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An American National Standard

Standard Test Method for Measuring Anionic Contaminants in High-Purity Water by On-Line Ion Chromatography[1]

This standard is issued under the fixed designation D 5996; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers on-line analysis of high-purity water by the ion chromatography technique. This test method is applicable for measuring various anionic contaminants in high-purity water, typically in the range of 0.02 to 100 µg/L. This test method is used to determine the concentration of acetate, formate, chloride, fluoride, phosphate, nitrate, and sulfate in a continuously flowing sample. The range of the test method is only as good as the reagent water available for preparing standards. At extremely low concentrations, <1.0 µg/L, preparing standards is difficult, and extra care must be taken in their preparation. The sample may have to be conditioned from higher pressures and temperatures to conditions that are suitable for use by on-line instruments. The range of the test method is only as good as the reagent water available for standard preparation.

1.2 *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:*

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for the Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis[2]

D 4453 Practice for Handling of Ultra-Pure Water Samples[2]

D 5542 Test Methods for Trace Anions in High Purity Water by Ion Chromatography[2]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analytical column,, n*—a column used to separate the anions of interest.

3.2.2 *analytical column set,, n*—a combination of one or more guard columns followed by one or more analytical columns.

3.2.3 *anion suppressor device,, n*—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.

3.2.4 *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. All of the columns in series contribute to the overall capacity of the analytical column set.

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

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

3.2.7 *guard column,, n*—a column used before the analytical column to protect it from contaminants, such as particulate matter or ionic species that may chemically foul the resins and degrade their performance.

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

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

4. Summary of Test Method

4.1 A continuously flowing sample is injected into the instrument through a sample injection valve. The sample is pumped through a concentrator column where the anions of interest are collected on ion-exchange resin. After a suitable volume of sample has been passed through the concentrator

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water.

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[2] *Annual Book of ASTM Standards,* Vol 11.01.

column, sample flow is diverted and an eluant is pumped through the concentrator column to remove the trapped anions. This eluant then flows through an analytical column set where the anions are separated based on the retention characteristic of each anion relative to the eluant used. The eluant stream containing the anions of interest passes through a suppressor device where the cations from the eluant are exchanged for hydrogen ions, converting the anions to their acid form. After the suppressor device, the eluant solution passes through a conductivity detector where the separated anions are detected. Detection limits for the anions are enhanced because the anions are in the acid form rather than the salt.

4.2 The anions are identified based on the retention time as compared to known standards. By measuring peak height or area and comparing the detector response to known standards, the anions can be quantified.

5. Significance and Use

5.1 In the power-generation industry, high-purity water is used to reduce corrosion from anions, such as sulfate, chloride, and fluoride. These anions are known to be detrimental to materials of construction used in steam generators, reactor vessel internals and recirculation piping, heat exchangers, connective piping, and turbines. Most electric generating plants try to control these anions to <1.0 µg/L in the steam generator feed water. Some nuclear power plants have been able to control anion contaminants at less than 0.02 µg/L.

5.2 These anions and others cause low product yields in semiconductor manufacturing. They are also monitored and controlled at similarly low levels as in the electric power industry.

5.3 Low molecular weight organic acids (acetate, formate, propionate) have been detected in steam generator feed water. These low molecular weight organic materials are believed to be high-temperature degradation products of chemicals used to control cycle water pH and organic contaminants in cycle makeup water.

5.4 In the semiconductor industry, anion contaminants may come from the breakdown of low molecular weight organic materials by ultraviolet light radiation, which is frequently used to produce bacteria-free water. These organic compounds may also contribute to low product yield.

5.5 The production of high-purity water for process makeup and use frequently employs the use of demineralizers to remove unwanted anion contaminants. Also in the electric power industry, demineralizers are used in the process stream to maintain low levels of these contaminants. As such, it is important to monitor this process to ensure that water quality standards are being met. These processes can be monitored for the above mentioned anions.

5.6 On-line measurements of these contaminants provide a greater degree of protection of the processes by allowing for frequent on-line measurement of these species. Early detection of contaminant ingress allows for quicker corrective action to locate, reduce, or eliminate, or combination thereof, the source. Grab samples will not provide the same level of protection because of their intermittent nature and the longer time required to obtain and then analyze the sample.

