Designation: D8234 – 19

Standard Test Method for Anions in High Ionic Water by Ion Chromatography using Tandem Suppressed Conductivity and UV Detection[1]

This standard is issued under the fixed designation D8234; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the simultaneous determination of fluoride (F^-), nitrite-N (NO_2-N), *ortho*-phosphate-P (o-PO_4-P), bromide (Br^-), nitrate-N (NO_3-N), and sulfate (SO_4^{-2}) ions in high saline water (up to 20 % sodium chloride (NaCl)) by suppressed ion chromatography and tandem ultra-violet (UV) detection.

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

1.2.1 *Exception*—The inch-pound and SI units shown for pressure measurements are to be individually regarded as standard.

1.3 *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.*

1.4 *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:*[2]

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.

4. Summary of Test Method

4.1 This test method measures NO_2-N, NO_3-N, and Br^- in presence of high level concentrations of chloride ion.

5. Significance and Use

5.1 Ion chromatography provides for both qualitative and quantitative determination of common anions, F^-, NO_2^-, hydrogen phosphate ion (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 for analysis.

5.2 Anion combinations such as chloride/bromide (Cl^- /Br^-) and nitrite/nitrate (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 potentially interfere for each other. Low molecular weight organic acid may interfere with fluoride ion. Selection of proper analytical column will permit resolution of these interfering compounds from fluoride ion.

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 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. Use of the UV detector enables detection of nitrite nitrogen in presence of high concentrations of chloride ion.

[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 July 1, 2019. Published August 2019. DOI: 10.1520/D8234-19.

[2] 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 Single Laboratory Detection Limits in HIW[A]

NOTE 1—n/a = not applicable.

Analyte	Peak No. (See Fig. 1 and Fig. 2)	LOQ mg/L
Fluoride	1	0.1
Chloride	2	n/a (matrix)
Nitrite-N	3	0.03 (UV det)
Bromide	4	0.1 (UV det)
Nitrate-N	5	0.02 (UV det)
o-PO_4-P	6	0.1
Sulfate	7	0.1

[A]

Data provided by US EPA-Region 6 Laboratory, Houston, TX.

B Column: as specified in 7.5.
Detector: as specified in 7.7.
Eluent: as specified in 8.3.
Pump rate: 0.7 mL/min.
Sample loop: 10 µL.

7. Apparatus

7.1 *Ion Chromatograph*—The ion chromatograph should have the components shown in Fig. 7.

7.2 *Eluent and Regenerant Containers.*

7.3 *Eluent Pump,* capable of delivering 0.1 to 5 mL/min of eluent at a pressure of up to 20 000 kPa (4000 psi).

7.4 *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.

7.5 *Analytical Column*—Anion exchange column capable of separating fluoride ion from the injection void volume, as well as resolving the anions Cl^- through sulfate.

NOTE 1—Any analytical column may be used. However, the user should be able to achieve the resolution and separation as shown in Figs. 1-5.

7.6 *Suppressor Device*—A suppressor device based upon cation-exchange principles. In this test method, a chemical exchange based suppressor device was used. An equivalent suppressor device may be used provided that comparable method detection limits are achieved and that adequate baseline stability at minimum of 0.2 µS/cm is attained. An electrolytic suppressor device may also be used.

7.7 *Detector*—Following detectors were used:

7.7.1 A low-volume, flow through, temperature-controlled electrical conductivity cell equipped with a meter capable of reading from 0 to 10 000 µS/cm on a linear scale or greater if applicable.

7.7.2 A low-volume UV detector capable of reading range from 190 to 900 nm wavelength with minimum four channels of data acquisition at one time.

NOTE 2—For this experiment, eight channel variable wavelength UV detector was used.

7.8 *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.

7.9 *Sample Loop*—A loop on the injection valve that is designed to contain an exact amount of the sample. For high saline waters use 10 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 100 µL may result in column overloading and nonlinear response. The chromatogram in Fig. 1 and Fig. 2 uses a 10-µL size sample loop.

