METHOD 6500

DISSOLVED INORGANIC ANIONS IN AQUEOUS MATRICES BY CAPILLARY ION ELECTROPHORESIS

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This test method is applicable for determination of the dissolved inorganic anions in aqueous matrices (drinking water, wastewater, and ground water) using capillary ion electrophoresis with indirect UV detection. The following analytes have been determined by this method:

Analytes	CAS Registry No.*
Bromide	24959-67-9
Chloride	16887-00-6
Fluoride	16984-48-8
Nitrate	14797-55-8
Nitrite	14797-65-0
o-Phosphate	14265-44-2
Sulfate	14808-79-8

*Chemical Abstracts Service Registry Number

1.2 This test method is applicable to drinking water, wastewater and ground water for the analysis of inorganic anions in the concentration range of 0.1 to 50 mg/L, except for fluoride, which has a range of 0.1 to 25 mg/L. It is the user's responsibility to ensure the applicability of this test method for other anion concentration ranges and other aqueous sample matrices.

1.3 Capillary ion electrophoresis provides a simultaneous separation and determination of several inorganic anions using nanoliters of sample in a single injection. Only 500 µL of sample is necessary to fill the analysis vial. Analysis time is less than 5 min.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for

demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel in the use of capillary ion electrophoresis. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Capillary ion electrophoresis (see Figs. 1 through 4) is a free-zone electrophoretic technique optimized for the analysis of anions with molecular weights of 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 flow (EOF) 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. 2 and 3).

2.2 The sample is introduced into the capillary using hydrostatic sampling. The inlet of the capillary, containing electrolyte, is immersed in the sample and the sample raised 10 cm for 30 sec where 36 nanoliter 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. Pressure injection may also be used as long as the performance specifications of this method are achievable.

2.3 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. 4). Detector output polarity is reversed to provide positive mV response to the data system, and to make the negative absorbance peaks appear positive.

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

3.0 DEFINITIONS

See the last pages of this method for a glossary of basic capillary ion electrophoresis and procedure-specific terms. Also refer to Chapter One, Chapter Three, and the manufacturer's instructions for other definitions that may be relevant to this method.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware.

4.2 The most difficult quantitation and possible comigration occur when one anion is in significant excess to other anions in close proximity. For two closely adjacent peaks, reliable quantitation can be achieved when the concentration differential is less than 100:1. As the resolution between two anion peaks increases so does the tolerated concentration differential.

4.3 Dissolved carbonate, as HCO_3^{-1}, is an anion present in all aqueous environmental samples, especially alkaline samples. Under the defined analysis conditions, carbonate at less than 1000:1 concentration differential to the anions will not interfere with the quantitation of the anions listed in Sec. 1.1.

4.4 Most monovalent organic acids and neutral organic compounds commonly found in wastewater and groundwater migrate later in the electropherogram, after carbonate, and do not interfere with the anions listed in Sec. 1.1. Formate, a common organic acid found in environmental samples, migrates shortly after fluoride but before phosphate. At high formate concentrations the quantification of fluoride may be incorrectly identified. Include 5 mg/L of formate into the mixed anion working solution to aid with fluoride identification and quantitation (see Fig. 5).

4.5 Other inorganic or organic anions present in the sample will be separated and detected yielding an anionic profile of the sample. Other matrix anions commonly found in drinking water or wastewater do not interfere with the analysis of anions given in Sec. 1.1. However, unknown matrix anions may co-migrate or be a direct interferant with the analyte anions of interest.

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

4.7 Chlorate also migrates in the phosphate region but does not interfere with phosphate identification or quantitation at concentrations less than 3 mg/L. For chlorate concentrations greater than 3 mg/L, add 5 mg/L of chlorate to the mixed anion working solution to aid in identification of phosphate and chlorate.

4.8 As the concentration of analyte increases, the analyte peak shape becomes asymmetrical. If adjacent analyte peaks are not baseline resolved, the data system will drop a perpendicular line 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, ensure that adjacent peaks are fully resolved, if they are not, dilute the sample 1:1 with reagent water.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A

reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 It is the responsibility of the user to prepare, handle, and dispose of electrolyte 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 with the appropriate safety features. See the manufacturer's instructions.

6.0 EQUIPMENT AND SUPPLIES

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Capillary ion electrophoresis system -- Consists of the following components, or equivalent.

6.1.1 High voltage power supply -- Capable of generating voltage potential between 0 and minus 30 kV relative to ground.

6.1.2 Covered sample carousel -- To prevent environmental contamination of the samples during a multi-sample analysis.

6.1.3 Sample introduction mechanism -- Capable of hydrostatic or pressure sampling techniques.

6.1.4 Capillary purge mechanism -- To automatically purge the capillary after every analysis to eliminate any cross contamination from the previous sample matrix and to replenish the capillary with fresh electrolyte; or to clean the capillary with other reagents, such as sodium hydroxide.

6.1.5 UV detector -- Capable of monitoring 254 nm with a time constant of 0.1 sec.

6.1.6 Fused silica capillary -- 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.

6.1.7 Constant temperature compartment -- To keep the samples, capillary and electrolytes at constant temperature.

6.2 Data system -- Computer system capable of acquiring data at 20 points per sec and an ability to express migration time or relative migration time in minutes to 3 decimal places, use midpoint of the analyte peak width to determine the migration time of the analyte, use reference peaks and normalized migration time relative to the reference peak for qualitative identification, report time corrected peak area, and express results in concentration units.

6.3 Anion exchange cartridge, hydroxide form or equivalent.

6.4 Plastic syringes, 20 mL disposable.

6.5 Vacuum filtration apparatus using a 0.45 µm aqueous compatible filter.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- All references to water in this method refer to reagent water unless otherwise specified. Reagent water should be interference free.

7.3 Individual anion solution, stock standard (1000 mg/L anion) -- Individual stock solution may be purchased from an appropriate vendor or may be prepared in the laboratory. The use of certified 1000 ppm stock standards is recommended.

NOTE: All weights given are for anhydrous or dried salts.

7.3.1 Bromide solution, standard -- Dry approximately 0.5 g of sodium bromide (NaBr) for 6 hrs at 150 EC and cool in a desiccator. In a 100-mL volumetric flask dissolve 0.129 g of the dry salt with water, and fill to mark with water.

7.3.2 Chloride solution, standard -- Dry approximately 0.5 g of sodium chloride (NaCl) for 1 hr at 100 EC and cool in a desiccator. In a 100-mL volumetric flask dissolve 0.165 g of the dry salt with water, and fill to mark with water.

7.3.3 Fluoride solution, standard -- Dry approximately 0.5 g of sodium fluoride (NaF) for 1 hr at 100 EC and cool in a desiccator. In a 100-mL volumetric flask dissolve 0.221 g of the dry salt with water, and fill to mark with water.

