METHOD 300.0

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

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Revision 2.1
August 1993

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1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions:

PART A.

Bromide	Nitrite
Chloride	Ortho-Phosphate-P
Fluoride	Sulfate
Nitrate	

PART B.

Bromate	Chlorite
Chlorate	

1.2 The matrices applicable to each method are shown below:

1.2.1 Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7), leachates (when no acetic acid is used).

1.2.2 Drinking water and reagent waters

1.3 The single laboratory Method Detection Limit (MDL defined in Section 3.2) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 Method A is recommended for drinking and wastewaters. The multilaboratory ranges tested for each anion are as follows:

Analyte	mg/L
Bromide	0.63 - 21.0
Chloride	0.78 - 26.0
Fluoride	0.26 - 8.49
Nitrate-N	0.42 - 14.0
Nitrite-N	0.36 - 12.0
Otho-Phosphate-P	0.69 - 23.1
Sulfate	2.85 - 95.0

1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.6   When this method is used to analyze unfamiliar samples for any of the above
       anions, anion identification should be supported by the use of a fortified
       sample matrix covering the anions of interest. The fortification procedure is
       described in Section 11.6.

1.7   Users of the method data should state the data-quality objectives prior to
       analysis. Users of the method must demonstrate the ability to generate
       acceptable results with this method, using the procedures described in
       Section 9.0.

2.0   SUMMARY OF METHOD

2.1   A small volume of sample, typically 2-3 mL, is introduced into an ion
       chromatograph. The anions of interest are separated and measured, using a
       system comprised of a guard column, analytical column, suppressor device,
       and conductivity detector.

2.2   The main differences between Parts A and B are the separator columns and
       guard columns. Sections 6.0 and 7.0 will elicit the differences.

2.3   An extraction procedure must be performed to use this method for solids
       (See Section 11.7).

2.4   Limited performance-based method modifications may be acceptable provided
       they are fully documented and meet or exceed requirements expressed in
       Section 9.0, Quality Control.

3.0   DEFINITIONS

3.1   **Calibration Blank (CB)** -- A volume of reagent water fortified with the same
       matrix as the calibration standards, but without the analytes, internal
       standards, or surrogate analytes.

3.2   **Calibration Standard (CAL)** -- A solution prepared from the primary dilution
       standard solution or stock standard solutions and the internal standards and
       surrogate analytes. The CAL solutions are used to calibrate the instrument
       response with respect to analyte concentration.

3.3   **Field Duplicates (FD)** -- Two separate samples collected at the same time and
       placed under identical circumstances and treated exactly the same throughout
       field and laboratory procedures. Analyses of field duplicates indicate the
       precision associated with sample collection, preservation and storage, as well
       as with laboratory procedures.

3.4   **Instrument Performance Check Solution (IPC)** -- A solution of one or more
       method analytes, surrogates, internal standards, or other test substances used
       to evaluate the performance of the instrument system with respect to a defined
       set of criteria.

3.5   **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6   **Laboratory Fortified Sample Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.7   **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8   **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.9   **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10   **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.11   **Performance Evaluation Sample (PE)** -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12   **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13   **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.0   INTERFERENCES

4.1   Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2   The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to l00 mL of each standard and sample.

4.3   Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4   Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5   Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6   The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7   The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.8   Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

5.0   SAFETY

5.1   The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2   Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3   The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1   Sulfuric acid (Section 7.4)

6.0   EQUIPMENT AND SUPPLIES

6.1   Balance -- Analytical, capable of accurately weighing to the nearest 0.000l g.

6.2   Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1   Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2   Anion separator column: This column produces the separation shown in Figures 1 and 2.

6.2.2.1 Anion analytical column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Section 9.2 can be met.

6.2.2.2 Anion analytical column (Method B): The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of Section 9.2 can be met.

6.2.3   Anion suppressor device: The data presented in this method were generated using a Dionex anion micro membrane suppressor (P/N 37106).

