



Designation: ~~D4327-03~~ Designation: D4327 - 11

Standard Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography¹

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 method² 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
<i>o</i> -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, quantified~~, in single laboratory work. Utilizing a 50- μ L sample volume loop and a sensitivity of 3 μ S/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 μ S/cm) or a larger sample injection loop (>100 μ L). The analyst must assure optimum instrument performance to maintain a stable baseline at more sensitive conductivity full-scale settings.~~ 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 formate or citrate to be determined. This is not the subject of this test method.~~

~~1.7~~

~~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 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 US 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 problems, if any, associated with its use. It is the responsibility

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. Current edition approved Jan. 10, 2003; 15, 2011. Published January 2003; March 2011. Originally approved in 1984. Last previous edition approved in 1997 as D4327-97; D4327 - 03. DOI: 10.1520/D4327-03; 10.1520/D4327-11.

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 Conductometric 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.

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

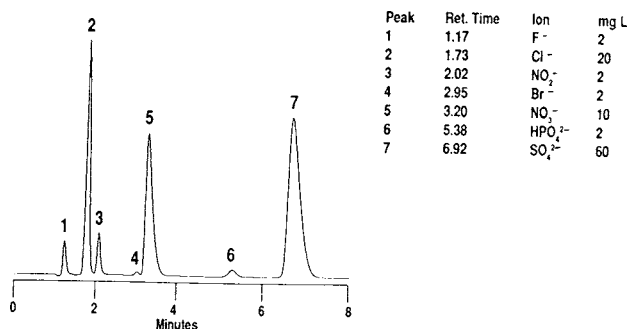


FIG. 1 Chromatogram Showing Separation Using the AS4A Column

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

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, 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 *chemical suppressor device, n*—a device that is placed between the analytical columns and the detector. Its

3.2.2.1 *Discussion*—The purpose of the suppressor is to inhibit/minimize detector response to the of ionic constituents in the eluent, so as to lower which lowers the detector background and at the same time enhances detector response to the ions of interest.

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

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

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.

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.

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

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

3.2.7 *separator column, n*—the ion-exchange or analytical 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 columns,~~ a suppressor device, and into a conductivity detector. The analytical column and the guard column are packed with low-capacity 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, in the milligram per liter range from a single analytical operation requiring only a few milliliters 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 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. 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.~~ 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 interferences 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. ~~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 quantitated. ~~quantified.~~ Some suggested techniques for elimination of the water dip are described in Appendix X1.

6.4 ~~Due to the effect of the~~ 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. 2:⁴

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. ~~psi.~~

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.

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

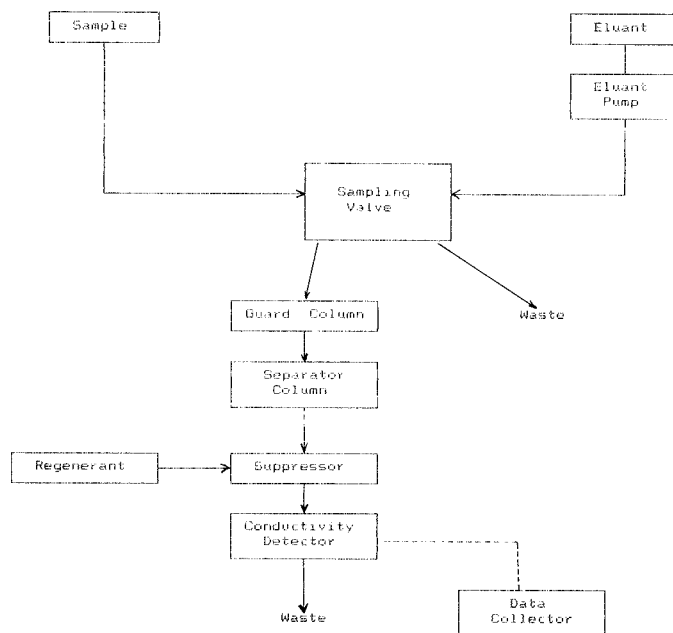


FIG. 2 Schematic of an Ion Chromatograph

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.—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. 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 $\mu\text{S}/\text{cm}$ 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 *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.

7.1.98.1 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; Type I may also be used. Column life may be extended by passing Type II water through a

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 "Analytical Standards for Laboratory Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia."

0.22-~~um~~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 $\mu\text{g/L}$ each are typical of this type of water.

8.3 *Eluent*—Dissolve 0.2856 g of sodium bicarbonate (1.7 mM) and 0.3816 g of sodium carbonate (1.8 mM) 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 use 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.

8.5 (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. —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. —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. —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. —) 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. — 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. —) 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. —) 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.

TABLE 2 Preparation of Standard Solutions for Instrument Calibration

Anion	High-Range Standard			
	Milliliters of Each Stock Solution (1.00 mL = 1.00 mg), Diluted to 1000 mL	Anion Concentration, mg/L	Intermediate-Range Standard, mg/L	Low-Range Standard, 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-Liter 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

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:

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. for example elution orders using carbonate based eluent. If hydroxide eluents are used, the elution order of sulfate and phosphate are reversed.~~

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.

NOTE 9—The mid-range combination anion standard may be used to verify resolution of all seven anions.

NOTE 10—Each analytical curve should be established using only one scale setting. Changing the scale setting may result in a slight change in the slope of the analytical curve.