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METHOD 300.1

DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY

Revision 1.0

John D. Pfaff (USEPA, ORD, NERL) - Method 300.0, (1993)

Daniel P. Hautman (USEPA, Office of Water) and David J. Munch (USEPA, Office of Water) - Method 300.1, (1997)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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1. SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions in reagent water, surface water, ground water, and finished drinking water. As a result of different specified injection volumes (See conditions in Tables 1A and 1B), these anions are divided between the common anions listed in Part A and the inorganic disinfection by-products listed in Part B. These different injection volumes are required in order to compensate for the relative concentrations of these anions in drinking water and maintain good chromatographic peak shape throughout the expected dynamic range of the detector. Bromide is included in both Part A, due to its importance as a common anion, as well as Part B due to its critical role as a disinfection by-product precursor.

PART A.-- Common Anions

Bromide	Nitrite
Chloride	ortho-Phosphate-P
Fluoride	Sulfate
Nitrate	

PART B.-- Inorganic Disinfection By-products

Bromate	Chlorite
Bromide	Chlorate

1.2 The single laboratory Method Detection Limits (MDL, defined in Sect. 3.11) for the above analytes are listed in Tables 1A, 1B and 1C. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.

1.2.1 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained and must be capable of yielding a baseline with no more than 5 nS noise/drift per minute of monitored response over the background conductivity.

1.3 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.

1.4 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 Sect. 9.4.1.

1.5 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 Sect. 9.0.

1.6 Bromide and nitrite react with most oxidants employed as disinfectants. The utility of measuring these anions in treated water should be considered prior to conducting the analysis.

2. SUMMARY OF METHOD

2.1 A small volume of sample, 10 µL for Part A and 50 µL for Part B, 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 ONLY difference between Parts A and B is the volume of sample analyzed by the ion chromatographic system. The separator columns and guard columns as well as eluent conditions are identical.

3. DEFINITIONS

3.1 ANALYSIS BATCH -- A group of no more than 20 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all Laboratory Fortified Sample Matrices). The analysis batch must include an Initial Calibration Check Standard, an End Calibration Check Standard, Laboratory Reagent Blank, and a Laboratory Fortified Blank. Within an ANALYSIS BATCH, for every group of ten field samples, at least one Laboratory Fortified Matrix (LFM) and either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM must be analyzed. When more than 10 field samples are analyzed, a Continuing Calibration Check Standard must be analyzed after the tenth field sample analysis.

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.2.1 INITIAL CALIBRATION STANDARDS -- A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions.

3.2.2 INITIAL CALIBRATION CHECK STANDARD -- An individual CAL solution, analyzed initially, prior to any sample analysis, which verifies previously established calibration curves.

3.2.3 CONTINUING CALIBRATION CHECK STANDARD -- An individual CAL solution which is analyzed after every tenth field sample analyses which verifies the previously established calibration curves and confirms accurate analyte quantitation for the previous ten field samples analyzed.

3.2.4 END CALIBRATION CHECK STANDARD -- An individual CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curves and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check.

3.3 FIELD DUPLICATES -- Two separate samples collected at the same time and place 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, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 LABORATORY DUPLICATE -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

3.6 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.

3.7 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.

3.8 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, 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.

3.9 LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.

3.10 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.

3.11 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.

3.12 MINIMUM REPORTING LEVEL (MRL) -- The minimum concentration that can be reported for an anion in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.13 PERFORMANCE EVALUATION SAMPLE (PE) -- A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst.

3.14 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.

3.15 SURROGATE ANALYTE -- An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a

sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.16 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. INTERFERENCES

4.1 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.1.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect.

4.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that **sample dilution will alter your Minimum Reporting Limit (MRL)** by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent as outlined in 11.9.

4.1.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. Prior to using any pretreatment, the analyst should be aware that all instrument calibration standards must be pretreated in exactly the same manner as the pretreated unknown field samples. The need for these cartridges have been greatly reduced with recent advances in high capacity anion exchange columns.

4.1.3.1 Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges

which can foul the guard and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) to insure proper separation and similar response ratios between the target analytes is observed.

4.2 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 baselines in an ion chromatogram. These interferences can lead to false positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

4.3 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.

4.4 Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. 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.

4.5 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of analytes of interest in a second, subsequent analysis. Normally, the elution of sulfate (retention time of 13.8 min.) indicates the end of a chromatographic run, but, in the ozonated and chlorine dioxide matrices, which were included as part of the single operator accuracy and bias study (See Table 2B), a small response (200 nS baseline rise) was observed for a very late eluting unknown peak at approximately 23 minutes. Consequently, a run time of 25 minutes is recommended to allow for the proper elution of any potentially interferant late peaks. It is the responsibility of the user to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

4.6 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, the sample must be purged with an inert gas (helium, argon or nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to ethylenediamine preservation and at time of sample collection.

5. 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 -- When used to prepared a 25 mN sulfuric acid regenerant solution for chemical suppression using a Dionex Anion Micro Membrane Suppressor (AMMS).

6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and a conductivity detector.

6.1.1 Anion guard column: Dionex AG9-HC, 2 mm (P/N 52248), or equivalent. This column functions as a protector of the separator column. If omitted from the system the retention times will be shorter.

6.1.2 Anion separator column: Dionex AS9-HC column, 2 mm (P/N 52244), or equivalent. The microbore (2 mm) was selected in the development of this method as a means to tighten the bromate elution band and thus reduce the detection limit. An optional column (2 mm or 4 mm) may be used if comparable resolution of peaks is obtained, and the requirements of Sect. 9.0 can be met. The AS9-HC, 2 mm column using the conditions outlined in Table 1A and 1B produced the separation shown in Figures 1 through 4.

6.1.2.1 If a 4 mm column is employed, the injection volume should be raised by a factor of four to 40 µL for Part A anions and 200 µL for Part B anions in order to attain comparable detection limits. A four fold increase in injection volume compensates for the four

fold increase in cross sectional surface area of the 4 mm standard bore column over the 2 mm microbore column.

6.1.2.2 Comparable results can be attained using the Dionex, AS9-HC, 4 mm column. MDLs for the part B, inorganic disinfection by-products using this 4 mm column are displayed along with analysis conditions in Table 1C.

6.1.3 Anion suppressor device: The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (ASRS, P/N 43187). An equivalent suppressor device may be utilized provided comparable detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity.

6.1.3.1 The ASRS was set to perform electrolytic suppression at a current setting of 100 mA using an external source DI water mode. Insufficient baseline stability was observed using the ASRS in recycle mode.

6.1.4 Detector -- Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in Sect. 9.2.

6.2 The Dionex Peaknet Data Chromatography Software was used to generate all the data in the attached tables. Systems using a strip chart 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 Sect. 9.2.

6.3 Analytical balance, ±0.1 mg sensitivity. Used to accurately weigh target analyte salts for stock standard preparation.

6.4 Top loading balance, ±10 mg sensitivity. Used to accurately weigh reagents to prepare eluents.

6.5 Weigh boats, plastic, disposable - for weighing eluent reagents.

6.6 Syringes, plastic, disposable, 10 mL - used during sample preparation.

6.7 Pipets, Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.

6.8 Bottles, high density polyethylene (HDPE), opaque or glass, amber, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions. Opaque or amber due to the photoreactivity of chlorite anion.

6.9 Micro beakers, plastic, disposable - used during sample preparation.

7. REAGENTS AND STANDARDS

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

7.2 Eluent solution : Sodium carbonate (CASRN 497-19-8) 9.0 mM. Dissolve 1.91 g sodium carbonate (Na_2CO_3) in reagent water and dilute to 2 L.

7.2.1 This eluent solution must be purged for 10 minutes with helium prior to use to remove dissolved gases which may form micro bubbles in the IC compromising system performance and adversely effecting the integrity of the data.

7.3 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade, potassium or sodium salts as listed below, for most analytes. Chlorite requires careful consideration as outline below in 7.3.5.1.

