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# METHOD 317.0 DETERMINATION OF INORGANIC OXYHALIDE DISINFECTION BY-PRODUCTS IN DRINKING WATER USING ION CHROMATOGRAPHY WITH THE ADDITION OF A POSTCOLUMN REAGENT FOR TRACE BROMATE ANALYSIS

**Revision 2.0**

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# METHOD 317.0

# DETERMINATION OF INORGANIC OXYHALIDE DISINFECTION BY-PRODUCTS IN DRINKING WATER USING ION CHROMATOGRAPHY WITH THE ADDITION OF A POSTCOLUMN REAGENT FOR TRACE BROMATE ANALYSIS

## 1. SCOPE AND APPLICATION

1.1 This method covers the determination of inorganic oxyhalide disinfection by-product anions in reagent water, surface water, ground water, and finished drinking water. In addition, bromide can be accurately determined in source or raw water and it has been included due to its critical role as a disinfection by-product precursor. Bromide concentration in finished water can differ significantly between preserved and unpreserved samples and should not be attempted due to numerous variables which can influence the concentration. Since this method, prior to the addition of the postcolumn reagent (PCR), employs the same hardware as EPA Method 300.1[1], the analysis of the common anions (using EPA Method 300.1, Part A[1]) can be performed using this instrument setup with the postcolumn hardware attached but "off-line" and with the appropriate smaller sample loop.

Inorganic Disinfection By-products by Conductivity Detection

| | |
|---|---|
| Bromate (report values > 15.0 ug/L) | Chlorite |
| Bromide (source or raw water only) | Chlorate |

Inorganic Disinfection By-product by Postcolumn UV/VIS Absorbance Detection

Bromate (report values > Minimum Reporting Limit (MRL) to 15.0 ug/L)

1.2 The single laboratory reagent water Method Detection Limits (MDL, defined in Section 3.14) for the above analytes are listed in Table 1. 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 on the conductivity detector, 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 nanosiemen (nS) noise/drift per minute of monitored response over the background conductivity.

1.2.2 In order to achieve acceptable detection limits on the postcolumn absorbance detector, the postcolumn reagent must be delivered pneumatically and some form of software signal filtering or smoothing of the absorbance signal from the absorbance detector must be incorporated.[2]

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 Section 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 Section 9.0.

## 2. SUMMARY OF METHOD

2.1 A volume of sample, approximately 225 µL (see Note), is introduced into an ion chromatograph (IC). The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, conductivity detector, a postcolumn reagent delivery system (pneumatically controlled), a heated postcolumn reaction coil, and a ultraviolet/visible (UV/VIS) absorbance detector.[2,3]

**NOTE:** A 225 uL sample loop can be made using approximately 111 cm (44 inches) of 0.02 inch i.d. PEEK tubing. Larger injection loops may be employed.[4] The volume should be verified to be within 5% by weighing the sample loop empty, filling the loop with deionized water and re-weighing the loop assuming the density of water is 1 mg/uL.

## 3. DEFINITIONS

3.1 ANALYSIS BATCH – A sequence of samples, which are analyzed within a 30 hour period and include no more than 20 field samples. An analysis batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20. The required QC samples include:

- Laboratory Reagent Blank (LRB)
- Initial Calibration Check Standard (ICCS)
- Laboratory Fortified Blank (LFB)
- Continuing Calibration Check Standard (CCCS), when the batch contains more than 10 field samples
- End Calibration Check Standard (ECCS)
- Laboratory Fortified Matrix (LFM)
- Either a Field Duplicate (FD), a Laboratory Duplicate (LD) or a duplicate of the LFM

3.2 CALIBRATION STANDARD (CAL) – A solution prepared from the primary dilution standard solution(s) or stock standard solutions and the surrogate analyte. The CAL

solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 INITIAL CALIBRATION STANDARDS – A series of CAL solutions (either individual or combined target analytes) used to initially establish instrument calibration and develop calibration curves for individual target anions (Section 10.2).

3.4 INITIAL CALIBRATION CHECK STANDARD (ICCS) – A CAL solution, (either individual or combined target analytes) which is analyzed initially, prior to any field sample analyses, which verifies previously established calibration curves. The concentration for the initial calibration check standard MUST be at or below the MRL (Section 3.15) level which is also the level of the lowest calibration standard (Section 10.3.1).