6.2.4   Detector -- Conductivity cell: Approximately 1.25 µL internal volume, (Dionex, or equivalent) capable of providing data as required in Section 9.2.

6.3   The Dionex AI-450 Data Chromatography Software was used to generate all
        the data in the attached tables. Systems using a stripchart recorder and
        integrator or other computer based data system may achieve approximately
        the same MDL's but the user should demonstrate this by the procedure
        outlined in Section 9.2.

7.0   REAGENTS AND STANDARDS

7.1   Sample bottles: Glass or polyethylene of sufficient volume to allow replicate
        analyses of anions of interest.

7.2   Reagent water: Distilled or deionized water, free of the anions of interest.
        Water should contain particles no larger than 0.20 microns.

7.3   Eluent solution (Method A and Method B): Sodium bicarbonate
        (CASRN 144-55-8) 1.7 mM, sodium carbonate (CASRN 497-19-8) 1.8 mM.
        Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium
        carbonate (Na_2CO_3) in reagent water (Section 7.2) and dilute to 2 L.

7.4   Regeneration solution (micro membrane suppressor): Sulfuric acid
        (CASRN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 L
        with reagent water.

7.5   Stock standard solutions, l000 mg/L (1 mg/mL): Stock standard solutions
        may be purchased as certified solutions or prepared from ACS reagent grade
        materials (dried at 105°C for 30 minutes) as listed below.

   7.5.1   Bromide (Br^-) 1000 mg/L: Dissolve 1.2876 g sodium bromide (NaBr,
            CASRN 7647-15-6) in reagent water and dilute to 1 L.

   7.5.2   Bromate (BrO_3^-) 1000 mg/L: Dissolve 1.1798g of sodium bromate
            ($NaBrO_3$, CASRN 7789-38-0) in reagent water and dilute to 1 L.

   7.5.3   Chlorate (ClO_3^-) 1000 mg/L: Dissolve 1.2753g of sodium chlorate
            ($NaC1O_3$, CASRN 7775-09-9) in reagent water and dilute to 1 L.

   7.5.4   Chloride (Cl^-) l000 mg/L: Dissolve 1.6485 g sodium chloride (NaCl,
            CASRN 7647-l4-5) in reagent water and dilute to 1 L.

   7.5.5   Chlorite (ClO_2^-) 1000 mg/L: Dissolve 1.3410g of sodium chlorite
            ($NaC1O_2$, CASRN 7758-19-2) in reagent water and dilute to 1 L.

   7.5.6   Fluoride (F^-) 1000 mg/L: Dissolve 2.2100g sodium fluoride (NaF,
            CASRN 7681-49-4) in reagent water and dilute to 1 L.

   7.5.7   Nitrate (NO_3^--N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$,
            CASRN 7631-99-4) in reagent water and dilute to 1 L.

   7.5.8   Nitrite (NO_2^--N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$,
            CASRN 7632-00-0) in reagent water and dilute to 1 L.

7.5.9 Phosphate ($PO_4^=$-P) 1000 mg/L: Dissolve 4.3937 g potassium phosphate (KH_2PO_4, CASRN 7778-77-0) in reagent water and dilute to 1 L.

7.5.10 Sulfate ($SO_4^=$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4, CASRN 7778-80-5) in reagent water and dilute to 1 L.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Except for the chlorite standard which is only stable for two weeks. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

7.6 Ethylenediamine preservation solution: Dilute 10 mL of ethylenediamine (99%) (CASRN 107-15-3) to 200 mL with reagent water. Use 1 mL of this dilution to each 1 L of sample taken.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

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

Analyte	Preservation	Holding Time
Bromate	None required	28 days
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	immediately
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Combined	conc. H_2SO_4	28 days
(Nitrate/Nitrite)	to a pH <2	
Nitrite-N	Cool to 4°C	48 hours
0-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

Note: If the determined value for the combined nitrate/nitrite exceeds 0.5 mg/L as N⁻, a resample must be analyzed for the individual concentrations of nitrate and nitrite.

