R08-5 amdt
R08-7 SDWA
R08-13 SDWA
PC 2 (Pet in 8-7)

From: <Fair.Pat@epamail.epa.gov>
To: MCCAMBM@ipcb.state.il.us
Date: 7/10/2008 7:46:26 AM
Subject: Re: Waters Methods

Mike,

Here's Waters 6508 method that was approved for drinking water. Aren't you limited to methods that are listed as approved for drinking water? Based on the info at the top of the method, I'm guessing this may now be an ASTM method. It was evaluated under the ATP program, so EPA was given the method prior to the ASTM process. I don't know this for sure and it will be something I investigate as we begin putting together our next Expedited Methods Approval FR action. (If it is the same method, we'll probably list it in Appendix A.)

(See attached file: Waters Method D 6508, Rev 2_EPA-HQ-OW-2003-0070-0063.pdf)

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Hope this helps,
Pat

"Mike McCambridge" <mccambridge@ipcb.state.il.us> 07/08/2008 03:29 PM

To: Pat Fair/CI/USEPA/US@EPA
cc:
Subject: Re: Waters Methods

Whatever you can do for me when you get back. I have continued to look into this today. I am convinced that Method 6500 added to SW-846 in Update IV in the end of 2007 is the method you have called "Method D6508" from Waters. See 73 Fed. Reg. 486 (Jan. 3, 2008); http://www.epa.gov/SW-846/pdfs/6500.pdf. If this is true, I will likely cite the SW-846 version of the method, since it is much easier to obtain than the method from Waters. As described, Waters initially acted like I spoke a foreign language when I asked for "Method D6508." As for

Method B-1011, it seems to distill down to me needing the title to the document in which the method appears.

Talk to you when you return.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 7/8/2008 2:18 PM >>>
Mike,

I'm working off site today, so I don't have access to the references I need to answer your questions. I should have copies of the methods that were added to 40 CFR 141 as part of the 2007 methods update rule. If these Waters methods are prior to that, I might not be able to help you. Unfortunately, I don't know who might have them other than Waters.

I'll see what I can find tomorrow and get back to you.

Pat

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To: Pat Fair/CI/USEPA/US@EPA
From: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
Date: 07/08/2008 01:57PM
Subject: Waters Methods

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The copy of Method B-1011 sent me by Waters is nearly identical to one that I found on the USEPA website. The only difference between the two is that the method from the USEPA website is headed "Waters." The document it appears to include pages 13 through 17 from some reference. It is undated, which means that I cannot use it for an incorporation by reference. Do you have a dated copy of Method B-1011 or a fuller copy of the posted reference that would include the date? It appears that the method is just one cited out of a fuller reference, and I should cite to that fuller reference by its own title. I will also approach Waters with this request.

Your rule cites "Waters Method D6508, Rev. 2," entitled "Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte." Waters sent me a document marked "Method 6500," "revision 0," and dated February 2007," and entitled "Dissolved Inorganic Anions In Aqueous Matrices By Capillary Ion Electrophoresis." That document appears to be Method 6500 from SW-846. Is "Waters Method D6508, Rev. 2" the same as Method 6500,

rev. 0 from SW-846? If so, why did USEPA cite this as "D6508"? If not, can you forward me a copy of Method D6508 or give me enough information to identify the method to Waters, that I might obtain a copy of the right method?

Michael J. McCambridge
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Mike McCambridge - Re: Waters Methods

From: <Fair.Pat@epamail.epa.gov>
To: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
Date: 7/10/2008 9:31 PM
Subject: Re: Waters Methods

Mike,

I haven't done a one-to-one check of the ASTM method against the Waters method, so I can't say for sure that they are the same. My comment was meant to let you know that I would do that BEFORE we issue the next set of method approvals. If they are the same or only have insignificant differences, then we will include the ASTM method as an approved method. Legally, it won't be an approved drinking water method until we publish a notice in the Federal Register.

It's my opinion that if the Waters methods aren't easily available from Waters, then you can easily justify not including them in your state regulations. Our ATP coordinator wasn't able to find a copy of the nitrate/nitrite method in his files. However, he is still checking on it.

I have the GA Tech method. I can email it to you on Monday. If you need it before then, you can go to the e-docket for the 2007 Methods Update Rule. I know the method is in the docket, because I put it there and it is available for download through the docket site.

I will see if I can find out how we should be referencing the GA Tech method. I thought our information was correct when we went final on the rule.

Hope this helps.
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> To: Pat Fair/CI/USEPA/US@EPA
> From: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
> Date: 07/10/2008 06:07PM
> Subject: Re: Waters Methods
>
> Thank you. That nails it down. I will cite it as an ASTM method.
>
> I have another method problem. I have been trying to obtain a copy of that Ra-226/Ra-228 method by gamma-ray spectometry developed by Georgia Insitute of Technology. The "Environmental Resources Center" has been disbanned or something, so that the number at 40 C.F.R. 141.74 is no longer valid. It may have become the Environmental Radiation Center or something. I have placed several calls and e-mails with Bernd Kahn and the Center in an attmpt to locate the method, but no luck so far.
>
> Can you help on this one too?

Michael J. McCambridge
Attorney
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>>> <Fair.Pat@epamail.epa.gov> 7/10/2008 7:43 AM >>>
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07/08/2008 03:29

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Michael J. McCambridge
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OW-2003-0070-0063 B1

This ASTM D6508, Rev2 method document has been reviewed by EPA Office of Drinking Water and Wastewater for EPA Tier 3 approval. Added updated QC criteria based upon statistical analysis by Dyncorp.

ATP Case #:	**N00-0002 and D00-0002**
Draft #:	**Second draft with EPA Modifications: ASTM D6508, Rev 2**
Date:	**December 2000**
Method Author:	**Jim Krol**
Telephone:	**508/482-2131**
FAX:	**508/482-3625**

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

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 Fig. 1 through 6.

1.2 The test method uses a chromate-based electrolyte and indirect UV detection at 254 nm. It is applicable for the determination of inorganic anions in the range of 0.2 to 50 mg/L except for fluoride whose range is 0.2 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 P&B 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 This method does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see sec. 9.

2 Referenced Documents

2.1 ASTM Standards

D 1066 Practice for Sampling Steam[1]
D 1129 Terminology Relating to Water[1]
D 1193 Specification for Reagent Water[1]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[1]
D 3370 Practices for Sampling Water[1]
D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[1]
D 5810 Standard Practice of Spiking Samples[1]
D 5847 Standard Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[1]
D 5905 Standard Specification for Substitute Wastewater[1]
F 488 Test Method for Total Bacterial Count in Water[2]

2.2 EPA 40 CFR Ch.1 (7-1-92 Edition), Pt 136, App. B, page 565 – 567: Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11.

2.3 Draft Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water, dated Mar 1999, EPA-821-B-98-003.

3 Terminology

3.1 Definitions - For definitions of terms used in this test method, refer to Terminology D1129.

3.2 Description of Terms Specific to This Test Standard:

3.2.1 Capillary Ion Electrophoresis -- an electrophoretic technique in which an UV absorbing electrolyte is placed in a 50 μm to 75 μm fused silica capillary. 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 their 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 -- 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. 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) -- 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) -- a cationic quaternary amine in the electrolyte that dynamically coats the negatively charged silica wall giving it a net positive charge. This 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 effects anion selectivity and resolution. See Fig. 7.

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1) Annual Book of ASTM Standards, Vol. 11.01
2) Annual Book of ASTM Standards, Vol. 11.02

3.2.5 Electrophoretic Mobility -- the specific velocity of a charged analyte in the electrolyte under specific electroosmotic flow conditions. 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.

3.2.6 Electropherogram -- a graphical presentation of UV detector response versus time of analysis; the x axis is migration time which is used to qualitatively identify the anion, and the y axis is UV response which can be converted to time corrected peak area for quantitation.

3.2.7 Hydrostatic Sampling -- 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. Nanolitres of sample are siphoned into the capillary by differential head pressure and gravity.

3.2.8 Indirect UV Detection -- 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. 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 -- CIE peaks are typically asymmetrical with the peak apex shifting with increasing concentration, and peak apex may not be indicative of true analyte migration time. 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 -- the time required for a specific analyte to migrate through the capillary to the detector. The migration time in capillary ion electrophoresis is analogous to retention time in chromatography.

3.2.11 Time Corrected Peak Area -- normalized peak area; peak area divided by migration time. CE principles state that peak area is dependent upon migration time, i.e. 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 Fig. 7 through Fig. 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 Fig. 7 and 8.

4.2 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 is 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 automatically vacuum purged by the system of any remaining sample, and replenished with fresh electrolyte. The system is now 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 min with sufficient sensitivity for drinking water, and wastewater applications. Time between samplings is less than 7 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.

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.

6.7 Samples containing high levels of TOC, total organic carbon, may effect the observed analyte migration times. The TOC binds to the capillary surface decreasing the EOF and increasing analyte migration times. Refer to Figure 7. However, the change in EOF does not effect analyte selectivity. Analytes are identified using normalized analyte migration times with respect to a reference peak, chloride, always the first peak in the electropherogram. The surface can be regenerated with a 5 minute wash with 500 mM NaOH.

7 .Apparatus

7.1 Capillary Ion Electrophoresis System -- the system consists of the following components, as shown in Fig. 10, or equivalent:[3]

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 multi-sample 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 reagents, 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 375 μm (outer diameter) x 60 cm (length) having a polymer coating for flexibility, and a non-coated section to act as the cell window for UV detection.[3]

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

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3) Available from Waters, 34 Maple St., Milford, Ma., 01757, 800/252-4752.

7.2 Data System -- computer system that can acquire data at 20 points per second minimum, express migration time in minutes to 3 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.[3]

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]

7.4 Plastic Syringe -- 20 mL, Disposable.

7.5 Vacuum Filtration Apparatus -- capable for filtering 100 mL of reagent through a 0.45 µm aqueous filter.

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.[5] 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 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 D1193. Freshly drawn water should be used for preparation of all stock and working standards, electrolytes, and solutions.[6] Performance and detection limits of this method are limited by the purity of reagent water, especially TOC.