5.7 Additionally, on-line monitoring significantly reduces the potential for contamination of high-purity water samples, a significant problem when sampling and testing high-purity water.

6. Interferences

6.1 When working with low concentration samples, blanks, and standards, contamination can be a serious problem. Extreme care must be exercised in all phases of this test method.

6.2 Improper sample line material or sample lines that have not been properly conditioned can give results that may not be truly representative of the process stream. Absorption/desorption of anions on sample line wall deposits can change analytical results. Maintaining a minimum sample flow of 1.8 m/s (6 ft/s) will minimize deposit buildup on sample line walls, reducing the potential for absorption/desorption of anions.

6.3 A single anion present at a concentration significantly higher than other anions could mask closely adjacent peaks on the chromatogram.

6.4 Low breakthrough volumes may be experienced when continuously monitoring for anions in water that has had its pH raised by ammonia, morpholine, or other additives. This interference can be eliminated by taking the sample from the effluent of a cation resin column.

6.5 Identification of the anion is based on retention time of the anion of interest. An interfering anion having the same retention time as one of the anions of interest will result in erroneously high values for that anion.

6.6 When loading a concentrator column, high concentrations of interfering anions may cause low breakthrough volumes of other anions. These interfering anions may act as an eluant and displace other anions from the concentrator column. See Annex A1 to determine breakthrough volume. Do not load a sample volume greater than 80 % of the breakthrough volume.

7. Apparatus

7.1 Ion chromatograph with the following components:

7.1.1 *Eluant Introduction System*—The wetted portion of the eluant pump should be nonmetallic or of a corrosion-resistant metal to prevent contamination of the chromatography columns.

7.1.2 *Sample Injection System*—The wetted portion of the sample pump should be nonmetallic or of a corrosion-resistant metal to prevent metal contamination of the chromatography columns.

7.1.3 *Anion Suppressor Device*.

7.1.4 *Conductivity Cell*, low dead volume (1 µL). Temperature compensated or corrected flow through conductivity detector should be capable of measuring conductivity from 0 to 1000 µS/cm. If temperature controlled conductivity detector is used, temperature control should be at ±0.5°C or better.

7.1.5 *Suppressor Device Regenerant System*—Some manufacturers provide integrated regenerant systems that reduce the consumption of eluant. Electrochemical suppressor regenerant systems can be used, eliminating the need to prepare regenerant solutions.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. [3] 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.

8.2 *Purity of Water*— Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Specification D 1193 Type 1 and shall contain less than 0.2 µg/L of the anions of interest. Freshly prepared water should be used for making the low-level standards used for calibration. Detection limits will be limited by the purity of the water and reagents used to make standards. The purity of the water used shall be checked by the use of Test Methods D 5542.

8.3 Prepare eluant for the specific columns used and for the anions of interest in accordance with manufacturer's directions.

8.4 Prepare regenerant for the specific suppressor used in accordance with the manufacturer's directions if required.

NOTE 1—There are numerous combinations of analytical columns, suppressors, eluants, and regenerants that may be used with this method. It is not practicable to list all the combinations. Users should use the appropriate combination of analytical column, suppressor, eluant, and regenerant to achieve the desired resolution and detection.

8.5 *Fluoride Solution, Stock* (1.00 mL = 1.00 mg F)—Dry sodium fluoride at 110°C for 2 ± 0.5 h and cool in a desiccator. Dissolve 2.210 g of dried salt in water and dilute to 1 L.

8.6 *Acetate Solution, Stock* (1.00 mL = 1.00 mg acetate)—Dissolve 1.389 g of sodium acetate in water and dilute to 1 L with water. Store in a brown glass bottle with a TFE-fluorocarbon lined cap in a refrigerator.

8.7 *Formate Solution, Stock* (1.00 mL = 1 mg formate)—Dissolve 1.511 g sodium formate in water and dilute to 1 L with water. Store in a brown glass bottle with a TFE-fluorocarbon lined cap in a refrigerator.

8.8 *Chloride Solution, Stock* (1.00 mL = 1.00 mg Cl)—Dry sodium chloride (NaCl) for 2 ± 0.5 h at 110°C and cool in a desiccator. Dissolve 1.648 g of the dry salt in water and dilute to 1 L.

