Designation: D5542 – 16

Standard Test Methods for
Trace Anions in High Purity Water by Ion Chromatography[1]

This standard is issued under the fixed designation D5542; 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 These test methods cover the determination of trace (µg/L) levels of fluoride, acetate, formate, chloride, phosphate, and sulfate in high purity water using ion chromatography in combination with sample preconcentration. Other anions, such as bromide, nitrite, nitrate, sulfite, and iodide can be determined by this method. However, since they are rarely present in significant concentrations in high purity water, they are not included in this test method. Two test methods are presented and their ranges of application, as determined by a collaborative study, are as follows:

	Range Tested (µg/L Added)	Limit of Detection[A] (Single Operator) (µg/L)	Sections
Test Method A:			7–16
Chloride	0–24	0.8	
Phosphate	0–39	[B]	
Sulfate	0–55	1.8	
Test Method B:			17–24
Fluoride	0–14	0.7	
Acetate	0–414	6.8	
Formate	0–346	5.6	

[A] Limit of detection is lowest measurable concentration not reportable as zero at 99 % level of confidence as per EPRI study as cited in Sections 16 and 24.
[B] Insufficient data to calculate limit of detection.

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

1.3 The common practical range of Test Method A is as follows: chloride, 1 to 100 µg/L, phosphate, 3 to 100 µg/L, and sulfate, 2 to 100 µg/L.

1.4 The common practical range of Test Method B is as follows: fluoride, 1 to 100 µg/L, acetate, 10 to 200 µg/L, and formate, 5 to 200 µg/L.

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

1.6 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]
D1193 Specification for Reagent 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]
D4453 Practice for Handling of High Purity Water Samples
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

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 *analytical columns, n*—a combination of one or more guard columns followed by one or more separator columns used to separate the ions of interest.

3.2.1.1 *Discussion*—It should be remembered that all of the columns in series contribute to the overall capacity of the analytical column set.

3.2.2 *breakthrough volume, n*—the maximum sample volume that can be passed through a concentrator column before the least tightly bound ion of interest is eluted.

Eluent: 0.75 mM Sodium bicarbonate
2.2 mM Sodium carbonate

Flow Rate: 2 mL/min

Columns: TAC-1 Concentrator
IonPac AG4A Guard
IonPac AS4A Analytical

Suppressor: AMMS Anion MicroMembrane
25 mN Sulfuric acid
3 mL/min

Detector: Conductivity

Sample: Deionized water
10 mL Concentrated

Peaks: 1. Chloride   5 ug/L
2. Nitrate   20 ug/L
3. Phosphate   20 ug/L
4. Sulfate   20 ug/L

FIG. 1 Anions by Test Method A

detector background and at the same time enhance detector response to the ions of interest.

4. Significance and Use

4.1 The anions fluoride, chloride, and sulfate have been identified as important contributors to corrosion of high pressure boilers, electric power turbines and their associated heat exchangers. Many electric power utilities attempt to reduce these contaminants in their boiler feed water to less than 1 µg/L.

4.2 In the semiconductor manufacturing process these ions, among others, have been identified as a cause of low product yield and, thus, must be monitored and controlled to levels similar to those required by the electric power industry.

4.3 Low molecular weight organic acids, such as acetate and formate, have been found in many steam generator feed waters and condensates. They are believed to come from the high temperature breakdown of organic matter found in boiler make up water. It is felt that these organic acids promote corrosion by lowering the pH of boiler waters and may even be corrosive themselves.

4.4 Such low molecular weight organics may also be produced when ultraviolet light is used to produce bacteria-free water for semiconductor processing. Such polar organic contaminants are suspected of causing reduced semiconductor yields.

4.5 Phosphates are commonly added to drum boilers in the low mg/L level to precipitate calcium and magnesium and thereby prevent scale formation. Ion chromatography can be used to monitor the concentration of such chemicals in boiler water, as well as detect unwanted carry-over into the steam.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. [4]

5.1.1 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.

5.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Column life may be extended by passing Type I water through a 0.22 µm filter prior to use. Freshly prepared water should be used for making the low level standards intended for calibration. The detection limits of this method will be limited by the purity of the water and reagents used to make the standards. The purity of the water may be checked by use of this method. Anion concentrations of less than 0.2 ppb each, is typical of Type I water.