7.3.1 Bromide (Br^-) 1000 mg/L: Dissolve 0.1288 g sodium bromide (NaBr, CASRN 7647-15-6) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 0.1180 g of sodium bromate ($NaBrO_3$, CASRN 7789-38-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.3 Chlorate (ClO_3^-) 1000 mg/L: Dissolve 0.1275 g of sodium chlorate ($NaClO_3$, CASRN 7775-09-9) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.4 Chloride (Cl^-) 1000 mg/L: Dissolve 0.1649 g sodium chloride (NaCl, CASRN 7647-14-5) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.5 Chlorite (ClO_2^-) 1000 mg/L: Assuming an exact 80.0 % $NaClO_2$ is amperometrically titrated from technical grade $NaClO_2$ (See Sect. 7.3.5.1). Dissolve 0.1676 g of sodium chlorite ($NaClO_2$, CASRN 7758-19-2) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.5.1 High purity sodium chlorite ($NaClO_2$) is not currently commercially available due to potential explosive instability.

Recrystallization of the technical grade (approx. 80%) can be performed but it is labor intensive and time consuming. The simplest approach is to determine the exact % $NaClO_2$ using the iodometric titration procedure (Standard Methods, 19th Ed., 4500-ClO_2.C). Following titration, an individual component standard of chlorite must be analyzed to determine if there is any significant contamination (greater than 1% of the chlorite weight) in the technical grade chlorite standard from any of the Part B components. These contaminants will place a high bias on the calibration of the other anions if all four Part B components are mixed in an combined calibration solution. If these other anions are present as contaminants, a separate chlorite calibration needs to be performed.

7.3.6 Fluoride (F^-) 1000 mg/L: Dissolve 0.2210 g sodium fluoride (NaF, CASRN 7681-49-4) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.7 Nitrate (NO^-_3-N) 1000 mg/L: Dissolve 0.6068 g sodium nitrate ($NaNO_3$, CASRN 7631-99-4) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.8 Nitrite (NO^-_2-N) 1000 mg/L: Dissolve 0.4926 g sodium nitrite ($NaNO_2$, CASRN 7632-00-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.9 Phosphate (PO_4^{3-}-P) 1000 mg/L: Dissolve 0.4394 g potassium dihydrogenphosphate (KH_2PO_4, CASRN 7778-77-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.10 Sulfate (SO_4^{2-}) 1000 mg/L: Dissolve 0.1814 g potassium sulfate (K_2SO_4, CASRN 7778-80-5) in reagent water and dilute to 100 mL in a volumetric flask.

NOTE: Stability of standards: Stock standards (7.3) for most anions are stable for at least 6 months when stored at 4°C. Except for the chlorite standard which is only stable for two weeks when stored protected from light at 4°C, and nitrite and phosphate which are only stable for 1 month when stored at 4°C. Dilute working standards should be prepared monthly, except those that contain chlorite, or nitrite and phosphate which should be prepared fresh daily.

7.4 Ethylenediamine (EDA) preservation solution, 100 mg/mL: Dilute 2.8 mL of ethylenediamine (99%) (CASRN 107-15-3) to 25 mL with reagent water. Prepare fresh monthly.

7.5 Surrogate Solution: 0.50 mg/mL dichloroacetate (DCA) prepared by dissolving 0.065 g dichloroacetic acid, potassium salt (Cl_2CHCO_2K, CASRN 19559-59-2) in reagent water and dilute to 100 mL in a volumetric flask.

7.5.1 Dichloroacetate is potentially present in treated drinking waters as the acetate of the organic disinfection by product, dichloroacetic acid (DCAA). Typical concentrations of DCAA rarely exceed 50 µg/L, which, for this worst case example, would represent only a five percent increase in the observed response over the fortified concentration of 1.00 mg/L. Consequently, the criteria for acceptable recovery (90% to 115%) for the surrogate is weighted to 115% to allow for this potential background.

7.5.2 Prepare this solution fresh every 3 months or sooner if signs of degradation are present.

8. 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 Special sampling requirements and precautions for chlorite.

8.2.1 Sample bottles used for chlorite analysis must be opaque to protect the sample from light.

8.2.2 When preparing the LFM, be aware that chlorite is an oxidant and may react with the natural organic matter in an untreated drinking water matrix as a result of oxidative demand. If untreated water is collected for chlorite analysis, and subsequently used for the LFM, EDA preservation will not control this demand and reduced chlorite recoveries may be observed.

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

PART A : Common Anions

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
ortho-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

PART B : Inorganic Disinfection By-products

Analyte	Preservation	Holding Time
Bromate	50 mg/L EDA	28 days
Bromide	None required	28 days
Chlorate	50 mg/L EDA	28 days
Chlorite	50 mg/L EDA, Cool to 4°C	14 days

8.4 When collecting a sample from a treatment plant employing chlorine dioxide, the sample must be sparged with an inert gas (helium, argon, nitrogen) prior to addition of the EDA preservative at time of sample collection.

8.5 All four anions, in Part B, can be analyzed in a sample matrix which has been preserved with EDA. Add a sufficient volume of the EDA preservation solution (Sect. 7.4) such that the final concentration is 50 mg/L in the sample. This would be equivalent to adding 0.5 mL of the EDA preservation solution to 1 L of sample.

8.6 EDA is primarily used as a preservative for chlorite. Chlorite is susceptible to degradation both through catalytic reactions with dissolved iron salts and reactivity towards free chlorine which exists as hypochlorous acid/hypochlorite ion in most drinking water as a residual disinfectant. EDA serves a dual purpose as a preservative for chlorite by chelating iron as well as any other catalytically destructive metal cations and removing hypochlorous acid/hypochlorite ion by forming an organochloroamine. EDA preservation of chlorite also preserves the integrity of chlorate which can increase in unpreserved samples as a result of chlorite degradation. EDA also preserves the integrity of bromate concentrations by binding with hypobromous acid/hypobromite which is an intermediate formed as by-product of the reaction of either ozone or hypochlorous acid/hypochlorite with bromide ion. If hypobromous acid/hypobromite is not removed from the matrix further reactions may form bromate ion.

8.7 Degradation of ortho-phosphate has been observed in samples held at room temperature for over 16 hrs (see table 3A). Therefore, samples to be analyzed for ortho-phosphate must not be held at room temperature for more than 12 cumulative hours.

9. QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory performance, and subsequent analysis in each analysis batch (Sect. 3.1) of a Laboratory Reagent Blank, Laboratory Fortified Blank, Instrument Performance Check Standard, calibration check standards, Laboratory Fortified Sample Matrices (LFM) and either Field, Laboratory or LFM duplicate sample analyses. This section details the specific requirements for each of these QC parameters. 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 accuracy through the analysis of the QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 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 ± 15% 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.

9.2.3 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of three to five 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 over at least three separate days. 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.

9.2.3.1 MDLs should be determined every 6 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 analysis batch (defined Sect 3.1). 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.

9.3.1.1 If conducting analysis for the Part B anions, EDA must be added to the LRB at 50 mg/L. By including EDA in the LRB, any bias as a consequence of the EDA which may be observed in the field samples, particularly in terms of background contamination, will be identified.

9.3.2 Laboratory Fortified Blank (LFB) -- The LFB should be prepared at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the LFM. Calculate accuracy as percent recovery (Sect. 9.4.1.3). If the recovery of any analyte falls outside the required concentration dependant control limits (Sect. 9.3.2.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.2.1 If conducting analysis for the Part B anions, EDA must be added to the LFB at 50 mg/L. The addition of EDA to all reagent water prepared calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples.

9.3.2.2 Control Limits for the LRB

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 - 125 %
10xMRL to highest calibration level	85 - 115 %

9.3.2.2.1 These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

9.3.2.3 The laboratory must use the LRB to assess laboratory performance against the required control limits listed in 9.3.2.2. 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:

$$\text{UPPER CONTROL LIMIT} = x + 3S$$
$$\text{LOWER CONTROL LIMIT} = x - 3S$$

The optional control limits must be equal to or better than those listed in 9.3.2.2. After each five to ten 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 monitored. These data must be kept on file and be available for review.