7.10 When volumes larger than the sample loop size are used to fill the loop, any volume above the sample loop size goes to waste. It is considered good technique to flush the sample loop prior to injection by filling with 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.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of this test method. Type II water was specified at the time of round robin testing of this test method.

8.3 *Eluent*—Dissolve 0.742 g of sodium carbonate (3.5 mM) in water and dilute to 2 L with 2 % acetonitrile (ACN). 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 3—Automatic eluent preparation systems (electrolytically or chemically) may be used.

8.4 *Suppressor Regenerant Solution*—Cautiously add 5.6 mL of sulfuric acid (H_2SO_4) (sp gr 1.84) to 1 L of water and also add 100 ml of acetonitrile solvent. Or, follow instrument manufacture recommendations.

8.5 *Stock Solutions:*

8.5.1 *Bromide Stock Solution* (1.00 mL = 1.00 mg Br^{-1})—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 –matrix solution. Alternatively, certified bromide stock solutions with right matrix may be commercially available through chemical supply vendors and may be used.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.

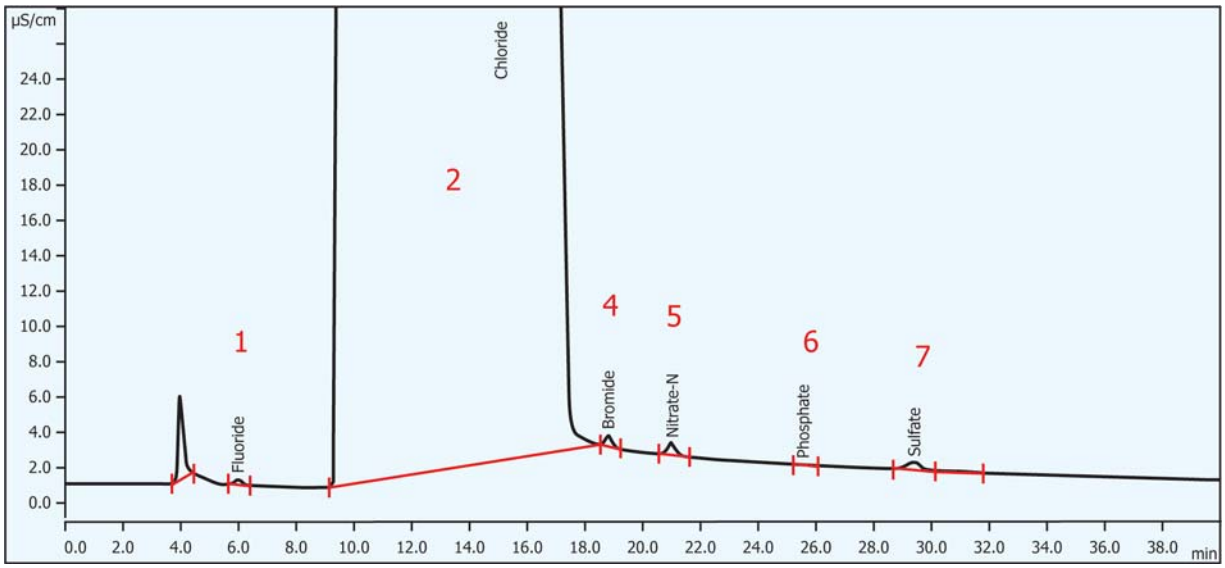

FIG. 1 Separation of Ions at 0.1 mg/L Each in a 30 000 mg/L Chloride Solution Using the MetroSep ASupp-7 Column with Suppressed Conductivity Signal