8.3 Reagent Blank: Reagent Water or any other solution used to preserve or dilute the sample.

8.4 Individual Anion Solution, Stock:

Note 4: It is suggested that certified individual 1000 mg/L anion standards be purchased for use with this test method.

Note 5: All weights given are for anhydrous or dried salts. Must account for reagent purity 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.

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4) Available from Alltech Associates, P/N 30254, 2051 Waukegan Rd, Deerfield IL., 60015, 847/948-8600.

5) 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.

6) Although the reagent water may exceed D1193 specification, 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 F 488 for analysis procedure.

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 desiccator. 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 a 0.2 mg/L and at least 3 different working standards concentrations for the analyte anions of interest bracketing the desired range of analysis, typically between 0.2 and 50 mg/L, and add 2 mg/L formate to all standards. Add an appropriate aliquot of Individual Anion Stock Solution (8.4) to a pre-rinsed 100 mL volumetric flask, and dilute to 100 mL with water.

Note 8: Use 100 µL of Individual Anion Stock Solution (8.4) per 100 mL for 1 mg/L anion.

Note 9: Anions of no interest may be omitted.

Note 10: The mid-range 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 1year.

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 1 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 1 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 [7] 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) [8]: Wash the anion exchange cartridge in the hydroxide form (7.3) using the 20 mL plastic syringe (7.4) with 10 mL of 500 mM NaOH (8.12) followed by 10 mL of water. Discard the washings. Slowly pass 4 mL of the 100 mM TTABr Solution (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 0.5 mL of 100 mM TTAOH and continue below

Into the 100 mL volumetric flask add 4.7 mL of Chromate Concentrate Solution (8.10) and 10 mL of Buffer solution (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 1 year.

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7) Available from Waters Corp. as IonSelect 100mM OFM Hydroxide Concentrate, 100 mM TTAOH, P/N 49387.
8) Availiable from Waters Corp. as IonSelect High Mobility Anion Electrolyte, P/N 49385.

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 D 3856.

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.

9.3 **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 D 3370.

10.2 Rinse samples 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 lab, filter samples containing suspended solids through a pre-rinsed 0.45 μm aqueous compatible membrane filter 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 (8.13), and allow 10 min for thermal equilibration.

11.3 Condition a new capillary (7.1.6) with 500 mM NaOH Solution (8.12) for 5 min followed by water for 5 min. Purge the capillary with electrolyte (8.13) for 3 min.

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 and/or blockage 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 then 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 37nL 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 a 1 min purge with the chromate electrolyte working solution between each analysis. Using a 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 per 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.

Note 13: Under the analysis conditions Cl is always the first peak in the electropherogram, and can be used as a 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 mid-range mixed anion standard working solution (8.5), described in Sec 11. Use the mid-point 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 (8.3), a 0.2 mg/L, and at least 3 working mg/L solutions (8.5), using the set-up described in sec 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 (1/X Weighting and 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, i.e. for the same analyte concentration, increasing migration time gives increasing peak area.

Note 16: EPA recommends calibration at the minimum concentration of 0.2 mg/L plus 3 additional points.

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 A2.

12.3 Calibrate daily and with each change in electrolyte, and validate by analyzing the CVS solution (8.6) according to procedure in Sec16.4.

12.4 After validation of linear multiple point calibration, a single point calibration solution can be used between 0.2 and 50 mg/L for recalibration provided the quality control requirements in Sec 16.4 are met.

13 Procedure

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

13.2 Analyze all blanks (8.3), standards (8.5), and samples as described in Sec 11 using the quality control criteria described in Sec 16.5 to 16.9. Refer to Fig. 1 through 5 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. Perform at least one matrix spike analysis in duplicate as part of the QC protocol, Sec 16.7. Optional: Duplicate analyses are preferred due to short analysis times.

Note 17: 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 (8.8). If necessary, recalibrate using a single mixed anion standard working solution (8.5), and replace analyte migration time.

Note 18: A change in analyte migration time of the mixed anion standard working solution by more than +5% suggests that components in the previously analyzed sample matrices have contaminated the capillary surface. Refer to sec 6.7. Continue but wash the capillary with NaOH solution (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 section 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:

Original Sample mg/L Analyte = (A x SF) where;
A = analyte concentration determined from the calibration curve, in mg/L,
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 3 decimal places, migration time ratio, peak area, time corrected peak area, sample dilution, and original solution analyte concentration. 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 quality control according to procedures recommended in Practice D5847, and Guide D5810.

16.2 The laboratory using this test must perform an initial demonstration of laboratory capability according to procedures outlined in Standard Practice D5847, and Appendix C.

Note 19: Certified Performance Evaluation Solutions (PES) and QC Solutions (QCS and CVS) are commercially available, and recommended.

16.3 Initial Demonstration of Performance: Analyze seven replicates of a Performance Evaluation Solution (PES, 8.7). Calculate analyte concentration mean and standard deviation of the seven replicates and compare to the precision and Initial %Recovery for the analyte in reagent water given in Table 8.

16.3.1 Repeat the 7 replicate analysis protocol before using a freshly prepared QVS solution (8.6) and QCS solution (8.8) for the first time. Calculate the standard deviation and compare with previous results using the student t-test. If no significant difference is noted then use the combined standard deviation to determine the QC limits, for the QVS and QCS solutions.

16.4 Calibration Verification: After calibration, verify the calibration linearity and acceptable instrument performance using a Calibration Verification Solution (8.6) treated as an unknown. If the determined CVS concentrations (8.6) are not within ± 3 standard deviations of the known true values as described in 16.3.1, the calibration solutions may be out of control. Reanalyze, and if analyte concentration still falls outside the acceptable limits, fresh calibration solutions (8.5) are required. Successful CVS analyte concentration must be confirmed after recalibration before continuing with the Test Method.

16.5 Analyze a reagent blank (8.3) with each batch to check for contamination introduced by the laboratory or use of the Test Method.

16.6 Quality Control Solution: Analyze one QCS (8.8) after 20 samples, or batch. The analyte concentrations for the QCS should fall within the lower limit (LL) and upper limits (UL) given in Table 8.

16.7 Matrix Spike Recovery: One Matrix Spike (MS) must be analyzed in duplicate with each batch of samples to test method recovery and relative %difference between them. Spike a portion of one sample from each batch with a known concentration of analyte, prepared in accordance with Guide D3856. The % recovery of the spike should fall within the MS/MSD lower and upper limits, and the Relative %Difference given in Table 8 for the appropriate sample matrix. If it does not, an interference may be present and the data for the set of similar samples matrices must be qualified with a warning that the data are suspect, or an alternate test method should be used. Refer to Guide D5810.

16.7.1 If the known analyte concentration is between 15 and 50 mg/L, then spike the sample solution to increase analyte concentration by 50%.

16.7.2 If the known analyte concentration is between 2 mg/L and 15 mg/L, then spike the sample solution to increase analyte concentration by 100%, but not less than 2 mg/L.

16.7.3 If the known analyte concentration is less than 2 mg/L, then spike the sample solution with 1 mg/L, 5 times the ML.

16.7.4 Calculate the percent recovery of the spike using the following formula:

$$\% \text{ Recovery} = 100\,[A\,(V_S + V) - B\,V_S] / C\,V \quad \text{where}$$

A = Analyte Concentration (mg/L) in Spiked Sample
B = Analyte Concentration (mg/L) in Unspiked Sample
C = Concentration (mg/L) of Analyte in Spiking Solution
V_S = Volume (mL) of Sample Used
V = Volume (mL) Added with Spike.

Evaluate performance according to Practice D5847.

16.8 Method Precision: One unknown sample should be analyzed in triplicate with each batch to test method precision. Calculate the standard deviation and use the F-Test to compare with the single operator precision given in Tables 1 through 7 for the equivalent analyte concentration and matrix type. Evaluate performance according to Practice D5847.

16.9 The laboratory may perform additional quality control as desired or appropriate.

17 Precision and Bias

17.1 The precision and bias data presented in this test method meet the requirements of Practice 2777-98, and are given in Tables 1 through 7. The full Research Report, RR# D19-1165, can be obtained from ASTM Headquarters.

17.2 This test method interlaboratory collaborative was performed by 11 laboratories using one operator each. Four Youden Pair spike concentrations for the 7 analytes anions yielding 8 analyte concentration levels. Test data was submitted for 11 Reagent Waters, 11 Substitute Wastewaters, 15 Drinking Waters, and 13 Wastewater sample matrices.

17.3 All data given in this method was quantitated using non-weighted linear calibration through zero, except where noted.

17.4 The precision, bias, and matrix recovery of this test method per anion analyte in the 4 tested sample matrices are based upon the analyte true value, calculated using weight, volume, and purity. True value spiking solution concentrations are given in Table A4.

17.5 The bias and matrix recovery statements for less than 2 mg/L of chloride, sulfate, and nitrate in naturally occurring sample matrices may be misleading due to spiking of small analyte concentration into a high naturally occurring analyte concentration observed with the matrix blank. The commonly occurring analyte concentrations observed in the sample matrix blanks for the naturally occurring tested matrices are given in Table A5.

17.6 The high nitrate bias and %recovery noted for the 0.5 mg/L NO_3 spike solution are attributed to the spiking solution containing 50 mg/L nitrite and 0.5 mg/L nitrate. Refer to Appendix Table A4, Solution 3. Some of the nitrite converted to nitrate prior to analysis. Similar NO_X conversion effect is observed with the 2 mg/L nitrate and 2 mg/L nitrite spike, Solution 7.

17.7 All collaborative participants used the premade Chromate electrolyte, (IonSelect High Mobility Anion Electrolyte, available from Waters Corp.) Ten laboratories used a Waters CIA Analyzer with Millennium Data Processing Software, and one laboratory used a Agilent CE System with Diode Array Detector that provided equivalent results, although different sampling and detection conditions were necessary for equivalent performance.
Note 20: Refer to reference B1.16 and Agilent (the former HP Company) website for recommended operating conditions.