9.3.3 Instrument Performance Check Solution (IPC) -- The Initial Calibration Check Standard is to be evaluated as the instrument performance check solution in order to confirm proper instrument performance. Proper chromatographic performance must be demonstrated by calculating the Peak Gaussian Factor (PGF), which is a means to measure peak symmetry and monitoring retention time drift in the surrogate peak over time. Critically evaluate the surrogate peak in the initial calibration check standard, and calculate the PGF as follows,

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where: W(1/2) is the peak width at half height
W(1/10) is the peak width at tenth height

9.3.3.1 The PGF must fall between 0.80 and 1.15 in order to demonstrate proper instrument performance.

9.3.3.2 The retention time for the surrogate in the IPC must be closely monitored on each day of analysis and throughout the lifetime of the analytical column. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if shifts of more than 2% are observed in the surrogate retention time, some type of instrument problem is present. Potential problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The chromatographic profile (elution order) of the target anions following an ion chromatographic analysis should closely replicate the profile displayed in the test chromatogram that was shipped when the column was purchased. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column may require cleaning or replacement. Particularly if resolution problems are beginning to become common between previously resolved peaks. A laboratory must retain a historic record of retention times for the surrogate and all the target anions to provide evidence of an analytical columns vitality.

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 field samples within an analysis batch. The LFM sample must be prepared from a sample matrix which has been analyzed prior to fortification. The analyte concentration must be high enough to be detected above the original sample and should adhere to the requirement of 9.4.1.2. It is recommended that the solutions used to fortify the LFM be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

9.4.1.1 If the fortified concentration is less than the observed background concentration of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration is so high.

9.4.1.2 The LFM should be prepared at concentrations no greater than five times the highest concentration observed in any field sample. If no analyte is observed in any field sample, the LFM must be

fortified no greater than five times the lowest calibration level which as outlined in 12.2 is the minimum reported level (MRL). For example, if bromate is not detected in any field samples above the lowest calibrations standard concentration of 5.00 µg/L, the highest LFM fortified concentration allowed is 25.0 µg/L.

9.4.1.3 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should 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.

9.4.1.4 Until sufficient data becomes available (usually a minimum of 20 to 30 analysis), assess laboratory performance against recovery limits of 75 to 125%. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery. The optional control limits must be equal to or better than the required control limits of 75-125%.

9.4.1.5 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 (Sect. 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.2 SURROGATE RECOVERY -- Calculate the surrogate recovery from all analyses using the following formula

$$R = \frac{SRC}{SFC} \times 100$$

where,
- R = percent recovery.
- SRC = Surrogate Recovered Concentration
- SFC = Surrogate Fortified Concentration

9.4.2.1 Surrogate recoveries must fall between 90-115% for proper instrument performance and analyst technique to be verified. The recovery of the surrogate is slightly bias to 115% to allow for the potential contribution of trace levels of dichloroacetate as the halogenated organic disinfection by-product (DBP) dichloroacetic acid (DCAA) Background levels of this organic DBP are rarely observed above 50 µg/L (0.05 mg/L) which constitutes only 5% of the 1.00 mg/L recommended fortified concentration.

9.4.2.2 If the surrogate recovery falls outside the 90-115% recovery window, a analysis error is evident and sample reanalysis is required. Poor recoveries could be the result of imprecise sample injection or analyst fortification errors.

9.4.3 FIELD OR LABORATORY DUPLICATES -- The laboratory must analyze either a field or a laboratory duplicate for a minimum of 10% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and insure the quality of the data. If none of the samples within an analysis batch have measurable concentrations, the LFM should be employed as a laboratory duplicate.

9.4.3.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_C) and duplicate quantitated concentration (D_c) using the following formula,

$$RPD = \frac{(I_C - D_c)}{([I_C + D_c]/2)} \times 100$$

9.4.3.2 Duplicate analysis acceptance criteria

Concentration range	%Diff Limits
MRL to 10xMRL	± 20 %
10xMRL to highest calibration level	± 10 %

9.4.3.3 If the %Diff fails to meet these criteria, the samples must be reanalyzed.

9.4.4 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.

9.4.5 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns, injection volumes, 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 Sect. 9.2 and adhere to the condition of baseline stability found in Sect. 1.2.1.

9.4.6 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. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B if employing a 2 mm column, Table 1C if employing a 4 mm column.

10.2 Estimate the Linear Calibration Range (LCR) -- The LCR should cover the expected concentration range of the field samples and should not extend over more than 2 orders of magnitude in concentration (For example, if quantitating nitrate in the expected range of 1.0 mg/L to 10 mg/L, 2 orders of magnitude would permit the minimum and maximum calibration standards of 0.20 mg/L and 20 mg/L, respectively.) The restriction of 2 orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

10.2.1 If quantification is desired over a larger range, then two separate calibration curves should be prepared.

10.2.2 For an individual calibration curve, a minimum of three calibration standards are required for a curve that extends over a single order of magnitude and a minimum of five calibration standards are required if the curve covers two orders of magnitude. (For example, using the nitrate example cited above in section 10.2, but in this case limit the curve to extend only from 1.0 mg/L to 10 mg/L or a single order of magnitude. A third standard is required somewhere in the middle of the range. For the calibration range of 0.20 mg/L to 20 mg/L, over two orders of magnitude, five calibrations standards should be employed, one each at the lower and upper concentration ranges and the other three proportionally divided throughout the middle of the curve.)

10.3 Prepare the calibration standards by carefully adding measured volumes of one or more stock standards (7.3) to a volumetric flask and diluting to volume with reagent water.

10.3.1 For the Part B anions, EDA must be added to the calibration standards at 50 mg/L. The addition of EDA to all reagent water prepared calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples.

10.3.2 Prepare a 10.0 mL aliquot of surrogate fortified calibration solution which can be held for direct manual injection or used to fill an autosampler vial. Add 20 µL of the surrogate solution (7.5) to a 20 mL disposable plastic micro beaker. Using a 10.0 mL disposable pipet, place exactly 10.0 mL of calibration standard into the micro beaker and mix. The calibration standard is now ready for analysis. The same surrogate solution that has been employed for the standards should also be used in the section 11.3.2 for the field samples.

10.4 Using a 2 mm column, inject 10 µL (Part A) or 50 µL (Part B) of each calibration standard. Using a 4 mm column, inject 50 µL (Part A) or 200 µL (Part B) of each calibration standard. Tabulate peak area responses against the concentration. The results are used to prepare calibration curves using a linear least squares fit for each analyte. Acceptable calibration curves are confirmed after reviewing the curves for linearity and passing the criteria for the initial calibration check standard in section 10.5.1. Alternately, if the ratio of response to concentration (response factor) is constant over the LCR (indicated by < 15% relative standard deviation (RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve,

10.4.1 Peak areas are strongly recommended since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites. Using peak areas, it is the analyst responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks since poorly drawn baselines will more significantly influence peak areas than peak heights.

10.5 Once the calibration curves have been established they must be verified prior to conducting any sample analysis using an initial calibration check standard (3.2.2). This verification must be performed on each analysis day or whenever fresh eluent has been prepared. A continuing calibration check standard (3.2.3) must be analyzed after every tenth sample and at the end of the analysis set as an end calibration check standard (3.2.4). The response for the initial, continuing and end calibration check must satisfy the criteria listed in 10.5.1. If during the analysis set, the response differs

by more than the calibration verification criteria shown in 10.5.1., or the retention times shift more than ± 5% from the expected values for any analyte, the test must be repeated, using fresh calibration standards. If the results are still outside these criteria, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable calibration check standard must be reanalyzed.

10.5.1 Control limits for calibration verification

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 - 125 %
10xMRL to highest calibration level	85 - 115 %

10.5.1.1 These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

10.5.2 CALIBRATION VERIFICATION REQUIREMENT FOR PART B

As a mandatory requirement of calibration verification, the laboratory MUST verify calibration using the lowest calibration standard as the initial calibration check standard.