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples

be cooled to 4°C and held for no longer than 28 days for Method A and analyzed immediately in Method B.

Note: If the sample cannot be analyzed for chlorite within ≤10 minutes, the sample may be preserved by adding 1 mL of the ethylenediamine (EDA) preservation solution (Section 7.6) to 1 L of sample. This will preserve the concentration of the chlorite for up to 14 days. This addition of EDA has no effect on bromate or chlorate, so they can also be determined in a sample preserved with EDA. Residual chlorine dioxide should be removed from the sample (per Section 4.8) prior to the addition of EDA.

9.0   QUALITY CONTROL

9.1   Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2   INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1   The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2   Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3   Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4   Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two

to three times the estimated instrument detection limit.[6] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where,   t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t= 3.14 for seven replicates]

S = standard deviation of the replicate analyses

MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3   ASSESSING LABORATORY PERFORMANCE

9.3.1   Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2   Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3   The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should

be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4   Instrument Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4   ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1   Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.1   If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

9.4.2   Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample

9.4.3   Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits for Method A of 80-120% and 75-125% for Method B. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery.

9.4.4   If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.5   Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

9.4.6   In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2.

9.4.7   It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

9.4.8   At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.4.9   When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

10.0   CALIBRATION AND STANDARDIZATION

10.1   Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B.

10.2   For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (Section 7.5) to a volumetric flask and diluting

to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3   Using injections of 0.1-1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

10.4   The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.

10.5   Nonlinear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

11.0   PROCEDURE

11.1   Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.2 are met.

11.2   Check system calibration daily and, if required, recalibrate as described in Section 10.0.

11.3   Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4   The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5   If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to 10 times the weight of dry solid material taken as a sample. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 μ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of fortified samples.

11.8 It has been reported that lower detection limits for bromate (≈7 μg/L) can be obtained using a borate based eluent[7]. The use of this eluent or other eluents that improve method performance may be considered as a minor modification of the method and as such still are acceptable.

11.9 Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3 Report results in mg/L.

12.4 Report NO_2^- as N
          NO_3^- as N
          HPO_4 as P

13.0 METHODS PERFORMANCE

13.1 Tables 1A and 2A give the single laboratory (EMSL-Cincinnati) MDL for each anion included in the method under the conditions listed.

13.2   Tables 2A and 2B give the single laboratory (EMSL-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the listed conditions.

13.3   Multiple laboratory accuracy and bias data (S_t) and estimated single operator values (S_o) for reagent, drinking and waste water using Method A are given for each anion in Tables 3 through 9. Data from 19 laboratories were used for this data.

13.4   Some of the bias statements, for example chloride and sulfate, may be misleading due to spiking small increments of the anion into large naturally occurring concentrations of the same anion.

14.0   POLLUTION PREVENTION

14.1   Pollution prevention encompasses any technique that reduces or eliminates the quantity 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   Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3   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's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4477.

15.0   WASTE MANAGEMENT

15.1   The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. 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 waste discharge permit 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 Section 14.3.

16.0   REFERENCES

1.   "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, No. 4, pg 192.

2.   Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography", 18th Edition of Standard Methods (1992).

3.   Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1988.

4.   Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater", J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

5.   American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).

6.   Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

7.   Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. of Chromatog., 602, (1992), 65-74.

17.0   TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART A)

Analyte	Peak #[*]	Retention Time (min)	MDL (mg/L)
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate-P	6	5.4	0.003
Sulfate	7	6.9	0.02

Standard Conditions:

Columns: as specified in Sesction 6.2.2.1
Detector: as specified in Section 6.2.4   Pump Rate: 2.0 mL/min.
Eluent: as specified in Section 7.3   Sample Loop: 50 μL

MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1 uMHO full scale.
*See Figure 1

TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART B)

Analyte	Peak #[*]	Retention Time (min)	MDL (mg/L)
Chlorite	1	2.8	0.01
Bromate	2	3.2	0.02
Chlorate	4	7.1	0.003