7.3.4 Formate solution, standard -- Dissolve 0.151 g of sodium formate in a 100-mL volumetric flask with water, and make to volume. This chemical is not dried in a desiccator because it may decompose at high temperatures.

7.3.5 Nitrate solution, standard -- Dry approximately 0.5 g of sodium nitrate ($NaNO_3$) for 48 hrs at 105 ^oC and cool in a desiccator. In a 100-mL volumetric flask dissolve 0.137 g of the dry salt with water, and fill to mark with water (1000 mg/L of NO_3 = 225.8 mg/L of $N\text{-}NO_3$).

7.3.6 Nitrite solution, standard -- Dry approximately 0.5 g of sodium nitrite ($NaNO_2$) for 24 hrs in a desiccator containing concentrated sulfuric acid. In a 100-mL volumetric flask dissolve 0.150 g of the dry salt with water, and fill to mark with water. Store in a sterilized glass bottle. Refrigerate and prepare monthly. (1000 mg/L NO_2 = 304.3 mg/L $N\text{-}NO_2$.)

CAUTION: Nitrite is easily oxidized, especially in the presence of moisture. Use only fresh reagent.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating for 1 hr at 170 EC in an air oven.

7.3.7 *o*-Phosphate solution, standard -- In a 100-mL volumetric flask dissolve 0.150 g of anhydrous dibasic sodium phosphate (Na_2HPO_4) with water, and fill to mark with water. (1000 mg/L PO_4 = 326.1 mg/L $P\text{-}PO_4$.)

7.3.8 Sulfate solution, standard -- Dry approximately 0.5 g of sodium sulfate (Na_2SO_4) for 1 hr at 105 EC and cool in a desiccator. In a 100-mL volumetric flask dissolve 0.148 g of the dry salt with water, and fill to mark with water.

7.4 Mixed anion solution, working -- Prepare a blank, and at least 3 different working standard concentrations for the anions of interest within the desired range of analysis, typically between 0.1 and 50 mg/L. To a pre-rinsed 100-mL volumetric flask add an appropriate aliquot of individual anion stock standard solution (Sec. 7.3), a 0.5-mL aliquot of standard formate solution (7.3.4) and dilute with water. The formate concentration in each working standard will be 5 mg/L.

NOTE: Use 0.1 mL of individual anion stock standard solution (Sec. 7.3) per 100 mL for 1 mg/L of anion.

NOTE: Anions of no interest may be omitted.

NOTE: The mid-range mixed anion working solution of this section may be used for the determination of migration times and resolution described in Sec. 10.1 and for the quality control evaluation described in Sec. 9.0.

7.5 Electrolyte reagents -- Although any electrolyte meeting the performance criteria of this method may be used, this method was validated using a chromate-based electrolyte.

7.5.1 Chromate concentrate (100 mM chromate) -- In a 1-L volumetric flask dissolve 23.40 g of sodium chromate tetrahydrate ($Na_2CrO_4 \bullet 4H_2O$) in 500 mL of 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.

7.5.2 Electroosmotic flow modifier (OFM) concentrate (100 mM tetradecyltrimethyl ammonium bromide, TTABr) -- In a 100-mL volumetric flask dissolve 3.365 g of tetradecyltrimethyl ammonium bromide (TTABr) in 70 mL of water, and dilute to 100 mL with water.

NOTE: TTABr needs to be converted to the hydroxide form using the anion exchange cartridge. TTAOH is commercially available from Waters Corp. (sole source).

7.5.3 Buffer solution (100 mM CHES/1mM calcium gluconate) -- In a 1-L volumetric flask dissolve 20.73 g of CHES (2-[N-cyclohexylamino]-ethane sulfonic acid) and 0.43 g of calcium gluconate in 500 mL of 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.

7.5.4 Sodium hydroxide solution (500 mM sodium hydroxide) -- In a 100-mL volumetric flask dissolve 2 g of sodium hydroxide in 50 mL of water and dilute to 100 mL with water.

7.5.5 Electrolyte solution, working (4.7 mM chromate/4 mM TTAOH/10mM CHES/0.1mM calcium gluconate) -- Wash the anion exchange cartridge in the hydroxide form using the 20-mL plastic syringe with 10 mL of 500 mM NaOH followed by 10 mL of water. Discard the washings. Slowly pass 4 mL of the 100 mM OFM concentrate solution (Sec. 7.5.2) 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: The above procedure is used to convert the TTABr to TTAOH which is used in the electrolyte. If using commercially available 100 mM TTAOH, this step is not necessary.

Into the 100-mL volumetric flask add 4.7 mL of chromate concentrate solution (Sec. 7.5.1) and 10 mL buffer solution (Sec. 7.5.3). Mix and dilute to 100 mL with water. The natural pH of the electrolyte should be 9.0 ± 0.1. Filter and degass using the vacuum filtration apparatus. Store the remaining electrolyte in a capped glass or plastic container at ambient temperature. The electrolyte is stable for one year. This electrolyte is commercially available from Waters Corp.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 Rinse sampling containers with the sample and discard to eliminate any contamination from the container, fill to overflowing, and cap to exclude air.

8.3 Analyze samples as soon as possible after collection. For nitrite, nitrate, and phosphate, refrigerate the sample at #6 EC after collection and warm to room temperature before dilution and analysis. Determine nitrite and nitrate within 48 hrs.

8.4 Filter samples containing suspended solids through a pre-rinsed 0.45-µm aqueous compatible membrane filter before transferring the sample to the analysis vial.

8.5 If sample dilution is necessary, dilute with reagent water only.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with the entire sample preparation and analytical procedure by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.2.1 Prepare the reference samples from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the

laboratory, the reference sample concentrate should be made using stock standards prepared independently from those used for calibration.

9.2.2 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. See the note in Sec. 9.3.1 for important information regarding spiking samples.

9.3 Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. Each time samples are analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of quantitation or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples.

9.4 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.4.2 A laboratory control sample (LCS) should be prepared as described in Chapter One and treated exactly as a field sample, including exposure to all glassare, equipment, and reagents that are used with field samples. An LCS should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.4.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Determination of migration times -- The migration time of an anion is dependent upon the electrolyte compositions, 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 minutes, to the third decimal place, of the mid-range mixed anion standard working solution (Sec. 7.4), using the analysis scheme described in Sec. 11.0. Use mid-point of analyte peak width as the determinant of analyte migration time (Fig. 5 and Table 2).

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

10.2 For each anion concentration (X-axis) plot the time-corrected peak area response (Y-axis). Determine the best linear calibration line through the data points, or use the linear regression calibration routine available in the data systems. Do not force the line through zero.