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[4] *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.
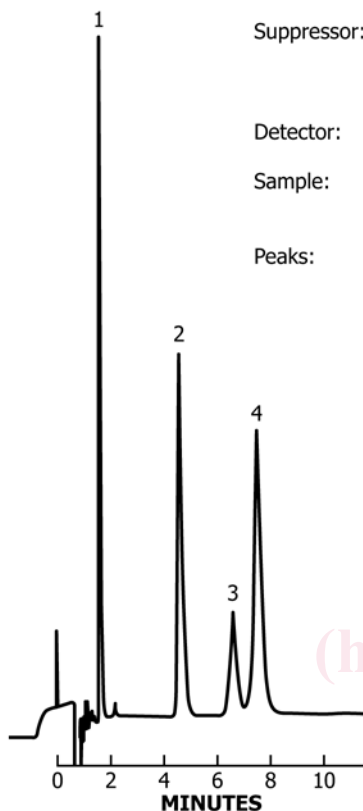
3.2.3 *concentrator column, n*—an ion exchange column used to concentrate the ions of interest and thereby increase method sensitivity.

3.2.4 *eluant, n*—the ionic mobile phase used to transport the sample through the exchange column.

3.2.5 *guard column, n*—a column used before the separator column to protect it from contaminants, such as particulate matter or irreversibly retained materials.

3.2.6 *ion chromatography, n*—a form of liquid chromatography in which ionic constituents are separated by ion exchange followed by a suitable detection means.

3.2.7 *resolution, n*—the ability of an analytical column to separate constituents under specific test conditions.

3.2.8 *separator column, n*—the ion exchange column used to separate the ions of interest according to their retention characteristics prior to their detection.

3.2.9 *suppressor device, n*—a device that is placed between the analytical columns and the detector.

3.2.9.1 *Discussion*—Its purpose is to inhibit detector response to the ionic constituents in the eluant, so as to lower the

6. Sampling

6.1 Collect samples in accordance with Practice D1066, Guide D1192, Practices D3370, and Practice D4453, as applicable.

6.2 Collect samples in polystyrene bottles that should be filled to overflow and capped, so as to exclude air. Glass sample bottles should not be used, as they can contribute ionic contamination.

6.3 Samples should be analyzed within 48 h of sampling. When acetate, formate or phosphate data are required, refrigerate at 4°C upon sampling.

6.4 To prevent added ionic contamination, no preservation or filtration of the sample shall be done.

TEST METHOD A—CHLORIDE, PHOSPHATE, AND SULFATE

7. Scope

7.1 This test method is optimized for the quantitative determination of trace levels of chloride, phosphate, and sulfate. Anions such as fluoride, acetate, and formate can be detected by this method, but are not reliably resolved from each other. See Fig. 1 for a typical chromatogram.

7.2 Using a concentrated sample volume of 20 mL, the test method is applicable in the range outlined in Section 1. The range of this test method may be extended by concentrating a smaller or a larger sample volume. Be sure not to exceed concentrator column breakthrough volume (see annex).

8. Quality Control

8.1 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. In order 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.

8.2 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 to the calibration standards, used to fortify reagent water. Ideally, the IPD solution should be prepared by an independent source from reference materials.

8.2.1 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.

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

8.3 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 of 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 ±15 % of the known values, the analyst shall reanalyze the CVS. If the values still fall outside acceptable limits, a new calibration curve is required which must be confirmed by a successful CVS before continuing with on-going analyses.

8.4 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 (±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.

8.5 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 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:

$$Upper\ Control\ Limit = x + 3S \quad (1)$$
$$Lower\ Control\ Limit = x - 3S \quad (2)$$

where:
x = percent mean recovery, and
S = standard deviation of the mean recovery, as determined from historical values for the equivalent concentration and matrix.

8.5.1 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 so as to pass these performance criteria, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

8.6 A reagent blank 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.

8.7 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 D5810 and section 11.11 of Guide D3856. The % recovery of the spike must fall within % recovery ± analyst % RSD for an equivalent spike concentration and matrix.