8.9 *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.

8.10 *Sulfate Solution, Stock* (1.00 mL = 1.00 mg SO_4)—Dry sodium sulfate for 2 ± 0.5 h at 110°C and cool in a desiccator. Dissolve 1.479 g of the dried salt in water and dilute to 1 L.

8.11 *Nitrate Solution, Stock* (1.00 mL = 1.00 mg NO_3)—Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105°C for 48 h. Dissolve exactly 1.371 g of the dried salt in water and dilute to 1 L with water.

8.12 *Anion Intermediate Solutions*—Prepare a 1000 µg/L standard of each anion by diluting 1.00 mL of each stock solution to 1 L. If acetate, formate, or phosphate are included in the standard, the solution must be prepared daily. It is recommended that these standards be prepared separately from the rest of the anions.

8.13 *Anion Working Solutions*—Prepare a blank and at least three different working solutions from the anion intermediate solution, containing the anions of interest. Prepare in dedicated volumetric flasks and transfer to sample containers in accordance with Practice D 4453. Prepare fresh daily. The range of the working solutions prepared should bracket the analytical range of interest. A typical range would be 5, 10, and 25 µg/L for each anion or consistent with analytical range of interest. Systems equipped with sample preparation modules are capable of automatic standard preparation at significantly lower concentrations.

NOTE 2—When working with very low concentration standards, it is advisable to use volumetric glassware that has been restricted for use only for preparing the low-level standards of choice. Contamination from volumetric pipettes can be reduced by preparing the standards gravimetrically.

9. Sampling

9.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, and Practices D 3370.

9.2 When volatile amines are used to control process pH, samples should be taken from the effluent of a rinsed strong acid resin exchange column. Typically on-line ion chromatography samples are taken from the effluent of cation resin columns used to continuously monitor cation conductivity. Samples taken from this source will have cation contaminants or additives such as ammonia removed by the cation resin. This will eliminate high pH conditions that can cause low breakthrough volumes. Process water such as boiling water reactor feedwater and water used in the semiconductor industry generally do not have pH additives, and sampling from the effluent of a cation resin column is not required.

9.3 Provide samples to the instrument that meet the manufacturer's required sample conditions, such as pressure, temperature, and minimum sample flow.

10. Calibration

10.1 Determine the retention time for the anions being determined by running an intermediate concentration solution containing only that anion and noting the retention time. The concentration of the anion in the solution used to determine the retention time should be in the mid range of the standards used to calibrate the instrument. Inject the working solutions in accordance with the manufacturer's recommendations.

10.2 Analyze a blank and the working solutions prepared in 8.12. Prepare a calibration curve in accordance with the manufacturer's directions.

11. Procedure

11.1 Set up the on-line ion chromatograph in accordance with the manufacturer's instructions.

11.2 Allow the system to equilibrate with eluant passing through all chromatography columns. Equilibrate with eluant

[3] *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 *Analar 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.

until a stable baseline is achieved. It is recommended that if the system is to be shut down for an extended time period that eluant flow be constantly maintained. This will reduce equilibration time when the system is returned to service.

11.3 Start sample flow in accordance with the manufacturer's instructions.

12. Precision and Bias

12.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D 2777 since this test method is an on-line determination. This inability of Practice D 2777 procedures to obtain precision and bias data for on-line determination is recognized and stated in the scope of Practice D 2777.

12.2 If it is desirable to validate the monitoring system results relative to the laboratory method, directions for performing this validation are given in of Guide D 3864. Use Test Methods D 5542 to validate the on-line instrument.

13. Keywords

13.1 anions; high purity; ion chromatography; on-line

ANNEX

(Mandatory Information)

A1. DETERMINATION OF CONCENTRATOR COLUMN BREAKTHROUGH VOLUME

A1.1 The breakthrough volume is that volume of sample that causes one or more ions of interest to be eluted from, rather than retained or concentrated on, the concentrator column. The breakthrough volume is dependent upon the following:

A1.1.1 The volume of sample loaded,

A1.1.2 The rate at which the sample is loaded,

A1.1.3 The pH of the sample,

A1.1.4 The ionic strength of the sample, and

A1.1.5 The ion exchange capacity of the resin in the column.