10.5.3 After satisfying the requirement of 10.5.2, the levels selected for the other calibration check standards should be varied between a middle calibration level and the highest calibration level.

11. 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 Sect. 9.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Sect. 10.

11.3 Sample Preparation

11.3.1 For refrigerated or samples arriving to the laboratory cold, ensure the samples have come to room temperature prior to conducting sample analysis by allowing the samples to warm on the bench for at least 1 hour.

11.3.2 Prepare a 10.0 mL aliquot of surrogate fortified sample which can be held for direct manual injection or used to fill an autosampler vial. Add 20 µL of the

surrogate solution (7.5) to a 20 mL disposable plastic micro beaker. Using a 10.0 mL disposable pipet, place exactly 10.0 mL of sample into the micro beaker and mix. Sample is now ready for analysis.

11.3.2.1 The less than 1% dilution error introduced by the addition of the surrogate is considered insignificant.

11.4 Using a Luer lock, plastic 10 mL syringe, withdraw the sample from the micro beaker and attach a 0.45 µm particulate filter (demonstrated to be free of ionic contaminants) directly to the syringe. Filter the sample into an autosampler vial (If vial is not designed to automatically filter) or manually load the injection loop injecting a fixed amount of well mixed sample. If using a manually loaded injection loop, flush the loop thoroughly between sample analysis using sufficient volumes of each new sample matrix.

11.5 Using a 2 mm column, inject 10 µL (Part A) or 50 µL (Part B) of each sample. Using a 4 mm column, inject 40 µL (Part A) or 200 µL (Part B) of each sample. Tabulate peak area responses against the concentration. During this procedure, retention times must be recorded. Use the same size loop for standards and samples. Record the resulting peak size in area units. An automated constant volume injection system may also be used.

11.6 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.

11.7 If the response of a sample analyte exceeds the calibration range, the sample may be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to ± 25% the estimated concentration. The latter procedure involves significantly more time than a simple sample dilution therefore, it is advisable to collect sufficient sample to allow for sample dilution or sample reanalysis, if required.

11.8 Shifts in retention time are inversely proportional to concentration. Nitrate, phosphate and sulfate will exhibit the greatest degree of change, although all anions can be affected. In some cases this peak migration may produce poor resolution or make peak identification difficult.

11.9 Should more complete resolution be needed between any two coeluting peaks, the eluent (7.2) can be diluted. This will spread out the run, however, and will cause late

eluting anions to be retained even longer. The analyst must determine to what extent the eluent is diluted. This dilution is not be considered a deviation from the method. If an eluent dilution is performed, section 9.2 must be repeated.

11.9.1 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely effect the MDLs for each analyte.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response, as peak area, against standard concentration. Compute sample concentration by comparing sample response with the standard curve. If a sample has been diluted, multiply the response by the appropriate dilution factor.

12.2 Report ONLY those values that fall between the lowest and the highest calibration standards. Samples with target analyte responses exceeding the highest standard should be diluted and reanalyzed. Samples with target analytes identified but quantitated below the concentration established by the lowest calibration standard should be reported as below the minimum reporting limit (MRL).

12.3 Report results for Part A anions in mg/L and for Part B anions in µg/L.

12.4 Report NO_2^- as N
NO_3^- as N
$HPO_4^=$ as P
Br^- in mg/L when reported with Part A
Br^- in µg/L when reported with Part B

13. METHODS PERFORMANCE

13.1 Tables 1A, 1B, and 1C give the single laboratory (OW OGWDW TSC-Cincinnati) retention times, standard conditions and MDL determined for each anion included in the method. MDLs for the Part A anions were determined in reagent water on the 2 mm column (Table 1A). MDLs for the Part B anions were conducted not only in reagent water but also a simulated high ionic strength water (HIW) on the 2 mm column (Table 1B) and in reagent water on the 4 mm column (Table 1C). HIW is designed to simulate a high ionic strength field sample. It was prepared from reagent water which was fortified with the common anions of chloride at 100 mg/L, carbonate at 100 mg/L, nitrate at 10.0 mg/L as nitrogen, phosphate at 10.0 mg/L as phosphorous, and sulfate at 100 mg/L.

13.2 Tables 2A and 2B give the single laboratory (OW OGWDW TSC-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the standard conditions identified in Table 1A and 1B, respectively.

13.3 Tables 3A and 3B shown stability data for the Part A and B anions, respectively. Each data point in these tables represent the mean percent recovery following triplicate analysis. These data were used to formulate the holding times shown in Sect. 8.3.

14. 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. 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 Sect. 14.3.

16. 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 DX500 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1996.

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.

8. Standard Methods for the Examination of Water and Wastewater, Method 4500-ClO_2,C "Amperometric Method I" (for the determination of Chlorine Dioxide), 19th Edition of Standard Methods (1995).

17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE COMMON ANIONS (PART A).

			MDL DETERMINATION		
ANALYTE	PEAK # [1]	RETENTION TIME (MIN.)	Fort Conc, mg/L	Number of Replicates	DI MDL mg/L
Fluoride	1	2.53	0.020	7	0.009
Chloride	2	4.67	0.020	7	0.004
Nitrite-N	3	6.01	0.010	7	0.001
Surrogate: DCA	4	7.03			
Bromide	5	8.21	0.040	7	0.014
Nitrate-N	6	9.84	0.010	7	0.008
ortho-Phosphate-P	7	11.98	0.040	7	0.019
Sulfate	8	13.49	0.040	7	0.019

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 2 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 0.40 mL/min
Sample Loop: 10 µL

System Backpressure: 2800 psi
Background Conductivity: 22 µS

Recommended method total analysis time: 25 minutes

(1) See Figure 1

TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN BOTH REAGENT WATER AND HIGH IONIC STRENGTH WATER FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

ANALYTE	PEAK # [1]	RETENTION TIME (MIN.)	MDL DETERMINATION			
			Fort Conc, µg/L	Number of Replicates	DI MDL µg/L	HIW[2] MDL µg/L
Chlorite	1	3.63	2.00	7	0.89	0.45
Bromate	2	4.19	2.00	7	1.44	1.28
Surrogate: DCA	4	7.28				
Bromide	5	8.48	2.00	7	1.44	2.51
Chlorate	6	9.28	2.00	7	1.31	0.78

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 2 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 0.40 mL/min
Sample Loop: 50 µL

System Backpressure: 2800 psi
Background Conductivity: 22 µS

Recommended method total analysis time: 25 minutes

(1) See Figure 2 and 3

(2) HIW indicates High Ionic Strength Water which is a simulated drinking water prepared from reagent water and fortified with chloride at 100 mg/L, carbonate at 100 mg/L, nitrate at 10.0 mg/L as nitrogen, phosphate at 10.0 mg/L as phosphorous, and sulfate at 100 mg/L.

TABLE 1C. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE INORGANIC DISINFECTION BY-PRODUCTS USING AN ALTERNATE 4 mm AS9-HC COLUMN (PART B).

ANALYTE	PEAK #	RETENTION TIME (MIN.)	MDL DETERMINATION		
			Fort Conc, µg/L	Number of Replicates	DI MDL µg/L
Chlorite	1	4.43	2.00	7	1.44
Bromate	2	5.10	2.00	7	1.32
Surrogate: DCA	4	8.82			
Bromide	5	10.11	2.00	7	0.98
Chlorate	6	10.94	2.00	7	2.55

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 4 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 300 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 1.25 mL/min
Sample Loop: 200 µL

System Backpressure: 1900 psi
Background Conductivity: 21 µS

Recommended method total analysis time: 25 minutes

TABLE 2A. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE COMMON ANIONS (PART A).

