Single-Column Indirect Conductivity Detection)

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.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,⁶ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without reducing the accuracy of the determination.

NOTE 1—Prepare all reagents, standards, and samples in plasticware. Sodium will leach from glassware and bias the quantification of sodium.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type IA. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the determination. For example, neutral organic compounds in the reagent water, measured as total organic carbon (TOC), may significantly erode the performance of this test method over time. It is recommended that reagent water with less than 10 ppb TOC be used for all prepared solutions in this test method.

8.3 *Eluent Concentrate; Suppressed Conductivity Detection (1.0 M methanesulfonic acid)*—Carefully add 48.040 g of concentrated methanesulfonic acid to approximately 400 mL of water in a 500-mL volumetric flask. Dilute to the mark and mix thoroughly.

NOTE 2—Methanesulfonic acid is a corrosive, strong acid that should be handled with care. Always handle this reagent in a fume hood while wearing gloves and eye protection.

8.4 *Eluent Analysis Solution; Suppressed Conductivity Detection (26 mM methanesulfonic acid)*—Add 26.0 mL of eluent stock (8.3) to a 1-L plastic volumetric flask containing approximately 500 mL of water. Dilute to the mark and mix thoroughly. The eluent analysis solution must be filtered through an appropriate 0.22- or 0.45- μm filter and degassed by vacuum sonication or helium sparging prior to use.

8.5 *Eluent Analysis Solution; Nonsuppressed Conductivity Detection (3 mM nitric acid)*—Add 29 mg of EDTA (as the free acid) to a 1-L plastic volumetric flask containing approximately 500 mL of water. Using a magnetic stir bar, mix for 10 min. Add 30 mL of 100 mM nitric acid, or 189 μL of concentrated nitric acid. Dilute to the mark and mix thoroughly. The eluent analysis solution must be filtered through an appropriate 0.22- to 0.45- μm filter and degassed by vacuum sonication or helium sparging prior to use.

8.6 *Standard Solutions, Stock (1000 mg/L)*—Prepare all standard solutions in plasticware. It is recommended that the user purchase certified stock standard solutions. Stock standards typically used for AAS are also suitable for the preparation of cation working standards.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

NOTE 3—Neutral pH cation standards are preferred. Alternatively, prepare stock standard solutions from the following salts, as described below:

8.6.1 *Ammonium Solution, Stock (1000 mg/L)*—Dissolve 2.965 g of anhydrous ammonium chloride in water and dilute to 1 L volumetrically; 1.00 mL = 1.00 mg NH_4^+ .

8.6.2 *Lithium Solution, Stock (1000 mg/L)*—Dissolve 6.108 g of anhydrous lithium chloride in water and dilute to 1 L volumetrically; 1.00 mL = 1.00 mg Li^+ .

8.6.3 *Sodium Solution, Stock (1000 mg/L)*—Dissolve 2.541 g of anhydrous sodium chloride in water and dilute to 1 L volumetrically; 1.00 mL = 1.00 mg Na^+ .

8.6.4 *Potassium Solution, Stock (1000 mg/L)*—Dissolve 3.481 g of anhydrous potassium phosphate monobasic in water and dilute to 1 L volumetrically; 1.00 mL = 1.00 mg K^+ .

8.6.5 *Magnesium Solution, Stock (1000 mg/L)*—Dissolve 10.144 g of magnesium sulfate heptahydrate in water and dilute to 1 L volumetrically; 1.00 mL = 1.00 mg Mg^{2+} .

8.6.6 *Calcium Solution, Stock (1000 mg/L)*—Dissolve 3.668 g of calcium chloride dihydrate in water and dilute to 1 L volumetrically; 1.00 mL = 1.00 mg Ca^{2+} .

8.7 *Cation Working Standards*—All calibration standards and standards used for analysis should be prepared in 100-mL volumetric flasks, as described below.

$$\text{Standard concentration (mg/L)} = \frac{(\text{stock volume added (mL)} \cdot 1000 \text{ mg/L})}{100 \text{ (mL)}}$$

Example:

$$10 \text{ mg/L Na} = \frac{(1 \text{ mL Na stock} \cdot 1000 \text{ mg/L Na})}{100 \text{ (mL)}}$$

8.8 *Blank*—The blank standard is a portion of the water used to prepare the cation working solutions.

8.9 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.22- μm or 0.45- μm membrane. Material such as fine-textured, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Precautions

9.1 These methods address the determination of low concentrations of cations. Accordingly, every precaution should be taken to ensure the cleanliness of sample containers, as well as other materials and apparatus that come in contact with the sample.

10. Sampling and Sample Preservation

10.1 Collect the sample in accordance with Practices D3370, as applicable.

10.2 Samples must be collected in plastic containers that are clean and free of artifacts and interferences. The suitability of the containers must be demonstrated for each new lot by performing a container blank and laboratory fortified container blank.

