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Designation: D4327 – 03

Standard Test Method for Anions in Water by Chemically 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] covers the sequential determination of fluoride, chloride, nitrite, *ortho*-phosphate, bromide, nitrate, and sulfate ions in water by chemically 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 quantitated, in single laboratory work. Utilizing a 50-µL sample volume loop and a sensitivity of 3 µS/cm full scale, the approximate detection limits shown in Table 1 can be achieved. If lower detection levels are required, the sensitivity may be improved by using a lower scale setting (<3 µS/cm) or a larger sample injection loop (>100 µL). The analyst must assure optimum instrument performance to maintain a stable baseline at more sensitive conductivity full-scale settings.

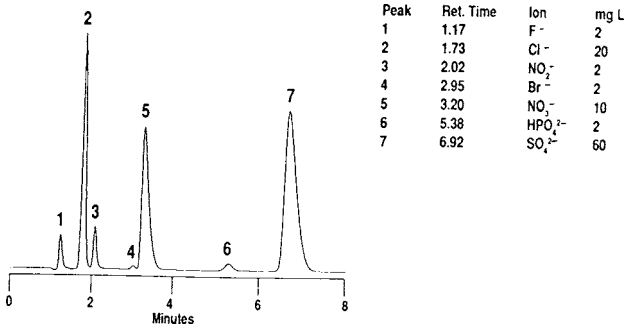

FIG. 1 Chromatogram Showing Separation Using the AS4A Column

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 formate or citrate to be determined. This is not the subject of this test method.

1.7 *This standard does not purport to address all of the safety problems, 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:*[3]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water

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[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] The following references may be consulted for additional information:

Small, H., Stevens, T. S., and Bauman, W. C., "Novel Ion Exchange Chromatographic Method Using Conductrimetric Detection," *Analytical Chemistry*, Vol 47, 1975, p. 1801.

Stevens, T. S., Turkelson, V. T., and Alve, W. R., "Determination of Anions in Boiler Blow Down Water with Ion Chromatography," *Analytical Chemistry*, Vol 49, 1977, p. 1176.

Sawicki, E., Mulik, J. D., and Witgenstein, E., Editors, *Ion Chromatographic Analysis of Environmental Pollutants*, Ann Arbor Science Publishers, Ann Arbor, MI, 1978.

Mulik, J. D., and Sawicki, E., Editors, *Ion Chromatographic Analysis of Environmental Pollutants*, Vol/No. 2, Ann Arbor Science Publishers, Ann Arbor, MI, 1979.

Weiss, J., *Handbook of Ion Chromatography*, Dionex Corp., Sunnyvale, CA, 1986.

Waters Innovative Methods for Anion Analysis, Waters Chromatography Division of Millipore, Method A 107 and A 116, 1990.

Haddad, P. R., and Jackson, P. E., *Ion Chromatography: Principles and Applications*, Elsevier Scientific Publishing Co., 1990.

[3] 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.**

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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 US 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.

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
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*—For definitions of terms used in this test method, refer to Terminology D1129.

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 *chemical 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 eluent, so as to lower the detector background and at the same time enhance detector response to the ions of interest.

3.2.3 *eluent*—the ionic mobile phase used to transport the sample through the system.

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

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

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

3.2.7 *separator column*—the ion exchange column used to separate the ions of interest according to their retention characteristics prior to their detection.

4. Summary of Test Method

4.1 An aliquot of sample is injected into an ion chromatograph. The sample is pumped through two columns and a suppressor device and into a conductivity detector. The analytical column and the guard column are packed with low-capacity anion exchanger. 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 a flow of dilute 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.

NOTE 2—This test method may be used to determine fluoride if its peak is in the water dip by adding one 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.

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.

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 quantitated. Some suggested techniques for elimination of the water dip are described in Appendix X1.