8.8 One matrix duplicate (MD) shall be analyzed with each sample batch (maximum of 20 samples) to test method
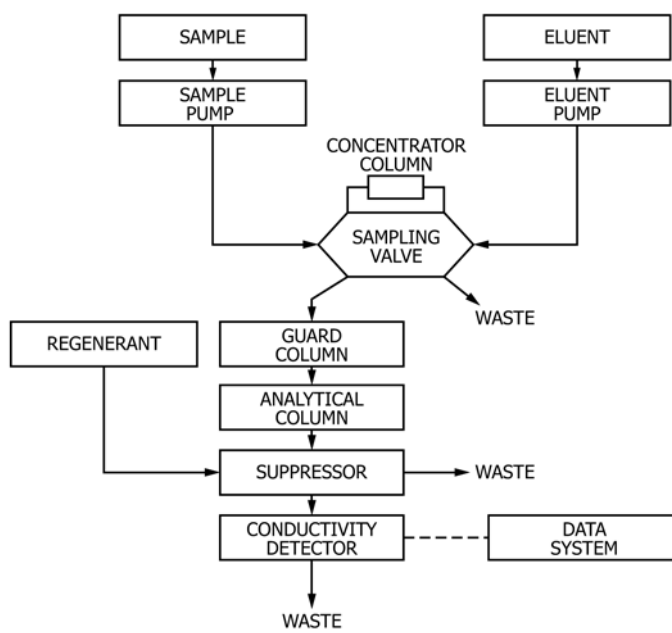
FIG. 2 Schematic of an Ion Chromatograph

precision. If non-detects 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 D5810 and D3856. The percent recovery of the spike must fall within % recovery ± analyst % RSD for an equivalent spike concentration and matrix. Calculate the standard deviation and use the F-test (see Practice D5847, 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 D5847.

8.9 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 1.1 of these test methods. The recovery values obtained for each test method analyte must fall within the control limits specified by the supplier of the IRM.

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

9. Summary of Test Method

9.1 A flow diagram of an ion chromatograph is shown in Fig. 2. With the sampling valve in the load position, the desired volume of sample (for example, 20 mL) is pumped through a concentrator column where the anions of interest are trapped. The sampling valve is then switched to the inject position and the pumped eluant, containing sodium carbonate and bicarbonate, sweeps these anions through the analytical columns where they are separated according to their retention characteristics relative to the anions in the eluant. The eluant stream next passes through a suppressor where all cations are exchanged for hydrogen ions. This converts the carbonate and bicarbonate in the eluant to the poorly ionized carbonic acid, thus reducing the background conductivity.

9.1.1 This also converts the anions to their acid form, thus enhancing their conductivity. The eluant stream then passes through an electrical conductivity detector, where the separated anions are detected. A strip chart recorder and/or a chromatographic integrator is used for data presentation.

9.2 The anions are identified based on their retention times, when compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

10. Interferences

10.1 When working at microgram per litre concentrations and lower, contamination can be a very serious problem. Extreme care must be exercised in all phases of the test method (sample collection, storage, and analysis) to eliminate contamination.

10.2 As with other types of chromatography, if one of the sample components is present at very high concentration levels, it may interfere by causing a very large peak on the chromatogram that could mask other peaks present. This type of interference may normally be minimized by dilution of the sample, depending on the concentration of other anions.

10.3 When loading concentrator columns, high concentrations of certain anions may cause low breakthrough volumes of other anions. These certain anions may act as eluants and displace other anions from the concentrator column. See annex to determine breakthrough volume. Do not attempt to concentrate a volume of sample greater than 80 % of the breakthrough volume.

10.4 Samples containing high (mg/L) concentrations of ammonia, morpholine, or other additives which raise the hydroxide concentration (pH) of the sample may cause low breakthrough volumes. This problem may be avoided by taking such samples after the cation resin of a cation conductivity detector.

11. Apparatus

11.1 *Ion Chromatograph*—The ion chromatograph should have the following components assembled, as shown in Fig. 2.

11.1.1 *Eluant and Regenerant Containers.*

11.1.2 *Eluant Pump,* capable of delivering 2 to 5 mL/min of eluant at a pressure of up to 2000 psig. Wetted parts of the pump should be nonmetallic, so as not to contaminate the concentrator or analytical columns with metals, or both.

11.1.3 *Sample Pump,* capable of delivering up to 5 mL/min of sample at a pressure of at least 200 psig. Wetted parts of the pump should be nonmetallic, so as not to contaminate the concentrator and/or analytical columns with metals.

11.1.4 *Concentrator Column*—Anion exchange column with sufficient capacity to concentrate at least 20 mL of sample before reaching chloride breakthrough.