10.3 Samples that will not be analyzed immediately must be preserved with sulfuric acid to a pH of 2. Whereas samples to

TABLE 1 Instrument Conditions for the Analysis of Dissolved Alkali and Alkaline Earth Cations and Ammonium by Ion Chromatography Using Suppressed Conductivity Detection

Eluent:	26 mM methanesulfonic acid
Flow rate:	1.5 mL/min
Column:	Dionex IonPac CG16/CS16
Sample Loop:	10 μ L
Detection:	Suppressed conductivity
Suppressor:	CSRS ULTRA
Background:	\sim 2 μ S
Solutes:	1 = lithium (1.0 mg/L), 2 = sodium (1.0 mg/L), 3 = ammonium (1.0 mg/L), 4 = potassium (1.0 mg/L), 5 = magnesium (1.0 mg/L), 6 = calcium (1.0 mg/L)

TABLE 2 Instrument Conditions for the Analysis of Dissolved Alkali and Alkaline Earth Cations and Ammonium by Ion Chromatography Using Nonsuppressed Conductivity Detection (Single-Column Indirect Conductivity Detection)

Eluent:	3 mM nitric acid / 0.05 mM EDTA
Flow rate:	1.0 mL/min
Column:	Waters IC-Pak TM CM/MD,
Injection Volume:	20 μ L
Detection:	Nonsuppressed conductivity, indirect conductivity
Background:	\sim 1300 μ S
Analytes:	1 = lithium (1.0 mg/L), 2 = sodium (4.0 mg/L), 3 = ammonium (5.0 mg/L), 4 = potassium (10.0 mg/L), 5 = magnesium (5.0 mg/L), 6 = calcium (10.0 mg/L)

be analyzed for cations are typically preserved with nitric acid, sulfuric acid is recommended for ammonium.⁷ Add 0.8 mL concentrated H₂SO₄/L of sample and store at 4°C. The pH of samples preserved in this manner should be between 1.5 and 2, although some wastewaters may require more concentrated H₂SO₄ to achieve this pH. This pH increases the holding time to 28 days.

11. Preparation of Apparatus

11.1 Set up the ion chromatograph according to the manufacturer's instructions.

11.2 Typical operating conditions for the ion chromatograph, in both suppressed and nonsuppressed conductivity modes, are summarized in Tables 1 and 2. A 10- μ L sample injection is recommended for calibration and sample analysis when using chemically suppressed conductivity detection. A larger injection volume, that is, up to 50 μ L, may be required when using nonsuppressed conductivity detection.

11.3 The detector ranges are variable. Choose a range consistent with the concentration range in the expected samples and within the operating requirements of the chromatographic system used.

11.4 Equilibrate the chromatographic system prior to use by pumping the eluent (8.4 or 8.5) through the system until a stable baseline is obtained (approximately 30 min).

12. Calibration and Standardization

12.1 Determine the range of concentrations that will be quantified for each analyte. For each individual calibration

curve, prepare calibration standards, at a minimum of three concentration levels, by accurately adding measured volumes of the stock standards (8.6) to a volumetric flask(s) and diluting to volume with water. A minimum of five concentration levels is recommended if the curve covers two orders of magnitude.

12.2 The order of peak elution and typical retention times are shown in Figs. 1 and 2 for suppressed and nonsuppressed conductivity detection, respectively. The retention time of each analyte can vary with the type and state of the guard and analytical columns and the eluent concentration, but should remain consistent within a given analysis batch.

12.3 To establish the calibration curve, analyze a reagent blank (8.8) and the calibration standards (8.7) in accordance with the procedure in Section 13. Tabulate peak area responses against concentration. These results are used to prepare a calibration curve using a linear least-squares fit for each analyte (with the exception of ammonium). The squared correlation coefficient of determination (r^2) should be ≥ 0.995 for accurate results. Ammonia is a weak base; hence the ammonium cation does not give linear response with suppressed conductivity detection and should be calibrated using a quadratic fit when using this detection method. However, a linear least-squares curve fit can be suitably used for calibration of ammonium using the nonsuppressed version of this method. Once the calibration curves have been established, verification must be performed on each analysis day, whenever fresh eluent is prepared, and once for each batch of samples.

13. Procedure

13.1 Inject the reagent blank, calibration standard, or sample into the eluent stream and record the chromatogram. With a fixed-loop manual injector, flush an excess of the sample (approximately 5 \times loop volume) through the sample injection port using a syringe prior to injection. Examples of method chromatograms are shown in Figs. 1 and 2 for the suppressed and nonsuppressed conductivity detection, ion chromatographic separation of the target cation analytes.