10.3 Initial calibration verification (ICV) -- Immediately after the calibration standards have been analyzed, the accuracy of the calibration must be verified by the analysis of an ICV standard. The ICV is prepared at a concentration level within the calibration range of the method and using a second source standard (prepared using standards different from the calibration standards) spiked into reagent water. The control limit for the ICV is ± 15% of the true value. When the ICV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4 Continuing calibration verification (CCV) -- Once the calibration curve has been established, the continuing accuracy must be verified by analysis of a CCV prior to conducting any field sample analysis, after every tenth field sample, and at the end of the analysis sequence. The CCV can be the single mixed anion working solution (see Sec. 7.4) or CCV concentrations can be alternated between the low- and mid-range calibration standard concentrations. The control limit for the low-range CCV is ± 50% and for the mid-range CCV is ± 15% of the true value. When the CCV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified. Samples that are not bracketed by acceptable CCV runs must be reanalyzed.

10.5 The calibration curve is validated if the single point calibration standard (or CCV) is within the control limits, and if analyte migration time is ± 5% of previous migration time determined in Sec. 10.1.

10.6 If the calibration curve is not validated, discard the spent electrolyte and replace with a fresh electrolyte. Calibrate as described in Sec. 10.1.

NOTE: Replace the electrolyte working solution in the instrument daily.

11.0 PROCEDURE

11.1 Set up the capillary electrophoresis system according to the manufacturer's instructions. Fill the electrolyte reservoirs with fresh electrolyte. Transfer the blank, standard, or sample into a prerinsed plastic sample analysis vial and place in the covered sample carousel.

11.2 Program the system according to the manufacturer's instructions using the following instrument settings as guidelines for analysis of standards and samples.

11.2.1 Condition a new 75-µm i.d. x 375-µm o.d. x 60-cm capillary with 100 mM NaOH for 5 min followed by working chromate electrolyte solution A for 5 min.

NOTE: This conditioning step should be repeated weekly in order to regenerate the capillary surface for optimum reproducibility.

Program the system for at least a one minute purge of the capillary with electrolyte between each standard or sample. Using a 15 psi vacuum purge mechanism, one 60 cm capillary volume can be displaced in 30 sec.

11.2.2 Program the system for the hydrostatic sampling technique for 30 sec. Different sampling times may be used provided that samples and standards are analyzed identically. Approximately 1.2 nL of sample per second is siphoned into a 75-µm capillary.

11.2.3 Program the system for constant current 14 µA and a run time of 5 min; if an anionic profile of the sample is of interest set the time to 7 min. Using a capillary 60 cm in length, the field strength at 15 µv applied voltage is 250 V/cm.

11.2.4 Program the integrator or computer for data acquisition rate of 20 points per second with a run time designated in Sec. 11.2.3. Set up data processing method according to the manufacturer's instructions.

11.2.5 Monitor UV response at 254 nm. Since detector ranges are variable, the range setting designated for analysis will depend on the concentration of anions in the sample and should be chosen accordingly.

11.2.6 The electropherogram of the working calibration standards (Sec. 7.4) should be similar to the inorganic anion electropherogram shown in Fig. 5.

11.3 Analyze all standards (Sec. 7.4) and samples as described in Sec. 11.2. Refer to Figs. 5 through 9 for representative anion standard, 0.1 mg/L anion standard, drinking water, and waste water (municipal and industrial).

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Relate the time-corrected peak area for each sample anion with the calibration curve generated in Sec. 10.2 to determine mg/L concentration of anion. If the sample was diluted prior to analysis, then multiply mg/L anion by the dilution factor to obtain the original sample concentration.

Original Sample mg/L Anion = (A x SF)

where:

A = mg/L anion determined from the calibration curve

SF = scale or dilution factor

12.2 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Tables 1 through 10 provide examples of collaborative design, migration time reproducibility, comparison of capillary ion electrophoresis (CIE) with other approved EPA methods, and interlaboratory reproducibility and precision for the capillary ion electrophoresis technique. These data are provided for guidance purposes only.

13.3 Table 11, entitled "Example Capillary Ion Electrophoresis Anion Analysis Round Robin Using Chromate Electrolyte (mg/L)," provides example precision data in some common environmental matrices. These data are provided for guidance purposes only.

13.4 Figures 6 through 12 display representative examples of electropherograms and linearity of calibration curves. These data are provided for guidance purposes only.

13.5 The following documents may provide additional information regarding this method and technique:

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

13.5.2 J. Romano, "Capillary Ion Analysis: A Method for Determining Ions in Water and Solid Waste Leachates," *Amer. Lab.*, May 1993, p. 48.

13.5.3 W. Jones, "Method Development Approaches for Ion Electrophoresis," *J. of Chromatography*, Vol. 640, 1993, p. 387.

13.5.4 W. Jones and P. Jandik, "Various Approaches to Analysis of Difficult Sample Matrices for Anions using Capillary Electrophoresis," *J. of Chromatography*, Vol. 608, 1992, p. 385.

13.5.5 G. Bondoux, P. Jandik and W. Jones, "New Approaches to the Analysis of Low Level of Anions in Water," *J. of Chromatography*, Vol. 602, 1992, p. 79.

13.5.6 P. Jandik, W. Jones, A. Weston and P. Brown, "Electrophoretic Capillary Ion Analysis: Origins, Principles, and Applications," *LC·GC*, Vol. 9, Number 9, 1991, p. 634.

13.5.7 J. Romano and P. Jackson, "Optimization of Inorganic Capillary Electrophoresis for the Analysis of Anionic Solutes in Real Samples," *J. of Chromatography*, Vol. 546, 1991, p. 411.

13.5.8 P. Jandik and W. Jones, "Optimization of Detection Sensitivity in the Capillary Electrophoresis of Inorganic Anions," *J of Chromatography*, Vol. 546, 1991, p. 431.

13.5.9 P. Jandik and W. Jones, "Controlled Changes of Selectivity in the Separation of Ions by Capillary Electrophoresis," *J. of Chromatography*, Vol. 546, 1991, p 445.

13.5.10 R. Foret, et.al., "Indirect Photometric Detection in Capillary Zone Electrophoresis," *J. of Chromatography*, Vol. 470, 1989, p. 299.

13.5.11 S. Hjerte'n, et. al.,"Carrier-free Zone Electrophoresis, Displacement Electrophoresis and Isoelectric Focusing in an Electrophoresis Apparatus," *J. of Chromatography*, Vol. 403, 1987, p. 47.

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

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Waters Chromatography, "Innovative Methods for Ion Analysis," Method N-601b, 1992.

2. Collection of validation data for Method 6500, from J. Romano, Waters Corporation, Waters Chromatography Division, Ion Analysis Group, Milford, Massachusetts. Data generated in 1995, reports submitted to EPA from J. Romano on January 9, 1998.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method. A flow diagram of the procedure and a glossary follow the tables and figures.

TABLE 1

EXAMPLE COLLABORATIVE DESIGN AS FOUR YOUDEN PAIR SETS[1]

Individual Youden Pair Standards, in mg/L

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

Source: Ref. 2

[1] The collaborative design is intended to demonstrate performance between 0.1 and 50 mg/L anion, except for fluoride between 0.1 and 25 mg/L. The concentrations among anions are varied so as not to have any one standard at all low or all high anion concentrations.