3.5 CONTINUING CALIBRATION CHECK STANDARDS (CCCS) – A CAL solution (either individual or combined target analytes) 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. The concentration for the continuing calibration check standards should be either at a middle calibration level or at the highest calibration level (Section 10.3.2).

3.6 END CALIBRATION CHECK STANDARD (ECCS) – A CAL solution (either individual or combined target analytes) which is analyzed after the last field sample analysis which verifies the previously established calibration curves and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check. The end calibration check standard should be either the middle or high level continuing calibration check standard (Section 10.3.2).

3.7 FIELD DUPLICATES (FD) – Two separate field samples collected at the same time and place under identical circumstances and handled 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.

3.8 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.

3.9 LABORATORY DUPLICATE (LD) – Two sample aliquots, taken in the laboratory from a single field sample bottle, and analyzed separately with identical procedures. Analysis of the initial sample ($I_C$) and the duplicate sample [($D_C$) Section 9.4.3.1] indicate precision associated specifically with the laboratory procedures by removing variation contributed from sample collection, preservation and storage procedures.

3.10 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water or other blank matrix 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.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) – An aliquot of an environmental field 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 field sample matrix contributes bias to the analytical result. The background concentrations of the analytes in the field sample matrix must be determined in a separate, unfortified aliquot and the measured values in the LFM corrected for background concentrations.

3.12 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is handled 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.

3.13 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.

3.14 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.[5]

3.15 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a target analyte 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 the ICCS are met.

3.16 PROFICIENCY TESTING (PT) or PERFORMANCE EVALUATION (PE) SAMPLE – A certified solution of method analytes whose concentration is unknown to the analyst. Frequently, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Often, results of these analyses are used as part of a laboratory certification program to objectively determine the capabilities of a laboratory to achieve high quality results.

3.17 QUALITY CONTROL SAMPLE (QCS) – A solution of method analytes of known concentrations that 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.

3.18 SURROGATE ANALYTE – An analyte added to all samples, standards, blanks, etc., which is unlikely to be found at a significant concentration, and which is added directly in a known amount before any sample processing procedures are conducted (except in the procedure for the removal of chlorite as described is Section 11.1.4). 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.

3.19 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 on 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. The analyst must verify that these changes do not induce any negative affects on method performance by repeating and passing all the QC criteria as described in Section 9.

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 Section 11.2.6.

4.1.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. With any proposed pretreatment, the analyst must verify that target analyte(s) are not affected by monitoring recovery after pretreatment. With advances in analytical separator column technology which employ higher capacity anion exchange resins, the need for these cartridges has been greatly reduced.

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 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 or subsequent analysis. Normally, in this analysis, the elution of sulfate (retention time of 17.5 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, a small response (200 nS baseline rise) was observed for a very late eluting unknown peak following the response for sulfate. 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.

4.5 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If residual chlorine dioxide is suspected in the sample, the sample must be purged with an inert gas (helium, argon or nitrogen) for approximately five minutes. This sparging must be conducted prior to ethylenediamine preservation and at the time of sample collection.

4.6 The presence of chlorite can interfere with the quantitation of low concentrations of bromate on the postcolumn UV/VIS absorbance detector. In order to accurately quantify bromate concentrations in the range 0.5 - 15.0 µg/L in this postcolumn system, the excess chlorite must be removed prior to analysis as outlined in Section 11.1.4.

## 5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established although the postcolumn reagent o-dianisidine, is listed as a potential human carcinogen. 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 Occupational Safety and Health Administration (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. Additional references on laboratory safety are available.[6-9]

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

5.3.1 Sulfuric acid – used to prepared a 25 mN sulfuric acid regenerant solution for chemical suppression using a Dionex Anion Micro Membrane Suppressor (AMMS) and for pretreatment for chlorite removal (Section 11.1.4)

5.3.2 Nitric acid – used to prepare the postcolumn reagent.

5.3.3 *o*-dianisidine [3, 3'- dimethoxybenzidine dihydrochloride (ODA)] – used as the postcolumn reagent.

## 6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph – Analytical system complete with ion chromatographic pump and all required accessories including syringes, analytical columns, compressed gasses, suppressor, conductivity detector, mixing "tee", postcolumn reagent delivery system, reaction coil, reaction coil heater, UV/VIS absorbance detector (Figure 1) and a PC based data acquisition and control system.