14. Calculations

14.1 Compare the peak areas for the cations in the sample to the calibration curves prepared in 12.3. Calculate and report the concentration of each cation in mg/L by comparing the analyte response to that of the standard curve according to the following equation:

$$\text{Cation Concentration, mg/L} = A \times F \quad (1)$$

where:

A = reading from the appropriate calibration plot, in mg/L, and
 F = dilution factor if the sample was diluted prior to analysis

14.1.1 Computing integrators and computer-based chromatographic data systems can be programmed to perform these calculations automatically.

15. Report

15.1 Report results as the constituent cation in mg/L. Ammonium results are frequently reported as mg of NH₃-N/L.

⁷ Standard Methods for the Examination of Water and Wastewater, APHA, Washington, DC, 1992.

To convert to mg of NH₃-N/L, multiply the ammonium result by a factor of 0.778 (14/18).

15.2 Report only those values that are bracketed within the range of the calibration curve. Any values that fall above that range shall be repeated with appropriate dilution(s).

16. Precision and Bias

16.1 The precision and bias data presented in this test method meet the requirements of Practice D2777, and are given in Tables 3-8. The full research report can be obtained from ASTM Headquarters.

16.2 A total of fourteen laboratories, employing one operator each, contributed data to the test method interlaboratory collaborative study. Three matrices were studied; reagent water, drinking water, and industrial wastewater. Each participant prepared and analyzed four Youden pairs for each of the six analytes in each of the three matrices. The Youden pair samples were prepared in matrices provided by the participants from spiking concentrates provided by the study organizer. Participants who requested it were provided with a substitute industrial wastewater matrix prepared by the study organizer according to Practice D5905.

16.3 The participants prepared seven separate Method Detection Limit (MDL) standards by pipetting aliquots of the supplied MDL concentrate into seven separate, clean, plastic volumetric flasks and diluting each to a total of 100 mL with reagent water. The participants were instructed to determine an appropriate dilution that yielded a response of the analyte peaks in the MDL sample of approximately 3 to 5 times the signal-to-noise of the instrument. Because the MDL sample concentrations were outside the calibration range for the purposes of this study, the calibrations were required to include the origin in the calibration curve. MDLs are given in Table 9.

16.4 The results of this collaborative study may not be typical of results for matrices other than those studied.

16.5 Precision and bias for this test method conforms to Practice D2777 – 98, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

17. Quality Control (QC)

17.1 Before this test is applied to analyzing unknown samples, the analyst shall establish quality control procedures as recommended in Practices D4210 and D5847, and Guide D3856. To be certain that analytical values obtained by this test method are valid and accurate within the confidence limits of the tests, the QC procedures described in this section must be followed.

17.2 Initial Demonstration of Laboratory Capability:

17.2.1 The laboratory using this test shall perform an initial demonstration of laboratory capability. Analyze seven replicates of an Initial Demonstration of Performance (IDP) solution. The IDP solution contains method analytes of known concentration, prepared from a different source than the calibration standards, used to fortify reagent water. Ideally, the IPD solution should be prepared by an independent source from reference materials. The level 3 (mid-level) standard used for the test method precision and bias study is recommended as an IDP solution.

17.2.2 The mean and standard deviation of seven values for each test method analyte shall then be calculated and compared, according to Practice D5847, to the single operator precision and recovery established for this test method. The upper limit for acceptable precision and the range of acceptable recoveries are detailed in Table 10.

17.2.3 If the values obtained for the IDP precision and recovery do not meet the criteria described in Table 10, initial demonstration of performance must be repeated until the results fall within these criteria.

TABLE 3 Precision and Bias for Lithium

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S _o , mg/L	S _o , %	S _i , mg/L	S _i , %
Reagent water	0.4	0.36	-10.0	11	0.01	2.7	0.01	3.5
	0.5	0.45	-9.6				0.02	5.0
	1.6	1.47	-8.1	11	0.01	0.8	0.04	2.8
	2.0	1.85	-7.6				0.05	2.7
	5.0	4.59	-8.2	11	0.07	1.4	0.14	3.0
	6.0	5.04	-16.0				0.15	3.1
Drinking water	0.4	0.36	-9.3	12	0.01	1.5	0.02	4.1
	0.5	0.46	-8.5				0.02	4.2
	1.6	1.48	-7.8	12	0.05	2.9	0.05	3.4
	2.0	1.82	-9.1				0.10	5.5
	5.0	4.54	-9.2	12	0.13	2.7	0.17	3.7
	6.0	5.09	-15.2				0.20	3.8
Wastewater	1.6	1.49	-6.8	12	0.01	0.8	0.06	4.2
	2.0	1.86	-6.9				0.07	3.5
	5.0	4.58	-8.4	12	0.18	3.7	0.14	3.0
	6.0	5.21	-13.2				0.32	6.2
	8.0	8.07	0.9	12	0.30	3.5	0.40	5.0
	10.0	9.00	-10.0				0.31	3.5