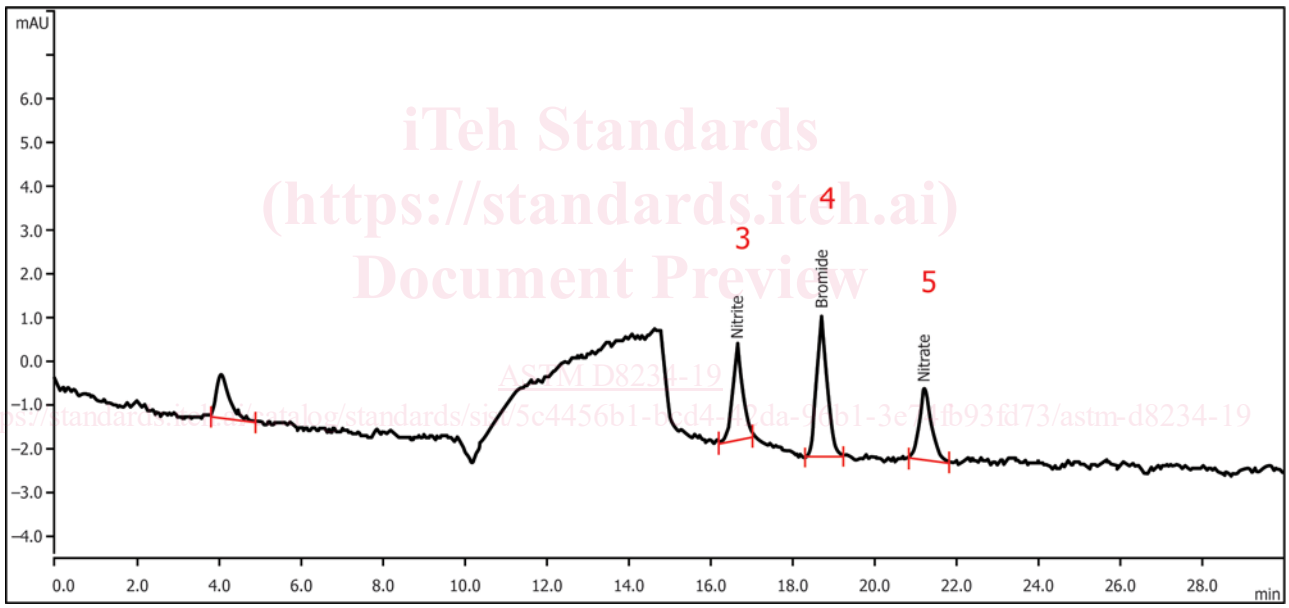

FIG. 2 Separation of Ions at 0.1 mg/L Each in a 30 000 mg/L Chloride Solution Using the MetroSep ASupp-7 Column with Tandem UV at 210 nm

8.5.2 *Chloride Stock Solution* (1.00 mL = 1.00 mg Cl^{-1})—Dry 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^{-1})—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^{-1})—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^{-1})—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 4—Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