These data are provided for guidance purposes only.

TABLE 2

EXAMPLE ANION MIGRATION TIME REPRODUCIBILITY FROM YOUDEN PAIR STANDARDS USING CHROMATE ELECTROLYTE AND CONSTANT CURRENT

Analyte Mid-Point Migration Time, Average of Triplicate Samplings

Youden Standards	Analyte	Cl	Br	NO_2	SO_4	NO_3	F	PO_4
	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	03015	0.027
	%RSD	0.67%	0.46%	0.55%	0.36%	0.56%	0.40%	0.68%

Average Migration Time Std Dev = 0.018 min = 1.1 sec Average %RSD = 0.53%

These data are provided for guidance purposes only.

TABLE 3

EXAMPLE COMPARISON OF CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE AND APPROVED METHODS USING A PERFORMANCE EVALUATION STANDARD

	Analyte	**Cl**	**NO_2**	**SO_4**	**NO_3**	**F**	**PO_4**
Performance Evaluation Standard[1]	True Value in mg/L	43.00	1.77	37.20	15.37	2.69	6.29
Official Anion Methods Wet Chem & IC	Measured Mean[2]	43.20	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
CIE Using Chromate Electrolyte[3]	Ave CIE n=18	42.51	1.78	37.34	14.06	2.63	6.34
	CIE/Mean CIE/True Value	0.984 0.989	1.006 1.006	1.009 1.003	0.911 0.945	0.956 0.978	0.994 1.008

Source: Ref. 2

[1] The performance evaluation standard was purchased from APG Laboratories and diluted 1:100 with Type I DI water.
[2] The measured result is the average from numerous laboratories using Approved Standard Methods and EPA wet chemistry and ion chromatography methods
[3] The CIE results were determined using Method 6500 and an ASTM method under development (no method number at the time), and are the average from four laboratories using the Youden Pair Standards for quantitation.

These data are provided for guidance purposes only.

TABLE 4

EXAMPLE CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE INTERLABORATORY REPRODUCIBILITY AND PRECISION[1]

Data given as mg/L

Analyte[2]	Cl	NO_2	SO_4	NO_3	F
Lab 1 n = 5	43.22 ± 0.22	1.58 ± 0.09	36.39 ± 0.33	14.57 ± 0.12	2.54 ± 0.10
Lab 2 n=5	43.68 ± 0.61	1.58 ± 0.08	37.01± 0.37	13.94 ± 0.09	2.69 ± 0.02
Lab 3 n=5	43.93 ± 0.39	1.60 ± 0.06	37.68 ± 0.24	15.05 ± 0.11	2.69 ± 0.03
Lab 4 n=3	42.51 ± 0.22	1.78 ± 0.06	37.34 ± 0.19	14.06 ± 0.07	2.69 ± 0.02
Average Mean ± Std Dev	43.34 ± 0.36	1.64 ± 0.07	37.11 ± 0.28	14.41 ± 0.10	2.64 ± 0.04
% RSD	0.83%	4.5%	0.77%	0.67%	1.61%

[1] Results from 4 laboratories analyzing the performance evaluation standard using the Youden Pair Standards for quantitation.

[2] Only one lab reported results for PO_4 as 6.34 ± 0.02 mg/L on triplicate samplings yielding an %RSD of 0.07%

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE KNOWN ADDITION RECOVERY AND PRECISION USING PERFORMANCE EVALUATION STANDARD WITH DRINKING WATER

Analyte	**Cl**	**NO_2**	**SO_4**	**NO_3**	**F**	**PO_4**
Milford Drinking Water n=3, as ppm	24.27 ± 0.18	Not Detected	7.99 ± 0.07	0.36 ± 0.05	Not Detected	Not Detected
%RSD	0.73%		0.91%	13.3%		
Performance Evaluation Std[1]	43.00	1.77	37.20	15.37	2.69	6.29
MDW + 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
%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%

Source: Ref. 2.

[1] The performance evaluation standard was diluted 1:100 with Drinking Water.

These data are provided for guidance purposes only.

TABLE 6

EXAMPLE COMPARISON OF APPROVED METHOD AND CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE FOR THE DETERMINATION OF CHLORIDE

Data given as mg/L

Analyte	Sample #	Titration[1]	IC[2]	CIE
Effluent	1	--[3]	149	147
	2	--	162	161
	3	--	153	152
	4	--	139	140
	5	--	111	110
	6	--	109	107
	7	--	3.6	3.5
Drinking Water	1	5.5	5.1	5.0
	2	5.5	5.0	4.9
	3	5.3	5.2	5.1
	4	5.5	5.1	5.1
	5	5.3	5.0	5.0
	6	5.3	4.9	4.9
	7	5.5	4.9	4.9
Landfill Leachate	1	0.1	<0.1	ND
	2	230	245	240

Source: Ref. 2.

[1] Chloride determined using "4500 Cl C, Iodometric Method."
[2] Chloride determined using "4110 C, Single Column Ion Chromatography Using Direct Conductivity Detection."
[3] A dash line indicates the test was not performed. ND indicates the anion was not detected.

These data are provided for guidance purposes only.

TABLE 7

EXAMPLE COMPARISON OF APPROVED METHOD AND CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE FOR THE DETERMINATION OF FLUORIDE

Analyte	Sample #	Electrode[1]	IC[2]	CIE
Effluent	1	1.7	1.2	1.5
	2	0.9	0.6	0.6
	3	0.8	0.5	0.6
	4	0.8	0.4	0.7
	5	0.9	0.5	0.8
	6	0.9	0.5	0.7
	7	<0.1	ND	<0.1
Drinking Water	1	1.2	0.9	0.9
	2	1.3	0.9	0.9
	3	1.3	0.9	0.9
	4	1.3	0.9	0.9
	5	1.3	0.9	0.9
	6	0.9	0.6	0.6
	7	1.3	0.9	0.9
Landfill Leachate	1	<0.2	ND	ND
	2	16	10.6	10.9

Source: Ref. 2.

[1] Fluoride determined using "4500-F C, Ion Selective Electrode Method."
[2] Fluoride determined using "4110 C, Single Column Ion Chromatography Using Direct Conductivity Detection."

These data are provided for guidance purposes only.

TABLE 8

EXAMPLE COMPARISON OF APPROVED METHOD AND CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE FOR THE DETERMINATION OF SULFATE

Data given as mg/L

Analyte	Sample #	Turbidimetric[1]	IC[2]	CIE
Effluent	1	98	87.5	98.0
	2	110	95.3	95.9
	3	130	118	115
	4	130	139	136
	5	110	113	110
	6	100	107	106
	7	6	5.6	5.8
Drinking Water	1	6	5.8	6.0
	2	6	5.8	6.0
	3	6	5.9	6.1
	4	6	5.9	6.1
	5	5	5.8	6.2
	6	4	3.0	3.4
	7	5	5.8	6.1
Landfill Leachate	1	<1	ND	ND
	2	190	211	201

Source: Ref. 2.

