<span id="page-0-0"></span>

# **Standard Test Method for Measuring Anionic Contaminants in High-Purity Water by On-Line Ion Chromatography<sup>1</sup>**

This standard is issued under the fixed designation D5996; 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  $(\varepsilon)$  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 0.01 to 100  $\mu$ g/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.

1.2 Online sample analysis of flowing streams does not lend itself to collaborative studies due to the nature of the sample and the possibility of contamination that may result from handling the sample as part of the collaborative study. Therefore this standard test method is not based on the results of a collaborative study but is intended to provide the best possible guidance for doing this type of analysis.

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

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.*

#### **2. Referenced Documents**

- 2.1 *ASTM Standards:*<sup>2</sup>
- [D1066](#page-3-0) [Practice for Sampling Steam](http://dx.doi.org/10.1520/D1066)
- D1129 [Terminology Relating to Water](http://dx.doi.org/10.1520/D1129)
- [D1192](#page-3-0) [Guide for Equipment for Sampling Water and Steam](http://dx.doi.org/10.1520/D1192) [in Closed Conduits](http://dx.doi.org/10.1520/D1192) (Withdrawn  $2003$ )<sup>3</sup>
- [D1193](#page-2-0) [Specification for Reagent Water](http://dx.doi.org/10.1520/D1193)
- [D2777](#page-3-0) [Practice for Determination of Precision and Bias of](http://dx.doi.org/10.1520/D2777) [Applicable Test Methods of Committee D19 on Water](http://dx.doi.org/10.1520/D2777)
- [D3370](#page-3-0) [Practices for Sampling Water from Closed Conduits](http://dx.doi.org/10.1520/D3370)

[D3864](#page-3-0) [Guide for On-Line Monitoring Systems for Water](http://dx.doi.org/10.1520/D3864) [Analysis](http://dx.doi.org/10.1520/D3864)

[D4453](#page-2-0) [Practice for Handling of High Purity Water Samples](http://dx.doi.org/10.1520/D4453) [D5542](#page-2-0) [Test Methods for Trace Anions in High Purity Water](http://dx.doi.org/10.1520/D5542)

[by Ion Chromatography](http://dx.doi.org/10.1520/D5542)

[D5810](#page-3-0) [Guide for Spiking into Aqueous Samples](http://dx.doi.org/10.1520/D5810)

[D5847](#page-3-0) [Practice for Writing Quality Control Specifications](http://dx.doi.org/10.1520/D5847) [for Standard Test Methods for Water Analysis](http://dx.doi.org/10.1520/D5847)

## **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 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.

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

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

<sup>&</sup>lt;sup>1</sup> This test method is under the jurisdiction of ASTM Committee [D19](http://www.astm.org/COMMIT/COMMITTEE/D19.htm) on Water and is the direct responsibility of Subcommittee [D19.03](http://www.astm.org/COMMIT/SUBCOMMIT/D1903.htm) on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved Feb. 15, 2016. Published June 2016. Originally approved in 1996. Last previous edition approved in 2009 as D5996 – 05 (2009). DOI: 10.1520/D5996-16.

<sup>2</sup> 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.

<sup>&</sup>lt;sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

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.

3.2.4.1 *Discussion—*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 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  $\langle 1.0 \mu g/L \rangle$  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.

<span id="page-2-0"></span>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](#page-4-0) 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 corrosionresistant 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  $\pm 0.5^{\circ}$ 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.<sup>4</sup> 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 [D1193](#page-0-0) 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 [D5542.](#page-3-0)

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 test method. It is not practicable to list all the combinations. Users should use the appropriate combination of concentrator column, 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  $2 \pm 0.5$  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 TFEfluorocarbon 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 TFEfluorocarbon lined cap in a refrigerator.

8.8 *Chloride Solution, Stock* (1.00 mL = 1.00 mg Cl)*—*Dry sodium chloride (NaCl) for  $2 \pm 0.5$  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<sub>4</sub>)— 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 SO4)*—*Dry sodium sulfate for  $2 \pm 0.5$  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 NO3)*—* Dry approximately 2 g of sodium nitrate (NaNO<sub>3</sub>) at  $105^{\circ}$ 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 [D4453.](#page-0-0) 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

<sup>4</sup> *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.

<span id="page-3-0"></span>volumetric pipettes can be reduced by preparing the standards gravimetrically.

# **9. Sampling**

9.1 Collect the sample in accordance with Practice [D1066,](#page-0-0) Guide [D1192,](#page-0-0) and Practices [D3370.](#page-0-0)

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.](#page-2-0) 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 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 D2777 since this test method is an on-line determination. This inability of Practice D2777 procedures to obtain precision and bias data for on-line determination is recognized and stated in the scope of Practice D<sub>2777</sub>.