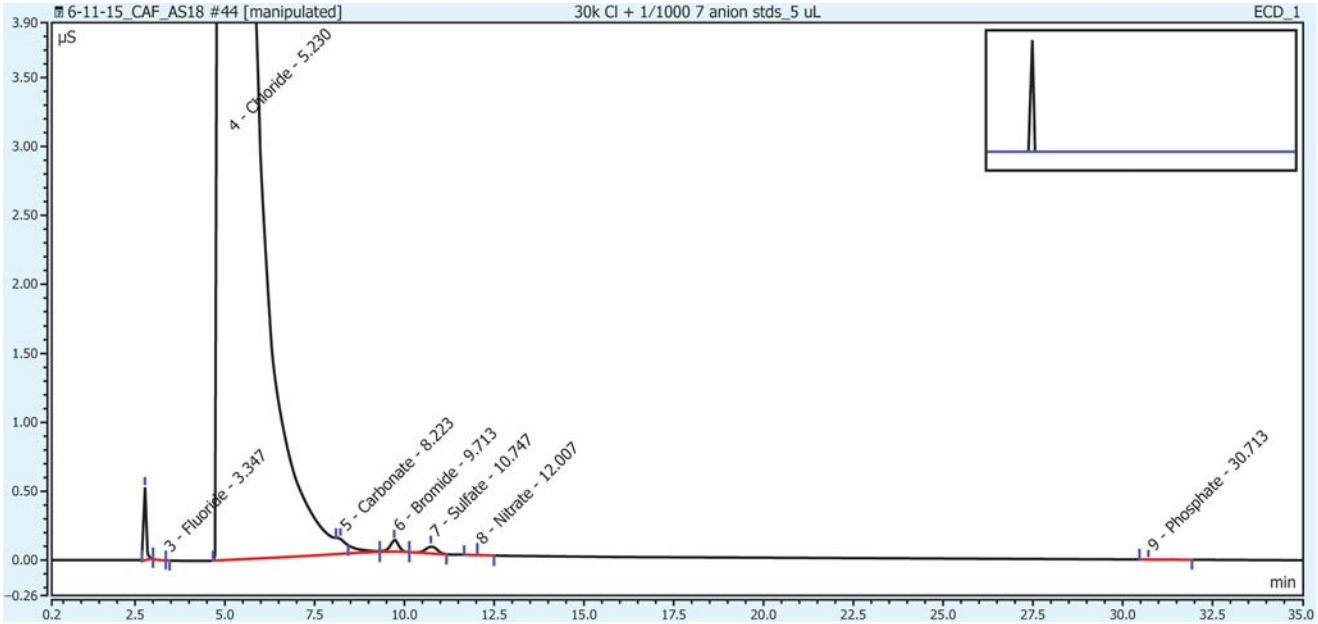

FIG. 3 Isocratic Separation of Ions at 0.1 mg/L Each in a 30 000 mg/L Chloride Solution by Hydroxide Eluent (23 mM Hydroxide Using Electrolytic Eluent Generation) Using the IonPac AG18 Guard (4 × 50 mm) and IonPac AS18 Analytical (4 × 250 mm) with Suppressed Conductivity Detection

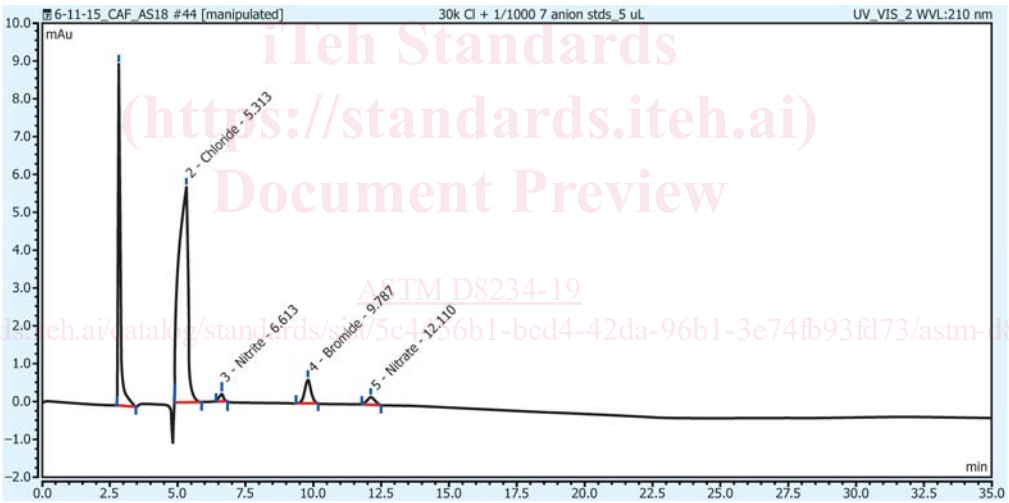

FIG. 4 Isocratic Separation of Nitrite, Bromide, and Nitrate at 0.1 mg/L Each in a 30 000 mg/L Chloride Solution by Hydroxide Eluent (23 mM Hydroxide Using Electrolytic Eluent Generation) Using the IonPac AG18 Guard (4 × 50 mm) and IonPac AS18 Separator (4 × 250 mm) Columns with Tandem UV Detection at 210 nm

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 matrix blank and at least five different working standards containing all anions of interest. The combination anion solutions should be prepared in volumetric flasks. These standards must be prepared fresh weekly (properly refrigerated). The concentration range for the five standards will be dependent on the levels expected in the samples.

8.6.1 The user should select the ranges of the five standards so as to cover the entire range of the chart. The ranges chosen should all fall into one attenuation setting. The standard concentrations given in Table 2 are for example purposes.