**NOTE**: Because of its acidic nature and high salt content, the PCR MUST be flushed from the reaction coil upon completion of the final analysis and prevented from draining through the reaction coil by gravity once the system is shut down. This can be accomplished either manually or by incorporating a column switching valve in combination with a flush and close method in the schedule.

6.1.1 Anion guard column – Dionex AG9-HC 4 mm (P/N 51791), 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, 4 mm (P/N 51786), or equivalent (see Note). The AS9-HC, 4 mm column using the conditions outlined in Table 1 produced the separations shown in Figures 2 and 3.

**NOTE**: The use of 2 mm columns is not recommended. A 50 uL sample loop would be required with the 2 mm columns. This reduced injection volume would decrease the "on-column" bromate and negatively affect PCR reactivity and the subsequent absorbance response. As well, the 2 mm columns require a flow rate approximately 4 times less than the 4 mm columns. At the lower flow rates, band broading may become an issue and it would be difficult, if not impossible, to accurately maintain the appropriate reduced flow rate for the PCR.

6.1.3 Anion suppressor device – The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (4 mm ASRS, P/N 46081). An equivalent suppressor device may be utilized provided comparable conductivity 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. The suppressor must be able to withstand approximately 80 - 120 psi back pressure which results from connecting the postcolumn hardware to the eluent out side of the suppressor.

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

6.1.3.2 This method was developed as a multiple component procedure employing both suppressed conductivity and postcolumn UV/VIS absorbance detectors in series. If a laboratory is exclusively interested in monitoring trace bromate using the PCR and the UV/VIS absorbance detector, the suppressor may not be required. The performance data presented within this method for the PCR and UV/VIS absorbance detector, is based upon a suppressed mobile phase system. A laboratory must generate comparable data as a result of a complete IDC (Section 9.2) in order to demonstrate comparability of a non suppressed system.

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

6.1.5 Detector – Absorbance detector (Dionex AD20 or equivalent with 10 mm cell pathlength, equipped with a tungsten source bulb, or equivalent and capable of measuring absorbance at 450 nm) capable of providing data as required in Section 9.2.

6.1.6 Postcolumn reagent delivery system (Dionex PC-10, or equivalent), pneumatically delivers the postcolumn reagent to mixing tee. The pressure settings will need to be established on an individual basis for each specific instrument configuration and at a level which yields the prescribed PCR flow rates.

6.1.7 Reaction Coil, 500 uL internal volume, knitted, potted or configured to fit securely in the postcolumn reaction coil heater. (Dionex P/N 39349, or equivalent).

6.1.8 Postcolumn Reaction Coil Heater, capable of maintaining a temperature of up to 80°C. (Dionex PCH-2, or equivalent).

6.2 Data System – The Dionex Peaknet Data Chromatography Software was used to generate all the data in the attached tables. Other computer based data systems may achieve approximately the same MDLs but the user must demonstrate this by the procedure outlined in Section 9.2.

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

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

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, used for sample collection and storage of calibration solutions. Opaque or amber bottles are required due to the photoreactivity of the chlorite anion.

6.9 Micro beakers – Plastic, disposable - used during sample preparation.

6.10 Particulate filters – Gelman ion chromatography Acrodisc 0.45 micron (PN 4485) syringe filters or equivalent. These cartridges are used to remove particulates and [$Fe(OH)_{3(s)}$] which is formed during the oxidation-reduction reaction between Fe (II) and $ClO_2^-$.

6.11 Hydrogen cartridges – Dionex OnGuard-H cartridges (PN 039596) or equivalent. These cartridges are conditioned according to the manufacturer's directions and are used to protect the analytical column and the suppressor membrane by removing excess ferrous iron [Fe (II)]. The ferrous iron is added to field samples to reduce chlorite levels prior to analysis of chlorine dioxide disinfected water samples.

## 7. REAGENTS AND STANDARDS

7.1 Reagent water – Distilled or deionized water 18 MΩ or better, 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. Alternatively, an in-line degas apparatus may be employed.

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 outlined below in Section 7.3.4.1.