ANALYTE	MATRIX	UNFORT MATRIX CONC., mg/L	FORT CONC mg/L	# OF REPLC	MEAN mg/L	MEAN %REC	SD(n-1)	%RSD
Fluoride	RW	<MDL[1]	2.00	9	1.79	89.7	0.02	1.18
	SW	0.139	2.00	9	1.75	80.4	0.01	0.56
	GW	0.280	2.00	9	1.97	84.3	0.02	0.85
	CDW	0.807	2.00	9	2.59	89.0	0.01	0.46
Chloride	RW	0.029	50.0	9	49.4	98.7	0.03	0.10
	SW	12.1	50.0	9	58.7	93.3	0.04	0.10
	GW	56.6	50.0	9	100.	---[2]	0.22	0.22
	CDW	16.0	50.0	9	64.9	97.8	0.11	0.16
Nitrite-N	RW	<MDL	1.00	9	0.851	85.1	0.00	0.51
	SW	<MDL	1.00	9	0.780	78.0	0.00	0.40
	GW	0.013	1.00	9	0.879	86.6	0.01	0.77
	CDW	<MDL	1.00	9	0.720	72.0	0.00	0.55
Bromide	RW	<MDL	0.500	9	0.480	96.1	0.00	0.92
	SW	0.028	0.500	9	0.469	88.1	0.00	0.94
	GW	0.153	0.500	9	0.634	96.3	0.00	0.52
	CDW	<MDL	0.500	9	0.431	86.2	0.01	1.28
Nitrate-N	RW	<MDL	10.0	9	9.50	95.0	0.01	0.14
	SW	2.12	10.0	9	10.9	87.7	0.03	0.30
	GW	0.016	10.0	9	9.64	96.3	0.03	0.27
	CDW	1.64	10.0	9	10.9	92.4	0.04	0.41
Phosphate-P	RW	<MDL	10.0	9	9.62	96.2	0.01	0.14
	SW	<MDL	10.0	9	8.70	87.0	0.02	0.18
	GW	<MDL	10.0	9	6.12	61.2	0.28	4.66
	CDW	<MDL	10.0	9	9.15	91.5	0.04	0.42
Sulfate	RW	<MDL	50.0	9	44.8	89.5	0.05	0.11
	SW	47.8	50.0	9	92.1	88.6	0.21	0.23
	GW	105	50.0	9	154	---[2]	0.60	0.39
	CDW	57.8	50.0	9	105	---[2]	0.33	0.32
Surrogate:	RW	----	5.00	9	5.12	102.3	0.50	0.49
	SW	----	5.00	9	5.09	102.3	1.12	1.09
	GW	----	5.00	9	5.16	101.8	0.67	0.66
	CDW	----	5.00	9	5.17	103.1	1.36	1.32

RW = Reagent Water
SW = Surface Water
GW = Ground Water
CDW = chlorine dioxide treated finished drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

ANALYTE	MATRIX	UNFORT CONC. µg/L	FORT CONC µg/L	# OF REPLC	MEAN µg/L	MEAN %REC	SD(n-1)	%RSD
Chlorite	RW	<MDL[1]	100	9	96.2	96.2	0.95	0.99
			500	9	523	105	3.13	0.60
	HIW	<MDL	100	9	102	102	2.19	2.15
			500	9	520	104	3.64	0.70
	SW	<MDL	100	9	91.4	91.4	1.22	1.33
			500	9	495	99.0	7.54	1.52
	GW	<MDL	100	9	92.9	92.9	1.65	1.77
			500	9	490	98.1	3.40	0.69
	ClW	<MDL	100	9	87.4	87.4	0.59	0.68
			500	9	485	97.1	6.36	1.31
	CDW	292	100	9	396	---[2]	1.64	0.41
			500	9	811	104	4.00	0.49
	O3W	<MDL	100	9	84.4	84.4	0.46	0.54
			500	9	481	96.1	3.24	0.67
Bromate	RW	<MDL	5.00	9	5.04	101	0.45	8.86
			25.0	9	26.5	106	1.71	6.47
	HIW	<MDL	5.00	9	4.88	97.5	0.95	19.5
			25.0	9	25.6	102	1.37	5.37
	SW	<MDL	5.00	9	4.46	89.2	0.58	13.0
			25.0	9	26.3	105	1.10	4.18
	GW	<MDL	5.00	9	5.10	102	0.50	9.75
			25.0	9	22.2	88.9	1.29	5.81
	ClW	<MDL	5.00	9	4.63	92.6	0.77	16.7
			25.0	9	25.1	100	1.64	6.55
	CDW	<MDL	5.00	9	4.14	82.7	0.62	15.1
			25.0	9	25.1	101	1.28	5.09
	O3W	1.45	5.00	9	5.49	80.9	0.61	11.1
			25.0	9	24.1	90.6	1.13	4.69

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B) (contd.).

ANALYTE	MATRIX	UNFORT CONC. µg/L	FORT CONC µg/L	# OF REPLC	MEAN µg/L	MEAN %REC	SD(n-1)	%RSD
Bromide	RW	<MDL[1]	20.0	9	20.9	104	0.80	3.82
			100	9	107	107	0.60	0.56
	HIW	3.24	20.0	9	21.8	92.5	0.79	3.63
			100	9	105	102	1.05	1
	SW	31.0	20.0	9	51.3	---[2]	0.97	1.9
			100	9	140.	109	1.88	1.35
	GW	151	20.0	9	172	---[2]	0.78	0.45
			100	9	265	---[2]	2.18	0.82
	ClW	16.3	20.0	9	39.3	115	0.64	1.62
			100	9	125	109	2.00	1.6
	CDW	11.5	20.0	9	34.4	115	0.76	2.22
			100	9	125	113	1.24	0.99
	O3W	39.8	20.0	9	65.4	---[2]	3.67	5.61
			100	9	153	113	1.00	0.65
Chlorate	RW	<MDL	100	9	98.3	98.3	0.80	0.82
			500	9	520	104	4.15	0.8
	HIW	<MDL	100	9	86.1	86.1	1.47	1.7
			500	9	502	100.	4.52	0.9
	SW	3.18	100	9	102	98.3	1.57	1.55
			500	9	513	102	7.11	1.39
	GW	<MDL	100	9	93.5	93.5	2.00	2.14
			500	9	510	102	3.84	0.75
	ClW	34.4	100	9	136	102	1.01	0.74
			500	9	549	103	3.11	0.57
	CDW	121	100	9	223	---[2]	3.20	1.44
			500	9	651	106	3.50	0.54
	O3W	6.15	100	9	106	100	1.20	1.13
			500.	9	523	103	2.45	0.47

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B)(contd.).

ANALYTE	MATRIX	FORT CONC mg/L	# OF REPLC	MEAN mg/L	MEAN %REC	SD(n-1)	%RSD
Surrogate: DCA (see NOTE below)	RW	5.00	9	5.11	102	0.93	0.91
				4.98	99.5	0.69	0.69
	HIW	5.00	9	5.00	100	0.79	0.79
				4.96	99.2	1.76	1.78
	SW	5.00	9	4.95	98.9	0.70	0.7
				4.99	99.8	1.60	1.61
	GW	5.00	9	5.12	102	0.50	0.49
				5.13	103	0.50	0.49
	ClW	5.00	9	5.15	103	1.73	1.68
				5.13	103	1.12	1.09
	CDW	5.00	9	5.01	100	1.02	1.02
				5.04	101	1.08	1.07
	O3W	5.00	9	4.99	99.8	0.70	0.7
				5.11	101	0.53	0.52

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

NOTE: The surrogate DCA was fortified at 5 mg/L but due to concerns about measuring trace concentrations of bromide with such high concentration of the neighboring surrogate peak, the recommended fortified concentration for the surrogate has been reduced to 1.00 mg/L.

TABLE 3A. STABILITY STUDY RESULTS FOR THE COMMON ANIONS (PART A).

