



# Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 6919; 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 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 method is 0.05–200 mg/L. The specific concentration ranges tested for this 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.

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

1.4 *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.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1193 Specifications for Reagent Water<sup>2</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water<sup>2</sup>
- D 3370 Practices for Sampling Water<sup>2</sup>
- D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water<sup>2</sup>

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

- D 4210 Practice for Interlaboratory Quality Control Procedures and Discussion on Reporting Low-Level Data<sup>2</sup>
- D 5810 Guide for Spiking into Aqueous Samples<sup>2</sup>
- D 5847 Practice for the Writing of Quality Control Specifications for Standard Test Methods for Water Analysis<sup>2</sup>
- D 5905 Practice for the Preparation of Substitute Wastewater<sup>2</sup>

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

## 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  $\mu$ L. 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.<sup>3</sup>

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

<sup>3</sup> International Standard ISO 14911.

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 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 method be able to tolerate acid concentrations up to 50 mM H<sup>+</sup> (pH 1.3), such as the IonPac<sup>®</sup> CS16 column. The columns used with nonsuppressed conductivity detection typically have lower capacity and can tolerate acid concentrations up to 10 mM H<sup>+</sup> (pH 2.0), such as the IC-Pak<sup>™</sup> 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 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 μS/cm on a linear scale.

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,<sup>4</sup> 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 D 1193, 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 method over time. It is recommended that reagent water with less than 10 ppb TOC be used for all prepared solutions in this method.

8.3 *Eluent Concentrate; Suppressed Conductivity Detection* (1.0 M methanesulfonic acid)—Carefully add 48.040 g of

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, by BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC) Rockville, MD.

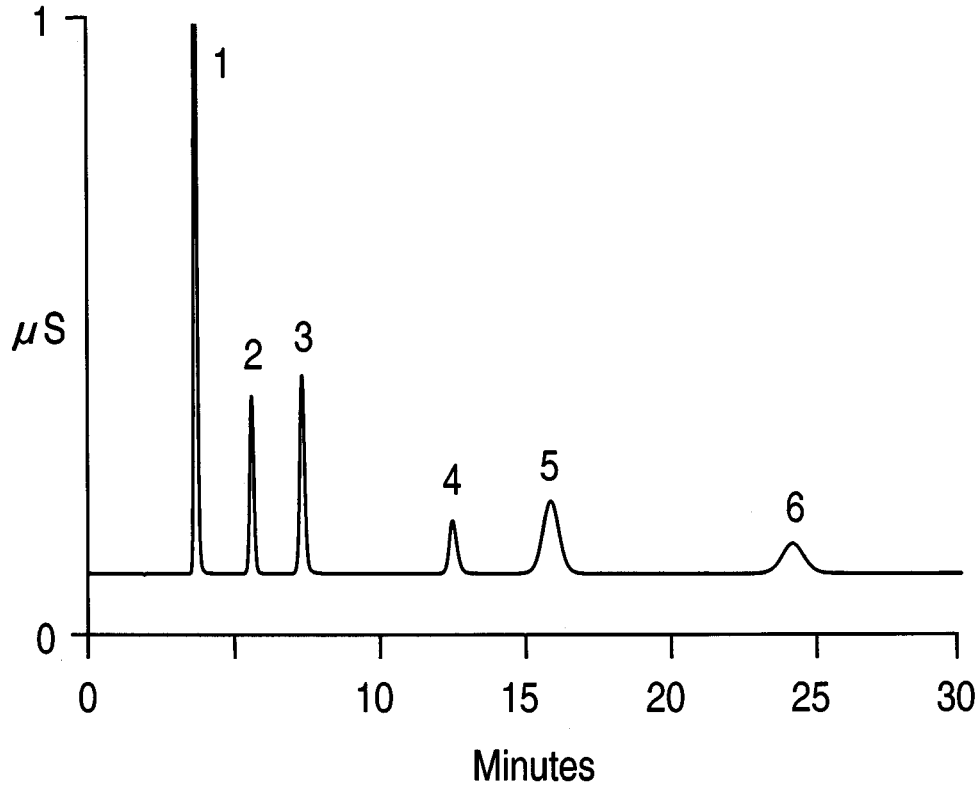


FIG. 1 Example Chromatogram of Dissolved Alkali and Alkaline Earth Cations, and Ammonium by Ion Chromatography Using Suppressed Conductivity Detection