[1] Sulfate determined using "4500 SO_4 E, Turbidimetric Method."
[2] Sulfate determined using "4110 C, Single Column Ion Chromatography Using Direct Conductivity Detection."

These data are provided for guidance purposes only.

TABLE 9

EXAMPLE COMPARISON OF APPROVED METHOD AND CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE FOR THE DETERMINATION OF NITRITE + NITRATE[3]

Data given as mg/L

Analyte	Sample #	Cd Red'n[1]	IC[2]	CIE
Effluent	1	0.3	ND	ND
	2	--	ND	ND
	3	--	ND	ND
	4	--	ND	0.5
	5	--	2.1	2.4
	6	2.4	1.9	2.2
	7	0.7	0.3	0.4
Drinking Water	1	0.6	0.3	0.4
	2	0.6	0.3	0.4
	3	0.4	0.3	0.4
	4	0.6	0.3	0.3
	5	0.6	0.3	0.4
	6	0.3	0.1	0.1
	7	0.5	0.3	0.4
Landfill Leachate	1	--	ND	ND
	2	--	ND	ND

Source: Ref. 2.

[1] Total nitrite + nitrate determined using "4500-NO3 F, Cadmium Reduction Method."
[2] Nitrite + nitrate determined using "4110 C, Single Column Ion Chromatography Using Direct Conductivity Detection."
[3] Each technique gave separate nitrate and nitrate values; their liability results were added for comparison purposes.

These data are provided for guidance purposes only.

TABLE 10

EXAMPLE COMPARISON OF APPROVED METHOD AND CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE FOR THE DETERMINATION OF ORTHO-PHOSPHATE

Data given as mg/L

Analyte	Sample #	Ascorbic Acid[1]	IC[2]	CIE
Effluent	1	3.4	ND	2.8
	2	4.9	ND	4.4
	3	4.7	ND	4.5
	4	5.3	ND	4.2
	5	3.0	ND	3.0
	6	2.9	ND	2.3
	7	<0.1	ND	<0.1
Drinking Water	1	<0.1	ND	ND
	2	<0.1	ND	ND
	3	--	ND	ND
	4	<0.1	ND	ND
	5	<0.1	ND	ND
	6	--	ND	ND
	7	--	ND	ND
Landfill Leachate	1	<0.1	ND	<0.1
	2	2.2	1.6	1.4

Source: Ref. 2.

[1] Phosphate determined using "4500 PO_4 E, Ascorbic Acid Method."
[2] Phosphate determined using "4110 C, Single Column Ion Chromatography Using Direct Conductivity Detection."

The values of "ND" were not given by the source reference.

These data are provided for guidance purposes only.

TABLE 11

EXAMPLE CAPILLARY ION ELECTROPHORESIS ANION ANALYSIS ROUND ROBIN[1]
USING CHROMATE ELECTROLYTE (mg/L)

Sample	Chloride	Bromide	Nitrite	Sulfate	Nitrate	Fluoride	Phosphate
1. Bleach waste	<0.046	<0.046	<0.072	0.30±0.37	<0.84	<0.020	<0.041
2. Creek water	3.06±0.27	<0.046	<0.072	3.00±0.30	0.37±0.19	0.11±0.09	<0.061
3. Wastewater	24.6±0.62	<0.046	<0.072	2.02±0.56	<0.084	0.08±0.08	3.74±0.75
4. Wastewater	59.7±2.9	0.85±0.52	<0.072	109±4.4	44.9±1.6	0.988±0.21	4.94±1.32
5. Wastewater	63.8±2.0	0.68±0.52	<0.072	115±3.9	44.3±1.06	1.04±0.17	4.78±1.55
6. Wastewater	72.0±5.4	0.05±0.01	<0.072	144±11.8	5.38±2.57	0.57±0.21	1.18±1.01
7. Wastewater	139±10.0	<0.046	4.0±1.3	584±35	353±25.5	3.01±0.80	9.34±5.17
8. Wastewater	51.4±7.7	<0.046	<0.072	40.2±6.1	39.9±7.9	1.17±0.24	6.99±1.31
9. Wastewater	29.9±4.3	<0.046	2.14±1.35	217±19	13.9±4.9	1.33±0.28	9.95±5.04
10. Wastewater	766±44	<0.046	<0.072	489±46	12.9±6.9	<0.020	41.3±8.5
11. Surface water	3.71±0.39	<0.046	<0.072	2.70±0.39	0.23±0.20	0.11±0.097	<0.041
12. Wastewater	22.1±0.62	8.47±0.30	<0.072	133±4.4	<0.084	0.76±0.11	<0.041
13. Drinking water	5.15±0.35	<0.046	<0.072	2.64±0.26	0.50±0.27	0.59±0.097	<0.041
14. Drinking water	4.95±0.24	<0.046	<0.072	2.62±0.21	0.54±0.25	0.56±0.09	<0.041

Source: Ref. 2.
[1] Five-laboratory interlaboratory precision. These data are provided for guidance purposes only.