ANALYTE	Preservative	Matrix	UNFORT CONC. mg/L	FORT CONC mg/L	Analyte % Recovery Day 0	Day 14	Day 28	See Note
Fluoride	None	RW	<MDL	2.00	89.8	88.3	88.4	
		SW	0.140	2.00	79.9	80.2	80.0	
		GW	0.280	2.00	84.7	87.8	87.0	
		CDW	0.929	2.00	82.9	83.6	81.6	
Chloride	None	RW	<MDL	50.0	98.8	99.1	98.1	
		SW	12.0	50.0	93.4	93.5	92.8	
		GW	56.6	50.0	87.6	87.6	86.5	
		CDW	16.0	50.0	97.9	98.4	97.8	
Nitrite-N	None	RW	<MDL	1.00	85.2	85.5	83.6	
		SW	<MDL	1.00	77.8	76.6	11.9	(1)
		GW	<MDL	1.00	88.2	85.4	56.1	(1)
		CDW	<MDL	1.00	71.9	71.7	73.9	(2)
Bromide	None	RW	<MDL	0.500	95.5	97.0	96.2	
		SW	0.028	0.500	87.5	88.3	86.7	
		GW	0.153	0.500	96.9	96.0	96.1	
		CDW	<MDL	0.500	85.7	87.1	89.2	(2)
Nitrate-N	None	RW	<MDL	10.0	94.9	94.7	94.2	
		SW	2.12	10.0	87.6	87.0	88.7	
		GW	<MDL	10.0	96.5	96.5	95.5	
		CDW	1.64	10.0	92.3	93.3	91.9	
Phosphate-P	None	RW	<MDL	10.0	96.3	95.8	95.2	
		SW	<MDL	10.0	86.9	86.4	85.1	
		GW	<MDL	10.0	62.8	93.1	89.5	(3)
		CDW	<MDL	10.0	91.6	91.4	90.8	
Sulfate	None	RW	<MDL	50.0	89.6	89.3	89.1	
		SW	47.8	50.0	89.0	89.0	88.1	
		GW	105	50.0	97.5	97.3	96.5	
		CDW	57.8	50.0	94.3	94.9	93.8	

NOTES:

(1) Degradation apparent.

(2) Analyte recovery will be adversely effected by reactions with free chlorine.

(3) Phosphate recovery on day 0 is believed to have been adversely effected by biological degradation since the sample sat in the autosampler for 18 hrs prior to analysis

TABLE 3B STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

ANALYTE	Preservative	Matrix	UNFORT CONC. µg/L	FORT CONC µg/L	Analyte % Recovery Day 0	Day 3	Day 10	Day 30	See Note
Chlorite	None	RW	<MDL	500	99.8	100	104	94.3	
		HIW	<MDL	500	99.3	98.5	106	89.3	
		SW	<MDL	500	92	88.5	82.	75.1	(1)
		GW	<MDL	500	93.9	94.5	96.	91.7	
		ClW	<MDL	500	93.7	NA[(1)]	90.	84.7	(2,3)
		CDW	286	500	98.6	101	91.	77.5	(1,3)
		O3W	<MDL	500	10	NA	82.	90.5	(2)
Chlorite	EDA	RW	<MDL	500	101	101	104	95.3	
		HIW	<MDL	500	98.4	98.7	104	95.4	
		SW	<MDL	500	98.3	97.3	97.	92.7	
		GW	<MDL	500	97.7	97.1	97.	92.6	
		ClW	<MDL	500	98.9	NA	96.	92.6	(2)
		CDW	297	500	103	107	102	94.5	
		O3W	<MDL	500	105	NA	96.	91.9	(2)
Bromate	None	RW	<MDL	25.0	93.6	94.1	110	96.1	
		HIW	<MDL	25.0	100	86.0	105	87.7	
		SW	<MDL	25.0	98.7	95.1	105	102	
		GW	<MDL	25.0	79.4	92.4	77.	82.2	
		ClW	<MDL	25.0	102	NA	101	103	(2)
		CDW	<MDL	25.0	104	96.8	98.	92.1	
		O3W	2.27	25.0	87.3	NA	84.	99.9	(2)
Bromate	EDA	RW	<MDL	25.0	97.3	95.3	99.	102	
		HIW	<MDL	25.0	86.9	86.1	107	91.2	
		SW	<MDL	25.0	100	104	103	94.9	
		GW	<MDL	25.0	83.2	101	88.	88.3	
		ClW	<MDL	25.0	105	NA	101	102	(2)
		CDW	<MDL	25.0	117	97.3	98.	83.9	
		O3W	2.32	25.0	92.6	NA	84.	88.9	(2)

See bottom of next page for explanation of notes

TABLE 3B. STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B)(contd.)

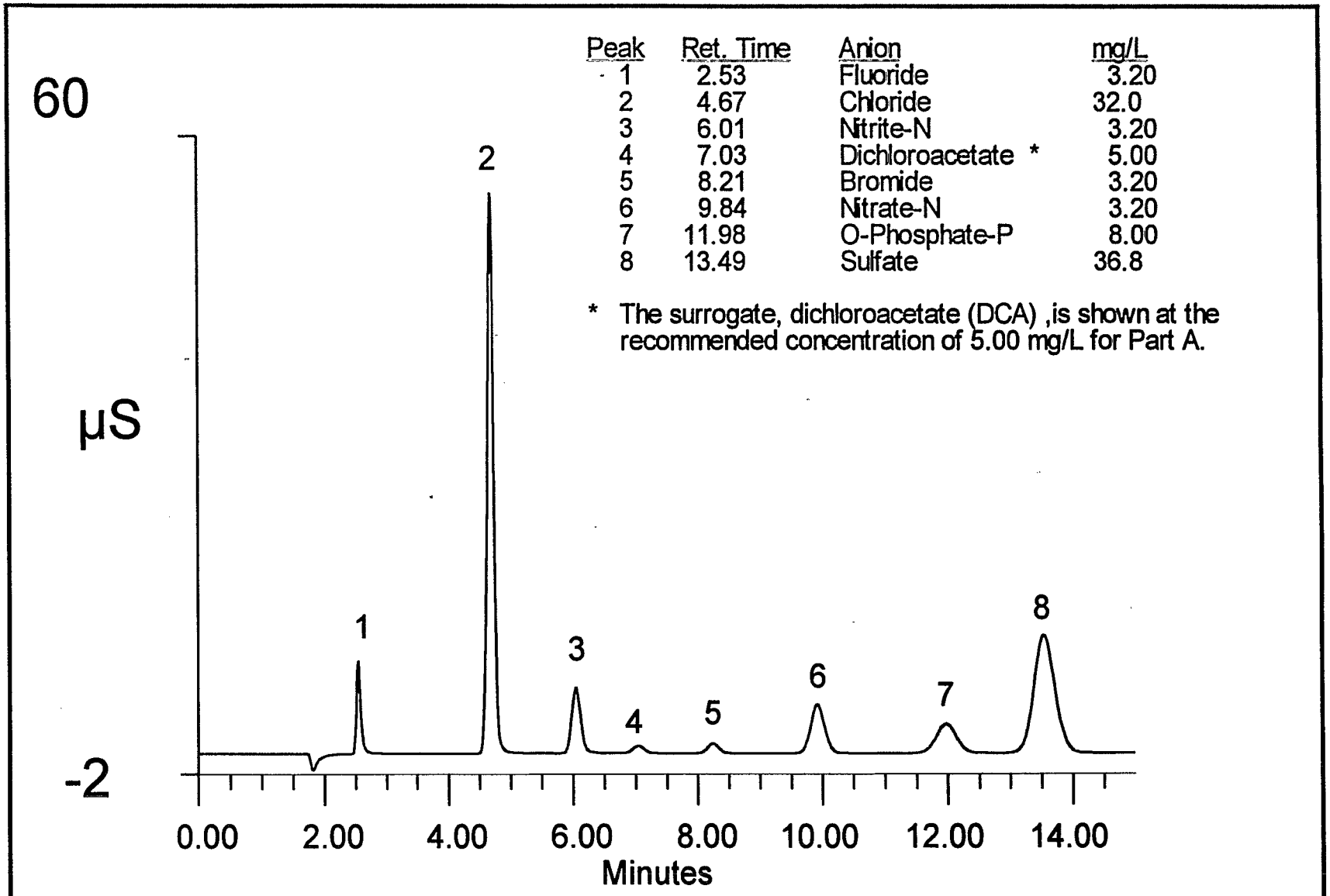
ANALYTE	Preservative	Matrix	UNFORT CONC. µg/L	FORT CONC µg/L	Analyte % Recovery Day 0	Day 3	Day 10	Day 30	See Note
Bromide	None	RW	<MDL	100	99.4	97.2	107	101	
		HIW	<MDL	100	102	103	105	105	
		SW	30.6	100	102	97.1	107	99.1	
		GW	149	100	97.7	95.3	109	100	
		ClW	4.73	100	8.9	NA(1)	37.	11.4	(2,3)
		CDW	<MDL	100	5.78	23.1	38.	51.3	(3)
		O3W	30.4	100	98.3	NA	120	108	(2)
Bromide	EDA	RW	<MDL	100	98.4	98.6	107	100	
		HIW	<MDL	100	104	103	106	105	
		SW	30.5	100	99.5	98.2	107	100	
		GW	149	100	100	97	114	97.7	
		ClW	11.9	100	101	NA	115	97.4	(2,3)
		CDW	6.14	100	101	96.5	119	110	(3)
		O3W	31.0	100	97.3	NA	122	102	(2)
Chlorate	None	RW	<MDL	500	102	102	105	97.4	
		HIW	<MDL	500	96.5	97.8	101	95.4	
		SW	5.84	500	99.8	97.8	100	96	
		GW	<MDL	500	99.5	98.7	101	99.8	
		ClW	37.8	500	102	NA	104	98.2	(2)
		CDW	125	500	102	99.9	104	99.6	
		O3W	8.34	500	100	NA	103	97.3	(2)
Chlorate	EDA	RW	<MDL	500	104	98.6	103	97.3	
		HIW	<MDL	500	97.3	103	100	95	
		SW	6.70	500	99.7	98.2	99.	95.6	
		GW	<MDL	500	102	97	101	99.3	
		ClW	38.2	500	101	NA	102	96.1	(2)
		CDW	123	500	102	96.5	105	97.7	
		O3W	8.62	500	98.4	NA	103	96.4	(2)