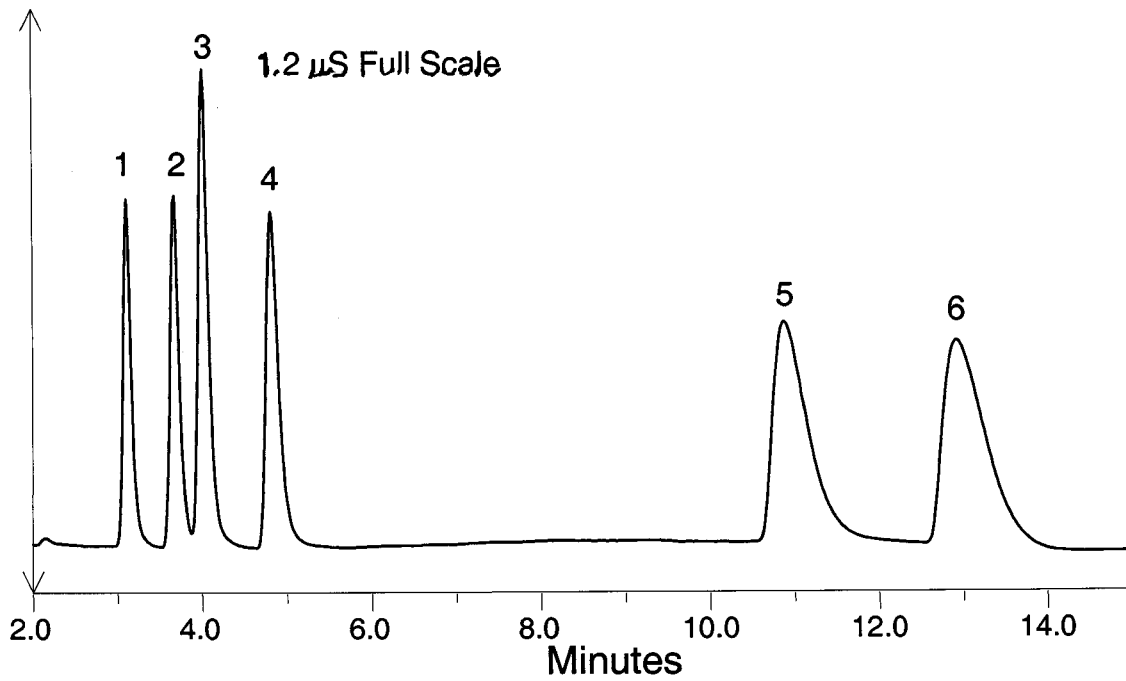


FIG. 2 Example QC Standard Chromatogram of Dissolved Alkali and Alkaline Earth Cations, and Ammonium by Ion Chromatography Using Nonchemically Suppressed Conductivity Detection (Single-Column Indirect Conductivity Detection)

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- $\mu$ m 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  $\mu$ L 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- $\mu$ m 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.

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  $\text{NH}_4^+$ .

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  $\text{Li}^+$ .

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  $\text{Na}^+$ .

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  $\text{K}^+$ .

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  $\text{Mg}^{2+}$ .

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  $\text{Ca}^{2+}$ .

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:

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

**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 $\mu$ L
Detection:	Suppressed conductivity
Suppressor:	CSRS ULTRA
Background:	~2 $\mu$ 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)

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

## 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 Practice D 3370, 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 be analyzed for cations are typically preserved with nitric acid, sulfuric acid is recommended for ammonium.<sup>5</sup> Add 0.8 mL concentrated  $\text{H}_2\text{SO}_4$ /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  $\text{H}_2\text{SO}_4$  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- $\mu$ 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  $\mu$ 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.

<sup>5</sup> Standard Methods for the Examination of Water and Wastewater, APHA, Washington, DC, 1992.

**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 <sup>®</sup> C/MD,
Injection Volume:	20 µL
Detection:	Nonsuppressed conductivity, indirect conductivity
Background:	~1300 µS
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)

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  $\geq 0.995$  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  
 $F$  = 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  $\text{NH}_3\text{-N/L}$ . To convert to mg of  $\text{NH}_3\text{-N/L}$ , 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 D 2777, 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 D 5905.

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.