18 Key Words

Anion
Capillary Electrophoresis
Drinking Water
Ion Analysis
Reagent Water
Substitute Wastewater
Wastewater

Appendix A
Mandatory Information

A1.1 All data presented in the following Tables conform and exceed the requirements of D2777-98. Data from eleven reagent waters, eleven substitute wastewater, fifteen Drinking Water, and thirteen wastewater sample matrices, were tested using a set of 4 Youden Pair concentrations for 7 analyte anions. All submitted individual data points are the average of duplicate samplings.

A1.2 Calibration Linearity

A1.2.1 All laboratories used a provided set of 4 certified, mixed anion calibration solutions in concentrations between 0.5 mg/L and 50 mg/L, formulated in random concentrations given in Table A1. They were prepared from certified, individual 1000 mg/L Stock Standards obtained from APG, Inc, Belpre, Ohio. No dilution was necessary.

Table A1: Collaborative Calibration Standard, mg/L Concentrations

Analyte Anion	Standard 1	Standard 2	Standard 3	Standard 4
Chloride	50	25	0.5	10
Bromide	0.5	25	10	50
Nitrite	25	0.5	50	10
Sulfate	10	25	0.5	50
Nitrate	25	0.5	50	10
Fluoride	5	0.5	10	25
Phosphate	50	25	0.5	10

A1.2.2 A Linear Through Zero, no weighting regression was used to calculate the calibration curve. The range coefficient of determination (r^2) values obtained from the collaborative is shown in Table A2

Table A2: Expected Range of (r^2) Coefficient of Determination

Anion / r^2	Average, n=29	Lowest	Highest
Chloride	0.99987	0.99959	0.99997
Bromide	0.99953	0.99878	0.99996
Nitrite	0.99983	0.99961	0.99999
Sulfate	0.99976	0.99901	0.99999
Nitrate	0.99957	0.99840	0.99999
Fluoride	0.99972	0.99797	0.99999
Phosphate	0.99982	0.99942	0.99999

A1.2.3 EPA requires that 1/X weighting be used for calibration. The P & B data were derived using unweighted calibration. Table A2a shows there is no significant difference in r^2 linearity between these 2 calibration routines.

Table A2a Coefficient of Determination r^2 from a Single Calibration

Analyte Anion	No Weighted Calibration	1/x Weighted Calibration
Chloride	0.99994	0.99996
Bromide	0.99942	0.99923
Nitrite	0.99975	0.99981
Sulfate	0.99971	0.99974
Nitrate	0.99975	0.99974
Fluoride	0.99986	0.99967
Phosphate	0.99999	0.99999

A1.3 Quality Control Solution Preparation

A1.3.1 The Quality Control Solution (QCS) was also used as the Calibration Verification Solution (CVS).

A1.3.2 Quality Control Solution (QCS) was manufactured, analyzed using ion chromatography, and certified by APG as 100X concentrate, to replicate typical Drinking Water concentrations. Required 1:100 dilution with water before analysis. The QCS analyte concentrations, required control limits, and interlaboratory determined control limits based upon n# analyses are given in Table A3.

Table A3: Quality Control Acceptance Limits

Analyte Anion	True Value mg/L	Certified Value mg/L	Required 99% Confidence Interval	Determined QCS Mean ± Std Dev, n = 82
Chloride	48.68	48.61 ± 0.12	43.99 – 52.96	47.64 ±1.53
Bromide	0.00	0.00	0.00	0.00
Nitrite	2.87	2.90 ± 0.07	2.39 – 3.26	2.88 ± 0.19
Sulfate	35.69	35.63 ± 0.25	29.54 – 40.53	35.02 ± 1.21
Nitrate	15.76	15.78 ± 0.15	12.80 – 18.39	15.33 ± 4.35
Fluoride	1.69	1.68 ± 0.01	1.49 – 1.87	1.67 ± 0.09
Phosphate	5.47	5.55 ± 0.12	4.78 – 6.20	5.58 ± 0.28

A1.3.3 A single day's QCS was reprocessed using a 1/X weighting linear calibration and remained within the QC Acceptance Limits.

Table A3a QC Standard Results: Reprocessed Using 1/x Calibration

Analyte Anion	No Weighted Calibration	1/x Weighted Calibration	QC Acceptance 99%Conf Interval
Chloride	48.64 ± 1.06	48.77 ± 1.07	43.99 – 52.96
Nitrite	2.93 ± .03	2.82 ± .03	2.39 – 3.26
Sulfate	34.49 ± .79	34.64 ± .79	29.54 – 40.53
Nitrate	15.28 ± .15	15.23 ± .18	12.80 – 18.39
Fluoride	1.74 ± .02	1.63 ± .02	1.49 – 1.87
Phosphate	5.75 ± .15	5.77 ± .15	4.78 – 6.20

A1.4 Youden Pair Spiking Solution Preparation

A1.4.1 Eight mixed anion, 100X concentrate, spiking solutions were prepared in accordance with Sec 8.3 (Reagents and Materials) of the test method using anhydrous sodium salts. The mg/L concentrations of the eight standards followed the approved Youden Pair design - 0.5 & 0.7, 2 & 3, 15 & 20, 40 & 50 mg/l for all anions except fluoride, which is 0.5 & 0.7, 2 & 3, 7& 10, 20 & 25mg/L. The analyte true value concentrations were randomized among the eight spiking solutions as described in Table A4.

A1.4.2 A ninth solution containing approximately 10 mg/L of each analyte was diluted 1:50 with water, and was used for method detection limit calculations.

Table A4: True Value Youden Pair Spiking mg/L Concentrations

Anion / TV	1	2	3	4	5	6	7	8	9
Chloride	0.71	2.00	2.98	14.92	39.81	19.91	49.76	0.50	10.20
Bromide	2.00	3.01	14.93	39.81	19.91	49.77	0.70	0.51	10.49
Nitrite	2.98	39.61	19.81	14.86	49.52	0.50	2.00	0.70	9.94
Sulfate	39.60	49.51	0.49	0.70	1.98	2.98	14.86	19.81	10.23
Nitrate	14.92	19.19	39.87	49.78	0.50	0.70	2.00	2.98	10.35
Fluoride	2.00	0.71	0.50	3.00	9.99	6.99	19.98	24.99	10.40
Phosphate	49.51	39.60	19.90	0.50	2.98	1.99	0.69	14.86	10.48

These solutions, kept at ambient temperature, were analyzed before and during the collaborative to monitor for accuracy and stability. The mg/L True Value in was used to determine bias, matrix recovery, and the single operator and interlaboratory precision in the P & B tables per the requirement of D 2777.

Solution 3 and 7 exhibited some conversion of nitrite to nitrate before analysis. This conversion is evident in the bias and % Recovery for 0.5 mg/L and 2 mg/l nitrite and nitrate.

A1.5 Sample Matrix Preparation

A1.5.1 All participating laboratories provided and tested reagent water, substitute wastewater, naturally occurring drinking water, and naturally occurring wastewater. Before matrix spiking with the Youden Pair solutions, the sample matrix was evaluated, then appropriately diluted to give the highest anion concentration below 50 mg/L. The diluted sample matrix was used to dilute each Youden Pair spiking solution 1:100.

A1.5.2 Reagent Water was used as-is. Substitute wastewater was diluted 1:20 with water. Naturally occurring drinking water was used as-is or diluted 1:5 with water. Naturally occurring wastewater was diluted between 1:3 and 1:20, except one which required a 1:1000 dilution due to high chloride.

A1.5.3 Due to the anion content of the naturally occurring drinking water and "real" wastewater matrices, some of the reported spike matrix results exceeded the scope of this test method. Linearity and matrix recovery data obtained from the collaborative indicated that these data are acceptable, and extended the useful range of this test method.

A1.5.4 Due to the anion content of the naturally occurring sample matrices given in Table A5, the low concentration bias and recovery may be misleading because of spiking a low anion concentration increment into a large naturally occurring concentration of the same anion.

Table A5: Blank Analyte Concentrations for Naturally Occurring Sample Matrices

Data in mg/L	Chloride	Sulfate	Nitrate
Drinking Water	0.7 to 41.9	0.5 to 33.6	0.2 to 6.5
Substitute Wastewater	20.5 to 25.5	3.2 to 4.0	Not Detected
"Real" Wastewater	0.9 to 43.4	0.5 to 50.4	0.3 to 23.0

A1.6 Test Method Detection Limits:

A1.6.1 Spiking Solution #9, containing 10 mg/L of each analyte, was diluted 1:50 with water and was used for detection limit calculations. Ten laboratories performed seven replicate samplings, and the mean and standard deviation from each laboratory was calculated. The mean time corrected peak area response for the 7 replicates was given the true value of the solution #9, and from a simple proportion, the standard deviation was calculated as mg/L.

$$\text{Std Dev, mg/L} = \frac{(\text{True Value Conc Sol'n \#9, mg/L})(\text{Response Std Dev})}{\text{Ave Response of Sol'n \#9}}$$

A1.6.2 Method detection limits (MDL) were derived using "pooled" EPA protocol and the student t-test at 6 degrees of freedom, as follows;
The method detection limit (MDL) =(3.14)(Std Dev, mg/L).

A1.6.3 The upper and lower confidence limits were calculated as;
95% Confidence Interval: LCL (Lower Confidence Limit) = 0.64 x MDL
UCL (Upper Confidence Limit) = 2.20 x MDL

A1.6.4 Method Detection Limits are given in Table A6.

