



Designation: **D8149—17** **D8149 – 20**

Standard Practice for Optimization, Calibration, and Validation of Ion Chromatographic Determination of Heteroatoms and Anions in Petroleum Products and Lubricants¹

This standard is issued under the fixed designation D8149; 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—Scope*

1.1 This practice covers the information on calibration, quality control, and operational guidance for anionic measurements using ion chromatography (IC).

1.2 *IC Related Standards*—Chemically or electrolytically regenerated suppressed ion chromatography standards for aqueous matrices include Test Methods **D2988**, **D4327**, **D5085**, **D5542**, **D5827**, **D5987**, **D5996**, **D6581**, **D7319**, **D7328**, **D7359**, **D7773**, **D7994**, and **D8150**; IC instrumentation requirements are described in Practices **E1151**, and **E1511**.

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

1.5 *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

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D975 Specification for Diesel Fuel

D1193 Specification for Reagent Water

D2988 Test Methods for Water-Soluble Halide Ion in Halogenated Organic Solvents and Their Admixtures

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4327 Test Method for Anions in Water by Suppressed Ion Chromatography

D5085 Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Ion Chromatography

D5542 Test Methods for Trace Anions in High Purity Water by Ion Chromatography

D5827 Test Method for Analysis of Engine Coolant for Chloride and Other Anions by Ion Chromatography

D5987 Test Method for Total Fluorine in Coal and Coke by Pyrohydrolytic Extraction and Ion Selective Electrode or Ion Chromatograph Methods (Withdrawn 2020)³

D5996 Test Method for Measuring Anionic Contaminants in High-Purity Water by On-Line Ion Chromatography

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6581 Test Methods for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Suppressed Ion Chromatography

D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee **D02.03** on Elemental Analysis.

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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.

³ The last approved version of this historical standard is referenced on www.astm.org.

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

- D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D7318 Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration
- D7319 Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography
- D7328 Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection
- D7359 Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)
- D7591 Test Method for Determination of Free and Total Glycerin in Biodiesel Blends by Anion Exchange Chromatography
- D7773 Test Method for Determination of Volatile Inorganic Acids (HCl, HBr, and HNO₃) Using Filter Sampling and Suppressed Ion Chromatography
- D7994 Test Method for Total Fluorine, Chlorine, and Sulfur in Liquid Petroleum Gas (LPG) by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)
- D8150 Test Method for Determination of Organic Chloride Content in Crude Oil by Distillation Followed by Detection Using Combustion Ion Chromatography
- E1151 Practice for Ion Chromatography Terms and Relationships
- E1511 Practice for Testing Conductivity Detectors Used in Liquid and Ion Chromatography
- 2.2 *Other Standards:*
- ISO/CEN 15492 Ethanol as a blending component for petrol—Determination of inorganic chloride—Ion chromatographic method⁴
- EPA Method 300.0 Determination of Inorganic Anions by Ion Chromatography⁵
- EPA Method 300.1 Determination of Inorganic Anions in Drinking Water by Ion Chromatography⁵

3. Terminology

3.1 Definition of terms relating to ion chromatography can be found in Practices E1151 and E1511.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *combustion ion chromatography, n*—an analytical system consisting of oxidative pyrohydrolytic combustion followed by ion chromatographic detection. **D7994, D8150**

3.2.2 *existent inorganic sulfate, n*—inorganic sulfate species actually present in the sample at the time of analysis with no oxidation treatment. **D7318, D7319, D7328**

3.2.3 *inorganic chloride, n*—chloride present as hydrochloric acid, ionic salts of this acid, or mixtures of these. **D7319, D7328**

3.2.4 *inorganic sulfate, n*—sulfate (SO₄)⁻² species present as sulfuric acid, ionic salts of this acid, or mixtures of these. **D7318, D7319, D7328**

3.2.5 *oxidative pyrohydrolytic combustion, n*—a process in which a sample is combusted in an oxygen-rich environment at temperatures greater than 900 °C and in the presence of excess water vapor not originating from the combustion of the sample.

