Designation: ~~D6508 – 10~~ D6508 – 15

Standard Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte[1]

This standard is issued under the fixed designation D6508; 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 determination of the inorganic anions fluoride, bromide, chloride, nitrite, nitrate, ortho-phosphate, and sulfate in drinking water, wastewater, and other aqueous matrices using capillary ion electrophoresis (CIE) with indirect UV detection. See Figs. 1-6.

1.2 The test method uses a chromate-based electrolyte and indirect UV detection at 254 nm. It is applicable for the determination or inorganic anions in the range of 0.1 to 50 mg/L except for fluoride whose range is 0.1 to 25 mg/L.

1.3 It is the responsibility of the user to ensure the validity of this test method for other anion concentrations and untested aqueous matrices.

NOTE 1—The highest accepted anion concentration submitted for precision and bias extend the anion concentration range for the following anions: Chloride to 93 mg/L, Sulfate to 90 mg/L, Nitrate to 72 mg/L, and ortho-phosphate to 58 mg/L.

1.4 The values stated in SI units are to be regarded as standard. ~~No other units of measurement are included in this~~ The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.5 *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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

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 Closed Conduits
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D5905 Practice for the Preparation of Substitute Wastewater
F488 Test Method for On-Site Screening of Heterotrophic Bacteria in Water (Withdrawn 2005)[3]

3. Terminology

3.1 ~~*Definitions—*~~*Definitions:* ~~For definitions of terms used in this test method, refer to Terminology D1129.~~

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

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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.
Current edition approved ~~Sept. 1, 2010~~Oct. 1, 2015. Published ~~October 2010~~October 2015. Originally approved in 2000. Last previous edition approved in ~~2005~~2010 as ~~D6508 – 00~~D6508 – 10. ~~(2005)ε2.~~ DOI: ~~10.1520/D6508-10.~~10.1520/D6508-15.

[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**

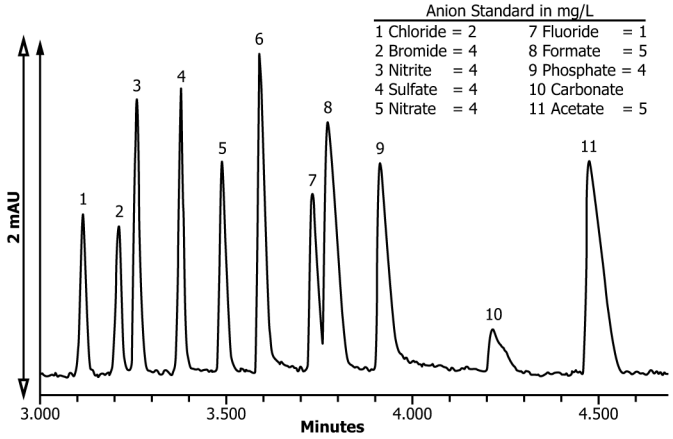


FIG. 1 Electropherogram of Mixed Anion Working Solution and Added Common Organic Acids