8.7 *Filter Paper*—Purchase suitable filter paper that are tested for anions of interest by rinsing with high purity water and analyzing for anions of interest. Typically the filter papers have a pore size of 0.22-µm membrane.

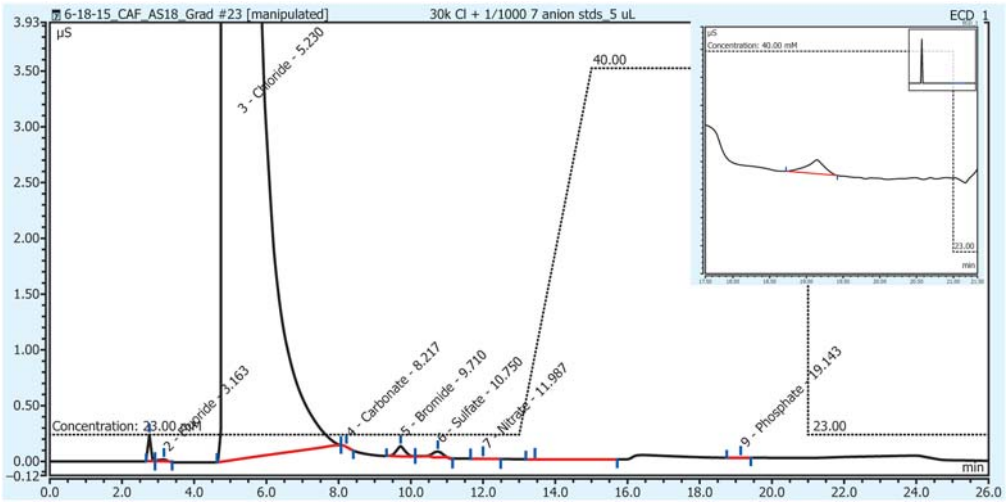

FIG. 5 Gradient Separation of Nitrite, Bromide, Nitrate, and Phosphate (See the Peak in the Zoomed Window) at 0.1 mg/L Each in a 30 000 mg/L Chloride Solution by Hydroxide Eluent Using Suppressed Conductivity Detection

Eluent:	23 mM hydroxide using electrolytic eluent generation
Loop size:	5 µL
Column:	IonPac AG18 (4 × 50 mm)
	IonPac AS18 (4 × 250 mm)
Suppressor:	AERS 500 electrolytic suppression
Detection:	**UV 210 nm**
Gradient conditions:	
	23 mM (0–13 min)
	23–40 mM (13–15 min)
	40 mM (15–21 min)
	23 mM (21–26 min)

FIG. 6 Gradient Separation of Nitrite, Bromide, Nitrate, and Phosphate at 0.1 mg/L Each in a 30 000 mg/L Chloride Solution by Hydroxide Eluent Using UV Detection

NOTE 5—Optional in-line cross flow filtration device may be used using commercially available 47-mm nylon filter paper. Syringe filters can also be used provided they have been tested to confirm absence of anions of interest.