3.2.5.1 *Discussion*—

In oxidative pyrohydrolytic combustion, the sample is pyrolyzed into carbon dioxide, water, hydrogen halides (HX), and elemental oxides such as NO_x and SO_x, and residual ash typically of elemental oxides. **D7359, D7994, D8150**

3.2.6 *potential sulfate, n*—total inorganic sulfate species present after the sample has been reacted with an oxidizing agent. **D7319, D7328**

4. Summary of Practice

4.1 Ion chromatography technique can be used to determine the anions in various liquid matrices. Often solid samples are converted into water-soluble forms after combustion, and are analyzed for anionic forms of elements of interest. This practice summarizes the protocols to be followed during such sample preparation, calibration, and verification of the analytical performance.

⁴ Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <http://www.iso.org>.

⁵ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

5. Principle of Analysis Technique

5.1 Ion chromatography (IC) is a combination of ion exchange chromatography, eluent suppression, and conductivity detection. Other detection devices can also be used such as amperometric, UV-fluorescence, mass spectrometry, inductively coupled plasma-mass spectrometry, and so on. Cations and polar organic compounds such as amines, sugars, and organic acids can also be determined using IC analysis. However, this practice covers only the determination of specific anions using conductivity detection.

5.2 For anion analysis, suppression is applied for minimizing the background conductivity and increasing the response of the anions of interest. Suppressor devices with ion exchanger resin in the H⁺ form and membrane-based devices are available. Regeneration is performed chemically in both versions or electrolytically in the membrane type.

5.2.1 A dilute base such as NaHCO₃, Na₂CO₃, and NaOH (or KOH) as mixtures or alone can be used as eluent which is conveniently neutralized to low conductivity acid in the suppressor and to increased sensitivity. Hydroxide eluents are neutralized to water with very low conductivity. Carbonate/hydrogen carbonate eluents are neutralized to carbonic acid with a low conductivity. An optional CO₂ removal device reduces the background conductivity further.

5.2.2 The anions are eluted through the separating column and detected by conductivity measurement. In the separator column, the anion exchange resin selectively causes the various anions of different types to migrate through the column at different respective rates, thus effecting their separation, and identification based on their retention times.

5.3 The non-selective nature of the conductimetric detection allows several ions to be sequentially determined in the same sample. The conductimetric detection is highly specific and relatively free from interferences. Different valence states of the same element can be determined. However, because of the non-selective nature of the detector, the chromatographic peaks are identified only by their retention times. Thus, it is important that there is separation of two ions having the same or close retention times to avoid detection as one broad peak giving erroneous results.

5.4 The advantages of IC analysis are (1) sequential multi-anion capability eliminating the individual anionic determinations by diverse techniques, such as those using wet chemistry, (2) small sample size used, usually < 1 mL, (3) rapid analysis ~ 10 min for several standard anions, (4) large dynamic range of over four orders of magnitude concentration, (5) ability to differentiate between different species of the same element, and (6) high sensitivity on the order of ppt to ppm.

5.5 On the other hand, the drawbacks of the technique include (1) possible interference if two anions have similar retention times, (2) in the presence of a large excess of one ion, the determination of another ion in much smaller concentration is challenging requiring use of a higher capacity column, and (3) the need for sample to be in an aqueous or water miscible solution. However, in spite of these drawbacks, the IC technique has become a workhorse in many industrial laboratories for the determination of multiple anions replacing antiquated and labor intensive wet chemistry techniques.

5.6 Further discussion on the IC technique can be found in references cited in Refs **1-6**⁶, and references cited therein.

6. Interferences

6.1 Although most ion chromatograms are simple and straight forward to interpret, in some instances artifacts appear in the chromatograms which need to be recognized and resolved if possible to avoid producing erroneous results.

6.1.1 *Water Dip*—There is usually a negative dip in the base line, early in the chromatogram. This small sharp dip occurs just before the fluoride peak. This is the void volume indication of the column set. It is often most seen when operating at low conductivity meter readings or when analyzing “clean” samples. A second depression in the chromatogram baseline closely follows the void volume indication. This second negative response is deeper and much broader and is called “water dip.”