## 17. Quality Control

17.1 Before this test is applied to analyzing unknown samples, the analyst shall establish quality control procedures

**TABLE 3 Precision and Bias for Lithium**

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S <sub>o</sub> , mg/L	S <sub>o</sub> , %	S <sub>i</sub> , mg/L	S <sub>i</sub> , %
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

**TABLE 4 Precision and Bias for Sodium**

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S <sub>o</sub> , mg/L	S <sub>o</sub> , %	S <sub>i</sub> , mg/L	S <sub>i</sub> , %
Reagent water	4.0	3.99	-0.3	10	0.13	2.9	0.13	3.3
	5.0	4.98	-0.4				0.22	4.3
	10.0	9.97	-0.3	11	0.10	0.9	0.33	3.3
	12.0	12.13	1.1				0.34	2.8
	20.0	20.26	1.3	11	0.51	2.2	0.94	4.6
	25.0	25.03	0.1				0.74	2.9
Drinking water	4.0	3.48	-13.1	11	0.20	5.0	0.46	13.2
	5.0	4.48	-10.5				0.65	14.5
	10.0	9.33	-6.7	12	0.15	1.5	0.86	9.2
	12.0	11.32	-5.7				0.87	7.7
	20.0	19.01	-5.0	12	0.80	3.7	1.40	7.4
	25.0	24.37	-2.5				1.20	4.9
Wastewater	10.0	9.41	-5.9	12	0.66	6.3	0.87	9.3
	12.0	11.26	-6.2				1.03	9.2
	20.0	18.70	-6.5	12	0.97	4.5	1.12	6.0
	25.0	24.61	-1.6				1.39	5.7
	32.0	31.00	-3.1	12	1.01	2.9	2.15	6.9
	40.0	38.70	-3.2				1.92	5.0

as recommended in Practices D 4210 and D 5847, and Guide D 3856. To be certain that analytical values obtained by this test method are valid and accurate within the confidence limits of the tests, the quality control procedures described in this section must be followed.

17.2 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 standard used for the method precision and bias study is recommended as an IDP solution.

17.2.1 The mean and standard deviation of seven values for each test method analyte shall then be calculated and compared, according to Practice D 5847, 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.

17.2.2 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.

17.3 When beginning use of this method, a Calibration Verification Standard (CVS) containing each test method analyte shall be analyzed to verify the calibration standards and acceptable instrument performance. This verification should be performed on each analysis day or whenever fresh eluent has been prepared. The CVS is a solution of method analytes with known concentration (mid-calibration range) used to fortify reagent water. The CVS must be prepared from a different source than the calibration standards. If the determined CVS concentrations are not within  $\pm 15\%$  of the known values, the analyst shall reanalyze the CVS. If the values still fall outside

**TABLE 5 Precision and Bias for Ammonium**

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S <sub>o</sub> , mg/L	S <sub>o</sub> , %	S <sub>t</sub> , mg/L	S <sub>t</sub> , %
Reagent water	0.4	0.42	4.5	11	0.04	9.2	0.05	11.3
	0.5	0.53	6.4				0.05	9.8
	1.6	1.62	1.1	12	0.02	1.1	0.12	7.6
	2.0	2.05	2.3				0.12	6.0
	5.0	4.98	-0.4	12	0.08	1.4	0.24	4.9
	6.0	5.94	-1.0				0.19	3.2
Drinking water	0.4	0.40	-1.2	13	0.03	7.0	0.07	18.2
	0.5	0.52	4.5	13	0.04	2.3	0.08	14.8
	1.6	1.65	3.2				0.17	10.4
	2.0	2.05	2.6	13	0.08	1.4	0.22	10.5
	5.0	4.96	-0.9				0.40	8.0
	6.0	5.97	-0.5	0.44	7.3			
Wastewater	1.6	1.66	3.7	11	0.11	6.0	0.27	16.5
	2.0	2.09	4.7	11	0.17	3.1	0.26	12.3
	5.0	4.95	-0.9				0.25	5.1
	6.0	5.96	-0.6	12	0.22	2.4	0.31	5.2
	8.0	7.95	-0.6				0.48	6.0
	10.0	9.83	-1.7	0.51	5.2			

**TABLE 6 Precision and Bias for Potassium**

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S <sub>o</sub> , mg/L	S <sub>o</sub> , %	S <sub>t</sub> , mg/L	S <sub>t</sub> , %
Reagent water	1.2	1.15	-4.0	11	0.05	3.7	0.11	9.5
	1.5	1.45	-3.5	10	0.03	0.5	0.08	5.8
	5.0	5.00	0.0				0.08	1.5
	6.0	6.05	0.8	11	0.18	1.6	0.06	0.9
	10.0	10.06	0.6				0.35	3.4
	12.0	11.99	-0.1	0.18	1.5			
Drinking water	1.2	1.18	-1.6	11	0.06	4.2	0.07	6.1
	1.5	1.49	-0.5	12	0.12	2.1	0.07	4.4
	5.0	5.02	0.3				0.21	4.2
	6.0	6.03	0.5	11	0.37	3.3	0.18	3.0
	10.0	10.00	0.0				0.27	2.7
	12.0	12.24	2.0	0.54	4.4			
Wastewater	5.0	5.20	4.0	11	0.10	1.8	0.31	6.0
	6.0	6.22	3.7	11	0.23	2.1	0.29	4.6
	10.0	10.08	0.8				0.36	3.6
	12.0	12.15	1.2	12	0.43	2.4	0.52	4.3
	16.0	15.96	-0.2				0.88	5.5
	20.0	19.91	-0.4	0.78	3.9			

