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.

[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of 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.

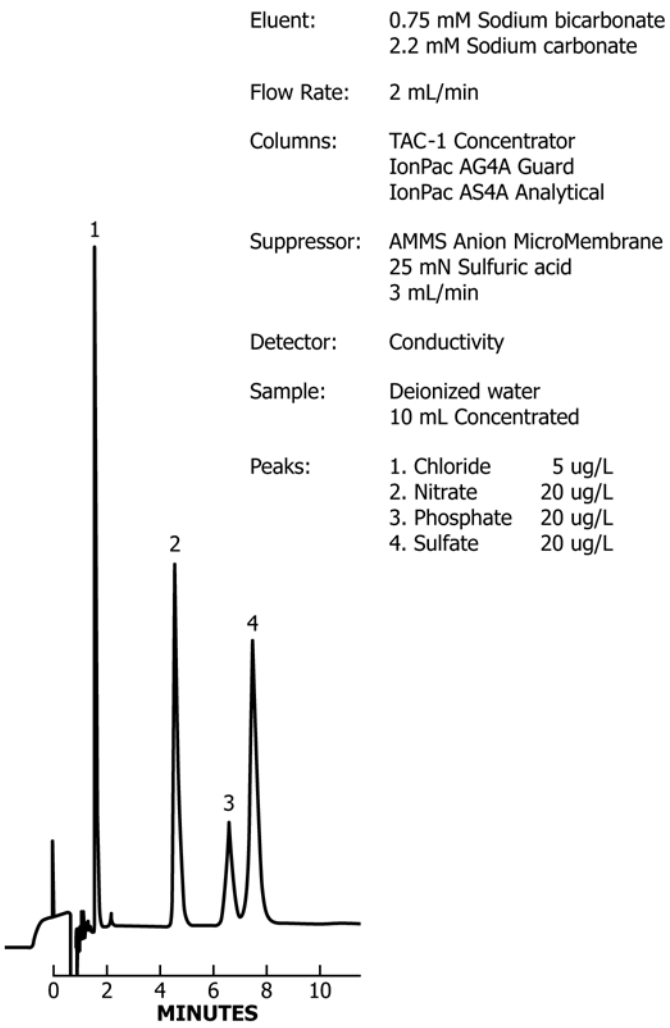

FIG. 1 Anions by Test Method A

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 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.

[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.

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:

$$\text{Upper Control Limit} = x + 3S \quad (1)$$

$$\text{Lower Control Limit} = x - 3S \quad (2)$$

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