Table A6: Method Detection Limits

Anion	mg/L Solution Concentration	Method Detection MDL, mg/L	95% Confidence Interval mg/L
Chloride	0.204	0.075	0.048 to 0.165
Bromide	0.210	0.120	0.077 to 0.264
Nitrite	0.199	0.103	0.066 to 0.227
Sulfate	0.205	0.065	0.042 to 0.143
Nitrate	0.207	0.076	0.049 to 0.167
Fluoride	0.208	0.032	0.020 to 0.070
Phosphate	0.210	0.097	0.062 to 0.213

Table 1
Precision, Bias, and Matrix Recovery for Chloride

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	9	0.50	0.55	0.05	110.0	0.11	19.8		
Water	10	0.71	0.69	-0.02	97.2	0.08	11.5	0.05	7.5
	10	2.00	1.97	-0.03	98.5	0.14	6.8		
	9	2.98	2.97	-0.01	99.7	0.11	3.8	0.05	2.1
	10	14.92	14.76	-0.16	98.9	0.61	4.2		
	10	19.91	19.81	-0.10	99.5	0.81	4.1	0.48	2.8
	10	39.81	38.58	-1.23	96.9	1.43	3.7		
	10	49.76	48.70	-1.06	97.9	1.94	4.0	1.36	3.1
Substitute	9	0.50	0.46	-0.04	92.0	0.51	111.1		
Wastewater	9	0.71	0.43	-0.28	60.6	0.69	160.7	0.42	93.8
	9	2.00	1.52	-0.48	76.0	0.68	45.0		
	9	2.98	2.58	-0.40	86.6	0.63	24.5	0.50	24.3
	9	14.92	14.29	-0.63	95.8	1.02	7.1		
	9	19.91	18.93	-0.98	95.1	1.24	6.6	0.60	3.6
	9	39.81	37.34	-2.47	93.8	5.44	14.6		
	9	49.76	47.54	-2.22	95.5	3.13	6.6	4.43	10.4
Drinking	12	0.50	0.63	0.13	126.0	0.67	106.1		
Water	12	0.71	0.75	0.04	105.6	0.34	45.5	0.40	57.2
	12	2.00	2.15	0.15	107.5	0.51	23.6		
	12	2.98	2.95	-0.03	99.0	0.39	13.1	0.47	18.5
	12	14.92	14.54	-0.38	97.5	0.71	4.9		
	12	19.91	19.09	-0.82	95.9	1.11	5.8	0.37	2.2
	12	39.81	38.38	-1.43	96.4	1.56	4.1		
		49.76	47.97	-1.79	96.4	2.19	4.6	1.26	3.9
"Real"	9	0.50	0.42	-0.08	84.0	0.34	81.0		
Wastewater	10	0.71	0.47	-0.24	66.2	0.34	72.6	0.26	59.3
	10	2.00	1.56	-0.44	78.0	0.51	32.7		
	9	2.98	2.78	-0.20	93.3	0.19	6.8	0.37	17.3
	10	14.92	14.29	-0.63	95.8	0.63	4.4		
	10	19.91	18.83	-1.08	94.6	0.78	4.1	0.46	2.8
	9	39.81	37.01	-2.80	93.0	2.78	7.5		
	10	49.76	48.24	-1.52	96.9	3.15	6.5	2.54	6.0

Table 2
Precision, Bias, and Matrix Recovery for Bromide

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.51	0.60	0.09	117.6	0.19	31.0		
Water	10	0.70	0.83	0.13	118.6	0.23	28.2	0.10	14.6
	10	2.00	2.06	0.06	103.0	0.14	6.6		
	10	3.01	2.88	-0.13	95.7	0.23	7.9	0.15	6.3
	10	14.93	15.00	0.07	100.5	0.58	3.9		
	10	19.91	19.32	-0.59	97.0	0.97	5.0	0.75	4.4
	10	39.81	39.66	-0.15	99.6	1.24	3.1		
	10	49.77	50.04	0.27	100.5	2.94	5.9	1.61	3.6
Substitute	9	0.51	0.67	0.16	131.4	0.19	28.8		
Wastewater	9	0.70	0.96	0.26	137.1	0.21	21.8	0.08	9.3
	9	2.00	2.14	0.14	107.0	0.22	10.2		
	9	3.01	2.72	-0.29	90.4	0.35	12.8	0.17	7.0
	9	14.93	14.70	-0.23	98.5	0.58	3.9		
	9	19.91	18.91	-1.00	95.0	2.62	13.8	1.63	9.7
	9	39.81	38.76	-1.05	97.4	1.11	2.9		
	9	49.77	48.81	-0.96	98.1	1.52	3.1	0.48	1.1
Drinking	13	0.51	0.58	0.07	113.7	0.25	43.4		
Water	13	0.70	0.83	0.13	118.6	0.22	26.5	0.14	19.9
	13	2.00	1.98	-0.02	99.0	0.25	12.5		
	13	3.01	2.56	-0.45	85.0	0.25	9.7	0.15	6.8
	13	14.93	14.63	-0.30	98.0	0.50	3.4		
	13	19.91	19.22	-0.69	96.5	1.10	5.7	0.77	4.6
	13	39.81	38.97	-0.84	97.9	1.99	5.1		
	13	49.77	48.74	-1.03	97.9	1.49	3.1	1.13	2.6
"Real"	11	0.51	0.59	0.08	115.7	0.11	19.3		
Wastewater	12	0.70	0.78	0.08	111.4	0.19	24.4	0.10	14.0
	11	2.00	2.08	0.08	104.0	0.13	6.3		
	12	3.01	2.70	-0.31	89.7	0.41	15.1	0.27	11.5
	12	14.93	15.16	0.23	101.5	0.90	6.0		
	11	19.91	19.46	-0.45	97.7	1.63	8.4	1.09	6.3
	12	39.81	40.24	0.43	101.1	2.27	5.7		
	12	49.77	49.97	0.20	100.4	2.52	5.0	0.91	2.0

Table 3
Precision, Bias, and Matrix Recovery for Nitrite

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	9	0.50	0.62	0.12	124.0	0.16	26.1		
Water	9	0.70	0.72	0.02	102.9	0.08	10.5	0.05	7.1
	10	2.00	1.31	-0.69	65.5	0.25	19.2		
	10	2.98	3.11	0.13	104.4	0.17	5.4	0.13	6.0
	10	14.86	14.70	-0.16	98.9	0.47	3.2		
	10	19.81	19.88	0.07	100.4	0.70	3.5	0.27	1.5
	10	39.61	39.90	0.29	100.7	0.88	2.2		
	10	49.52	48.24	-1.28	97.4	1.34	2.8	1.25	2.8
Substitute	9	0.50	0.37	-0.13	74.0	0.22	59.7		
Wastewater	9	0.70	0.59	-0.11	84.3	0.28	48.1	0.21	43.2
	10	2.00	1.25	-0.75	62.5	0.38	30.8		
	9	2.98	2.62	-0.36	87.9	0.82	31.4	0.43	22.1
	9	14.86	14.40	-0.46	96.9	0.58	4.0		
	10	19.81	19.50	-0.31	98.4	1.66	8.5	0.81	4.8
	10	39.61	39.97	0.36	100.9	2.02	5.0		
	9	49.52	49.09	-0.43	99.1	3.03	6.2	2.11	4.7
Drinking	11	0.50	0.52	0.02	104.0	0.08	14.4		
Water	12	0.70	0.74	0.04	105.7	0.17	23.3	0.09	13.5
	12	2.00	1.30	-0.70	65.0	0.21	15.9		
	12	2.98	2.97	-0.01	99.7	0.14	4.6	0.16	7.4
	11	14.86	14.60	-0.26	98.3	0.40	2.8		
	11	19.81	19.82	0.01	100.1	0.59	3.0	0.26	1.5
	11	39.61	39.35	-0.26	99.3	0.99	2.5		
	12	49.52	49.14	-0.38	99.2	1.93	3.9	0.64	1.5
"Real"	9	0.50	0.55	0.05	110.0	0.13	24.5		
Wastewater	10	0.70	0.73	0.03	104.3	0.24	32.9	0.07	10.8
	9	2.00	1.27	-0.73	63.5	0.18	14.2		
	10	2.98	2.99	0.01	100.3	0.19	6.2	0.15	7.0
	10	14.86	14.55	-0.31	97.9	0.46	3.1		
	10	19.81	19.68	-0.13	99.3	0.71	3.6	0.38	2.2
	9	39.61	39.21	-0.40	99.0	1.03	2.6		
	9	49.52	47.27	-2.25	95.5	3.50	7.4	2.40	5.6

Table 4
Precision, Bias, and Matrix Recovery for Sulfate

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	9	0.49	0.49	0.00	100.0	0.18	37.5		
Water	10	0.70	0.71	0.01	101.4	0.20	29.2	0.05	8.3
	10	1.98	2.04	0.06	103.0	0.19	9.7		
	10	2.98	3.09	0.11	103.7	0.24	7.9	0.06	2.5
	10	14.86	14.67	-0.19	98.7	0.57	4.0		
	10	19.81	19.67	-0.14	99.3	0.73	3.8	0.44	2.6
	10	39.60	39.66	0.06	100.2	0.92	2.4		
	10	49.51	49.27	-0.24	99.5	1.26	2.6	0.49	1.1
Substitute	9	0.49	0.38	-0.11	77.6	0.25	66.9		
Wastewater	9	0.70	0.51	-0.19	72.9	0.08	16.4	0.18	39.3
	9	1.98	1.83	-0.15	92.4	0.29	16.2		
	9	2.98	2.86	-0.12	96.0	0.31	11.2	0.20	8.6
	9	14.86	14.19	-0.67	95.5	1.06	7.7		
	9	19.81	19.23	-0.58	97.1	0.97	5.2	0.46	2.8
	9	39.60	38.45	-1.15	97.1	1.33	3.6		
	9	49.51	47.75	-1.76	96.4	1.43	3.1	0.75	1.8
Drinking	12	0.49	0.41	-0.08	83.7	0.21	52.8		
Water	12	0.70	0.41	-0.29	58.6	0.20	50.3	0.14	34.3
	13	1.98	1.77	-0.21	89.4	0.53	30.3		
	13	2.98	2.68	-0.30	89.9	0.42	16.2	0.27	12.1
	13	14.86	14.25	-0.61	95.9	1.11	8.0		
	12	19.81	19.31	-0.50	97.5	1.39	7.4	1.48	8.9
	12	39.60	38.58	-1.02	97.4	1.96	5.2		
	13	49.51	48.43	-1.08	97.8	2.04	4.3	1.44	3.3
"Real"	10	0.49	0.37	-0.12	75.5	0.39	106.4		
Wastewater	11	0.70	0.16	-0.54	22.9	1.19	765.2	0.47	179.6
	11	1.98	1.57	-0.41	79.3	0.87	55.4		
	11	2.98	2.53	-0.45	84.9	0.64	25.4	0.24	11.9
	11	14.86	14.69	-0.17	98.9	1.26	8.6		
	10	19.81	19.38	-0.43	97.8	0.90	4.6	0.57	3.4
	11	39.60	38.74	-0.86	97.8	1.71	4.4		
	10	49.51	48.36	-1.15	97.7	1.51	3.1	0.47	1.1

