Designation: D4327 – 17

Standard Test Method for Anions in Water by Suppressed Ion Chromatography[1]

This standard is issued under the fixed designation D4327; 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[2,3] covers the sequential determination of fluoride, chloride, nitrite, *ortho*-phosphate, bromide, nitrate, and sulfate ions in water by suppressed ion chromatography.

NOTE 1—Order of elution is dependent upon the column used; see Fig. 1.

1.2 This test method is applicable to drinking and wastewaters. The ranges tested for this test method for each anion were as follows (measured in mg/L):

Fluoride	0.26 to 8.49
Chloride	0.78 to 26.0
Nitrite-N	0.36 to 12.0
Bromide	0.63 to 21.0
Nitrate-N	0.42 to 14.0
o-Phosphate	0.69 to 23.1
Sulfate	2.85 to 95.0

1.3 It is the user's responsibility to ensure the validity of this test method for other matrices.

1.4 Concentrations as low as 0.01 mg/L were determined depending upon the anions to be quantified, in single laboratory work. Utilizing a 50-µL sample volume loop and a sensitivity of 3000 µS/cm full scale, the approximate detection limits shown in Table 1 can be achieved. Lower detection limits have been observed with newer instrumentation, column technology and eluents. The analyst must assure optimum instrument performance to maintain a stable baseline at more sensitive conductivity full-scale settings.

1.5 The upper limit of this test method is dependent upon total anion concentration and may be determined experimentally as described in Annex A1. These limits may be extended by appropriate dilution or by use of a smaller injection volume.

1.6 Using alternate separator column and eluents may permit additional anions such as acetate, formate, or citrate to be determined. This is not the subject of this test method.

1.7 This test method update approves the use of electrolytically generated eluent, electrolytically regenerated eluent, electrolytic suppression (not autozeroing), and electrolytic trap columns also known as reagent-free ion chromatography. This approval is based on acceptance by the U.S. EPA as referenced in Appendix X2.

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

1.9 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.10 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Flowing Process Streams
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.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] Refs. (**1-7**)[3] may be consulted for additional information.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

[4] 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.

***A Summary of Changes section appears at the end of this standard**

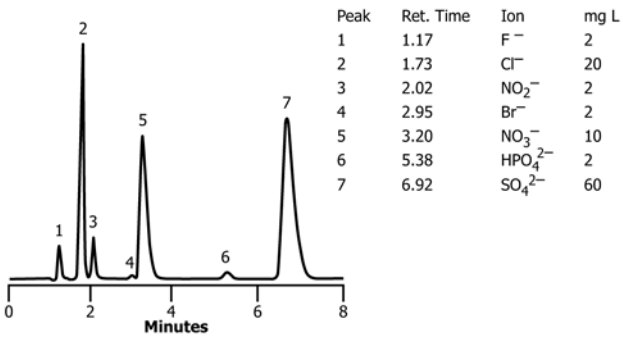

FIG. 1 Chromatogram Showing Separation Using the AS4A Column

TABLE 1 Approximate Single Laboratory Detection Limits in Reagent Water[A,B]

Analyte	Peak No.	Retention Time, min	MDL mg/L
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate	6	5.4	0.003
Sulfate	7	6.9	0.02

[A] Data provided by U.S. EPA/EMSL Laboratory, Cincinnati, OH.
[B] Column: as specified in 7.1.4.
Detector: as specified in 7.1.6.
Eluent: as specified in 8.3.
Pump rate: 2.0 mL/min.
Sample loop: 50 µL.

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 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.3 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.4 *eluent, n*—the ionic mobile phase used to transport the sample through the system.

3.2.5 *guard column, n*—a column used before the separator column to protect the analytical column 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.

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 or analytical column used to separate the ions of interest according to the ion 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*—The purpose of the suppressor is to minimize detector response of ionic constituents in the eluent, which lowers the detector background and at the same time enhances detector response to the ions of interest.