FIGURE 1

HARDWARE SCHEMATIC OF A CAPILLARY
ION ELECTROPHORESIS SYSTEM

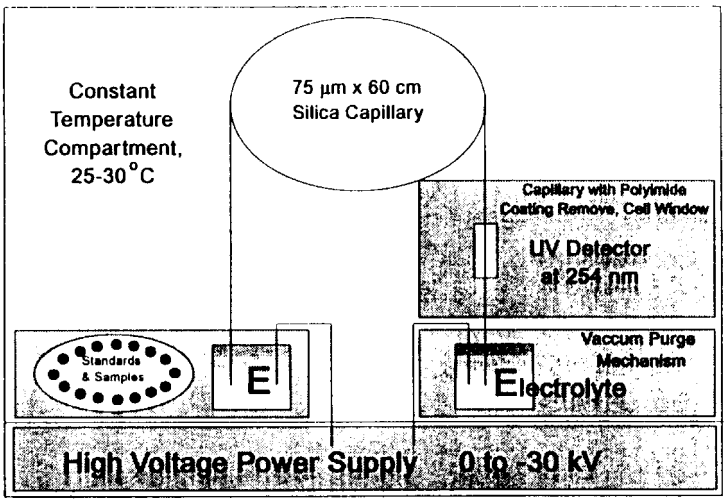


FIGURE 2

PICTORIAL DIAGRAM OF ANION MOBILITY AND
ELECTROOSMATIC FLOW MODIFIER

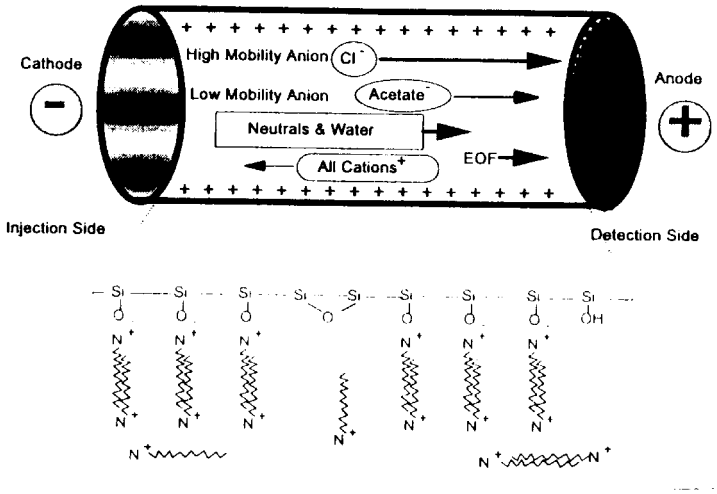


FIGURE 3

SELECTIVITY DIAGRAM OF ANION MOBILITY
USING CAPILLARY ION ELECTROPHORESIS

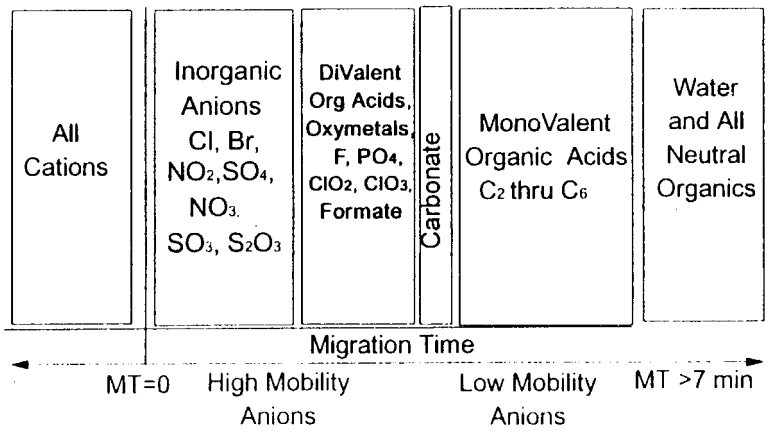


FIGURE 4

PICTORIAL DIAGRAM OF INDIRECT UV DETECTION

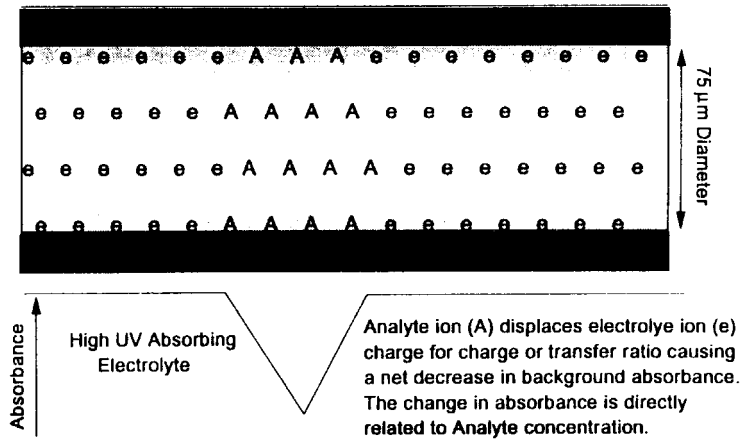
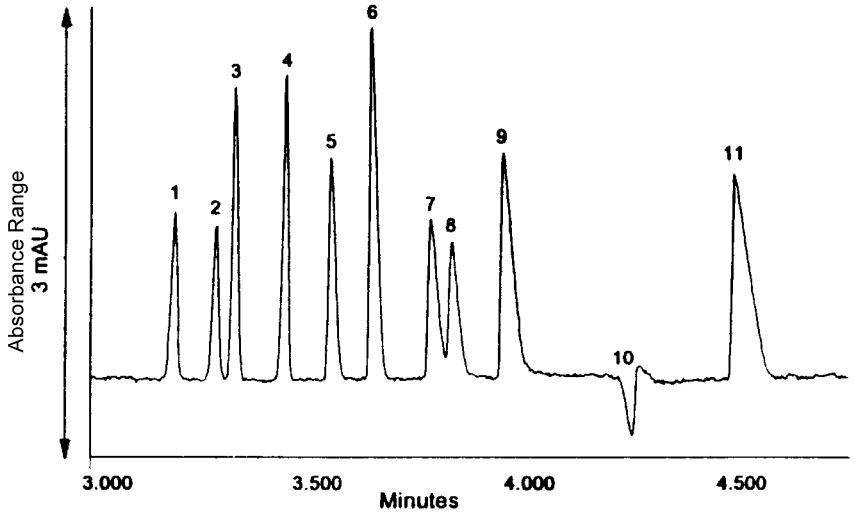


FIGURE 5

ELECTROPHEROGRAM OF THE INORGANIC ANIONS AND TYPICALLY FOUND ORGANIC ACIDS USING CAPILLARY ION ELECTROPHORESIS WITH CHROMATE ELECTROLYTE



Electrolyte: 4.7 mM Na_2CrO_4/4.0 mM TTAOH / 10 mM CHES / 0.1 mM Calcium Gluconate
Capillary: 75 µm (id) x 375 µm x 60 cm (length), Uncoated Silica
Voltage: 15 kV using a Negative Power Supply
Current: 14 ± µA, Constant Current
Sampling: Hydrostatic at 10 cm for 30 secs
Detection: Indirect UV using a Hg Lamp and 254 nm Filter
The y-axis is UV response expressed as Absorbance Units, or in this case, as absorbance range in milliAbsorbance Units or mAU.

Anion	Conc. Mg/L	Migration Time in Mintues	Migration Time Ratio to Cl	Peak Area	Time[1] Corrected Peak Area
1. Chloride	2.0	3.200	1.000	1204	376.3
2. Bromide	4.0	3.296	1.030	1147	348.0
3. Nitrite	4.0	3.343	1.045	2012	601.9
4. Sulfate	4.0	3.465	1.083	1948	562.2
5. Nitrate	4.0	3.583	1.120	1805	503.8
6. Oxalate	5.0	3.684	1.151	3102	842.0
7. Fluoride	1.0	3.823	1.195	1708	446.8
8. Formate	5.0	3.873	1.210	1420	366.6
9. *o*-Phosphate	4.0	4.004	1.251	2924	730.3
10. Carbonate	--	4.281	1.338	--	--
11. Acetate	5.0	4.560	1.425	3958	868.0

[1] Time Corrected Peak Area = Peak area divided by migration time.

FIGURE 6

ELECTROPHEROGRAM OF 0.1 MG/L INORGANIC ANIONS
EXAMPLE MINIMUM DETECTION LIMIT WITH CHROMATE ELECTROLYTE

Seven replicates of the 0.1 mg/L inorganic anion standard were used to calculate the example minimum detection limits, as mg/L, using analytical protocol described in Standard Methods 1030 E.