6.4 Due to the effect of the 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

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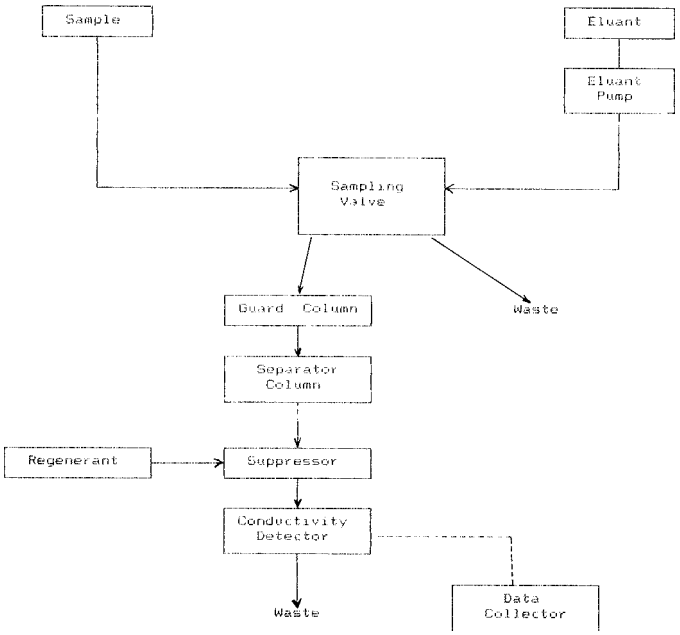

FIG. 2 Schematic of an Ion Chromatograph

until separation of fluoride and carbonate is accomplished. This will cause an increase in retention time for anions such as sulfate to elute.

7. Apparatus

7.1 *Ion Chromatograph*—The ion chromatograph should have the following components assembled, as shown in Fig. 2:[4]

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 psig.

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 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.

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.

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 *Data System*—An electronic integrator, such as is used with gas and liquid chromatographs, may be used to quantitate peak area, as well as peak height. The peak area data can be used in the same way peak height is used to quantitate results. Computer and software.

7.1.9 *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.

7.1.9.1 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

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.[5] 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, references to water shall be understood to mean reagent water conforming to Specification D1193, Type II. 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.

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.

[4] Available from Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086. An equivalent may be used. Other manufacturers' components may provide equivalent data.

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., 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."

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.

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.

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.

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.

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.

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.

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.

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.

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.

9.3 Filter the samples containing particulates through a prewashed 0.22-µm filter prior to analysis to avoid fouling or clogging the resin of the columns.

10. Calibration

10.1 *Determination of Retention Times*:

TABLE 2 Preparation of Standard Solutions for Instrument Calibration

Anion	High-Range Standard		Intermediate-Range Standard, mg/L	Low-Range Standard, mg/L
	Millilitres of Each Stock Solution (1.00 mL = 1.00 mg), Diluted to 1000 mL	Anion Concentration, mg/L		
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (HPO_4^{-2})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{-2})	100	100	10.0	2.0

TABLE 3 Preparation of Standard Solutions for Determination of Retention Times

Stock Solution (1 mL = 1.00 mg)	Volume of Stock Solution per Litre of Water, mL	Anion Concentration, mg/L
Fluoride	4	4
Chloride	4	4
Nitrite	10	10
Phosphate	50	50
Bromide	10	10
Nitrate	30	30
Sulfate	50	50

10.1.1 The retention time for each anion is determined by injecting a standard solution containing only the anion of interest and noting the time required for a peak to appear on the chromatogram. Retention times vary with operating conditions and are influenced by the concentration of ion(s) present. Prepare separate standard solutions in accordance with Table 3 by pipetting the designated aliquots of stock solutions prepared in Section 8 (8.5.1 through 8.5.7) into separate 1-L volumetric flasks. Analyze each standard of interest as defined in Section 11. Note the time in minutes for each peak to appear on the chromatogram.

NOTE 7—Some operators have reported unusually large shifts in retention time for nitrate with changes in concentration. If this occurs, care must be taken to ensure integration of the correct peak when integration is used for calculation.

10.1.2 Concentrations other than those listed in Table 3 may be used if they better approximate concentrations expected in the samples. Those concentrations listed will give about midscale response with a 1-V recorder input and a conductivity meter full-scale setting of 10 µS/cm.

10.1.3 Retention times as well as elution order vary with the column used. See Fig. 1 for example elution orders.

10.2 Analyze the blank and each of the prepared calibration solutions described in 8.7 in accordance with the defined procedure (see Section 11).

NOTE 8—If the concentrations of the sample ions of interest are known or estimated, the concentration of standard solutions prepared for instrument calibration may be varied to better approximate or bracket the concentration range of interest. Anions of no interest may be omitted.

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