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

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:			7–15
Chloride	0–24	0.8	
Phosphate	0–39	[B]	
Sulfate	0–55	1.8	
Test Method B:			16–23
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 15 and 23.
[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]
D 1066 Practice for Sampling Steam
D 1129 Terminology Relating to Water
D 1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water
D 3370 Practices for Sampling Water from Closed Conduits
D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water
D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]
D 4453 Practice for Handling of Ultra-Pure Water Samples
D 5810 Guide for Spiking into Aqueous Samples
D 5847 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 these test methods refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analytical columns*—a combination of one or more guard columns followed by one or more separator columns used to separate the ions of interest. 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*—the maximum sample volume that can be passed through a concentrator column before the least tightly bound ion of interest is eluted.

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

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

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

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

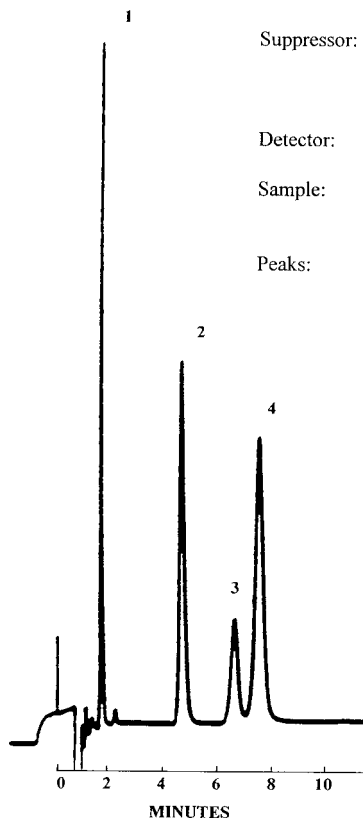| Peaks:		
	1. Chloride	5 ug/L
	2. Nitrate	20 ug/L
	3. Phosphate	20 ug/L
	4. Sulfate	20 ug/L

FIG. 1 Anions by Test Method A

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

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

3.2.8 *separator column*—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*—a device that is placed between the analytical columns and the detector. Its purpose is to inhibit detector response to the ionic constituents in the eluant, so as to lower the 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 D 1193, 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.

6. Sampling

6.1 Collect samples in accordance with Practice D 1066, Specification D 1192, Practice D 3370, and Practice D 4453, 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.

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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.
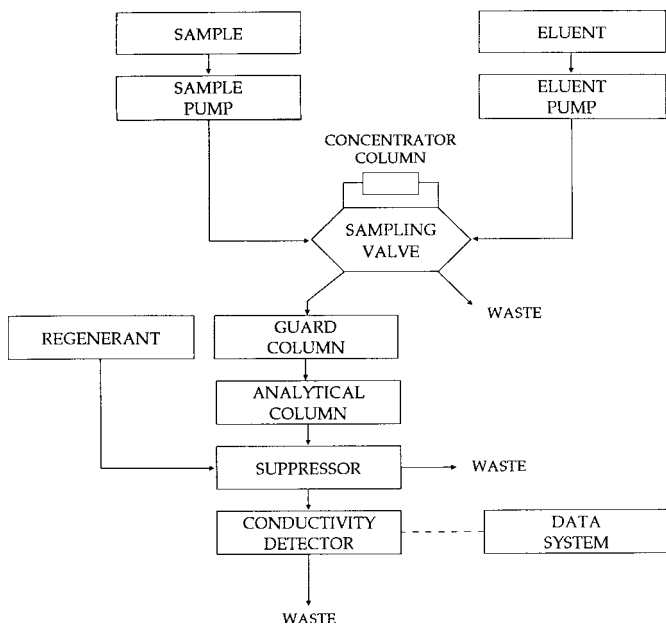
FIG. 2 Schematic of an Ion Chromatograph

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. Summary of Test Method

8.1 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.

8.1.1 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.

8.2 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.

9. Interferences

9.1 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.

9.2 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.

9.3 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.

9.4 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.

10. Apparatus

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

10.1.1 *Eluant and Regenerant Containers*.

10.1.2 *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.

10.1.3 *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.

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

10.1.5 *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.

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

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