11.1.5 *Guard Column*— Anion exchange column, typically of the same anion exchange material used in the separator column. The purpose of this column is to protect the separator column from particulate matter and irreversibly retained materials.

11.1.6 *Separator Column*—Anion exchange column capable of separating chloride from the injection void volume, as well as resolving the anions chloride, phosphate, and sulfate.

11.1.7 *Suppressor Column*—A cation exchanger which is continuously regenerated by a flow of dilute sulfuric acid.

11.1.8 *Detector*—A low-volume, flow-through, temperature-compensated electrical conductivity cell equipped with a meter capable of reading from 0 to 15 000 uS/cm on a linear scale.

11.1.9 *Recorder,* compatible with the detector output with a full-scale response time of 2 s or less.

11.1.10 *Integrator*—An electronic integrator, such as is used with gas and liquid chromatographs, may be used to quantitate peak area, as well as peak height. The peak area data can be used in the same way peak height is used to quantitate results.

11.1.11 *Sample Bottles*—Polystyrene culture bottles with a total capacity of approximately 270 mL have been found satisfactory.

11.1.12 The following is a summary of the columns and suppressor components used in the collaborative study.

> Concentrator column: AG-4A
> Guard column: AG-4A
> Separator column: AS-4A
> Suppressor device: Anion MicroMembrane Suppressor[A]

[A] Anion MicroMembrane Suppressor is a registered trademark of Dionex Corp.

12. Reagents

12.1 *Eluant*—Dissolve 0.25 g of sodium bicarbonate (0.75 millimolar) and 0.93 g of sodium carbonate (2.2 millimolar) in water and dilute to 4 L with water. Other eluants may also prove to be acceptable, provided they give the proper resolution between the component peaks.

12.2 *Suppressor Regenerant*—Cautiously add 3 mL of concentrated sulfuric acid to 4 L of water.

12.3 *Stock Solutions:*

12.3.1 *Fluoride Solution, Stock* (1.00 mL = 1.00 mg F)—Dissolve 2.210 g of sodium fluoride (NaF) in water and dilute to 1 L with water.

12.3.2 *Acetate Solution Stock* (1.00 mL = 1 mg acetate)—Dissolve 1.389 g of sodium acetate in water and dilute to 1 L with water.

12.3.3 *Formate Solution Stock* (1.00 mL = 1 mg formate)—Dissolve 1.511 g sodium formate in water and dilute to 1 L with water.

12.3.4 *Chloride Solution Stock* (1.00 mL = 1.00 mg chloride)— Dry sodium chloride (NaCl) for 1 h at 100°C and cool in a desiccator. Dissolve 1.648 g of the dry salt in water and dilute to 1 L with water.

12.3.5 *Phosphate Solution Stock* (1.00 mL = 1.00 mg PO_4)—Dissolve 1.433 g of potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 L with water.

12.3.6 *Sulfate Solution Stock* (1.00 mL = 1.00 mg SO_4)—Dry sodium sulfate for 1 h at 105°C and cool in a desiccator. Dissolve 1.479 g of the dried salt in water and dilute to 1 L with water.

12.4 *Intermediate Standard Solutions*—Prepare a 1000 µg/L standard of each anion by diluting 1.00 mL of each standard stock solution to 1 L. These solutions should be prepared fresh weekly and should be stored in polypropylene or polystyrene bottles.

12.5 *Working Standard Solutions*—Prepare a blank and at least three different working standards containing the anions of interest. The combination anion solutions should be prepared in volumetric flasks and then transferred to polystyrene bottles. These standards must be prepared fresh daily. The concentration range for the three standards will be dependent on the levels expected in the samples. If desired, a standard may be prepared that contains all six anions. A typical range would be 5, 10, and 25 µg/L of each anion per standard. This would be prepared by taking 5, 10, and 25 mL of the standard stock solution and diluting to 1 L with water for each standard. The blank standard is a portion of the same water used to prepare the working standard solutions.

12.6 Some investigators prefer to work with standard solutions that are prepared by diluting microlitre qualities of stock standards (or low level standards) using push-button microlitre pipettes. These have been found to be adequate for many purposes, but their precision may be limited.

13. Calibration

13.1 Determine the retention time for each anion by analyzing a standard solution containing only the anion of interest and noting the time required for a peak to appear on the chromatogram.