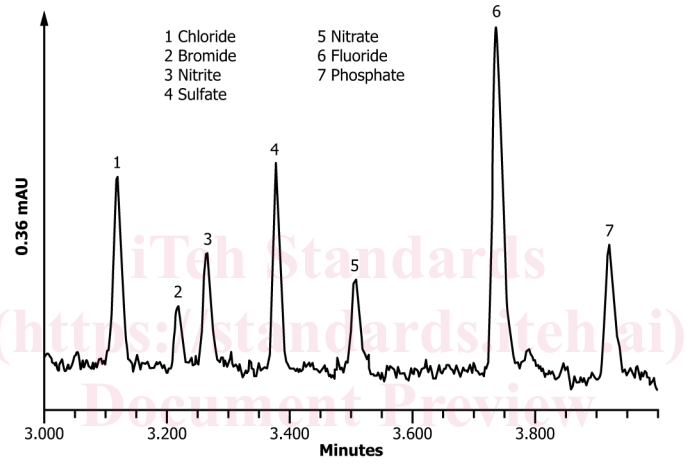


FIG. 2 Electropherogram of 0.2 mg/L Anions Used to Determine MDL

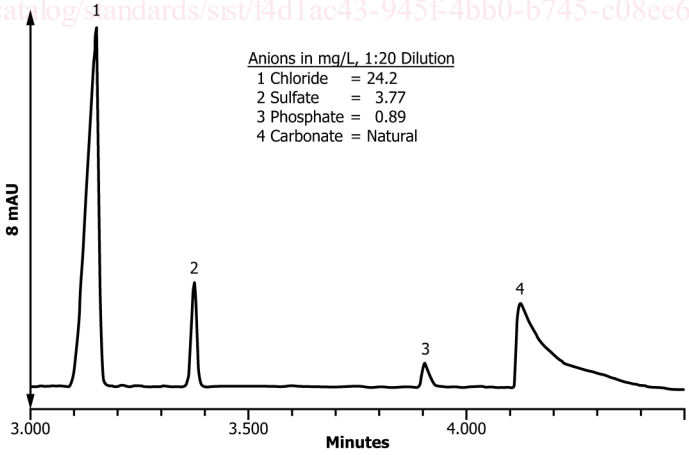
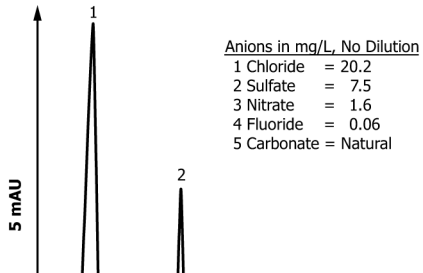


FIG. 3 Electropherogram of Substitute Wastewater

3.2.1 *capillary ion electrophoresis, n*—an electrophoretic technique in which a UV-absorbing electrolyte is placed in a 50 µm to 75 µm fused-silica capillary.



3.2.1.1 *Discussion*—

FIG. 4 Electropherogram of Drinking Water

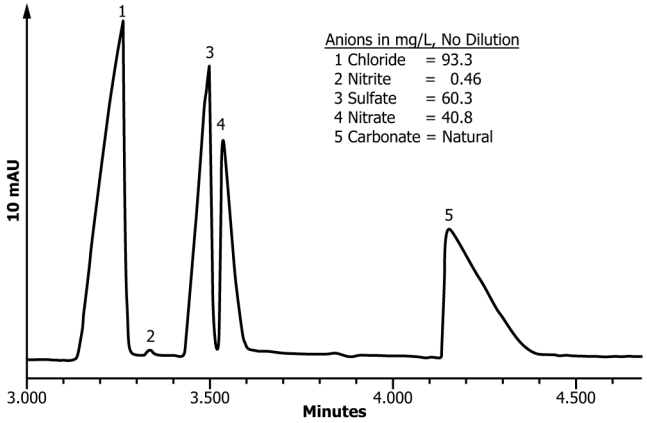


FIG. 5 Electropherogram of Municipal Wastewater Treatment Plant Discharge

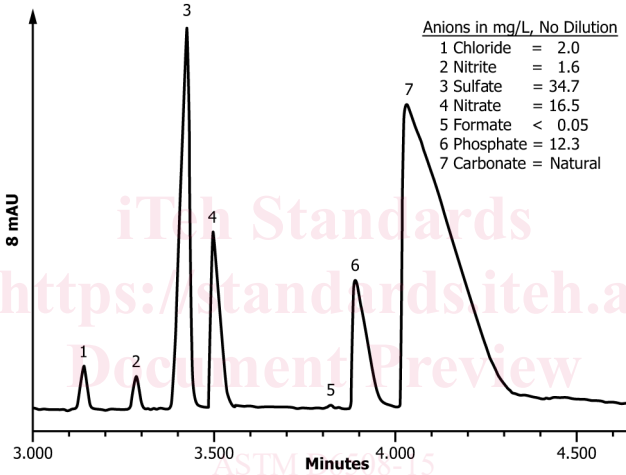


FIG. 6 Electropherogram of Industrial Wastewater

Voltage is applied across the capillary causing electrolyte and anions to migrate towards the anode and through the capillary's UV detector window. Anions are separated based upon the differential rates of migration in the electrical field. Anion detection and quantitation are based upon the principles of indirect UV detection.

3.2.2 *electrolyte, n*—a combination of a UV-absorbing salt and an electroosmotic-flow modifier placed inside the capillary, used as a carrier for the analytes, and for detection and quantitation.

3.2.2.1 *Discussion*—

The UV-absorbing portion of the salt must be anionic and have an electrophoretic mobility similar to the analyte anions of interest.

3.2.3 *electroosmotic flow (EOF), n*—the direction and velocity of electrolyte-solution flow within the capillary under an applied electrical potential (voltage); the velocity and direction of flow is determined by electrolyte chemistry, capillary-wall chemistry, and applied voltage.

3.2.4 *electroosmotic-flow modifier (OFM), n*—a cationic quaternary amine in the electrolyte that dynamically coats the negatively charged silica wall giving it a net positive charge.

3.2.4.1 *Discussion*—

This modifier reverses the direction of the electrolyte's natural electroosmotic flow and directs it towards the anode and detector. This modifier augments anion migration and enhances speed of analysis. Its concentration secondarily affects anion selectivity and resolution, (see Fig. 7).