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 Chlorite ($ClO_2^-$) 1000 mg/L – If the amperometric titration of the technical grade sodium chlorite ($NaClO_2$), specified in 7.3.4.1, had indicated the purity of the salt to be 80.0 % $NaClO_2$, the analyst would 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.

7.3.4.1 High purity sodium chlorite ($NaClO_2$) is not currently commercially available due to its 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 purity of the $NaClO_2$ using the iodometric titration procedure.[10] 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) from chlorate, bromate or bromide (as other method target anions) in the technical grade chlorite standard.

**NOTE**: Stability of standards – Stock standards (Section 7.3) for most anions are stable for at least 6 months when refrigerated at <6°C. The chlorite standard is only stable for two weeks when stored refrigerated at <6°C and protected from light. Dilute working standards should be prepared monthly, except those that contain chlorite, which must be prepared every two weeks or sooner if signs of degradation are indicated by repeated QC failure.

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) – Prepare by dissolving 0.065 g dichloroacetic acid, potassium salt ($Cl_2CHCO_2K$, CASRN 19559-59-2) in reagent water and diluting 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 indicated by the repeated failure of the surrogate QC criteria.

7.5.3 If the analyst is exclusively interested in monitoring trace bromate using the PCR and the UV/VIS absorbance detector, the surrogate may be omitted since it only yields a signal on the conductivity detector. If the surrogate is removed, the laboratory must adhere to the alternate QC requirements found in Section 9.3.3.3 in order to monitor and demonstrate proper instrument performance.

7.6 Postcolumn reagent – The postcolumn reagent is prepared by adding 40 mL of 70% redistilled nitric acid (purity as 99.999+%, Aldrich, Cat. No. 22,571-1, Milwaukee, WI, or equivalent) to approximately 300 mL reagent water (see Note 1) in a well rinsed 500 mL volumetric flask (see Note 2) and adding 2.5 grams of ACS reagent grade KBr (Sigma, Cat. No. P-5912, St. Louis, MO, or equivalent). Two-hundred-and-fifty milligrams of purified grade o-dianisidine, dihydrochloride salt [(ODA), (Sigma, Cat. No. D-3252, or equivalent)] are dissolved, with stirring, in 100 mL methanol (Spectrophotometric grade, Sigma, Cat. No. M-3641, St. Louis MO, or equivalent). After dissolution, the o-dianisidine solution is added to the nitric acid/KBr solution and diluted to volume with reagent water. The reagent is stable for 24 hours and should be prepared fresh daily prior to analysis.

7.6.1 The purity of all reagents employed in the preparation of the postcolumn reagent is critical. Some commercial manufacturers/suppliers of laboratory chemicals sell inferior grades of o-dianisidine dihydrochloride. ONLY the purified grade of this reagent is acceptable (see Notes 3 and 4). The purified ODA dihydrochloride salt is a white, fine powder.

**NOTE 1:** For selected lots of ODA, the method sensitivity monitored by the UV-vis detector may be increased by as much as 2-fold if the reagent water used to prepare the ODA PCR is purged with helium for 30 minutes prior to preparing the ODA solution.

**NOTE 2:** All glassware used to prepare the postcolumn reagent must be thoroughly rinsed with reagent water prior to use. A champagne or light amber coloration of the PCR reagent may be evident when freshly prepared. Over several hours, this slight coloration will fade. Consequently, the PCR must be prepared in advance and allowed to sit until it is clear, for a minimum of 4 hours (preferably overnight) prior to use. Occasionally, no matter how well all the glassware used to prepare the postcolumn reagent is rinsed, a darkly colored solution (oxidized ODA) may result. These solutions MUST be discarded. For this reason, it is recommended that the PCR be made in a series of 500 mL lots with dedicated glassware. The clear solution should be filtered using a 0.45 micron membrane to remove particulates before use.

**NOTE 3:** Differences in purity as indicated by variations in the physical appearance of different lots of ODA, even from the same manufacturer can effect method sensitivity. Although considerably more expensive, a pelletized form of ODA from one supplier (Sigma, Cat. No. D-9154, St. Louis, MO) has shown to increase method sensitivity by as much as 2-fold over impure lots of ODA. Care must be exercised when switching ODA lots to ensure the method sensitivity is not compromised.