Standard Conditions:

Column: as specified in Section 6.2.2.2
Detector: as specified in Section 6.2.4   Pump Rate: 1.0 mL/min.
Eluent: as specified in Section 7.3   Sample Loop: 50 μL
                                                               Attentuation - 1
                                                               y-axis - 500 ns

[*]See Figure 2

TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS (METHOD A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	99	0.08
	DW	5.0	7	105	0.10
	SW	5.0	7	95	0.13
	WW	5.0	7	105	0.34
	GW	5.0	7	92	0.34
	SD	2.0	7	82	0.06
Chloride	RW	20.0	7	96	0.35
	DW	20.0	7	108	1.19
	SW	10.0	7	86	0.33
	WW	20.0	7	101	5.2
	GW	20.0	7	114	1.3
	SD	20.0	7	90	0.32
Fluoride	RW	2.0	7	91	0.05
	DW	1.0	7	92	0.06
	SW	1.0	7	73	0.05
	WW	1.0	7	87	0.07
	GW	0.4	7	95	0.07
	SD	5.0	7	101	0.35
Nitrate-N	RW	10.0	7	103	0.21
	DW	10.0	7	104	0.27
	SW	10.0	7	93	0.17
	WW	10.0	7	101	0.82
	GW	10.0	7	97	0.47
	SD	10.0	7	82	0.28
Nitrite	RW	10.0	7	97	0.14
	DW	10.0	7	121	0.25
	SW	5.0	7	92	0.14
	WW	5.0	7	91	0.50
	GW	10.0	7	96	0.35
	SD	2.0	7	98	0.08
o-Phosphate-P	RW	10.0	7	99	0.17
	DW	10.0	7	99	0.26
	SW	10.0	7	98	0.22
	WW	10.0	7	106	0.85
	GW	10.0	7	95	0.33
Sulfate	RW	20.0	7	99	0.40
	DW	50.0	7	105	3.35
	SW	40.0	7	95	1.7
	WW	40.0	7	102	6.4
	GW	40.0	7	112	3.2

TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS (METHOD A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)

RW = Reagent Water   WW = Mixed Domestic and Industrial Wastewater

DW = Drinking Water   GW = Groundwater

SW = Surface Water   SD = USEPA QC Solid (shale)

TABLE 2B. SINGLE-OPERATOR ACCURACY AND BIAS OF BY-PRODUCT (PART B)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	103	0.07
		1.0	7	98	0.04
		0.1	7	155	0.005
		0.05	7	122	0.01
	DW	5.0	7	95	0.04
		1.0	7	85	0.02
		0.1	7	98	0.005
		0.05	7	98	0.005
Chlorate	RW	5.0	7	101	0.06
		1.0	7	97	0.01
		0.1	7	100	0.01
		0.05	7	119	0.05
	DW	5.0	7	101	0.04
		1.0	7	115	0.01
		0.1	7	121	0.005
		0.05	7	110	0.01
Chlorite	RW	5.0	7	100	0.04
		1.0	7	98	0.01
		0.1	7	86	0.01
		0.05	7	94	0.01
	DW	5.0	7	96	0.03
		1.0	7	100	0.02
		0.1	7	76	0.00
		0.05	7	96	0.01

RW = Reagent Water
DW = Drinking Water

TABLE 3. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR FLUORIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.26	0.25	0.08	0.11	-3.8
	0.34	0.29	0.11		-14.7
	2.12	2.12	0.07	0.12	0.0
	2.55	2.48	0.14		-2.7
	6.79	6.76	0.20	0.19	-0.4
	8.49	8.46	0.30		-0.4
Drinking	0.26	0.24	0.08	0.05	-7.7
	0.34	0.34	0.11		0.0
	2.12	2.09	0.18	0.06	-1.4
	2.55	2.55	0.16		0.0
	6.79	6.84	0.54	0.25	+0.7
	8.49	8.37	0.75		-1.4
Waste	0.26	0.25	0.15	0.06	-3.8
	0.34	0.32	0.08		-5.9
	2.12	2.13	0.22	0.15	+0.5
	2.55	2.48	0.16		-2.7
	6.79	6.65	0.41	0.20	-2.1
	8.49	8.27	0.36		-2.6