Table 5
Precision, Bias, and Matrix Recovery for Nitrate

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.50	1.02	0.52	204.00	0.08	7.4		
Water	10	0.69	0.71	0.02	102.90	0.08	11.6	0.06	6.4
	11	1.99	2.83	0.84	142.21	0.23	8.1		
	11	2.97	2.89	-0.08	97.31	0.18	6.4	0.14	5.0
	11	14.91	14.77	-0.14	99.06	0.44	3.0		
	11	19.18	19.77	0.59	103.08	0.64	3.2	0.24	1.4
	10	39.86	39.09	-0.77	98.07	1.43	3.7		
	10	49.77	48.93	-0.84	98.31	1.72	3.5	0.62	1.4
Substitute	11	0.50	1.18	0.68	236.00	0.41	34.9		
Wastewater	10	0.69	0.55	-0.14	79.71	0.30	55.3	0.42	4.9
	10	1.99	2.70	0.71	135.68	0.42	15.4		
	10	2.97	2.33	-0.64	78.45	1.10	47.3	0.39	15.4
	9	14.91	14.29	-0.62	95.84	0.78	5.4		
	10	19.18	18.69	-0.49	97.45	1.46	7.8	0.25	1.5
	11	39.86	37.70	-2.16	94.58	1.93	5.1		
	11	49.77	47.78	-1.99	96.00	2.18	4.6	1.62	3.8
Drinking	11	0.50	1.06	0.56	212.00	0.19	18.1		
Water	11	0.69	0.65	-0.04	94.20	0.06	8.7	0.12	14.4
	12	1.99	3.05	1.06	153.27	0.39	12.8		
	11	2.97	3.01	0.04	101.35	0.22	7.2	0.33	10.8
	12	14.91	14.69	-0.22	98.52	0.62	4.2		
	12	19.18	20.05	0.87	104.54	0.88	4.4	0.46	2.7
	12	39.86	39.31	-0.55	98.62	1.67	4.3		
	12	49.77	48.93	-0.84	98.31	1.43	2.9	0.78	1.8
"Real"	11	0.50	0.94	0.44	188.00	0.80	84.7		
Wastewater	10	0.69	0.69	0.00	100.00	0.09	13.3	0.39	47.6
	10	1.99	3.00	1.01	150.75	0.38	12.7		
	10	2.97	3.01	0.04	101.35	0.20	6.6	0.23	7.8
	11	14.91	14.52	-0.39	97.38	0.66	4.6		
	11	19.18	19.26	0.08	100.42	0.77	4.0	0.77	4.6
	11	39.86	39.13	-0.73	98.17	1.78	4.6		
	11	49.77	49.17	-0.60	98.79	2.26	4.6	0.93	2.1

Table 6
Precision, Bias, and Matrix Recovery for Fluoride

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.50	0.51	0.01	102.00	11.00	11.4		
Water	10	0.71	0.73	0.02	102.82	7.90	8.1	0.02	2.9
	10	2.00	2.05	0.05	102.50	3.60	3.7		
	10	3.00	2.96	-0.04	98.67	4.40	4.6	0.09	3.4
	10	6.99	7.02	0.03	100.43	5.40	5.6		
	10	9.99	9.79	-0.20	98.00	4.60	4.8	0.13	1.6
	10	19.98	19.60	-0.38	98.10	3.80	3.9		
	10	24.99	24.51	-0.48	98.08	4.80	4.9	0.74	3.4
Substitute	10	0.50	0.50	0.00	100.00	0.09	18.0		
Wastewater	10	0.71	0.71	0.00	100.00	0.09	12.0	0.01	2.3
	10	2.00	1.98	-0.02	99.00	0.12	6.0		
	10	3.00	2.94	-0.06	98.00	0.10	3.4	0.06	2.6
	10	6.99	6.92	-0.07	99.00	0.28	4.1		
	9	9.99	9.94	-0.05	99.50	0.46	4.7	0.28	3.3
	10	19.98	19.67	-0.31	98.45	0.94	4.8		
	10	24.99	24.78	-0.21	99.16	1.09	4.4	0.63	2.8
Drinking	13	0.50	0.48	-0.02	96.00	0.06	12.9		
Water	13	0.71	0.68	-0.03	95.77	0.06	9.5	0.02	3.4
	13	2.00	1.96	-0.04	98.00	0.08	3.9		
	13	3.00	2.90	-0.10	96.67	0.10	3.4	0.08	3.5
	13	6.99	6.91	-0.08	98.86	0.25	3.6		
	13	9.99	9.91	-0.08	99.20	0.37	3.7	0.18	2.2
	13	19.98	19.94	-0.04	99.80	0.68	3.4		
	12	24.99	24.27	-0.72	97.12	1.63	6.7	1.30	5.9
"Real"	11	0.50	0.47	-0.03	94.00	0.08	16.9		
Wastewater	11	0.71	0.68	-0.03	95.77	0.08	11.7	0.04	7.6
	11	2.00	1.96	-0.04	98.00	0.12	6.3		
	11	3.00	2.93	-0.07	97.67	0.18	6.2	0.09	3.5
	11	6.99	6.85	-0.14	98.00	0.26	3.8		
	10	9.99	9.56	-0.43	95.70	0.73	7.7	0.44	5.3
	11	19.98	20.06	0.08	100.40	1.23	6.1		
	11	24.99	25.12	0.13	100.52	1.34	5.3	0.32	1.4

Table 7
Precision, Bias, and Matrix Recovery for o-Phosphate

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.50	0.41	-0.09	82.00	0.12	29.6		
Water	9	0.69	0.51	-0.18	73.91	0.13	26.6	0.03	7.2
	10	1.99	1.88	-0.11	94.47	0.16	8.3		
	10	2.98	2.76	-0.22	92.62	0.14	4.9	0.08	3.2
	10	14.86	14.93	0.07	100.47	0.64	4.3		
	9	19.80	19.76	-0.04	99.80	1.00	5.1	0.85	4.9
	10	39.60	39.79	0.19	100.48	1.38	3.5		
	10	49.51	50.10	0.59	101.19	1.76	3.5	0.72	1.6
Substitute	11	0.50	0.49	-0.01	98.00	0.15	30.0		
Wastewater	10	0.69	0.59	-0.10	85.51	0.17	28.8	0.13	24.4
	11	1.99	1.92	-0.07	96.48	0.28	14.6		
	10	2.98	2.89	-0.09	96.98	0.22	7.6	0.18	7.5
	11	14.86	15.31	0.45	103.03	1.74	11.4		
	11	19.80	19.78	-0.02	99.90	1.16	5.9	0.84	4.8
	11	39.60	39.58	-0.02	99.95	2.72	6.9		
	11	49.51	49.19	-0.32	99.35	3.98	8.1	2.18	4.9
Drinking	12	0.50	0.46	-0.04	92.00	0.14	30.0		
Water	13	0.69	0.55	-0.14	79.71	0.20	36.3	0.07	13.4
	13	1.99	1.89	-0.10	94.97	0.22	11.9		
	13	2.98	2.87	-0.11	96.31	0.24	8.5	0.07	2.8
	12	14.86	15.09	0.23	101.55	0.91	6.1		
	13	19.80	20.28	0.48	102.42	0.96	4.7	1.06	6.0
	13	39.60	40.37	0.77	101.94	2.15	5.3		
	13	49.51	50.75	1.24	102.50	3.14	6.2	1.03	2.3
"Real"	11	0.50	0.43	-0.07	86.00	0.17	39.1		
Wastewater	11	0.69	0.53	-0.16	76.81	0.24	46.5	0.12	25.8
	11	1.99	1.72	-0.27	86.43	0.27	15.8		
	11	2.98	2.52	-0.46	84.56	0.48	19.2	0.30	14.0
	11	14.86	14.93	0.07	100.47	0.91	6.1		
	11	19.80	19.90	0.10	100.51	1.35	6.8	0.91	5.2
	11	39.60	38.98	-0.62	98.43	1.45	3.7		
	10	49.51	48.26	-1.25	97.48	1.80	3.7	0.82	1.9