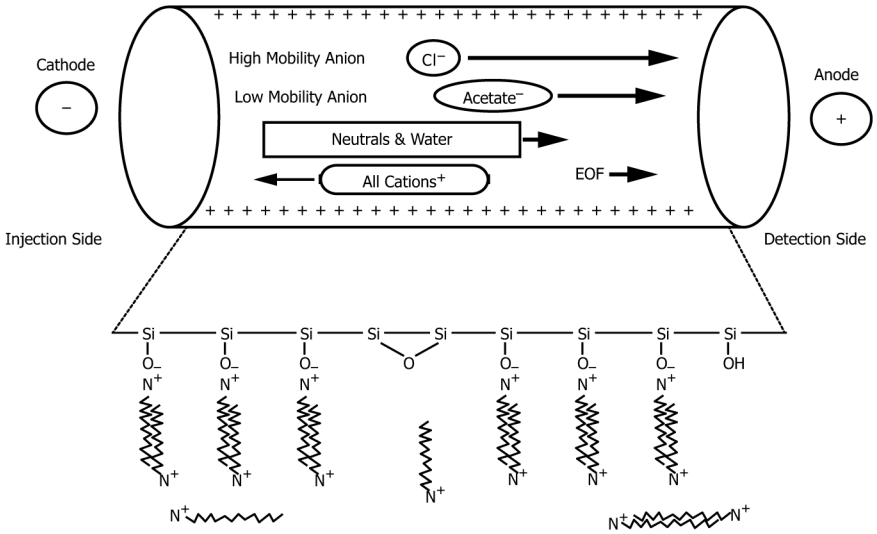


FIG. 7 Pictorial Diagram of Anion Mobility and ElectroOsomotic Flow Modifier

3.2.5 *electropherogram, n*—a graphical presentation of UV-detector response versus time of analysis; the ~~x-axis~~X-axis is migration time, which is used to identify the anion qualitatively, and the ~~y-axis~~Y-axis is UV response, which can be converted to time-corrected peak area for quantitation.

3.2.6 *electrophoretic mobility, n*—the specific velocity of a charged analyte in the electrolyte under specific electroosmotic-flow conditions.

3.2.6.1 *Discussion*—

The mobility of an analyte is directly related to the analyte's equivalent ionic conductance and applied voltage, and is the primary mechanism of separation.

3.2.7 *hydrostatic sampling, n*—a sample-introduction technique in which the capillary with electrolyte is immersed in the sample, and both are elevated to a specific height, typically 10 cm, above the receiving-electrolyte reservoir for a preset amount of time, typically less than 60 s.

3.2.7.1 *Discussion*—

Nanolitres of sample are siphoned into the capillary by differential head pressure and gravity.

3.2.8 *indirect UV detection, n*—a form of UV detection in which the analyte displaces an equivalent net-charge amount of the highly UV-absorbing component of the electrolyte causing a net decrease in background absorbance.

3.2.8.1 *Discussion*—

The magnitude of the decreased absorbance is directly proportional to analyte concentration. Detector-output polarity is reversed in order to obtain a positive mV response.

3.2.9 *midpoint of peak width, n*—CIE peaks typically are asymmetrical with the peak apex's shifting with increasing concentration, and the peak apex may not be indicative of true analyte-migration time.

3.2.9.1 *Discussion*—

Midpoint of peak width is the midpoint between the analyte peak's start and stop integration, or the peak center of gravity.

3.2.10 *migration time, n*—the time required for a specific analyte to migrate through the capillary to the detector.

3.2.10.1 *Discussion*—

The migration time in capillary ion electrophoresis is analogous to retention time in chromatography.

3.2.11 *time-corrected peak area, n*—normalized peak area; peak area divided by migration time.

3.2.11.1 *Discussion*—

CE principles state that peak area is dependent upon migration time, that is, for the same concentration of analyte, as migration time increases (decreases) peak area increases (decreases). Time-corrected peak area accounts for these changes.

4. Summary of Test Method

4.1 Capillary ion electrophoresis, see Figs. 7-10, is a free zone electrophoretic technique optimized for the determination of anions with molecular weight less than 200. The anions migrate and are separated according to their mobility in the electrolyte when an electrical field is applied through the open tubular fused silica capillary. The electrolyte's electroosmotic low modifier dynamically coats the inner wall of the capillary changing the surface to a net positive charge. This reversal of wall charge reverses the natural EOF. The modified EOF in combination with a negative power supply augments the mobility of the analyte anions towards the anode and detector achieving rapid analysis times. Cations migrate in the opposite direction towards the cathode and are removed from the sample during analysis. Water and other neutral species move toward the detector at the same rate as the EOF. The neutral species migrate slower than the analyte anions and do not interfere with anion analysis (see Figs. 7 and 8).

4.2 The sample is introduced into the capillary using hydrostatic sampling. The inlet of the capillary containing electrolyte is immersed in the sample and the height of the sample raised 10 cm for 30 s where low nanolitre volumes are siphoned into the capillary. After sample loading, the capillary is immediately immersed back into the electrolyte. The voltage is applied initiating the separation process.