NOTES:

(1) Degradation in the unpreserved matrix is apparent.

(2) NA indicates "NOT ANALYZED"

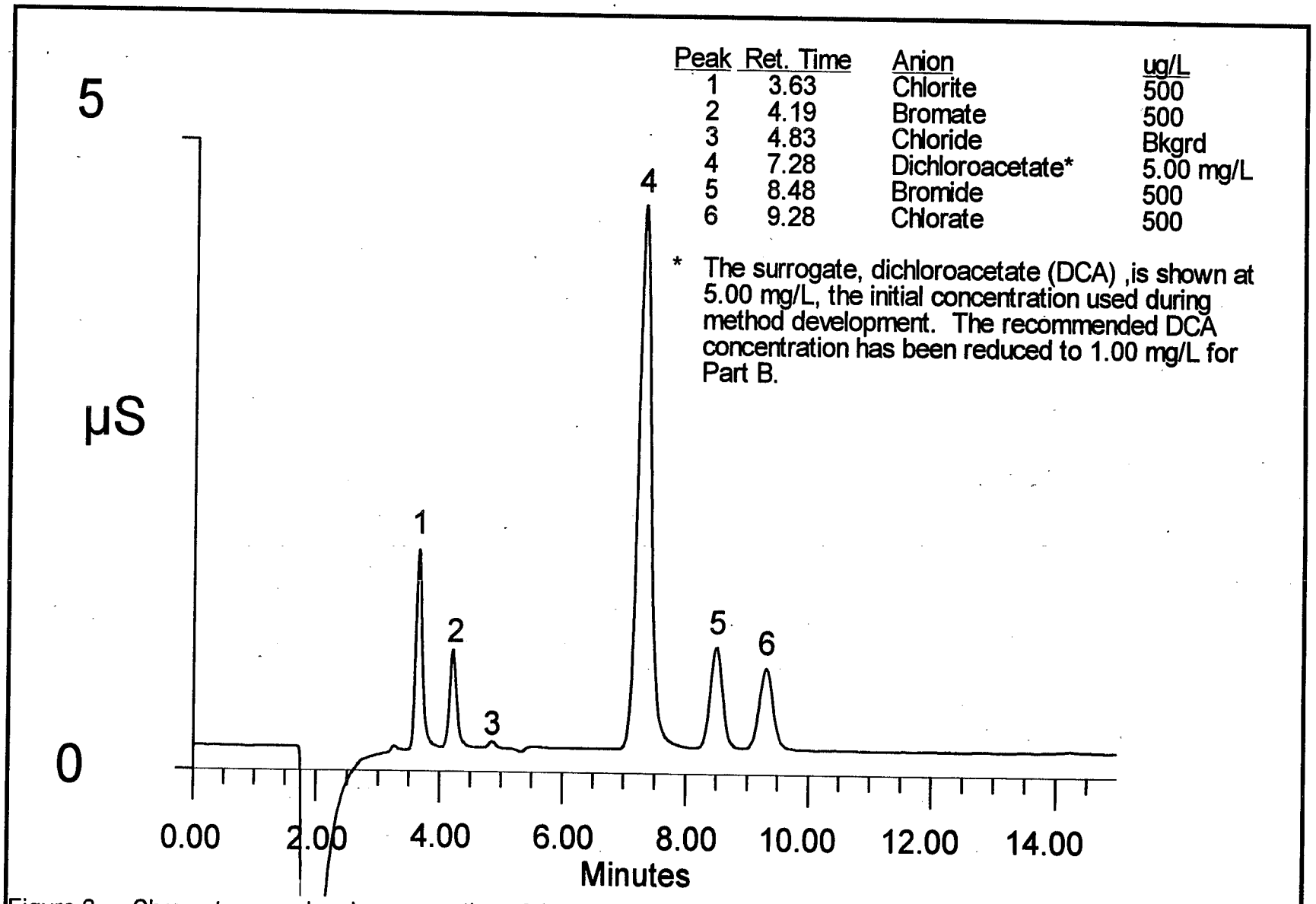
(3) Analyte recovery will be adversely effected by reactions with free chlorine.



Peak	Ret. Time	Anion	mg/L
1	2.53	Fluoride	3.20
2	4.67	Chloride	32.0
3	6.01	Nitrite-N	3.20
4	7.03	Dichloroacetate *	5.00
5	8.21	Bromide	3.20
6	9.84	Nitrate-N	3.20
7	11.98	O-Phosphate-P	8.00
8	13.49	Sulfate	36.8

* The surrogate, dichloroacetate (DCA) ,is shown at the recommended concentration of 5.00 mg/L for Part A.

Figure 1. Chromatogram showing separation of the Part A common anions on the AS9-HC column. See Table 1A for analysis conditions.



Peak	Ret. Time	Anion	ug/L
1	3.63	Chlorite	500
2	4.19	Bromate	500
3	4.83	Chloride	Bkgrd
4	7.28	Dichloroacetate*	5.00 mg/L
5	8.48	Bromide	500
6	9.28	Chlorate	500

* The surrogate, dichloroacetate (DCA) ,is shown at 5.00 mg/L, the initial concentration used during method development. The recommended DCA concentration has been reduced to 1.00 mg/L for Part B.

Figure 2 Chromatogram showing separation of the Part B inorganic DBPs and bromide on the AS9-HC column. See Table 1B for analysis conditions.