6.1.1.1 The shape of the dip depends on the sample volume injected, the eluent concentration, the sample concentration. Matching the sample to the eluent concentration minimizes the water dip. If the concentration of eluent is almost equal in the sample and the eluent, the dip would be eliminated. A second remedy is to use a weaker eluent which increases the species retention times. The depth of the dip is less because the conductivity offset is lower than with the standard eluent.

6.1.1.2 Usually for chloride and sulfate determinations, the water dip should not be a problem since the chloride and sulfate peaks are far enough away from the water dip. It is primarily a concern for fluoride determination because it typically elutes just after this dip.

6.1.1.3 With hydroxide based eluents or other eluents after CO₂ removal, a minimal or no water dip is seen. This allows injection of a large sample volume.

6.1.2 *Peak Interferences*—Overlapping peaks is a common problem in all chromatographic methods. There are a number of ways that this could be minimized. These steps may be used singly or in combination to reduce the peak interferences.

6.1.2.1 Pre-treating the sample, for example oxidizing the sulfide ion to sulfate ion by treating with H₂O₂ will eliminate the sulfide interference in the chloride determination.

6.1.2.2 Using a longer or higher capacity separator column may increase the separation between the succeeding ions.

⁶ The boldface numbers in parentheses refer to the list of references at the end of this standard.

6.1.2.3 Changing the eluent strength, the ratio of the eluting species, or the actual eluting species themselves or sample pre-treatment. Generally, a single large change in the eluent strength is more efficient than several small changes.

6.1.2.4 Gradient ion chromatography can facilitate resolution of co-eluting peaks. This approach uses an eluent concentration change with time. Using weak eluent concentrations to resolve early co-eluting peaks and increasing strength further helps in shortening the time of the chromatographic separation to elute strongly retained anions.

(1) A gradient might not actually result in a significantly longer run, and may even shorten it, depending on how high and how quickly the eluent concentration is increased. Time is needed at the end of the run to allow the lower eluent concentration to equilibrate in the column.

6.1.2.5 Altering the temperature of the column compartment.

6.1.2.6 Using a column with a different selectivity.

6.1.3 *Peak Shifts* are observed with increase in sample concentration, interaction between the sample and the eluent, and temperature. Peak shifts can also occur as a column ages and becomes contaminated and loses ion exchange sites. Dilution of the sample is the easiest way of solving this high concentration sample problem. Another way is to spike the sample with a very small amount of a standard solution and then reanalyzing the solution. This helps to verify the identity of the shifted peak. Peaks can also shift from run to run if eluent was not prepared properly, or not allowing the column to equilibrate at the end of a gradient run.

6.1.4 *High Matrix Constituents* sometimes cause peak shifts. This occurs most often when the major constituent has a high affinity for the resin. One solution to this problem is to dilute or pretreat the sample to keep the total ionic strength of the solution low. Another solution is to use a smaller injection loop which decreases the amount of sample deposited onto the column and serves the same purpose as dilution. The use of high capacity separation columns allows greater disparate ratios of anions to be resolved.

6.1.5 *Drifting or Shifting Baseline*—Main cause here is slow elution of strongly retained ions and changes in the room temperature. Thermostating the column sets and detector will minimize temperature effects.

6.1.6 *Excessive Analysis Time*—The analysis time can be shortened by several methods. Use of a shorter separator column decreases the analysis time but also may give poor peak resolution. An increase in the eluent strength also decreases the analysis time. Increasing the flow rate shortens the analysis time but will decrease the peak resolution. Smaller particle size columns (for example, 4 μm) are another option to decrease run times because of their increased peak efficiency, which allows shorter columns to be used while maintaining adequate resolution. Introduction of a solvent such as acetone into the mobile phase can shorten analysis time of late eluting peaks such as thiosulfate. Dependent on the separation, chemical suppression may offer advantages in solvent considerations to electrolytically regenerated suppression. However, another option for reducing retention times for slow eluting peaks is to consider a different column suited to resolving the analytes of interest.