TABLE 4. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR CHLORIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.78	0.79	0.17	0.29	+1.3
	1.04	1.12	0.46		+7.7
	6.50	6.31	0.27	0.14	-2.9
	7.80	7.76	0.39		-0.5
	20.8	20.7	0.54	0.62	-0.5
	26.0	25.9	0.58		-0.4
Drinking	0.78	0.54	0.35	0.20	-30.8
	1.04	0.51	0.38		-51.0
	6.50	5.24	1.35	1.48	-19.4
	7.80	6.02	1.90		-22.8
	20.8	20.0	2.26	1.14	-3.8
	26.0	24.0	2.65		-7.7
Waste	0.78	0.43	0.32	0.39	-44.9
	1.04	0.65	0.48		-37.5
	6.50	4.59	1.82	0.83	-29.4
	7.80	5.45	2.02		-30.1
	20.8	18.3	2.41	1.57	-11.8
	26.0	23.0	2.50		-11.5

TABLE 5. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR NITRITE-NITROGEN

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.36	0.37	0.04	0.04	+2.8
	0.48	0.48	0.06		0.0
	3.00	3.18	0.12	0.06	+6.0
	3.60	3.83	0.12		+6.4
	9.60	9.84	0.36	0.26	+2.5
	12.0	12.1	0.27		+0.6
Drinking	0.36	0.30	0.13	0.03	-16.7
	0.48	0.40	0.14		-16.7
	3.00	3.02	0.23	0.12	+0.7
	3.60	3.62	0.22		+0.6
	9.60	9.59	0.44	0.28	-0.1
	12.0	11.6	0.59		-3.1
Waste	0.36	0.34	0.06	0.04	-5.6
	0.48	0.46	0.07		-4.2
	3.00	3.18	0.13	0.10	+6.0
	3.60	3.76	0.18		+4.4
	9.60	9.74	0.49	0.26	+1.5
	12.0	12.0	0.56		+0.3

TABLE 6. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR BROMIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.63	0.69	0.11	0.05	+9.5
	0.84	0.85	0.12		+1.2
	5.24	5.21	0.22	0.21	-0.6
	6.29	6.17	0.35		-1.9
	16.8	17.1	0.70	0.36	+1.6
	21.0	21.3	0.93		+1.5
Drinking	0.63	0.63	0.13	0.04	0.0
	0.84	0.81	0.13		-3.6
	5.24	5.11	0.23	0.13	-2.5
	6.29	6.18	0.30		-1.7
	16.8	17.0	0.55	0.57	+0.9
	21.0	20.9	0.65		-0.4
Waste	0.63	0.63	0.15	0.09	0.0
	0.84	0.85	0.15		+1.2
	5.24	5.23	0.36	0.11	-0.2
	6.29	6.27	0.46		-0.3
	16.8	16.6	0.69	0.43	-1.0
	21.0	21.1	0.63		+0.3

TABLE 7. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR NITRATE-NITROGEN

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.42	0.42	0.04	0.02	0.0
	0.56	0.56	0.06		0.0
	3.51	3.34	0.15	0.08	-4.8
	4.21	4.05	0.28		-3.8
	11.2	11.1	0.47	0.34	-1.1
	14.0	14.4	0.61		+2.6
Drinking	0.42	0.46	0.08	0.03	+9.5
	0.56	0.58	0.09		+3.6
	3.51	3.45	0.27	0.10	-1.7
	4.21	4.21	0.38		0.0
	11.2	11.5	0.50	0.48	+2.3
	14.0	14.2	0.70		+1.6
Waste	0.42	0.36	0.07	0.06	-14.6
	0.56	0.40	0.16		-28.6
	3.51	3.19	0.31	0.07	-9.1
	4.21	3.84	0.28		-8.8
	11.2	10.9	0.35	0.51	-3.0
	14.0	14.1	0.74		+0.4