4.3 Anion detection is based upon the principles of indirect UV detection. The UV-absorbing electrolyte anion is displaced charge-for-charge by the separated analyte anion. The analyte anion zone has a net decrease in background absorbance. This decrease in UV absorbance in quantitatively proportional to analyte anion concentration (see Fig. 9). Detector output polarity is reversed to provide positive mV response to the data system, and to make the negative absorbance peaks appear positive.

4.4 The analysis is complete once the last anion of interest is detected. The capillary is vacuum purged automatically by the system of any remaining sample and replenished with fresh electrolyte. The system now is ready for the next analysis.

5. Significance and Use

5.1 Capillary ion electrophoresis provides a simultaneous separation and determination of several inorganic anions using nanolitres of sample in a single injection. All anions present in the sample matrix will be visualized yielding an anionic profile of the sample.

5.2 Analysis time is less than 5 minutes with sufficient sensitivity for drinking water and wastewater applications. Time between samplings is less than seven minutes allowing for high sample throughput.

5.3 Minimal sample preparation is necessary for drinking water and wastewater matrices. Typically, only a dilution with water is needed.

5.4 This test method is intended as an alternative to other multi-analyte methods and various wet chemistries for the determination of inorganic anions in water and wastewater. Compared to other multi-analyte methods the major benefits of CIE are speed of analysis, simplicity, and reduced reagent consumption and operating costs.

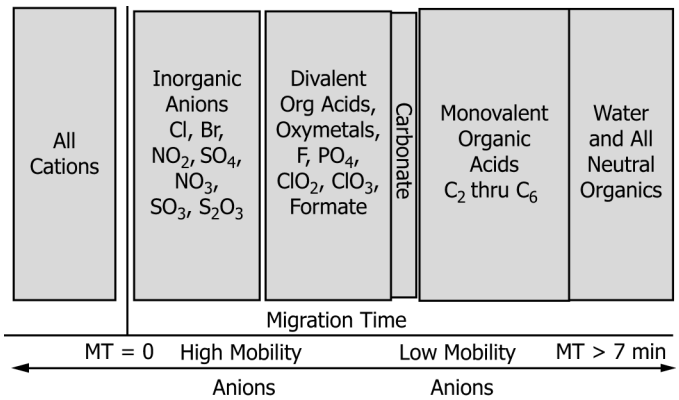


FIG. 8 Selectivity Diagram of Anion Mobility Using Capillary Ion Electrophoresis

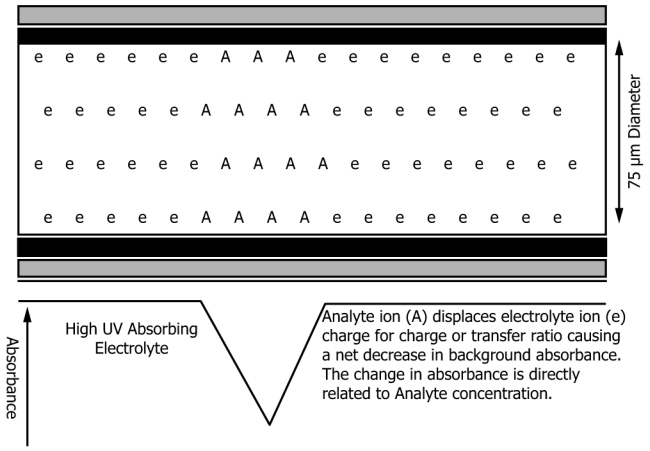


FIG. 9 Pictorial Diagram of Indirect UV Detection

6. Interferences

6.1 Analyte identification, quantitation, and possible comigration occur when one anion is in significant excess to other anions in the sample matrix. For two adjacent peaks, reliable quantitation can be achieved when the concentration differential is less than 100:1. As the resolution between two anion peaks increase so does the tolerated concentration differential. In samples containing 1000 mg/L Cl, 1 mg/L SO_4 can be resolved and quantitated, however, the high Cl will interfere with Br and NO_2 quantitation.

6.2 Dissolved carbonate, detected as HCO_3^{-1}, is an anion present in all aqueous samples, especially alkaline samples. Carbonate concentrations greater than 500 mg/L will interfere with PO_4 quantitation.

6.3 Monovalent organic acids, except for formate, and neutral organics commonly found in wastewater migrate later in the electropherogram, after carbonate, and do not interfere. Formate, a common organic acid found in environmental samples, migrates shortly after fluoride but before phosphate. Formate concentrations greater than 5 mg/L will interfere with fluoride identification and quantitation. Inclusion of 2 mg/L formate into the mixed anion working solution aids in fluoride and formate identification and quantitation.

6.4 Divalent organic acids usually found in wastewater migrate after phosphate. At high concentrations, greater than 10 mg/L, they may interfere with phosphate identification and quantitation.