9. Sampling

9.1 Collect the sample in accordance with Practice D1066 or D3370 as applicable.

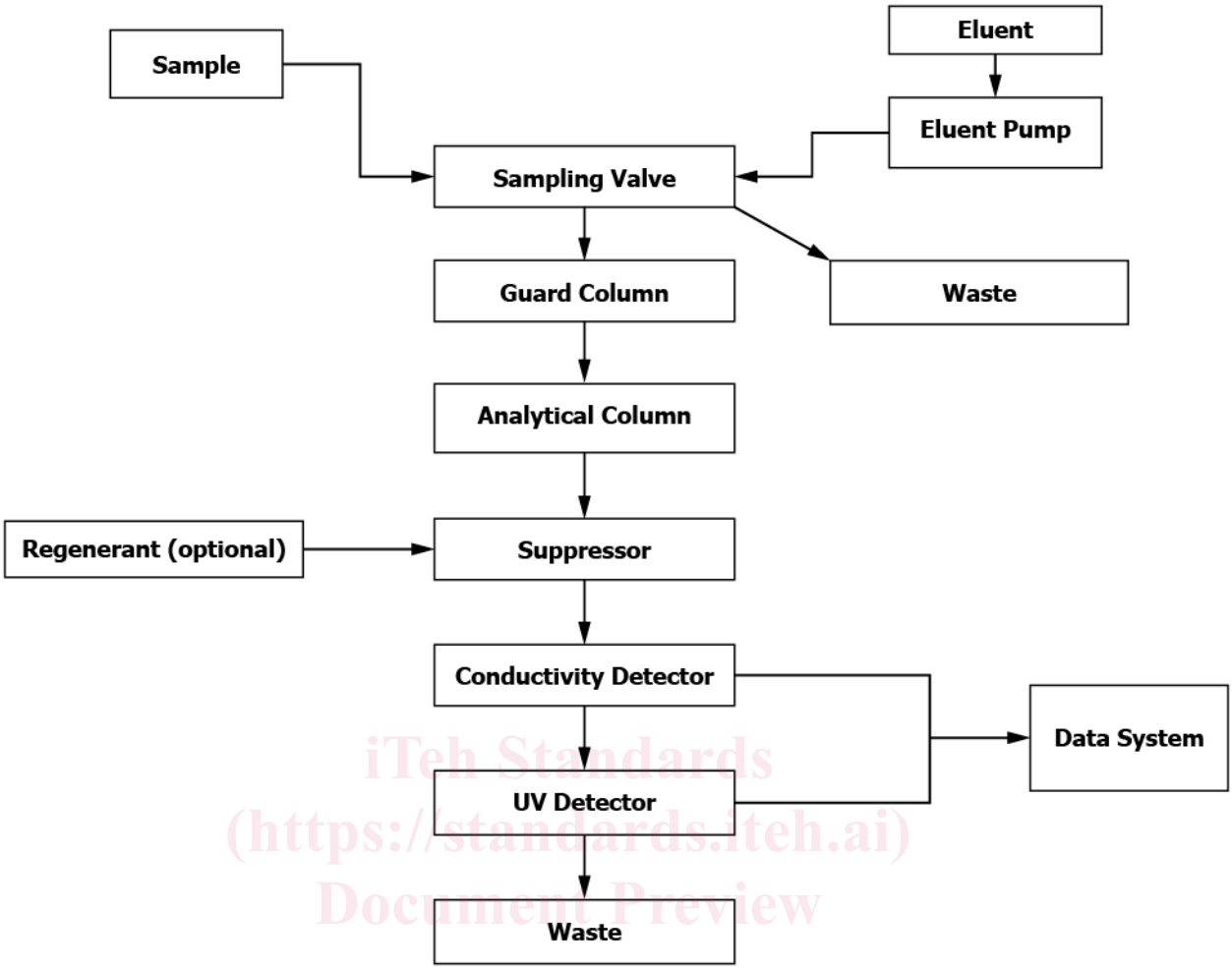

FIG. 7 Schematic of Ion Chromatography System

TABLE 2 Calibration Ranges

NOTE 1—n/a = not applicable.

Analyte	Low Standard Concentration, mg/L	High Standard Concentration, mg/L
Fluoride	0.1	10
Chloride	n/a (matrix)	n/a (matrix)
Nitrite-N	0.03	3.3
Bromide	0.1	10
Nitrate-N	0.02	2.5
o-PO_4-P	0.03	3.3
Sulfate	0.1	10

9.2 Samples should be collected in plastic or glass bottles. If fluoride is required, only use plastic bottles. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

9.3 Sample preservation and holding times for the anions that can be determined by this test method are as follows:

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Fluoride	None required	28 days
Nitrite-N	Cool to 4°C	48 hours
Nitrate-N	Cool to 4°C	48 hours
o-PO_4-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

9.4 The method of preservation and the holding time for samples analyzed by this test method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples be cooled to 4°C and held for no longer than 28 days.

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 2 by pipetting the designated aliquots of stock solutions prepared in 8.5 (8.5.1 – 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.