6.1.7 *Inadequate Sensitivity*—Ways of increasing sensitivity include using a larger injection loop, decreasing the distance between the conductivity cell electrodes, or using a concentrator column. Newer digital signal processing detectors offer full scale sensitivity across a range of ~~0 micro-Siemens to 15 000 micro-Siemens~~ 0 μS to 15 000 μS without any range changes. Gradient eluents provide for peak focusing allowing narrower, taller peaks. Also, carbonate removal devices offer equally low background conductivity for hydroxide and carbonate eluents eliminating a substantial sensitivity difference.

6.1.8 *Sample Problems*—Highly concentrated solutions can cause problems as mentioned above. Dilution or pre-treatment will usually eliminate these problems. Unstable constituents or particulates present in the sample solution will also cause problems in the analysis. For particulate contamination, samples should be filtered to remove the particles larger than 0.25 μm .

6.2 Given the trace amounts of anions to be determined in these methods, interferences can be caused by contamination of glassware, eluents, reagents, and so on. Hence, great care must be taken to ensure that the contamination is kept to a minimum. The instrument must be clean and properly maintained to address potential sources of contamination, or carryover, or both. Multiple injections shall be completed until a stable background is attained. This is considered to be achieved when the analysis of a minimum of three consecutive system blanks have area counts equal to or less than 5 % relative standard deviation (RSD) for the anions of interest. The use of powder-free gloves is highly recommended to prevent sample contamination. Only deionized water with ~~18.0 M Ω –18.0 M Ω~~ resistance must be used to minimize contamination in the preparation of calibration standards or dilution of samples.

7. Significance and Use

7.1 Accurate elemental analysis of petroleum products and lubricants is necessary for the determination of chemical properties, which are used to establish compliance with commercial and regulatory specifications.

7.2 Ion chromatography is often used in cases where anion content of the material is desired. Some of the hetero-atoms can be converted by combustion in an oxygen atmosphere followed by aqueous dissolution to convert them into anions before ion chromatographic determination. A number of ion chromatographic ASTM standards issued are listed in Section 2. Of these, the D02, D05, and D16 Committee standards which use ion chromatography are listed in [Table 1](#).

8. Apparatus

8.1 An ion chromatographic analysis system uses a sample introduction device, an elution reservoir or eluent generation device, a non-metallic pump, a guard column, the separator column where the anionic species are resolved by conventional elution

TABLE 1 Ion Chromatography Standards Used in Analysis of Fossil Fuels

Standard	Analysis	Matrix	ASTM Committee
D5987	Total Fluorine Content	Coal and Coke	D05
D7319	Existent and Potential Sulfate and Inorganic Chloride	Fuel Ethanol and Butanol	D02
D7328	Existent and Potential Inorganic Sulfate and Total Inorganic Sulfate	Fuel Ethanol	D02
D7359	Total Fluorine, Chlorine, and Sulfur	Aromatic Hydrocarbons	D16
D7591	Free and Total Glycerin	Diesel and Biodiesel	D02
D7994	Total Fluorine, Chlorine, and Sulfur	Liquid Petroleum Gases	D02
D8150	Organic Chloride	Crude Oil	D02

chromatography, the suppressor where the eluent coming from the separator column is converted to a lower conductivity, a detector, software to calculate the concentration of the measured anions, and a printout device, if desired.

NOTE 1—Many different instrument companies manufacture automatic ion chromatographs. Consult the specific manufacturer’s instruction manual for details regarding setup and operation.

8.1.1 One key to successful IC analysis is suppression of the eluent conductivity while converting the sample ions to a more conductive form. A dilute mixture of Na_2CO_3 , NaHCO_3 or hydroxide can be used as an eluent, because carbonate and bicarbonate are conveniently neutralized to low conductivity species, and the different combinations of carbonate-bicarbonate give variable buffered pH values, allowing the ions of interest, which can be in a large range of affinity to be separated. The anions are separated through the separating column in the background of carbonate-bicarbonate and conveniently detected based on electrical conductivity.