6.5 Chlorate also migrates after phosphate and at concentrations greater than 10 mg/L will interfere with phosphate identification and quantitation. Inclusion of 5 mg/L chlorate into the mixed anion working solution aids in phosphate and chlorate identification and quantitation.

6.6 As analyte concentration increases, analyte peak shape becomes asymmetrical. If adjacent analyte peaks are not baseline resolved, the data system will drop a perpendicular between them to the baseline. This causes a decrease in peak area for both analyte peaks and a low bias for analyte amounts. For optimal quantitation, insure that adjacent peaks are fully resolved, if they are not, dilute the sample 1:1 with water.

7. Apparatus

7.1 *Capillary Ion Electrophoresis System*—~~the~~The system consists of the following components, as shown in Fig. 10 or equivalent:

7.1.1 *High Voltage Power Supply,* capable of generating voltage (potential) between 0 and minus 30 kV relative to ground with the capability working in a constant current mode.

7.1.2 *Covered Sample Carousel,* to prevent environmental contamination of the samples and electrolytes during a multisample batch analysis.

7.1.3 *Sample Introduction Mechanism,* capable of hydrostatic sampling technique, using gravity, positive pressure, or equivalent.

7.1.4 *Capillary Purge Mechanism,* to purge the capillary after every analysis with fresh electrolyte to eliminate any interference from the previous sample matrix, and to clean the capillary with other reagent, such as sodium hydroxide.

7.1.5 *UV Detector,* having the capability of monitoring 254 nm, or equivalent, with a time constant of 0.3 s.

7.1.6 *Fused Silica Capillary*—a 75 µm (inner diameter) ~~x~~x 375 µm (outer diameter) ~~x~~x 60 cm (length) having a polymer coating for flexibility, and noncoated section to act as the cell window for UV detection.[4,5]

[4] The sole source of supply of the apparatus known to the committee at this time is Waters Corp., 34 Maple St., Milford, MA 01757.

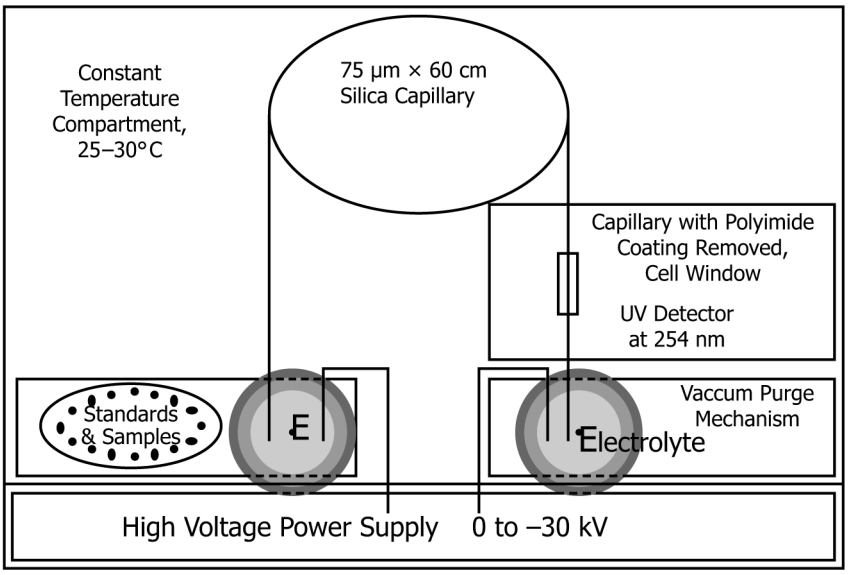


FIG. 10 General Hardware Schematic of a Capillary Ion Electrophoresis System

7.1.7 *Constant Temperature ~~Compartment—~~Compartment,* to keep the samples, capillary, and electrolytes at constant temperature.

7.2 *Data System—~~a~~A* computer system that can acquire data at 20 points/s minimum, express migration time in minutes to three decimal places, use midpoint of the analyte peak width, or center of gravity, to determine the analyte migration time, use normalized migration times with respect to a reference peak for qualitative identification, use time corrected peak area response for analyte quantitation, and express results in concentration units.[4]

NOTE 2—It is recommended that integrators or standard chromatographic data processing not be used with this test method.

7.3 *Anion Exchange Cartridges in the Hydroxide Form.*[4,6]

7.4 *Plastic Syringe,* 20-mL, disposable.

7.5 *Vacuum Filtration ~~Apparatus ,~~ Apparatus,* capable for filtering 100 mL of reagent through a ~~0.45 µm aqueous filter.~~0.45-µm aqueous filter (see 8.14).

8. Reagents and Materials

8.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the reagent grade specification of the 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 sufficient high purity to permit its use without lessening the performance or accuracy of the determination. Reagent chemicals shall be used for all tests.