TABLE 8. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR ORTHO-PHOSPHATE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.69	0.69	0.06	0.06	0.0
	0.92	0.98	0.15		+6.5
	5.77	5.72	0.36	0.18	-0.9
	6.92	6.78	0.42		-2.0
	18.4	18.8	1.04	0.63	+2.1
	23.1	23.2	0.35		+2.4
Drinking	0.69	0.70	0.17	0.17	+1.4
	0.92	0.96	0.20		+4.3
	5.77	5.43	0.52	0.40	-5.9
	6.92	6.29	0.72		-9.1
	18.4	18.0	0.68	0.59	-2.2
	23.1	22.6	1.07		-2.0
Waste	0.69	0.64	0.26	0.09	-7.2
	0.92	0.82	0.28		-10.9
	5.77	5.18	0.66	0.34	-10.2
	6.92	6.24	0.74		-9.8
	18.4	17.6	2.08	1.27	-4.1
	23.1	22.4	0.87		-3.0

TABLE 9. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR SULFATE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	2.85	2.83	0.32	0.52	-0.7
	3.80	3.83	0.92		+0.8
	23.8	24.0	1.67	0.68	+0.8
	28.5	28.5	1.56		-0.1
	76.0	76.8	3.42	2.33	+1.1
	95.0	95.7	3.59		+0.7
Drinking	2.85	1.12	0.37	0.41	-60.7
	3.80	2.26	0.97		-40.3
	23.8	21.8	1.26	0.51	-8.4
	28.5	25.9	2.48		-9.1
	76.0	74.5	4.63	2.70	-2.0
	95.0	92.3	5.19		-2.8
Waste	2.85	1.89	0.37	0.24	-33.7
	3.80	2.10	1.25		-44.7
	23.8	20.3	3.19	0.58	-14.7
	28.5	24.5	3.24		-14.0
	76.0	71.4	5.65	3.39	-6.1
	95.0	90.3	6.80		-5.0

Method A

Peak	Ret. Time	Ion	mg/L
1	1.17	F^-	2
2	1.73	Cl^-	20
3	2.02	NO_2^-	2
4	2.95	Br^-	2
5	3.20	NO_3^-	10
6	5.38	HPO_4^{2-}	2
7	6.92	SO_4^{2-}	60
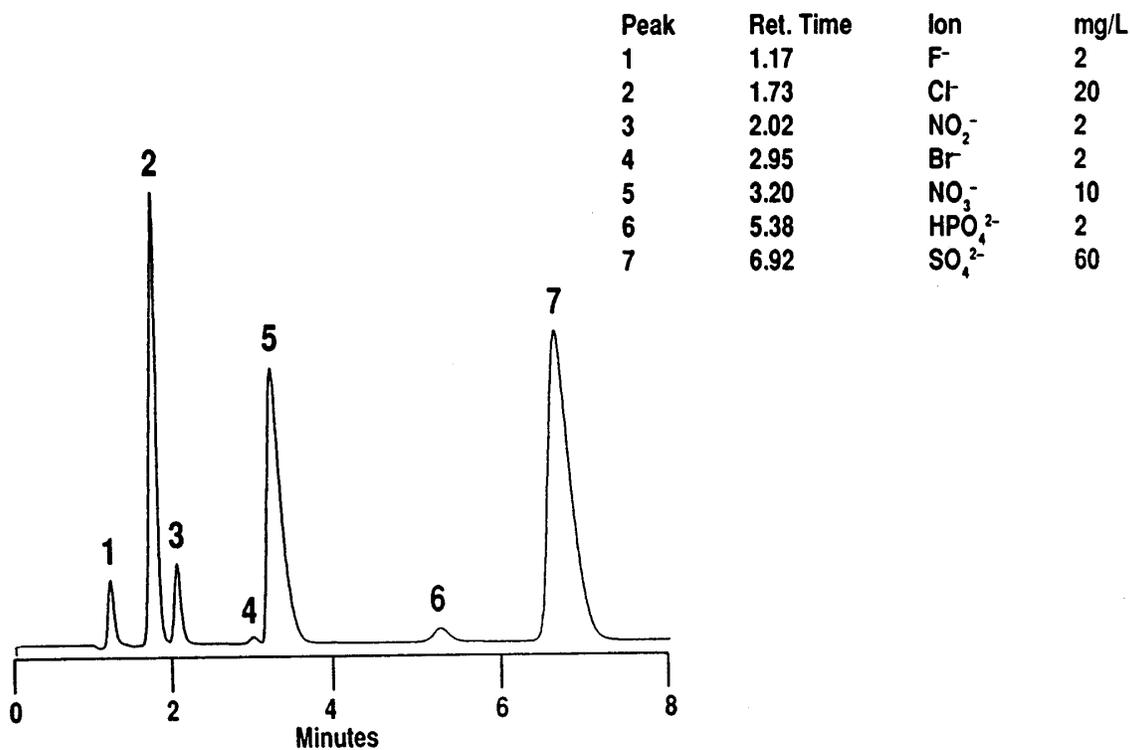
Figure 1. Chromatogram showing separation using the AS4A column