8.2 An IC detection system uses a conductivity detector (most commonly), an amperometric detector, or an UV/visible light absorbance detector. Because IC is typically non-destructive, it can also be combined with mass spectrometry to provide increased sensitivity and to confirm peak identity.

8.2.1 The conductivity detectors used should conform to the performance criteria given in ASTM Standard Practice E1511. This practice requires four different tests to be performed to characterize a detector: (1) noise and drift; (2) linear range; (3) dependence of response on flow rate; and (4) response time. Constant temperature must be maintained by the detector to avoid signal drift. Usually it is expected that the conductivity detector supplied by the ion chromatograph vendor will meet these requirements.

8.3 Fig. 1 shows a schematic representation of an ion chromatography system. Fig. 2 shows a typical chromatogram of a mixture of several common inorganic anions. Not all the species shown in this figure are going to be detected in all samples.

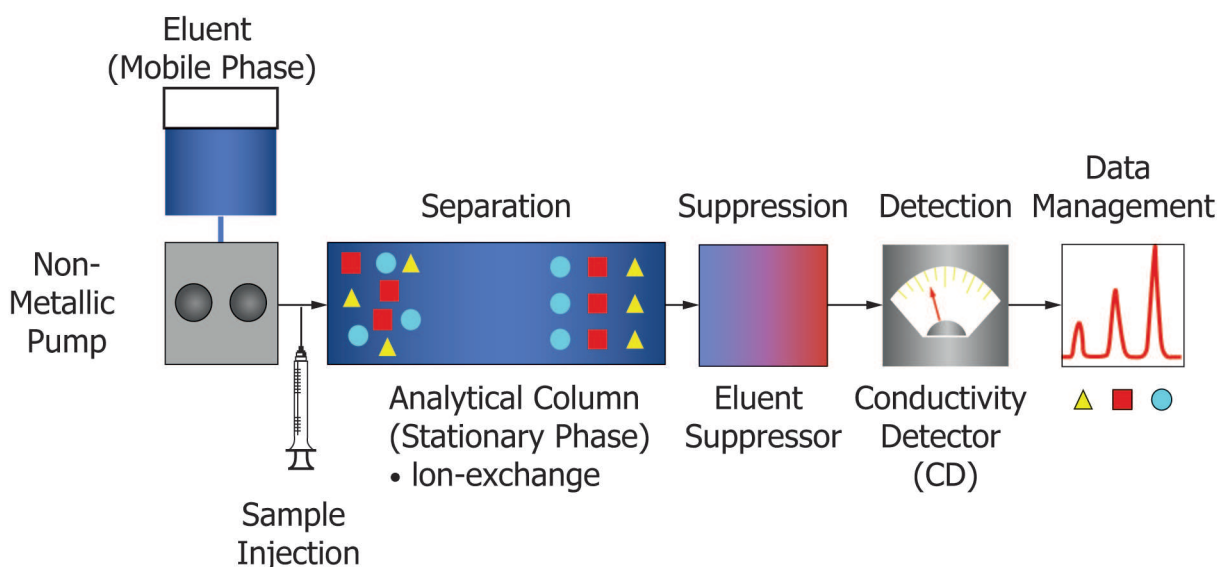
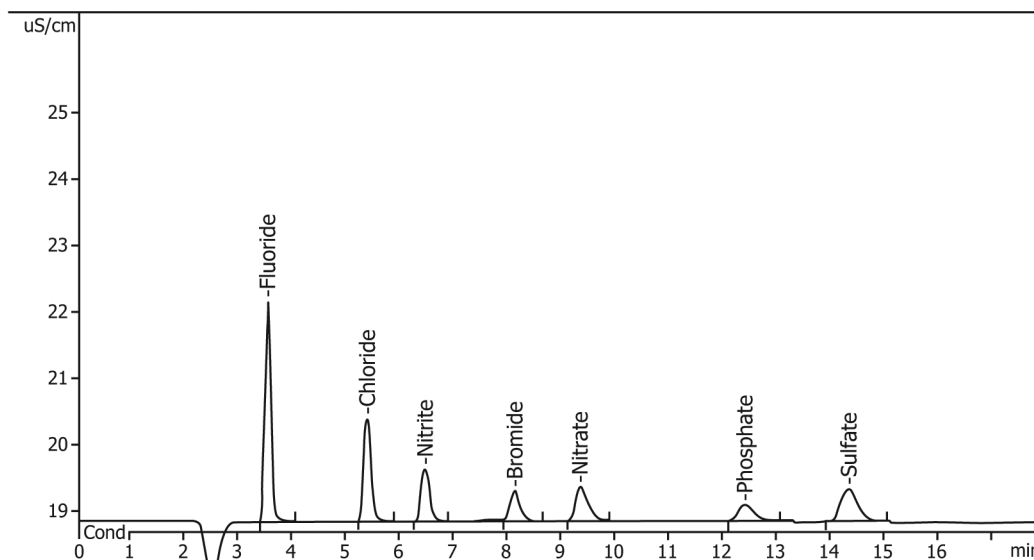