A1.2 Ion exchange resins have a finite capacity in that they can retain only a fixed number of ions at any given time. The number of ions that can be retained is dependent upon the charge of the ion. An ion(s) may act as an eluant if its affinity for the ion exchange resin is greater than the affinity of the ions associated with the resin. Early breakthrough is possible when one or more ions act as an eluant phase.

A1.3 The breakthrough volume is determined as follows:

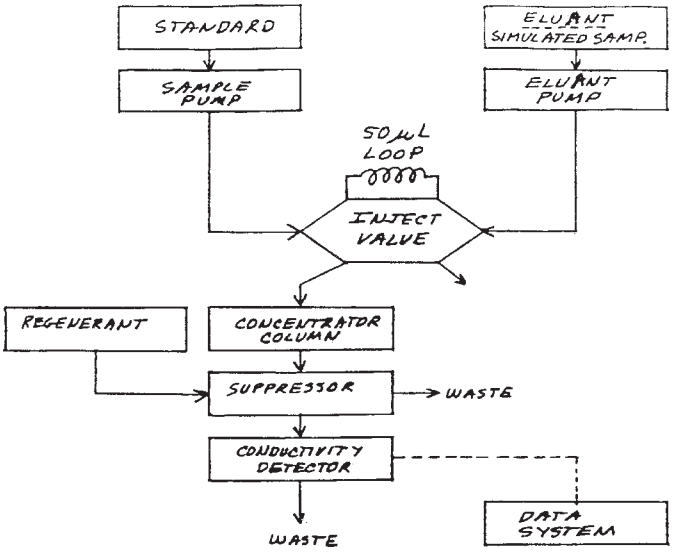
A1.3.1 Prepare 1 L of a solution that closely simulates the type of sample to be analyzed. For example, if the sample contains ammonia, the simulated sample should also contain ammonia. Ammonia in solution exists as ammonium hydroxide and ammonium anion. The resulting hydroxide (OH^-) ion will act as an eluant.

A1.3.2 Prepare a 1 mg/L standard solution of the first eluting ion of interest (for example, chloride).

A1.3.3 Set up the ion chromatograph in accordance with the manufacturer's recommendations to flush the system with eluant and flush the concentrator column with eluant to a stable baseline. See Fig. A1.1.

A1.3.4 Switch to the simulated sample as an eluant and inject a 50µ L portion of the 1 mg/L standard.

A1.3.5 Record the resulting chromatogram and calculate the breakthrough volume as shown in Fig. A1.2.



NOTE 1—Flush concentrator column with eluant.

NOTE 2—Load 50 µL loop with 1 mg/L standard of first eluting ion of interest.

NOTE 3—Switch from eluant to simulated sample and inject 50 µL of standard.

NOTE 4—Determine breakthrough volume as in Fig. A1.2.

FIG. A1.1 Typical Instrument Configuration for Determining Breakthrough Volume

A1.3.6 Do not attempt to concentrate a volume of sample greater than 80 % of the breakthrough volume.

A1.3.7 Calculate the breakthrough volume (BTV) as follows:

$$BTV = EF \times RT \quad \text{(A1.1)}$$

where:

BTV = breakthrough volume,

EF = eluant flow in mL/min, and

RT = retention time that first anion of interest elutes, min.

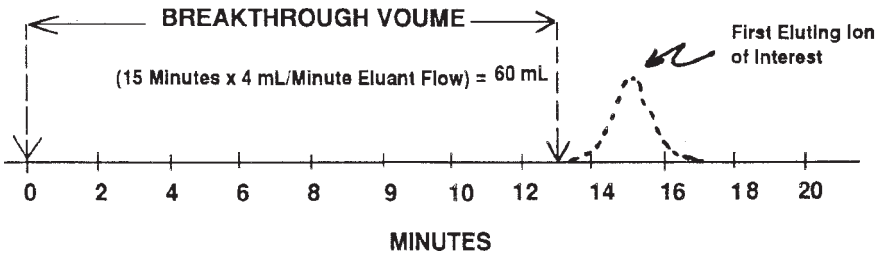


FIG. A1.2 Determination of Breakthrough Volume