Table 8
QC Acceptance Criteria

Analyte	Matrix	Precision % RSD	Average %Recovery	Initial LL - UL	Ongoing LL - UL	MS/MSD LL - UL	MS/MSD RPD
Chloride	RW	6.30	98.5	90.8 - 106.2	88.7 - 108.3	89.4 - 107.5	12.0
	DW	10.00	97.0	84.0 - 110.0	81.1 - 113.0	81.9 - 112.5	18.6
	WW	7.00	92.8	83.0 - 102.6	81.4 - 104.2	81.8 - 103.8	13.2
Bromide	RW	10.10	99.7	92.2 - 107.2	86.7 - 112.7	88.5 - 111.0	19.2
	DW	12.70	95.8	85.9 - 105.6	79.8 - 111.8	81.8 - 109.8	23.3
	WW	14.40	99.2	87.2 - 111.2	80.1 - 118.3	82.4 - 116.0	26.9
Nitrite	RW	6.40	100.6	95.1 - 106.0	91.9 - 109.2	92.8 - 108.3	12.1
	DW	4.30	99.6	92.4 - 106.7	91.5 - 107.7	91.8 - 107.4	8.1
	WW	4.90	98.9	91.3 - 106.5	90.2 - 107.6	90.5 - 107.3	9.2
Sulfate	RW	9.40	100.4	90.9 - 109.9	86.9 - 113.9	88.2 - 112.6	17.9
	DW	16.1	95.6	82.6 - 108.6	74.9 - 116.2	77.5 - 113.7	29.7
	WW	19.60	95.3	78.9 - 111.7	70.1 - 120.5	72.6 - 118.0	36.9
Nitrate	RW	8.40	99.5	93.1 - 105.9	88.6 - 110.4	90.0 - 108.9	15.9
	DW	9.40	100.2	93.0 - 107.4	88.0 - 112.4	89.4 - 111.0	17.4
	WW	6.70	99.1	90.7 - 107.6	88.6 - 109.7	89.2 - 109.1	12.4
Fluoride	RW	7.90	99.5	92.2 - 106.7	88.7 - 110.3	89.8 - 109.1	14.9
	DW	4.86	98.3	91.9 - 104.8	90.5 - 106.2	90.9 - 105.7	9.0
	WW	7.90	98.5	90.0 - 107.1	87.0 - 110.1	88.0 - 109.1	14.7
Phosphate	RW	10.60	98.2	91.9 - 104.5	85.4 - 111.0	87.4 - 109.0	20.1
	DW	9.40	100.2	89.3 - 111.1	85.8 - 114.6	87.0 - 113.4	17.4
	WW	16.90	94.6	81.5 - 107.7	73.5 - 115.8	76.1 - 113.1	31.5

All data determined as spike recovery from ASTM method validation and EPA Tier 3 Criteria

Reagent water (RW) data between 0.5 and 50 mg/L, except Fluoride 0.5 and 25 mg/L
consisting of 4 Youden Pairs
Drinking (DW) and Wastewater (WW) data between 2 and 50 mg/L except Fluoride 2 and 25 mg/L
consisting of 3 Youden Pairs

RSD = %Relative Standard Deviation; (std dev / mean)(100)
LL = Lower Limit of %Recovery
UL = Upper Limit of %Recovery
RPD = Relative % Difference between MSD

Appendix B
(Non-mandatory Information)

B.1 Suggested Background References

B1.1 EPA Method 6500, "Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis", SW846, Rev 0, January 1998.

B1.2 Method 4140, "Inorganic Anions by Capillary Ion Electrophoresis", Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, p 4-12 to 4-20.

B1.3 Krol, Benvenuti, and Romano, "Ion Analysis Methods for IC and CIA and Practical Aspects of Capillary Ion Analysis Theory", Waters Corp, Lit Code WT-139, 1998.

B1.4 Jandik, P., Bonn, G., "Capillary Electrophoresis of Small Molecules and Ions", VCH Publishers, 1993

B1.5 Romano, J., Krol, J, "Capillary Ion Electrophoresis, An Environmental Method for the Determination of Anions in Water", J. of Chromatography, Vol. 640, 1993, p. 403.

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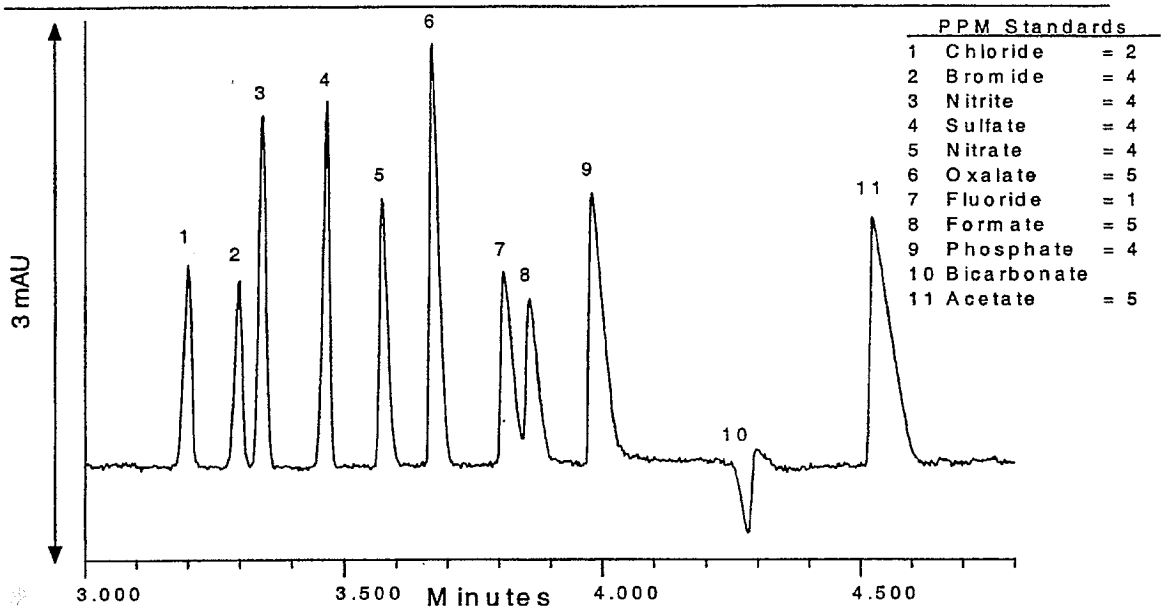
Appendix C
Capillary Ion Electrophoresis
Initial Demonstration of Performance
Single Operator

General Inorganic Anion & Organic Acid Analysis with Indirect UV Detection
Basis for EPA Method 6500, ASTM D6508, and Standard Methods 4140

The performance data given in this appendix was provided in the collaborative instruction booklet to evaluate initial demonstration of performance required by the collaborative design.



Analysis Conditions:

Electrolyte:	IonSelect High Mobility Anion Electrolyte, P/N 49385
Capillary:	75 µm (id) x 375 µm (od) x 60 cm (length)
Temperature:	25°C (5°C Above Ambient)
Power Supply:	Negative
Voltage:	15 kV
Current:	14 ± 1 µA (Use Constant Current for Analysis)
Sampling:	Hydrostatic for 30 Seconds
Detection:	Indirect UV at 254 nm, Hg Lamp, 185 or 254 nm Window
Time Constant:	0.3 Seconds, or less
Sampling Rate:	20 Data Points per Second
Analyte MT:	Mid-Point of Analyte Peak Width at Baseline
Quantitation:	Time Corrected Peak Area (Peak Area / MT)

Millennium Data Processing Method:

CIE Processing Method using Mid-Point of Peak Width for Migration Time

Integration
Peak Width = 2.25 - 3.00 Threshold = 100 ± 25
Min Area = 100 Min Height = 50
Inhibit Intg. = 0 to 3 min

Calibration
Averaging = None MT Window = 2%
Update MT = Average Standards
Peak Match = First for Chloride
(Cl is always first in the pherogram, use as a ref peak)
Cl MT Window = 10%
Other Analytes = Closest
Quantitate By = Time Corrected Peak Area
Fit Type = Linear Through Zero

Report
Analyte Name
Analyte Migration Time
Analyte Migration Time Ratio (respect to Cl Ref Peak)
Peak Area
Time Corrected Peak Area
Amounts

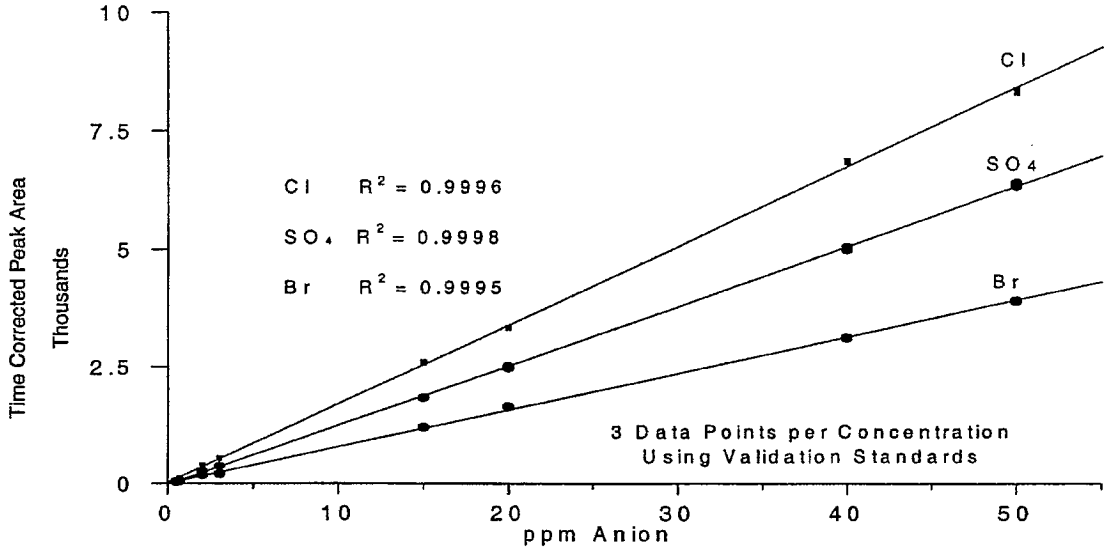
Use fresh electrolyte daily; recalibrate with every change in electrolyte.
Clear previous calibration (in Quick Set Page) before recalibration.
Do Not use analyte peak height for quantitation due to asymmetrical peak shapes.