acceptable limits, a new calibration curve is required that must be confirmed by a successful CVS before continuing with on-going analyses.

17.4 One continuing CVS shall be analyzed with each sample batch (maximum of 20 samples) to verify the previously established calibration curves. If the determined analyte concentrations fall outside acceptable limits ( $\pm 15\%$ ), that analyte is judged out of control, and the source of the problem must be identified before continuing with on-going analyses. All samples following the last acceptable CVS should be reanalyzed.

17.5 One Laboratory Control Sample (LCS) shall be analyzed with each sample batch (maximum of 20 samples) to ensure the test method is in control. The LCS is a solution of the test method analytes spiked at concentration levels of the IDP solution (see 17.2) added to a matrix that sufficiently challenges the test method. The LCS must be taken through all

of the steps of this analytical method including sample preservation and pretreatment. The analyte recoveries for the LCS must fall within the control limits listed below:

$$\text{Upper Control Limit} = x + 3S$$

$$\text{Lower Control Limit} = x - 3S$$

where:

$x$  = percent mean recovery

$S$  = standard deviation of the mean recovery, as determined from historical values for the equivalent concentration and matrix

**TABLE 7 Precision and Bias for Magnesium**

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S <sub>o</sub> , mg/L	S <sub>o</sub> , %	S <sub>i</sub> , mg/L	S <sub>i</sub> , %
Reagent water	2.4	2.48	3.2	11	0.06	2.3	0.09	3.7
	3.0	3.07	2.4				0.12	3.8
	5.0	5.22	4.5	11	0.03	0.5	0.14	2.6
	6.0	6.33	5.5				0.15	2.4
	10.0	10.15	1.5	10	0.18	1.6	0.22	2.2
	12.0	12.32	2.7				0.37	3.0
Drinking water	2.4	2.44	1.6	11	0.11	3.9	0.13	5.3
	3.0	3.06	1.9				0.15	4.8
	5.0	5.15	3.1	11	0.15	2.6	0.26	5.1
	6.0	6.17	2.8				0.22	3.5
	10.0	9.92	-0.8	12	0.27	2.5	0.47	4.7
	12.0	12.22	1.9				0.36	2.9
Wastewater	5.0	5.29	5.9	11	0.09	1.6	0.23	4.3
	6.0	6.43	7.2				0.21	3.3
	10.0	10.27	2.7	12	0.15	1.3	0.38	3.7
	12.0	12.41	3.4				0.40	3.2
	16.0	16.31	1.9	12	0.42	2.3	0.53	3.3
	20.0	20.12	0.6				0.57	2.8

**TABLE 8 Precision and Bias for Calcium**

Matrix	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Number Retained Pairs	S <sub>o</sub> , mg/L	S <sub>o</sub> , %	S <sub>i</sub> , mg/L	S <sub>i</sub> , %
Reagent water	4	3.86	-3.4	10	0.11	2.5	0.14	3.5
	5	4.80	-4.0				0.21	4.3
	10	9.52	-4.8	11	0.08	0.7	0.30	3.1
	12	11.75	-2.1				0.37	3.1
	20	16.64	-16.8	9	1.81	9.7	2.20	13.2
	25	20.73	-17.1				4.03	19.4
Drinking water	4	3.92	-2.0	12	0.22	5.1	0.27	6.8
	5	4.90	-2.0				0.44	8.9
	10	9.57	-4.3	12	0.17	1.6	0.45	4.7
	12	11.65	-2.9				0.39	3.3
	20	16.75	-16.2	10	1.14	6.2	3.09	18.4
	25	19.78	-20.9				4.16	21.0
Wastewater	10	9.64	-3.6	12	0.15	1.4	0.38	4.0
	12	11.83	-1.4				0.39	3.3
	20	17.53	-12.3	10	1.28	6.7	2.78	15.9
	25	20.49	-18.1				3.88	18.9
	32	25.54	-20.2	10	2.35	8.3	6.15	24.1
	40	31.22	-22.0				8.16	26.1