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 Guide [D3864.](#page-0-0) Use Test Methods [D5542](#page-0-0) to validate the on-line instrument.

## **13. Quality Control**

13.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing anions in water.

13.2 *Calibration and Calibration Verification:*

13.2.1 Analyze at least three working standards containing concentrations of anions in water that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis. In many situations for online analysis of ultrapure water the calibration blank and the sample are one and the same.

13.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within  $\pm 15$  % of the known concentration.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

#### 13.3 *Initial Demonstration of Laboratory Capability:*

13.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

13.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of anions in water. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Guide [D5810,](#page-4-0) Tables 4-11. This study should be repeated until the recoveries are within the limits given in Tables 4-11. If a concentration other than the recommended concentration is used, refer to Practice [D5847](#page-4-0) for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

13.4 *Laboratory Control Sample (LCS):*

13.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of anions in water with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within  $\pm 15\%$  of the known concentration.

<span id="page-4-0"></span>13.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

### 13.5 *Method Blank:*

13.5.1 Analyze a reagent water test blank with each batch. The concentration of anions in water found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of anions in water is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.5.2 In many situations for online analysis of ultrapure water the calibration blank and the sample are one and the same. If this is the case, use of a method blank may not be feasible.

### 13.6 *Matrix Spike (MS):*

13.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of anions in water and taking it through the analytical method.

13.6.2 The spike concentration plus the background concentration of anions in water must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

13.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$
P = 100 \left[ A \left( V_s + V \right) - B V_s \right] / CV \tag{1}
$$

where:

- *A* = analyte concentration (mg/L) in spiked sample,<br>*B* = analyte concentration (mg/L) in unspiked sample
- $=$  analyte concentration (mg/L) in unspiked sample,
- $C =$  concentration (mg/L) of analyte in spiking solution,
- $V<sub>s</sub>$  = volume (mL) of sample used, and

## $V =$  volume (mL) added with spike.

13.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Tables 4-11. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 3—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide [D5810](#page-0-0) for additional information.

#### 13.7 *Duplicate:*

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

13.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice [D5847](#page-0-0) for information on applying the *F* test.

13.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 13.8 *Independent Reference Material (IRM):*

13.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory. If an IRM is not commercially available (for example: Ultrapure water) a suitable substitute may be made up by the laboratory.

#### **14. Keywords**

14.1 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 50 µL 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.](#page-6-0)

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:

$$
BTV = EF \times RT \tag{A1.1}
$$

where:

*BTV* = breakthrough volume,

 $EF$  = eluant flow in mL/min, and

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



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.](#page-6-0)

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

<span id="page-6-0"></span>

**FIG. A1.2 Determination of Breakthrough Volume**

#### **APPENDIX**

#### **(Nonmandatory Information)**

#### **X1. APPENDIX FROM D5996**

#### **X1.1 Benefits of On-Line Analysis**

X1.1.1 The two major benefits of on-line analysis of trace level contaminants in high purity water is (*1*) there is no need for a chemistry lab analyst to be involved in everyday ion analysis procedures and (*2*) the sample analyzed is never exposed to sources of accidental ionic contamination to which samples collected and brought to the laboratory are subject.

X1.1.2 The balance of this Appendix is devoted to a brief summary of advances in ion chromatography (IC) technology that have taken place since this test method (guidance) was introduced in 1996. The innovations presented here are applicable to high purity water analysis, whether it is used in the power or semiconductor fabrication industry, or in any other industry that requires ionic-contamination-free water for proper operation.

### **X1.2 Electrolytic Generation of Eluent**

X1.2.1 IC has become simpler and more automated with the invention of electrolytic generation of a hydroxide eluent and a corresponding development of hydroxide selective anion exchange columns. Now, anion separations can be made without manual preparation of eluent reagents. Further, when the hydroxide eluent passes through the suppressor, it is converted to water, which results in a very low and stable baseline, compared to carbonate-based eluents. This stable baseline delivers less baseline noise, thus increasing method sensitivity.

#### **X1.3 Electrolytic Regeneration of Suppressor**

X1.3.1 The traditional regenerant for the suppressor cited in this document is dilute sulfuric acid. Now, electrolytically generated acid can be used to supply the hydrogen ion required for regenerating an anion suppressor.

## **X1.4 Reagent-Free IC**

X1.4.1 The invention of electrolytic generation of hydrogen ion and hydroxide ion has brought the reagent-free technology to ion analysis.

## **X1.5 Example of Results with These Advances**

X1.5.1 The example chromatogram below shows the separation and concentration of example anions with these advances in place.

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/*