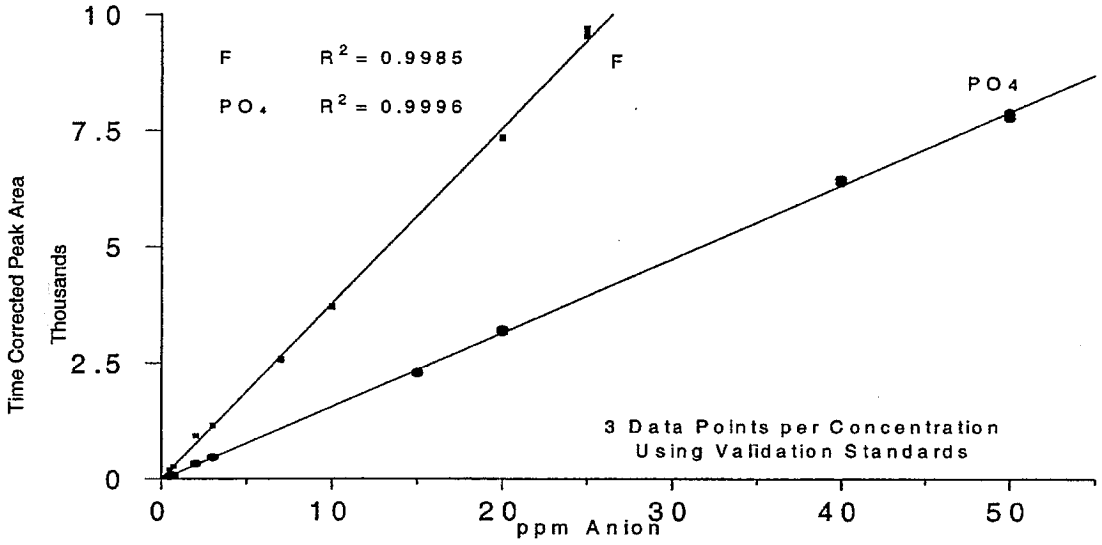
Method Validation:
The single operator performance given below using the ASTM validation design is intended as a basis to evaluate Initial Demonstration of Performance.

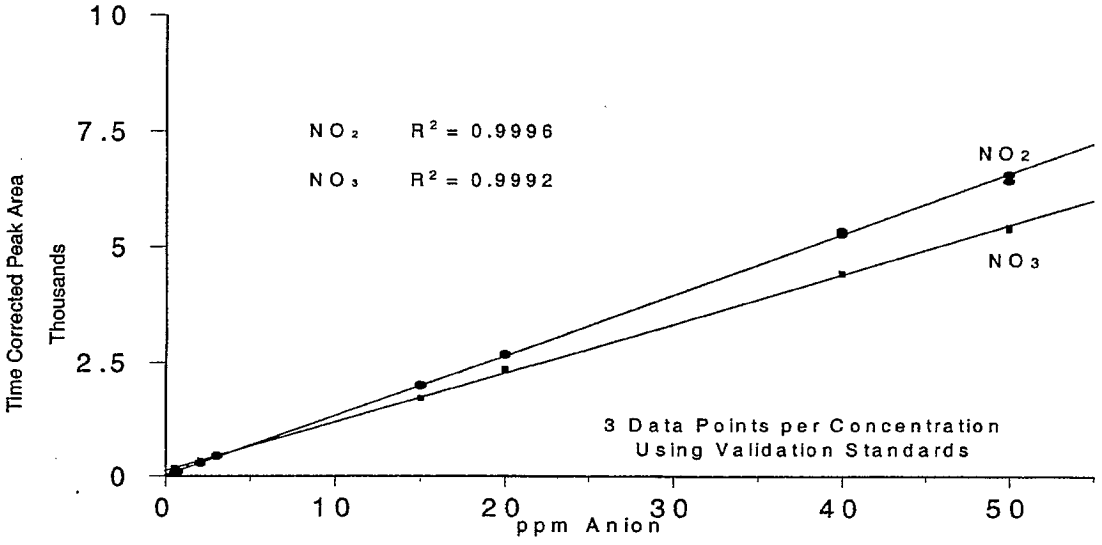
Individual Youden Pair Standard, in ppm

Analyte Anion	1	2	3	4	5	6	7	8
Cl	0.7	2.0	3.0	15.0	40.0	20.0	50.0	0.5
Br	2.0	3.0	15.0	40.0	20.0	50.0	0.7	0.5
NO_2	3.0	40.0	20.0	15.0	50.0	0.5	2.0	0.7
SO_4	40.0	50.0	0.5	0.7	2.0	3.0	15.0	20.0
NO_3	15.0	20.0	40.0	50.0	0.5	0.7	2.0	3.0
F	2.0	0.7	0.5	3.0	10.0	7.0	20.0	25.0
PO_4	50.0	40.0	20.0	0.5	3.0	2.0	0.7	15.0

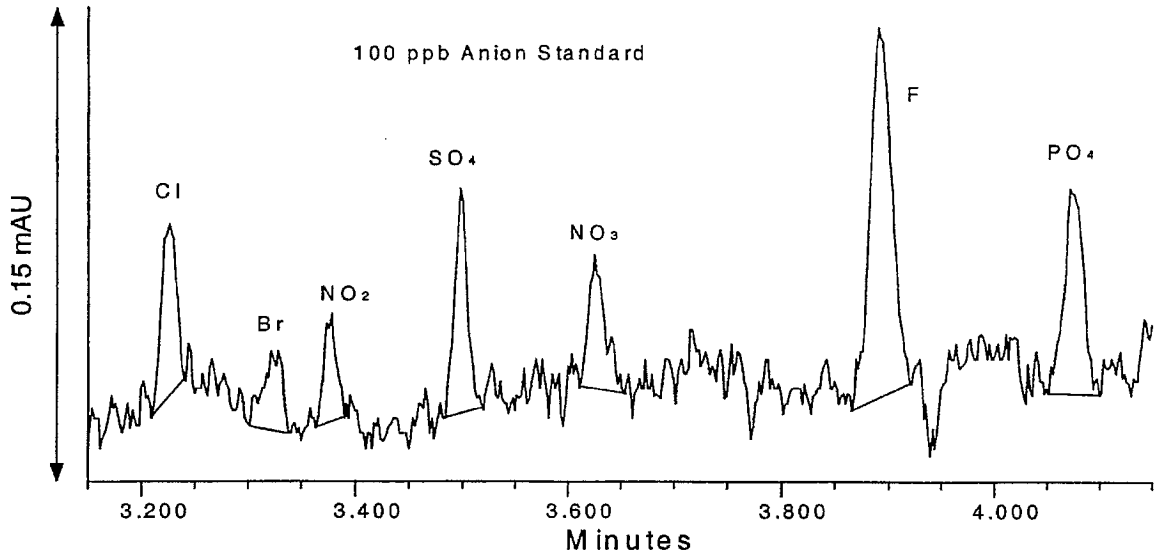
Method Linearity:







Method Detection Limits:



Seven replicates of the above 100 ppb anion standard were used to calculate time corrected peak area precision. Using EPA and Standard Methods protocols, the detection limits, as ppb, for these analytes are:

Chloride = 46	Bromide = 90	Nitrite = 72	Sulfate = 32
Nitrate = 84	Fluoride = 20	Phosphate = 41	

This method has been validated between 0.1 to 50 ppm. Quantitation below 0.1 ppm is not advised.

Migration Time Reproducibility:

Use mid-point of analyte peak width at the baseline as the analyte migration time determinant. Data given as average absolute migration time for each validation standard analyzed in triplicate.

Analyte		Cl	Br	NO_2	SO_4	NO_3	F	PO_4
Validation Standard	1	3.132	3.226	3.275	3.405	3.502	3.761	3.906
	2	3.147	3.239	3.298	3.431	3.517	3.779	3.931
	3	3.138	3.231	3.283	3.411	3.497	3.771	3.925
	4	3.158	3.244	3.307	3.434	3.510	3.781	3.963
	5	3.184	3.271	3.331	3.435	3.551	3.787	3.981
	6	3.171	3.260	3.312	3.418	3.537	3.776	3.964
	7	3.191	3.272	3.315	3.437	3.544	3.773	3.978
	8	3.152	3.248	3.294	3.418	3.526	3.739	3.954
Std Dev		0.021	0.015	0.018	0.012	0.20	0.015	0.027
%RSD		0.67%	0.46%	0.55%	0.36%	0.56%	0.40%	0.68%

Average Standard Deviation = 0.018 min = 1.1 sec
Average %RSD of Analyte Migration Time = 0.53%

Quantitation Precision:

Time Corrected Peak Area Precision, given as %RSD, based upon 3 samplings per concentration.

Analyte		Cl	Br	NO_2	SO_4	NO_3	F	PO_4
ppm concentration	0.1	12.36	18.89	16.19	13.25	23.13	9.82	14.00
	0.5	10.51	20.00	3.90	2.25	2.18	2.03	7.71
	0.7	1.23	13.36	2.01	2.95	0.37	2.72	4.41
	2	0.32	3.76	4.14	1.79	2.17	0.73	1.91
	3	0.63	1.80	1.72	1.70	0.58	0.98	2.70
	15	0.43	0.27	0.48	0.07	0.36	0.15	1.37
	20	0.45	0.66	0.17	0.13	0.88	0.16	0.81
	40	0.36	0.56	0.36	0.46	0.58		0.47
	50	0.45	0.51	0.48	0.16	0.46		0.46

Quantitation Accuracy:
Used a Certified Performance Evaluation Standard diluted 1:100 with DI water. Amounts based upon multi-point calibration curve prepared from certified standards.

	Analyte	Cl	NO_2	SO_4	NO_3	F	PO_4
Performance Evaluation Standard	True Value in ppm	43.00	1.77	37.20	15.37	2.69	6.29
Official Anion Methods Wet Chem & IC	Measured Mean	43.30	1.77	37.00	15.42	2.75	6.38
	Measured Std Dev	3.09	0.07	2.24	1.15	0.26	0.21
CIA Using Chromate Electrolyte	Ave CIA n=18	43.34	1.64	37.11	14.41	2.64	6.34
	CIA/Mean	1.003	0.927	1.003	0.935	0.959	0.993
	CIA/TrueValue	1.008	0.927	0.996	0.938	0.981	1.008

A CIA/True Value, or Mean = 1.000 indicates perfect agreement between CIA and official anion methods.