4. Summary of Test Method

4.1 An aliquot of sample is injected into an ion chromatograph. The sample is pumped through two columns, a suppressor device, and into a conductivity detector. The analytical column and the guard column are packed with anion exchange resin. Ions are separated based on their affinity for the exchange sites of the resin. The suppressor device contains a fiber- or membrane-based cation exchanger that is continuously regenerated by either a flow of dilute sulfuric acid or an electrolytic suppressor which does not require sulfuric acid. The suppressor device reduces the background conductivity of the eluent to a low or negligible level by replacing the cations with the hydrogen ion, thereby converting the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times 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.

5. Significance and Use

5.1 Ion chromatography provides for both qualitative and quantitative determination of seven common anions, F^-, Cl^-, NO_2^-, HPO_4^{-2}, Br^-, NO_3^-, and SO_4^{-2}, in the milligram per litre range from a single analytical operation requiring only a few millilitres of sample and taking approximately 10 to 15 min for completion. Additional anions, such as carboxylic acids, can also be quantified.

NOTE 2—This test method may be used to determine fluoride if its peak is in the water dip by adding 1 mL of eluent (at 100× the concentration in 8.3) to all 100-mL volumes of samples and standards to negate the effect of the water dip. (See 6.3, and also see 6.4.) The quantitation of unretained peaks should be avoided. Anions such as low molecular weight organic acids (formate, acetate, propionate, etc.) that are conductive coelute with fluoride and would bias fluoride quantitation in some drinking waters and most wastewaters. The water dip can be further minimized if measures are taken to remove carbonic acid which remain in the eluent after suppression using carbonate based eluents. There is no water dip if hydroxide eluents are used.

5.2 Anion combinations such as Cl^-/Br^- and NO_2^-/NO_3^-, which may be difficult to distinguish by other analytical methods, are readily separated by ion chromatography.

6. Interferences

6.1 Since chloride and nitrite elute very close together, they are potential interferents for each other. It is advisable not to have one of these anions present in a ten-fold excess over the other; that is, Cl^-/NO_2^- ratios higher than 1:10 or 10:1 if both ions are to be quantitated or refer to newer column technology.

6.2 As with other types of chromatography, if one of the sample components is present at very high levels, it may interfere by causing a very large peak on the chromatogram

that could mask other peaks present. This type of interference is normally minimized by dilution of the sample (see Annex A1) and in some instances may be corrected if the concentration of that anion is of interest. However, care should be taken not to dilute the analyte concentration below its detectable limit.

6.3 Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes, because its conductivity is less than that of the suppressed eluent. This dip usually occurs before Cl^-. Any peak of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantified. Some suggested techniques for elimination of the water dip are described in Appendix X1.

6.4 There may be a water dip and the interference of organic acids and due to the presence of carbonate ions in the separator column, the user of this test method is urged to use caution when determining fluoride (see Note 2). If the user wishes to be certain of good results and has interfering anions present when determining fluoride, the eluent can be diluted until separation of fluoride and carbonate is accomplished. This will cause an increase in retention time for anions such as sulfate to elute. Additional steps to avoid the water dip are mentioned in Appendix X1.

7. Apparatus

7.1 *Ion Chromatograph*—The ion chromatograph should have the following components assembled, as shown in Fig. 2:[5]

7.1.1 *Eluent and Regenerant Containers.*

7.1.2 *Eluent Pump,* capable of delivering 1 to 3 mL/min of eluent at a pressure of up to 2000 psi.

[5] The Dionex ion chromatograph available from Dionex Corporation, Sunnyvale, CA, or equivalent, may be used. Other manufacturers' components may provide equivalent data.