**TABLE 9 Method Detection Limits**

Analyte	Injected Concentration Range, µg/L <sup>A</sup>	Number of Labs	Pooled mean, µg/L	Pooled SD, µg/L	Pooled MDL, µg/L <sup>B</sup>
Lithium	3 to 18	10	8.3	0.9	2.9
Sodium	12 to 120	10	52.7	8.5	26.6
Ammonium	15 to 125	11	56.9	5.0	15.6
Potassium	30 to 90	10	73.9	11.4	35.9
Magnesium	15 to 60	10	38.9	6.1	19.1
Calcium	30 to 300	10	134.6	12.2	38.4

<sup>A</sup>Labs could choose the dilution of the MDL stock solution as appropriate for their instrumentation.

<sup>B</sup>On average, MDLs obtained using suppressed detection were approximately 2.1 times lower than those obtained using non-suppressed conductivity. This difference was not considered significant for the purposes of this study, as the analytes for the P&B study were spiked at a concentration level approximately two orders of magnitude greater than the calculated MDL values.

17.5.1 If the results do not fall within these limits, analysis of samples is halted until the problem is corrected. Either all samples in the batch must be reanalyzed to pass these perfor-

mance criteria, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

**TABLE 10 Upper Limits for Acceptable Precision and the Range of Acceptable Recoveries**

Analyte	IDP Solution Amount	Method $S_o$	Acceptable IDP Precision, $n = 7$	Acceptable IDP Range, $n = 7$	Method Mean Recovery	Lower Acceptable IDP Recovery	Upper Acceptable IDP Recovery
Lithium	1.6 mg/L	0.01 mg/L	0.0314 mg/L	0.1266 mg/L	1.47 mg/L	1.344 mg/L	1.597 mg/L
Sodium	10.0 mg/L	0.10 mg/L	0.2349 mg/L	1.0035 mg/L	9.97 mg/L	8.965 mg/L	10.972 mg/L
Ammonium	1.6 mg/L	0.02 mg/L	0.0457 mg/L	0.3774 mg/L	1.62 mg/L	1.241 mg/L	1.996 mg/L
Potassium	5.0 mg/L	0.03 mg/L	0.0637 mg/L	0.2338 mg/L	5.00 mg/L	4.764 mg/L	5.231 mg/L
Calcium	10.0 mg/L	0.08 mg/L	0.1771 mg/L	0.9235 mg/L	9.52 mg/L	8.601 mg/L	10.448 mg/L
Magnesium	5.0 mg/L	0.03 mg/L	0.0639 mg/L	0.4290 mg/L	5.22 mg/L	4.794 mg/L	5.652 mg/L

17.6 A reagent blank (8.8) shall be analyzed as part of the initial generation of calibration curves. A reagent blank shall also be analyzed with each sample batch (maximum of 20 samples) to check for contamination introduced by the laboratory or use of the test method.

17.7 One Matrix Spike (MS) shall be analyzed with each sample batch (maximum of 20 samples) to test method recovery. Spike a portion of one sample from each batch with a known concentration of the method analytes. The MS shall be prepared in accordance with that outlined in Guide D 5810 and section 11.11 of Guide D 3856. The percent recovery of the spike must fall within % recovery  $\pm$  analyst % RSD for an equivalent spike concentration and matrix given in Tables 3-8.

17.8 One Matrix Duplicate (MD) shall be analyzed with each sample batch (maximum of 20 samples) to test method precision. If nondetects are expected in all the samples to be analyzed, a Matrix Spike Duplicate (MSD) shall be analyzed instead of a MD. Prepare the MSD as outlined in Guides D 5810 and D 3856. The percent recovery of the spike must fall within % recovery  $\pm$  analyst % RSD for an equivalent

spike concentration and matrix given in Tables 3-8. Calculate the standard deviation and use the F-test (see Practice D 5847, section 6.3.1.1) to compare with the single operator precision given in Tables 3-8 for the equivalent analyte concentration and matrix type. Evaluate performance according to Practice D 5847.

17.9 An Independent Reference Material (IRM) shall be analyzed at least once per quarter in order to verify the quantitative values produced by the test method. The analyte concentrations of the reference material should be in appropriate range as cited in 1.2 of this test method. The recovery values obtained for each test method analyte must fall within the control limits specified by the supplier of the IRM.

17.10 The laboratory may perform additional quality control as desired or as required for regulatory compliance.

## 18. Keywords

18.1 alkali and alkaline earth cations; ammonium cation; conductivity detection; ion chromatography; wastewater; water

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