NOTE 3—Calibration and detection limits of this test method are biased by the purity of the reagents.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I reagent water conforming or exceeding ~~specification~~Specification D1193. Freshly drawn water should be used for preparation of all stock and working standards, electrolytes, and solutions.[8] Performance and detection limits of this test method are limited by the purity of reagent water, especially TOC. 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 bias and precision of the test method.

8.3 *Reagent Blank*—Reagent water, or any other solution, used to preserve or dilute the sample.

8.4 *Individual Anion Solution, ~~Stock~~Stock:*

[5] If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[6] The sole source of supply of the apparatus known to the committee at this time is Alltech Associates, P/N 30254, 2051 Waukegan Rd., Deerfield, IL, 60015.

[7] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chem. 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 and National Formulary*, U.S. Pharmacopoeia Convention, Inc. (USPC), Rockville, Md.

[8] Although the reagent water may exceed Specification D1193, the reagent water needs to be periodically tested for bacterial contamination. Bacteria and their waste products may adversely affect system performance. As a guide, ASTM Type IA water specifies a total bacteria count of 10 colonies/L. Refer to Test Method F488 for analysis procedure.

NOTE 4—It is suggested that certified individual 1000 mg/L anion standards of appropriate known purity be purchased for use with this test method.

NOTE 5—All weights given are for anhydrous or dried salts. Reagent purity must be accounted for in order to calculate true value concentration. Certify against NIST traceable standards.

8.4.1 *Bromide Solution, Standard (1.0 mL = 1.00 mg Bromide)*—Dry approximately 0.5 g of sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Dissolve 0.128 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.2 *Chloride Solution, Standard (1.0 mL = 1.00 mg Chloride)*—Dry approximately 0.5 g of sodium chloride (NaCl) for 1 h at 100°C and cool in a desiccator. Dissolve 0.165 g of the dry salt in a 100 mL a volumetric flask with water, and fill to mark with water.

8.4.3 *Fluoride Solution, Standard (1.0 mL = 1.00 mg Fluoride)*—Dry approximately 0.5 g of sodium fluoride (NaF) for 1 h at 100°C and cool in a desiccator. Dissolve 0.221 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.4 *Formate Solution, Standard (1.0 mL = 1.00 mg Formate)*—Dissolve 0.151 g of sodium formate in a 100-mL volumetric flask with water, and fill to mark with water.

8.4.5 *Nitrate Solution, Standard (1.0 mL = 1.00 mg Nitrate)*—Dry approximately 0.5 g of sodium nitrate ($NaNO_3$) for 48 h at 105°C and cool in a desiccator. Dissolve 0.137 g of the dry salt in a 100-mL volumetric flask with water, and fill to mark with water.

8.4.6 *Nitrite Solution, Standard (1.0 mL = 1.00 mg Nitrite)*—Dry approximately 0.5 g of sodium nitrite ($NaNO_2$) for 24 h in a desiccator containing concentrated sulfuric acid. Dissolve 0.150 g of the dry salt in a 100-mL volumetric flask with water, and fill to mark with water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE 6—Nitrite is easily oxidized, especially in the presence of moisture. Use only fresh reagent.

NOTE 7—Prepare sterile bottles for storing nitrite solutions by heating for 1 h at 170°C in an air oven.

8.4.7 *Ortho-Phosphate Solution, Standard (1.0 mL = 1.00 mg o-Phosphate)*—Dissolve 0.150 g of anhydrous dibasic sodium phosphate (Na_2HPO_4) in a 100-mL volumetric flask with water, and fill to mark with water.

8.4.8 *Sulfate Solution, Standard (1.0 mL = 1.00 mg Sulfate)*—Dry approximately 0.5 g of anhydrous sodium sulfate (Na_2SO_4) for 1 h at 110°C and cool in a dessicator. Dissolve 0.148 g of the dry salt in a 100-mL volumetric flask with water, and fill to mark with water.

8.5 *Mixed Anion Solution, Working*—Prepare at least three different working standard concentrations for the analyte anions of interest bracketing the desired range of analysis, typically between 0.1 and 50 mg/L, and add 2 mg/L formate to all standards. Add an appropriate aliquot of Individual anion stock solution (see 8.4) to a prerinsed 100-mL volumetric flask, and dilute to 100 mL with water.

NOTE 8—Use 100 µL of Individual anion stock solution (see 8.4) per 100 mL for 1 mg/L anion.

NOTE 9—Anions of no interest may be omitted.

NOTE 10—The midrange mixed anion solution, working may be used for the determination of migration times and resolution described in 12.1.

8.6 *Calibration Verification Solution (CVS)*—A solution formulated by the laboratory of mixed analytes of known concentration prepared in water. The CVS solution must be prepared from a different source to the calibration standards.

8.7 *Performance Evaluation Solution (PES)*—A solution formulated by an independent source of mixed analytes of known concentration prepared in water. Ideally, the PES solution should be purchased from an independent source.

8.8 *Quality Control Solution (QCS)*—A solution of known analyte concentrations added to a synthetic sample matrix such as substitute wastewater that sufficiently challenges the test method.