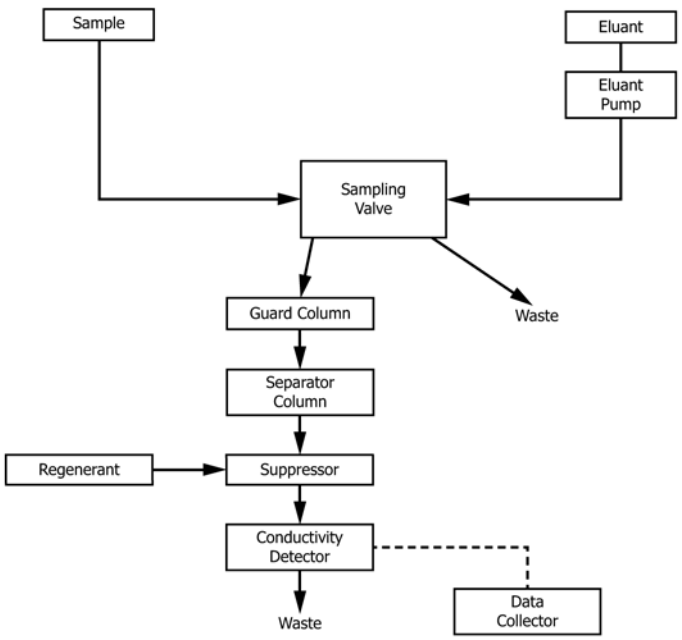

FIG. 2 Schematic of an Ion Chromatograph

7.1.3 *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 analytical column from particulate matter and irreversibly retained materials.

7.1.4 *Analytical Column*—Anion exchange column capable of separating chloride from the injection void volume, as well as resolving the anions chloride through sulfate.

NOTE 3—Any analytical column may be used. However, the user should be able to achieve the resolution and separation as shown in Fig. 1.

7.1.5 *Suppressor Device*—A suppressor device based upon cation-exchange principles. In this test method a membrane-based self-regenerating suppressor device was used. An equivalent suppressor device may be used provided that comparable method detection limits are achieved and that adequate baseline stability is attained. An electrolytic suppressor device can be used which does not require the addition of an acid but is a plug in electrolytic device. The suppressed eluent (water) is simply recirculated from the conductivity cell back to the electrolytic suppressor to back flush the suppressor device. Alternative pumps are also typically not required.

7.1.6 *Detector*—A low-volume, flow through, temperature-compensated electrical conductivity cell equipped with a meter capable of reading from 0 to 1000 µS/cm on a linear scale or greater if applicable.

7.1.7 *Recorder, Integrator, Computer*—A device compatible with the detector output capable of recording detector response as a function of time for the purpose of measuring peak height or area.

7.1.8 *Sample Loop*—A loop on the injection valve that is designed to contain an exact amount of the sample. The most common size is 100 µL. The sample volume injected onto the separator column is controlled by this loop. Use of a larger size loop will usually cause peak broadening and a loop size greater than 1 mL may result in column overloading and nonlinear response. The chromatogram in Fig. 1 uses a 100-µL size sample loop.

7.1.8.1 When injections of volumes larger than the sample loop size are made, any volume above the sample loop size goes to waste. It is considered good technique to flush the sample loop upon injection by injecting 2 to 3 times the sample loop volume.

8. Reagents and Materials

8.1 *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.[6] 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.

[6] *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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type II; Type I may also be used. Column life may be extended by passing Type II water through a 0.22-µm filter prior to use. Freshly prepared water should be used for making the standards intended for calibration. The detection limits of this test 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 test method. Anion concentrations of less than 0.2 µg/L each are typical of this type of water.

8.3 *Eluent*—Dissolve 0.2856 g of sodium bicarbonate (1.7 m*M*) and 0.3816 g of sodium carbonate (1.8 m*M*) in water and dilute to 2 L with water. Other eluents may also prove to be acceptable, provided they give the proper resolution between the component peaks. This eluent will act as a growth media for algae. For this reason the eluent should not be kept for longer than one month.