Method B

Peak	Ret. Time	Ion	mg/L
1	2.75	ClO_2^-	0.1
2	3.23	BrO_3^-	0.1
3	3.63	Cl^-	0.1
4	7.08	ClO_3^-	0.1
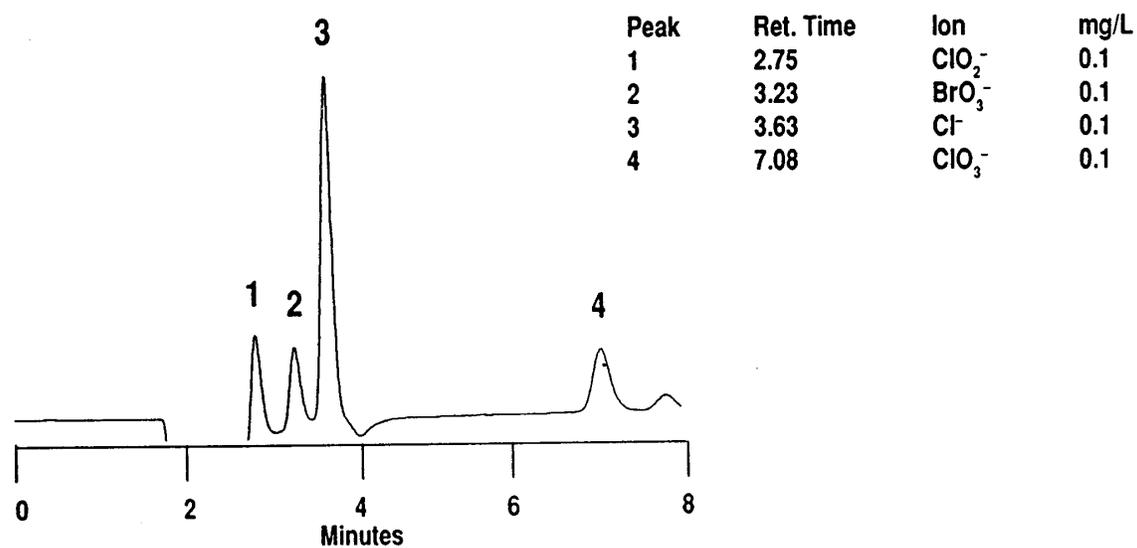
Figure 2. Chromatogram showing separation using the AS9 column