FIG. 1 Ion Chromatography System



Note – Chromatogram retention times may be different depending on instruments or columns used.

NOTE 1—Chromatogram retention times may be different depending on instruments or columns used.

FIG. 2 Analysis of Standard Inorganic Anions by Ion Chromatography (Test Method D7328)

9. Reagents and Materials

9.1 *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.⁷ 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.

NOTE 2—Purity of reagents is of particular importance when performing trace ion analysis of samples containing $\pm 1 \text{ mg/mg/kg/kg}$ or less in concentration of the elements (anions) of interest. The sample system blank should provide a chromatographic area response no greater than 50%–50% of the lowest calibration standard used for calibration.

9.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type I or better in Specification D1193. This shall be used for all eluent preparation, calibration standards preparation, and handling of such solutions. The quality of required Type 1 water is given in Table 2, excerpted from Specification D1193.

9.3 Eluent buffer stock solutions, suppressor reagent solutions, and so on should be prepared per the ion chromatograph manufacturer’s instructions. Additional information on these solution preparations is also given in Test Methods D7319, D7328, and D8150. Recipes for preparation of commonly used eluents are given in Table 3. All solid reagent chemicals should be properly dried before weighing the required amounts.

TABLE 2 Quality Requirements for Reagent Water Type I

Parameter	Limits
$\mu\text{S}/\text{cm}^2$ @25°C (max)	0.055
$\mu\text{S}/\text{cm}^2$ @25°C (max)	0.055
Electrical Conductivity @ 25°C, M Ω .cm (min)	18
Total Organic Carbon, $\mu\text{g}/\text{L}$ (max)	50
Sodium, $\mu\text{g}/\text{L}$ (max)	1
Chloride, $\mu\text{g}/\text{L}$ (max)	1
Total Silica, $\mu\text{g}/\text{L}$ (max)	3
HBC, clu/mL (max)	10/10 to 1000
Endotoxin, EU/mL (max)	0.093 to 0.25

⁷ *Reagent Chemicals, American Chemical Society Specifications, ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

TABLE 3 Preparation of Commonly Used Eluents

Eluent	Amount of a 4 L Solution in Deionized Water
0.003 M NaHCO ₃ + 0.0024M Na ₂ CO ₃	1.0008 g NaHCO ₃ + 1.0176 g Na ₂ CO ₃
0.003 M Na ₂ CO ₃ + 0.002 M NaOH	1.272 g Na ₂ CO ₃ + 80 mL of 0.1 M NaOH
0.1 N HCl	33.3 mL Conc. HCl
0.025 N H ₂ SO ₄	2.8 mL Conc. H ₂ SO ₄
0.001 M HCl	4 mL of 1 M HCl
0.1 M H ₂ SO ₄	22.4 mL Conc. H ₂ SO ₄

10. Sampling

10.1 Obtain samples in accordance with Practice **D4057** or Practice **D4177**. Samples should be well-mixed to ensure homogeneity. A representative portion shall be taken from each sample for analysis. Samples should be collected in clean (preferably glass or polyethylene) containers with closures that seal well to prevent evaporation. Sample containers shall not contain any residual or extractable anions of interest. If containers have been cleaned and rinsed with water, they shall be thoroughly rinsed with Type I reagent water and dried prior to use.