Chloride = 0.046	Bromide = 0.090	Nitrite = 0.072	Sulfate = 0.032
Nitrate = 0.084	Fluoride = 0.020	Phosphate = 0.041	

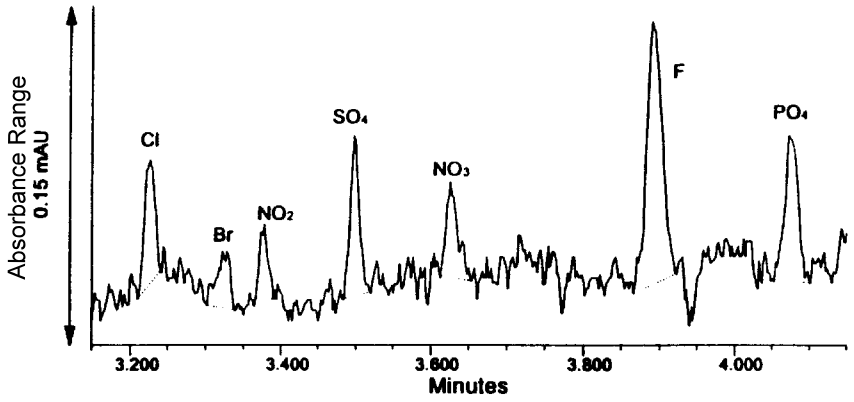


FIGURE 7

ELECTROPHEROGRAM OF TYPICAL DRINKING WATER
USING CHROMATE ELECTROLYTE

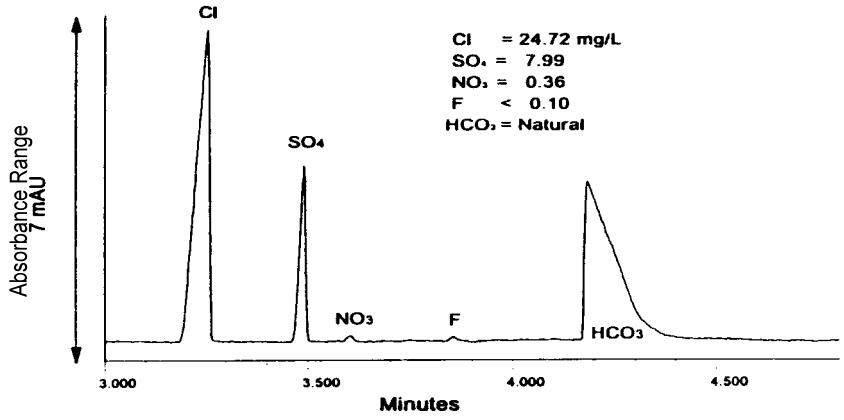


FIGURE 8

ELECTROPHEROGRAM OF TYPICAL MUNICIPAL WASTEWATER DISCHARGE
USING CHROMATE ELECTROLYTE

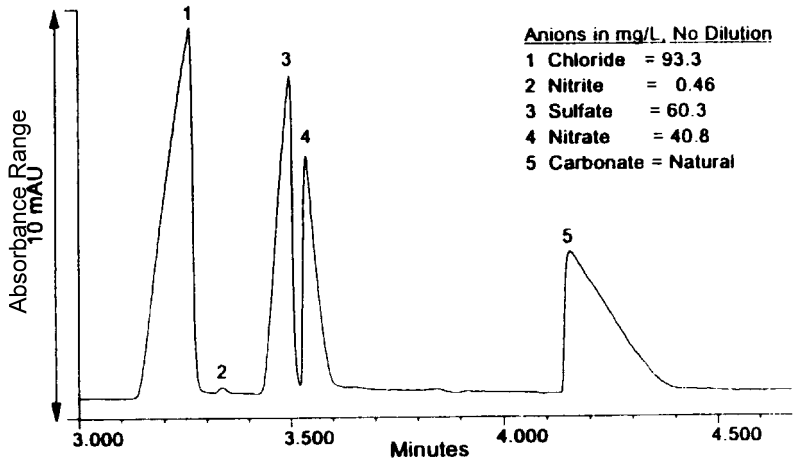


FIGURE 9

ELECTROPHEROGRAM OF TYPICAL INDUSTRIAL WASTEWATER DISCHARGE
USING CHROMATE ELECTROLYTE

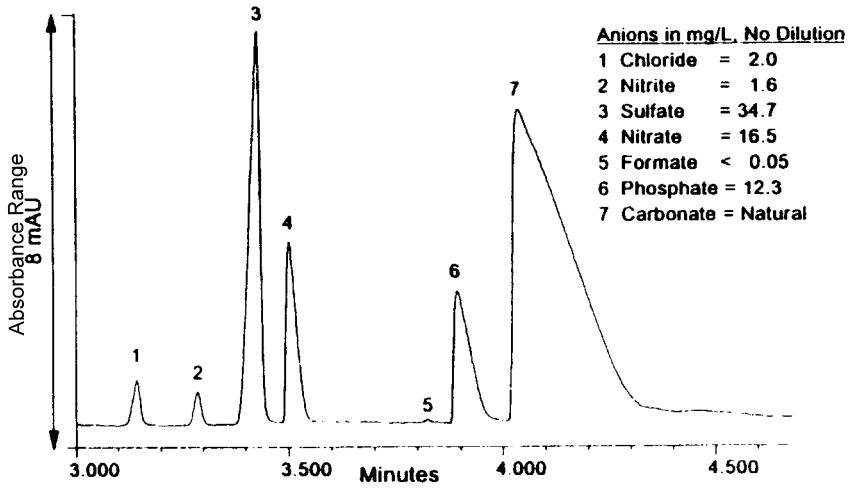


FIGURE 10

LINEARITY CALIBRATION CURVE FOR CHLORIDE, BROMIDE, AND SULFATE USING CHROMATE ELECTROLYTE

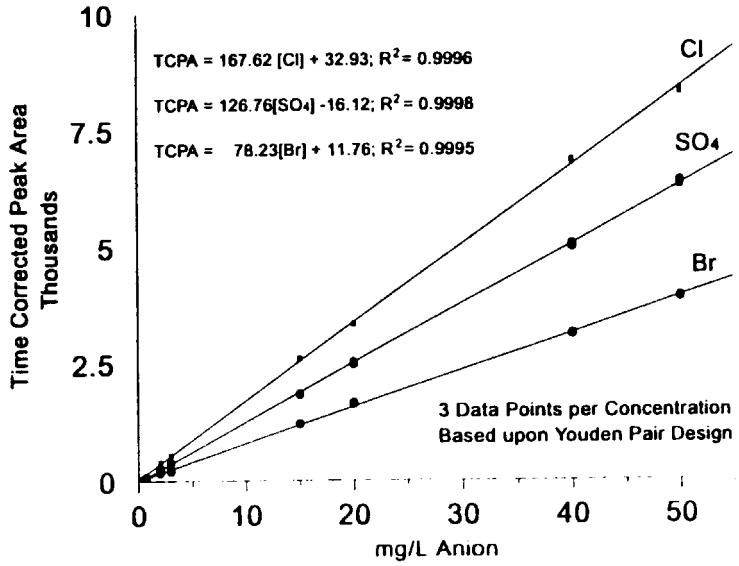


FIGURE 11

LINEARITY CALIBRATION CURVE FOR FLUORIDE AND *o*-PHOSPHATE
USING CHROMATE ELECTROLYTE

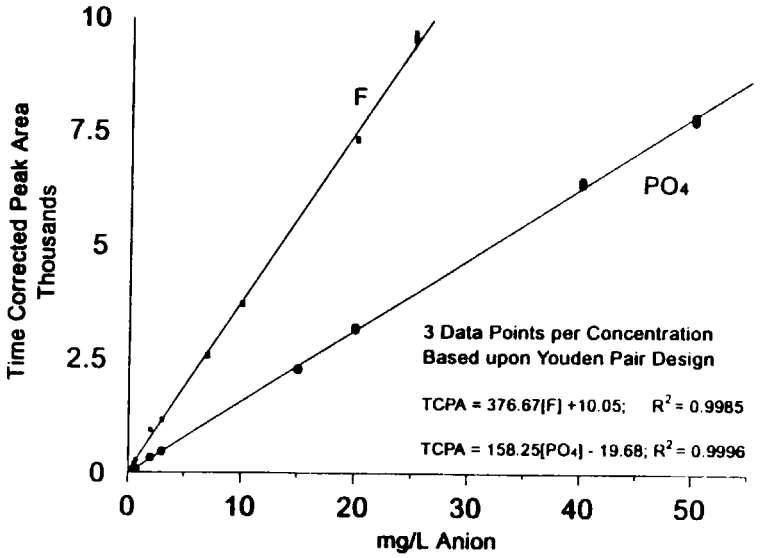
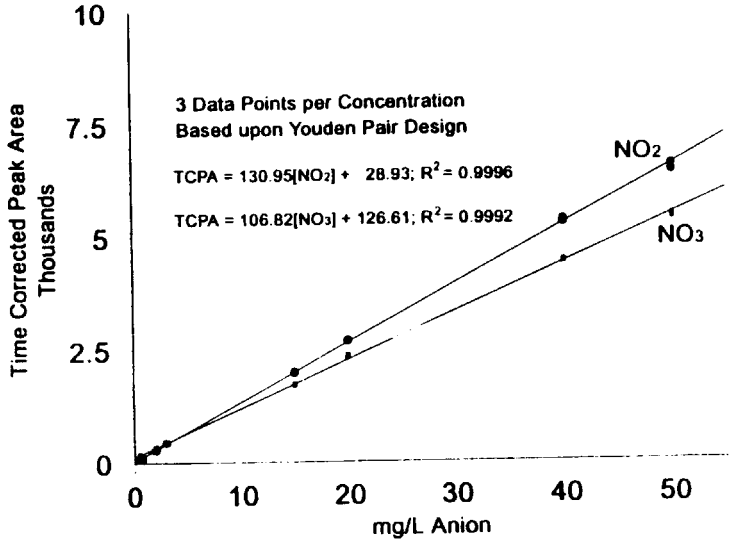
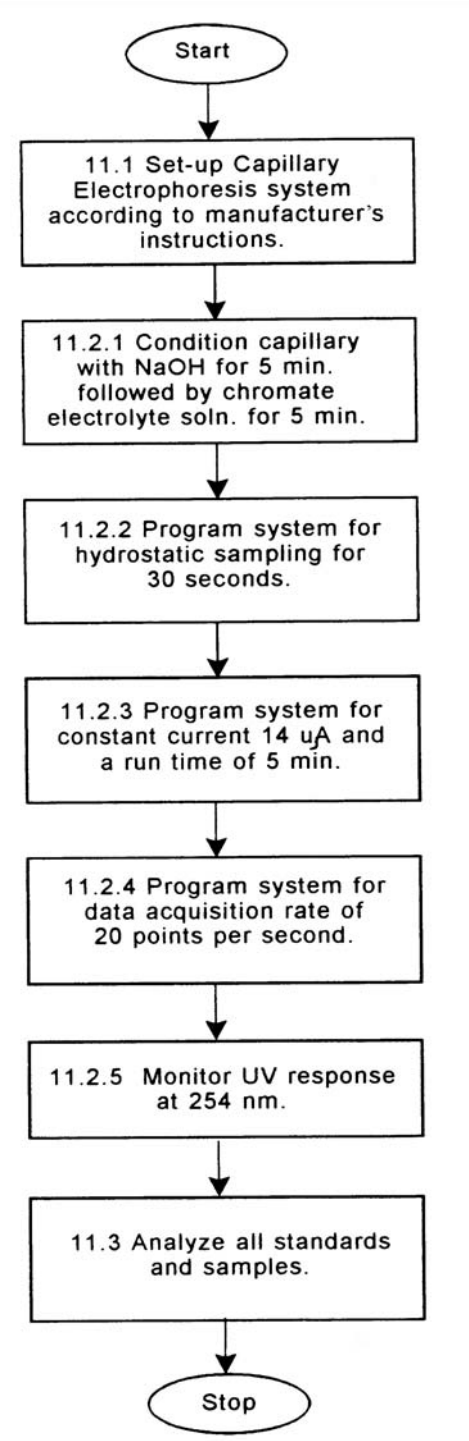


FIGURE 12

LINEARITY CALIBRATION CURVE FOR NITRITE AND NITRATE
USING CHROMATE ELECTROLYTE



DISSOLVED INORGANIC ANIONS IN AQUEOUS MATRICES
BY CAPILLARY ION ELECTROPHORESIS



Capillary ion electrophoresis -- An electrophoretic technique in which a UV absorbing electrolyte is placed in a 75-µm fused silica capillary. Voltage is applied through the capillary causing electrolyte and anions to migrate towards the anode and through the capillary UV detector window. Anions are separated based upon the anion's differential rates of migration in the electrical field which is directly related to the anion's equivalent ionic conductance. Anion detection and quantitation are based upon the principles of indirect UV detection.

Electrolyte -- 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 anion 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.

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, power supply polarity and applied voltage.

Electroosmotic flow modifier (OFM) -- A cationic amine in the electrolyte that dynamically coats the negatively charged silica wall reversing the direction of the electrolyte's natural electroosmotic flow and directing it towards the anode and detector. This modifier augments anion migration and enhances speed of analysis. See Fig. 2.

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.

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

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

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 switched in order to obtain a positive mV response.

Migration time -- The time designated 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.

Time corrected peak area (normalized peak area) -- Peak area divided by migration time. CIE principles state that peak area is dependant on migration time, i.e. for same concentration of analyte, as migration time increases (decreases) peak area increases (decreases). Timed corrected peak area accounts for these changes.

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.