8.3.1 *Hydroxide Eluent*—If NaOH is manually prepared as 50 % (w/w) NaOH using degassed, deionized water (18.2 megaohm-cm) to a final volume of 1000 µL using a volumetric flask. Avoid the introduction of carbon dioxide from the air into the 50 % NaOH or the distilled water being used to make the eluent. Do not shake the 50 % NaOH or pipette the required aliquot from the top of the solution where sodium carbonate may have formed. Eight grams or 5.25 mL of 50 % NaOH makes a 100 mM solution. A positive pressure of an inert gas should be maintained over the headspace to avoid carbon dioxide contamination. The use of electrolytically generated hydroxide by reagent-free ion chromatography to generate carbonate free hydroxide is also acceptable. In addition, electrolytically generated carbonate eluent is also acceptable. If using electrolytically prepared eluents only distilled water needs to be added to the system.

NOTE 4—Use of other eluents may change the order of elution of the anions from that using the carbonate-bicarbonate eluent.

8.4 *Fiber or Membrane Suppressor Regenerant Solution*—Cautiously add 3 mL of H_2SO_4 (sp gr 1.84) to 4 L of water. Not required for electrolytic or electronic based suppression.

8.5 *Stock Solutions:*

8.5.1 *Bromide Stock Solution* (1.00 mL = 1.00 mg Br^-)—Dry approximately 2 g of sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Dissolve 1.2877 g of the dried salt in water and dilute to 1 L with water. Alternatively, certified bromide stock solutions are commercially available through chemical supply vendors and may be used.

8.5.2 *Chloride Stock Solution* (1.00 mL = 1.00 mg Cl^-)—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. Alternatively, certified chloride stock solutions are commercially available through chemical supply vendors and may be used.

8.5.3 *Fluoride Stock Solution* (1.00 mL = 1.00 mg F^-)—Dissolve 2.210 g of sodium fluoride (NaF) in water and dilute to 1 L with water. Alternatively, certified fluoride stock solutions are commercially available through chemical supply vendors and may be used.

8.5.4 *Nitrate Stock Solution* (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. Alternatively, certified nitrate stock solutions are commercially available through chemical supply vendors and may be used.

8.5.5 *Nitrite Stock Solution* (1.00 mL = 1.00 mg NO_2^-)—Place approximately 2 g of sodium nitrite ($NaNO_2$) in a 125-mL beaker and dry to constant weight (about 24 h) in a desiccator containing concentrated H_2SO_4. Dissolve 1.500 g of the dried salt in water and dilute to 1 L with water. Store in a sterilized glass bottle. Refrigerate and prepare monthly. Alternatively, certified nitrite stock solutions are commercially available through chemical supply vendors and may be used.

NOTE 5—Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE 6—Prepare sterile bottles for storing nitrite solutions by heating for 1 h at 170°C in an air oven.

8.5.6 *Phosphate Stock Solution*(1.00 mL = 1.00 mg HPO_4^{-2})—Dissolve 1.433 g of potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 L with water. Alternatively, certified phosphate stock solutions are commercially available through chemical supply vendors and may be used.

8.5.7 *Sulfate Stock Solution* (1.00 mL = 1.00 mg SO_4^{-2})—Dry sodium sulfate (Na_2SO_4) 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. Alternatively, certified sulfate stock solutions are commercially available through chemical supply vendors and may be used.

8.6 *Anion Working Solutions*—Prepare a blank and at least 3 different working standards containing the anions of interest. The combination anion solutions should be prepared in volumetric flasks. 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 single standard may be prepared that contains all six anions.

8.6.1 The user should select the ranges of the three standards so as to cover the entire range of the chart. The ranges chosen should all fall into one attenuation setting. If a second attenuation setting must be used, it must be calibrated using three standards and a blank. The standard concentrations given in Table 2 and Table 3 are for example purposes.

8.7 *Filter Paper*—Purchase suitable filter paper or filters in a plastic housing with a luer lock syringe. Typically the filter papers have a pore size of 0.22-µm membrane. Material such as fine-textured, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Sampling

9.1 Collect the sample in accordance with Practices D1066 and D3370 as applicable.

9.2 Analyze the samples as soon as possible after collection. Preservation by refrigeration at 4°C is required for nitrite, nitrate, or phosphate.