13.2 Analyze the blank and each of the working standard solutions described in 12.5, according to the following:

13.2.1 Analyze the blank (known volume of water loaded onto the concentrator column).

13.2.2 Analyze the standard solutions (known volume of standard solution loaded onto the concentrator column).

13.2.3 If a measurable peak is noted on the blank chromatogram that coincides in retention time with a peak of interest, determine the concentration of each of the ions in the blank by plotting the standard concentration on the abscissa and the peak height or area on the ordinate of linear graph paper.

13.2.4 Extrapolate the line through the abscissa. The point at which the line intercepts the abscissa represents the concentration of the anion in the blank.

13.2.5 Add the concentration of the anion in the blank to the nominal concentration of the prepared standard solution.

13.2.5.1 *Example*—A 10-µg/L prepared chloride standard solution with a blank correction of 0.2 µg/L would be plotted as 10.2 µg/L chloride.

13.3 Reconstruct a calibration curve by plotting the adjusted concentration of the standards versus peak area or peak height or adjust the concentration of the standard values entered into a computer or computing integrator for direct read-out in concentration units.

13.3.1 The concentration of standard solutions prepared for instrument calibration should approximate or bracket the concentration of the sample whenever possible.

13.3.2 Each analytical curve should be established using only one scale setting. Changing the scale setting may result in a slight change in the slope of the analytical curve.

13.3.3 When working with concentrator columns, the volume of standard and sample must be kept constant.

13.3.4 The scale setting used (μS) should be adequate to observe peaks of interest with minimal noise. This is especially true at very low sensitivity settings.

13.4 Alternatively, computing integrators or computerized chromatographic data systems can be used to accomplish the essential features of the calibration procedure described above.

14. Procedure

14.1 Set-up the Ion Chromatograph according to the manufacturer's instructions.

14.1.1 The detector ranges are variable. Normal operating ranges are from 1 to 30 μS/cm full scale. The range setting required for analysis will depend on the concentration of anions in the sample and the volume loaded on the concentrator column and should be chosen accordingly.

14.2 Equilibrate the system by pumping eluant through all three columns until a stable baseline is obtained (approximately 15 to 20 min). This equilibration can normally be accomplished while the samples and standards are being prepared.

14.3 Set up the instrument as directed by the manufacturer. The concentrator column should be installed where the normal sample loop is located on the LOAD/INJECT valve. (**Warning**—Do not handle the fittings where they may come in contact with the eluant stream. Chloride contamination may result.)

14.4 Inject the sample loaded on the concentrator column into the eluant stream as per manufacturer's instructions. Record the ion chromatogram.

15. Calculation

15.1 Refer the peak height or area for the anion(s) of interest to the appropriate analytical curve(s) to determine the anion concentration in μg/L.

15.2 *Anion Concentration:*

$$\mu g/L = A \times F$$

where:
A = μg/L read from appropriate calibration curve, and
F = concentration factor.

15.3 The concentration factor should be equal to unity if equal volumes of standard and sample have been loaded on the concentrator column.

16. Precision and Bias (Test Method A)

16.1 Precision and bias of this test method for chloride, phosphate, and sulfate in demineralized water was determined by collaborative testing conducted under the auspices of the Electric Power Research Institute, who provided the collaborative study design and the precision and bias presented in Table

1.[5] The inclusion of this data had the approval of the results advisor when this standard was first approved in 2004.

TEST METHOD B—FLUORIDE, ACETATE, AND FORMATE

17. Scope

17.1 This test method is optimized for the quantitative determination of trace levels of fluoride, acetate, and formate in high purity water and in water containing up to 2000 mg/L boron from boric acid. The range of the method is summarized in Section 1. See Fig. 3 for a typical chromatogram.

17.2 This test method does not respond to sulfate, since its elution time is very long.

17.3 Using a concentrated sample volume of 20 mL, the test method is applicable in the range outlined in Section 1. The range of this method may be extended upward by concentrating a smaller sample volume, or downward by concentrating a larger sample volume. When analyzing samples containing high amounts of boric acid (for example, 1 %), the volume concentrated should not exceed 30 mL, so as not to exceed the breakthrough volume for fluoride.

18. Quality Control

18.1 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. In order 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.

18.2 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 to the calibration standards, used to fortify reagent water. Ideally, the IPD solution should be prepared by an independent source from reference materials.

18.2.1 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.

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

18.3 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