8.9 *Buffer Solution (100 mM CHES/1 mM Calcium Gluconate)*—Dissolve 20.73 g of CHES (2-[N-Cyclohexylamino]-Ethane Sulfonic Acid) and 0.43 g of calcium gluconate in a 1-L volumetric flask with water, and dilute to 1 L with water. This concentrate may be stored in a capped glass or plastic container for up to one year.

8.10 *Chromate Concentrate Solution (100 mM Sodium Chromate)*—Dissolve 23.41 g of sodium chromate tetrahydrate ($Na_2CrO_4 \cdot 4\ H_2O$) in a 1-L volumetric flask with water, and dilute to 1 L with water. This concentrate may be stored in a capped glass or plastic container for up to one year.

8.11 *OFM Concentrate Solution (100 mM Tetradecyltrimethyl Ammonium Bromide)*—Dissolve 33.65 g of Tetradecyltrimethyl Ammonium Bromide (TTABr) in a 1-L volumetric flask with water, and dilute to 1 L with water. Store this solution in a capped glass or plastic container for up to one year.

NOTE 11—TTABr needs to be converted to the hydroxide form (TTAOH) for use with this test method. TTAOH is commercially available as 100 mM TTAOH, which is an equivalent substitute.

8.12 *Sodium Hydroxide Solution (500 mM Sodium Hydroxide)*—Dissolve 20 g of sodium hydroxide (NaOH) in a 1-L plastic volumetric flask with water, and dilute to 1 L with water.

8.13 *Electrolyte Solution, Working (4.7 mM Chromate/4 mM TTAOH/10 mM CHES/0.1 mM Calcium Gluconate)*[4,9]—Wash the anion exchange cartridge in the hydroxide form (see 7.3) using the 20-mL plastic syringe (see 7.4) with 10 mL of 500 mM NaOH (see 8.12) followed by 10 mL of water. Discard the washings. Slowly pass 4-mL of the 100 mM TTABr solution (see 8.11) through the cartridge into a 100-mL volumetric flask. Rinse the cartridge with 20 mL of water, adding the washing to the volumetric flask.

NOTE 12—The above procedure is used to convert the TTABr to TTAOH, which is used in the electrolyte. If using commercially available 100 mM TTAOH, the above conversion step is not necessary; substitute 4 mL of 100 mM TTAOH and continue below.

8.13.1 Into the 100-mL volumetric flask add 4.7 mL of chromate concentrate solution (see 8.10) and 10 mL of buffer solution (see 8.9). Mix and dilute to 100 mL with water. The natural pH of the electrolyte should be 9 ± 0.1. Filter and degas using the vacuum filtration apparatus. Store the any remaining electrolyte in a capped glass or plastic container at ambient temperature. The electrolyte is stable for one year.

8.14 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Precautions

9.1 Chemicals used in this test method are typical of many useful laboratory chemicals, reagents, and cleaning solutions, which can be hazardous if not handled properly. Refer to Guide D3856.

9.2 It is the responsibility of the user to prepare, handle, and dispose of chemical solutions in accordance with all applicable federal, state, and local regulations. (**Warning—**This capillary electrophoresis method uses high voltage as a means for separating the analyte anions, and can be hazardous if not used properly. Use only those instruments that have all proper safety features.)

10. Sampling

10.1 Collect samples in accordance with ~~Practice~~Practices D3370 or ~~Practice~~ D1066.

10.2 Rinse sample containers with sample and discard to eliminate any contamination from the container. Fill to overflowing and cap to exclude air.

10.3 Analyze samples, as soon as possible, after collection. For nitrite, nitrate, and phosphate refrigerate the sample at 4°C after collection. Warm to room temperature before dilution and analysis.

10.4 At the laboratory, filter samples containing suspended solids through a prerinsed ~~0.45 µm~~ 0.45-µm aqueous compatible membrane filter (8.14) before analysis.

10.5 If sample dilution is required to remain within the scope of this test method, dilute with water only.

11. Preparation of Apparatus

11.1 Set up the CE and data system according to the manufacturer's instructions.

11.2 Program the CE system to maintain a constant temperature of 25 ± 0.5°C, or 5°C above ambient laboratory temperature. Fill the electrolyte reservoirs with fresh chromate electrolyte working solution (see 8.13), and allow 10 minutes for thermal equilibration.

11.3 Condition a new ~~capability~~capillary (see 7.1.6) with 500 mM NaOH solution (see 8.12) for 5 minutes followed by water for 5 minutes. Purge the capillary with electrolyte (see 8.13) for 3 minutes.

11.4 Apply 15 kV of voltage and test for current. The current should be 14 ± 1 µA. If no current is observed, then there is a bubble, or blockage, or both, in the capillary. Degas the chromate electrolyte working solution and retry. If still no current, replace the capillary.