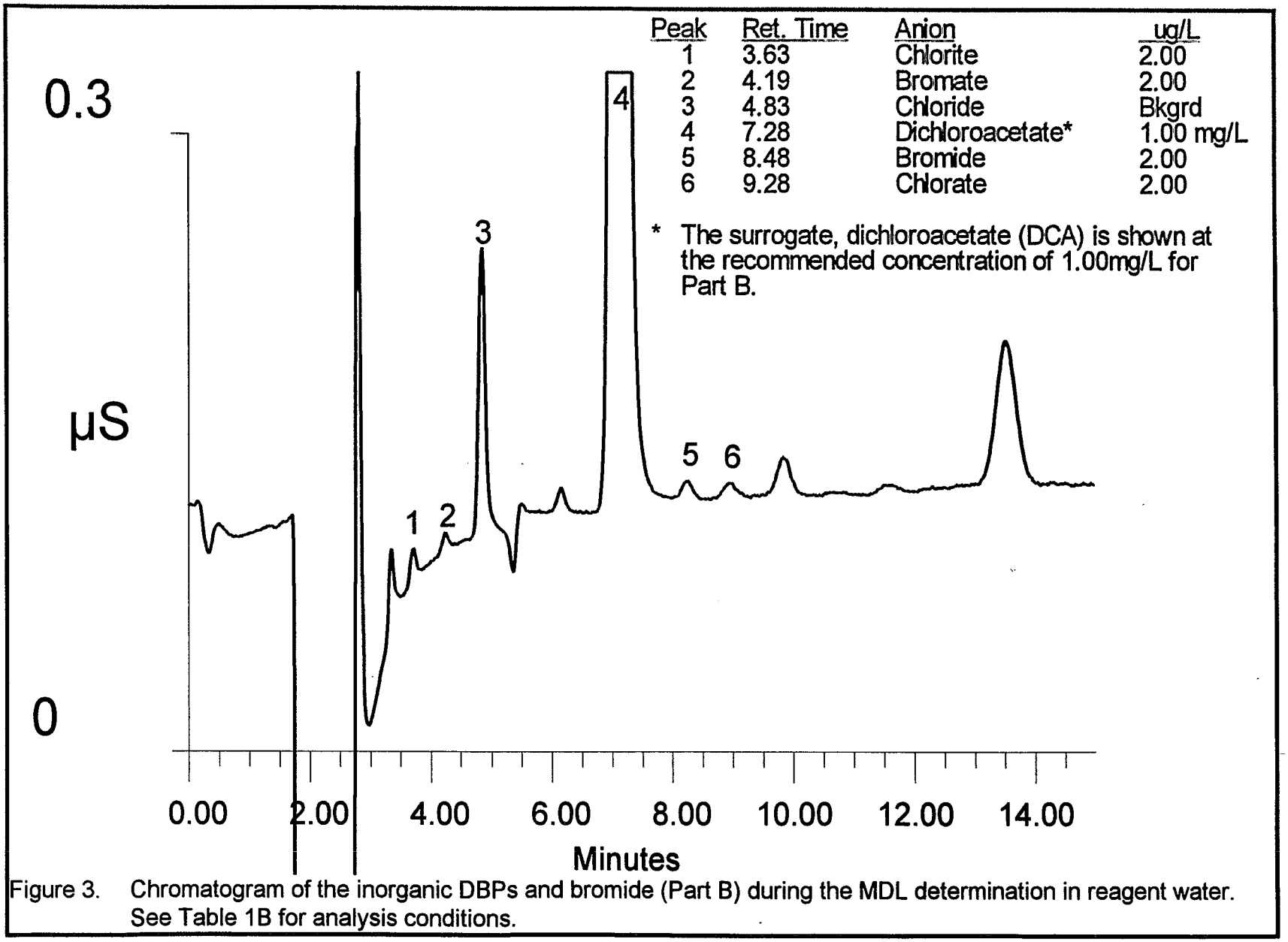
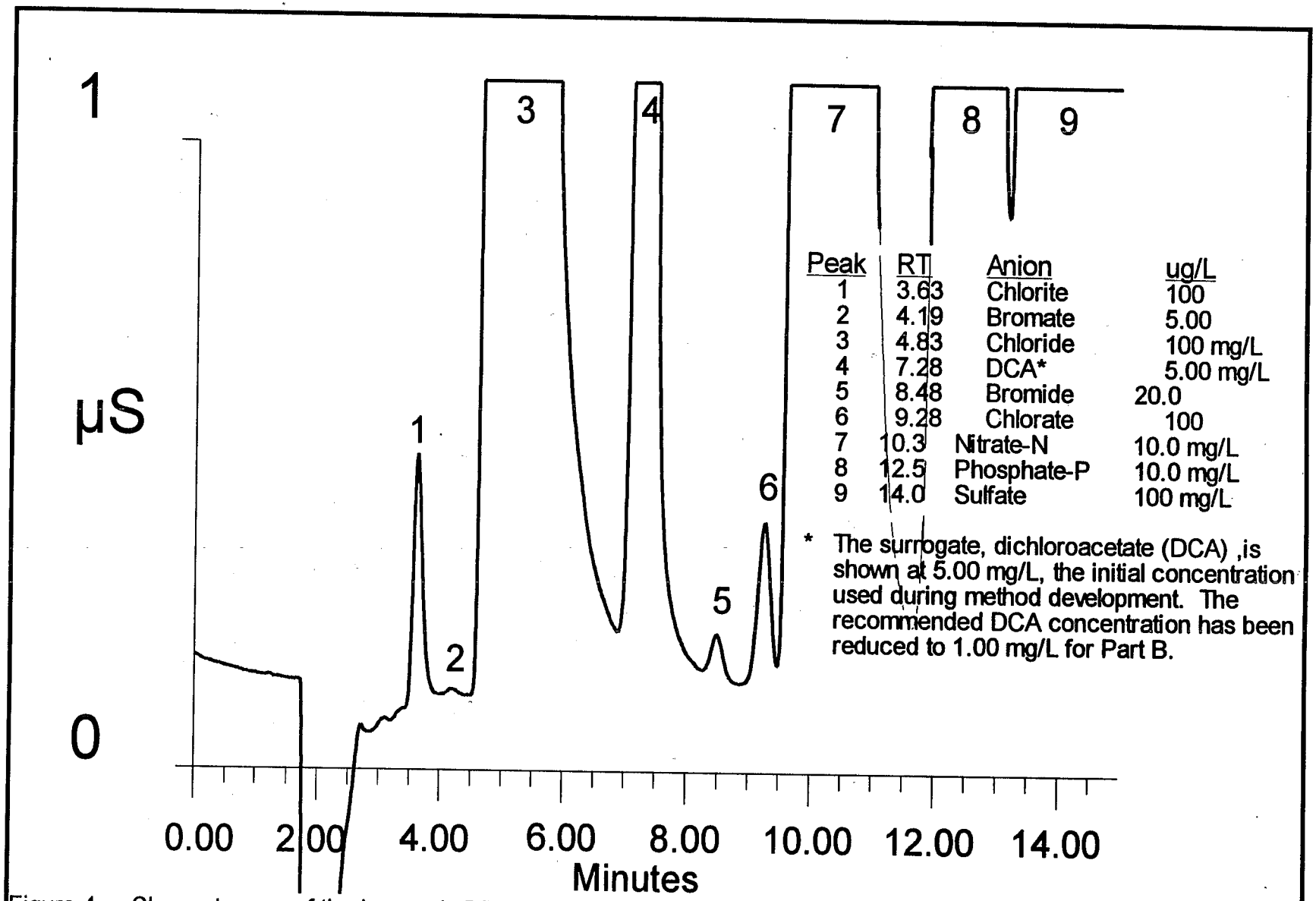


Figure 3. Chromatogram of the inorganic DBPs and bromide (Part B) during the MDL determination in reagent water. See Table 1B for analysis conditions.



Peak	RT	Anion	ug/L
1	3.63	Chlorite	100
2	4.19	Bromate	5.00
3	4.83	Chloride	100 mg/L
4	7.28	DCA*	5.00 mg/L
5	8.48	Bromide	20.0
6	9.28	Chlorate	100
7	10.3	Nitrate-N	10.0 mg/L
8	12.5	Phosphate-P	10.0 mg/L
9	14.0	Sulfate	100 mg/L

* The surrogate, dichloroacetate (DCA) ,is shown at 5.00 mg/L, the initial concentration used during method development. The recommended DCA concentration has been reduced to 1.00 mg/L for Part B.

Figure 4. Chromatogram of the inorganic DBPs and bromide (Part B) in high ionic strength water (HIW). See Table 1B for analysis conditions.