Method Recovery:
A Certified Performance Evaluation Standard (PES) was diluted 1:100 with Typical Drinking Water (DW). Amounts based upon multi-point calibration curve prepared from certified standards.

Analyte	Cl	NO_2	SO_4	NO_3	F	PO_4
Drinking Water n=3, as ppm	24.72 ± 0.18	Not Detected	7.99 ± 0.07	0.36 ± 0.05	Not Detected	Not Detected
Amount %RSD	0.73%		0.91%	13.3%		
Performance Evaluation Std	43.00	1.77	37.20	15.37	2.69	6.29
DW + PES n=3; as ppm	66.57 ± 0.34	1.74 ± 0.03	45.19 ± 0.17	15.42 ± 0.12	2.62 ± 0.07	5.55 ± 0.31
Amount %RSD	0.51%	1.85%	0.38%	0.79%	2.69%	5.52%
% Recovery	97.9%	98.3%	100.2%	98.1%	97.4%	88.2%

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

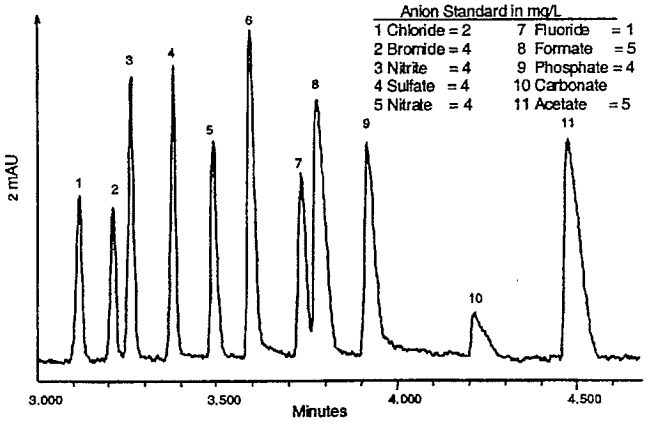


Fig. 2 Electropherogram of 0.2 mg/L Anions Used to Determine MDL

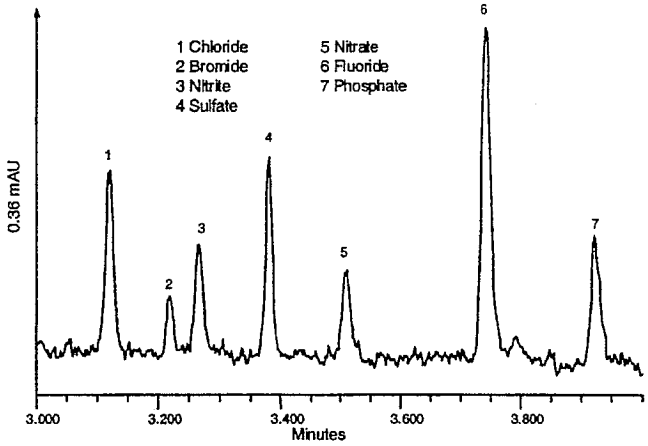


Fig. 3 Electropherogram of Substitute Wastewater

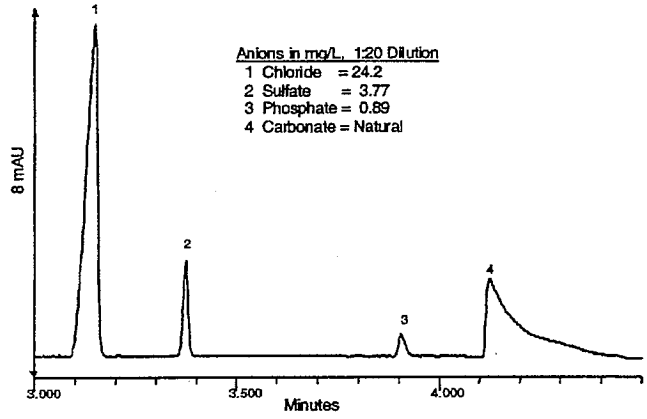


Fig. 4 Electropherogram of Drinking Water

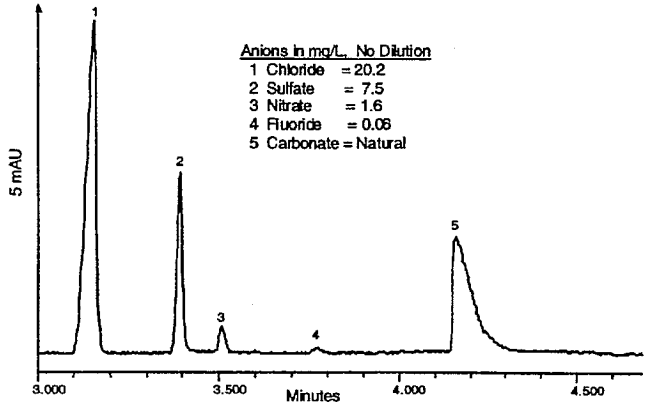


Fig. 5 Electropherogram of Municipal Wastewater Treatment Plant Discharge

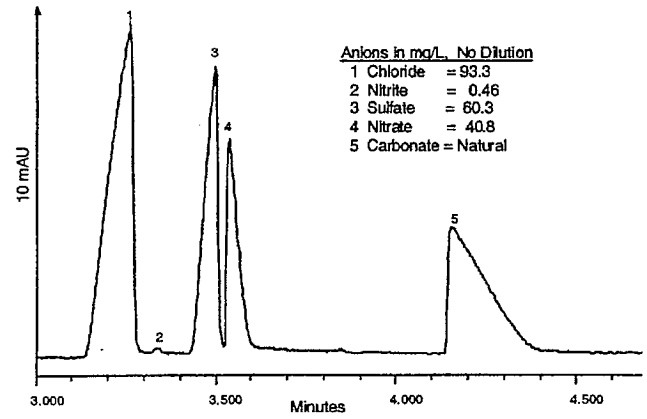


Fig. 6 Electropherogram of Industrial Wastewater

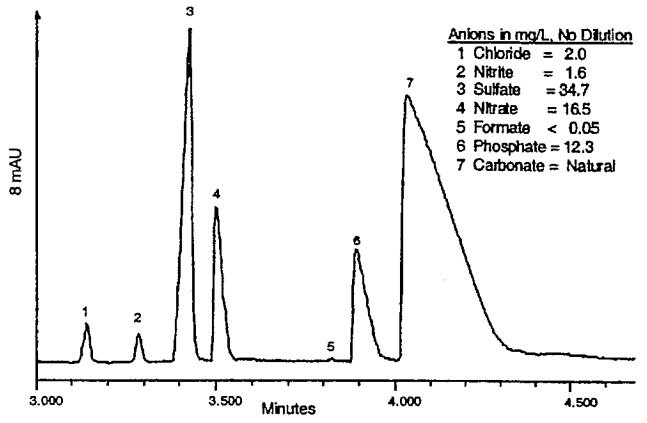


Fig. 7 Pictorial Diagram of Anion Mobility and ElectroOsomotic Flow Modifier

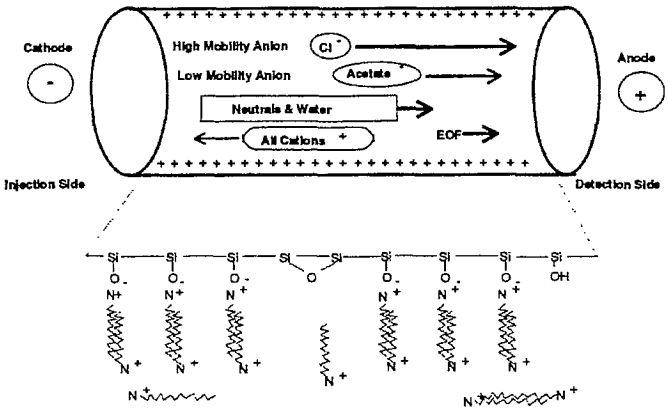


Fig. 8 Selectivity Diagram of Anion Mobility Using Capillary Ion Electrophoresis

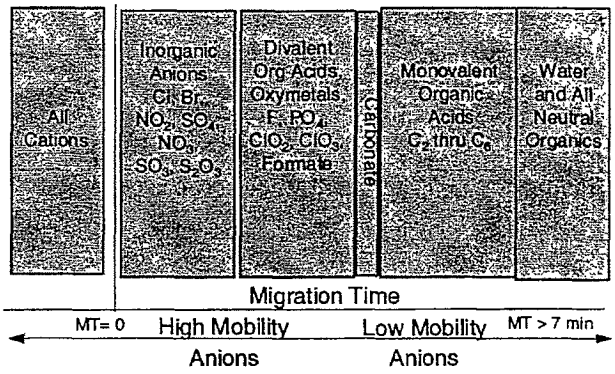


Fig. 9 Pictorial Diagram of Indirect UV Detection

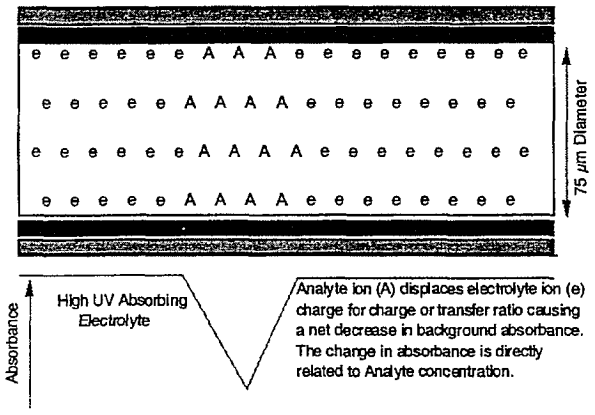


Fig. 10 General Hardware Schematic of a Capillary Ion Electrophoresis System