11.5 Set the UV detector to 254 nm detection, or equivalent. Zero the detector to 0.000 absorbance. UV offset is less than 0.1 AU.

11.6 Program the CE system for constant current of 14 µA.

11.7 Program the CE system for a hydrostatic sampling of 30 s. Approximately 37 nL of sample is siphoned into the capillary. Different sampling times may be used provided that the samples and standards are analyzed identically.

11.8 Program the CE system for 1 minute purge with the chromate electrolyte working solution between each analysis. Using a ~~15 psi~~ 103 kPa (15 psi) vacuum purge mechanism, one 60-cm capillary volume can be displaced in 30 s.

11.9 Program the data system for an acquisition rate of at least 20 points/s. Program the data system to identify analyte peaks based upon normalized migration time using Cl as the reference peak, and to quantitate analyte peak response using time corrected peak area.

[9] The sole source of supply of the apparatus known to the committee at this time is Waters Corp., 34 Maple St., Milford, MA 01757, as IonSelect High MobilityAnion Electrolyte, P/N 49385..

NOTE 13—Under the analysis conditions Cl is always the first peak in the electropherogram, and can be used as migration time reference peak.

12. Calibration

12.1 *Determination of Migration Times (Calibrate Daily)*—The migration time of an anion is dependent upon the electrolyte composition, pH, capillary surface and length, applied voltage, the ionic strength of the sample, and temperature. For every fresh electrolyte determine the analyte migration time, in min to the third decimal place, of the midrange mixed anion standard working solution (see 8.5), described in Section 11. Use the midpoint of analyte peak width as the determinant of analyte migration time.

NOTE 14—Analyte peak apex may be used as the migration time determinant, but potential analyte misidentification may result with asymmetrical peak shape at high analyte concentrations.

12.2 Analyze the blank (see 8.3) and at least three working mg/L solutions (see 8.5), using the set-up described in Section 11. For each anion concentration (X-axis) plot time corrected peak area response (Y-axis). Determine the best linear calibration line through the data points, or use the linear regression calibration routine (linear through zero) available in the data system.

NOTE 15—Do not use peak height for calibration. Peak area is directly related to migration time, that is, for the same analyte concentration, increasing migration time give increasing peak area.

12.2.1 The r^2 (coefficient of determination) values should be greater than 0.995; typical r^2 values obtained from the interlaboratory collaborative are given in Table A1.2.

12.3 Calibrate daily and with each change in electrolyte, and validate by analyzing the CVS solution (see 8.6) according to procedure in 16.4.

12.4 After validation of linear multiple point calibration, a single point calibration solution can be used between 0.1 and 50 mg/L for recalibration provided the quality control requirements in 16.4 are met.

13. Procedure

13.1 Dilute the sample, if necessary with water, to remain within the scope (see 1.2 and 1.3) and calibration of this test method. Refer to A1.5.1.

13.2 Analyze all blanks (see 8.3), standards (see 8.5), and samples as described in Section 11 using the quality control criteria described in 16.5 – 16.9. Refer to Figs. 1-6 for representative anion standard, detection limit standard, substitute wastewater, drinking water, and wastewater electropherograms.

13.3 Analyze all blanks, calibration standards, samples, and quality control solutions in singlicate.

13.3.1 *Optional*—Duplicate analyses are preferred due to short analysis times.

NOTE 16—Collaborative data was acquired, submitted and evaluated as the average of duplicate samplings.

13.4 After 20 sample analyses, or batch, analyze the QCS solution (see 8.8) If necessary, recalibrate using a single mixed anion standard working solution (see 8.5), and replace analyte migration time.

NOTE 17—A change in analyte migration time of the mixed anion standard working solution by more than ~~+5%~~ +5 % suggests that components in the previously analyzed sample matrices have contaminated the capillary surface. Continue but wash the capillary with NaOH solution (see 8.12) before the next change in electrolyte.

14. Calculation

14.1 Relate the time corrected peak area response for each analyte with the calibration curve generated in 12.2 to determine mg/L concentration of analyte anion. If the sample was diluted prior to analysis, then multiply mg/L anion by the dilution factor to obtain the original sample concentration, as follows:

$$\text{Original Sample mg/L Analyte} = (A \times SF) \quad (1)$$

where:

A = analyte concentration determined from the calibration curve, in mg/L, and
SF = scale or dilution factor.

15. Report Format

15.1 The sample analysis report should contain the sample name, analyte anion name, migration time reported to three decimal places, migration time ratio, peak area, time corrected peak area, sample dilution, and original solution analyte concentration.

15.1.1 *Optional*—Report analysis method parameters, date of sample data acquisition, and date of result processing for documentation and validation purposes.

16. Quality Control

16.1 Before this test method is applied to the analysis of unknown samples, the analyst should establish control according to procedures recommended in Practice D5847, and Guide D5810.