10.2 Thoroughly mix the samples in their containers immediately prior to withdrawing the test specimen aliquot for analysis.

10.3 Mixing samples using sonication or mechanical shaking for at least 5 min is suggested to ensure sample homogeneity.

10.4 Take care to ensure that all glassware and containers are thoroughly dry before introduction of samples. If cleaned and/or rinsed with Type I water, this can also include a follow up rinse with an anion of interest free organic solvent.

11. Calibration Standards

11.1 Use appropriately dried reagent grade or higher purity inorganic compounds for preparing calibration standards. Check reagent information sheet about proper drying conditions to be used. Some of these compounds may be deliquescent in moist air. Usually drying for an hour at ~100 °C in an air oven may be adequate. Store the dried reagents in a desiccator over appropriate dessicant (for example, silica gel, Drierite, and so on).

11.2 Pre-made stock solutions can also be used and diluted as necessary. Store prepared solutions in clean glass or polyethylene containers with securely closed tops. Store in a dry humidity and temperature controlled environment away from light. Some examples of preparation of specific calibration solutions are given in **Table 4**. Other alternative compounds and alternative quantities may also be prepared. Two typical calibration graphs for sulfate and chloride obtained in Test Method **D7319** IC analysis are shown in **Fig. 3**.

11.3 Some ions may have limited calibration ranges. Analytes with peak areas exceeding the calibration should be diluted with Type I water and re-tested. For a complex sample, multiple dilutions may be needed to measure all of the analytes in appropriate linear range. For larger dilutions, the reporting limits would be increased.

12. Sample Analysis

12.1 Obtain samples in accordance with Practice **D4057** or Practice **D4177**. Samples should be well mixed to ensure homogeneity. Take a representative aliquot for analysis. Collect samples in containers with closures that seal well to prevent

TABLE 4 Preparation of Calibration Standard Solutions

Anion	Dissolve x g in 1 L Deionized Water	Final Ion Concentration, mg/L
Borate (BO ₃ ⁻)	1.0 g H ₃ BO ₃	95
Bromate (BrO ₃ ⁻)	1.3057 g KBrO ₃	1000
Bromide (Br ⁻)	1.2877 g NaBr	1000
Chlorate (ClO ₃ ⁻)	1.2765 g NaClO ₃	1000
Chloride (Cl ⁻)	1.6484 g NaCl	1000
Fluoride (F ⁻)	2.2102 g NaF	1000
Iodate (IO ₃ ⁻)	1.1315 g NaIO ₃	1000
Iodide (I ⁻)	1.1813 g NaI	1000
Nitrate (NO ₃ ⁻)	1.3707 g NaNO ₃	1000
Nitrite (NO ₂ ⁻)	1.4998 NaNO ₂	1000
Phosphate (PO ₄ ⁻³)	3.7710 g Na ₂ HPO ₄ · 12.H ₂ O ^A	1000
Sulfate (SO ₄ ⁻²)	1.8142 g K ₂ SO ₄	1000
Sulfite (SO ₃ ⁻²)	1.5747 g Na ₂ SO ₃ ^B	1000
Thiocyanate (SCN ⁻)	1.3961 g NaSCN	1000
Thiosulfate (S ₂ O ₃ ⁻²)	1.4103 g Na ₂ S ₂ O ₃	1000

^A Use fresh undried compound.

^B Stabilize with 1 % formaldehyde, otherwise the solution will oxidize to sulfate.