NOTE 4: The PCR reaction temperature was optimized at 60 °C with the granular ODA that was available during the original method development. Investigation of recent changes in physical appearance/decreased sensitivity and stability of the ODA PCR indicated that, the method sensitivity with the ODA currently available, can be dramatically increased (up to 180%) or increased by up to a factor of 1.8) by increasing the reaction temperature to 80 °C. Use of temperatures ranging from 60 to 80 °C may be used in this method.

7.7 Ferrous iron [1000 mg/L Fe (II)] solution – Dissolve 0.124 g ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, Sigma, F-7002) in approximately 15 mL reagent water containing 6 uL concentrated nitric acid and dilute to 25 mL with reagent water in a volumetric flask (final pH ~2). The Fe (II) solution must be prepared fresh every two days.

7.8 Sulfuric acid (0.5 N) – Dilute 1.4 mL of concentrated sulfuric acid (Fisher Scientific Certified ACS Plus, A 300-500) to 100 mL.

## 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. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis and laboratory fortified matrix 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 or amber 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 are as follows:

| Analyte | Preservation | Holding Time |
|---|---|---|
| Bromate | 50 mg/L EDA, refrigerate at <6°C | 28 days |
| Chlorate | 50 mg/L EDA, refrigerate at <6°C | 28 days |
| Chlorite | 50 mg/L EDA, refrigerate at <6°C | 14 days |
| Bromide (source/raw water only) | EDA permitted, refrigerate at <6°C | 28 days |

**NOTE:** Samples for chlorite analysis must arrive at the laboratory within 48 hours of collection and must be received at 10°C or less.

8.4 When collecting a field sample from a treatment plant employing chlorine dioxide, the field 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 (bromate > 15.0 ug/L) can be analyzed by conductivity, in a sample matrix which has been preserved with EDA. Add a sufficient volume of the EDA preservation solution (Section 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 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.[11] 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 organochloramine. 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 ion which is an intermediate formed as a by-product of the reaction of either ozone or hypochlorous acid/hypochlorite ion with bromide ion. If hypobromous acid/hypobromite ion is not removed from the matrix, further reactions may form bromate ion.

## 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 capability (IDC), and subsequent analysis in each analysis batch (Section 3.1) of a Laboratory Reagent Blank (LRB), Initial Calibration Check Standard (ICCS), Laboratory Fortified Blank (LFB), Instrument Performance Check Standard (IPC), Continuing Calibration Check Standards (CCCS), Laboratory Fortified Sample Matrix (LFM) and either a Field, Laboratory or LFM duplicate sample analysis. This section details the specific requirements for each of these QC parameters for both the conductivity and absorbance detectors used in this application. Although this method involves both conductivity and absorbance detection, the MDLs and MRLs may differ but the QC requirements and acceptance criteria are the same for both detectors. The QC criteria discussed in the following sections are summarized in Section 17, Tables 4 and 5. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF CAPABILITY

9.2.1 The Initial Demonstration of Capability (IDC) – This is used to characterize instrument and laboratory performance prior to performing analyses by this method. The QC requirements for the IDC discussed in the following section are summarized in Section 17, Table 4.

9.2.2 Initial demonstration of low system background – Section 9.3.1.

9.2.3 Initial Demonstration of Precision (IDP) – For the 4 conductivity detector analytes, prepare 7 replicate LFBs fortified at a recommended concentration of 20 ug/L. For the absorbance detector, prepare 7 replicate LFBs fortified at a recommended concentration of 2.0 ug/L bromate. The percent relative standard deviation (RSD) of the results must be less than 20%.

9.2.4 Initial Demonstration of Accuracy (IDA) – Using the data generated for Section 9.2.3, calculate the average recovery. The average recovery of the replicate values must be within ± 15% of the true value.

9.2.5 Quality Control Sample (QCS) – After calibration curves have initially been established or have been re-established, on a quarterly basis or as required to meet data quality needs, verify both the calibration and acceptable instrument performance with the preparation and analyses of an external/second source QCS. If the determined concentrations are not within ± 20% of the stated values, performance of the method is unacceptable. The source of the problem must be identified and corrected before proceeding with the IDC.

9.2.6 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.[4] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. The replicates must be prepared and analyzed over three days. 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], and
S = standard deviation of the replicate analyses.

9.2.6.1 MDLs should be periodically verified, but MUST be initially determined when a new operator begins work or whenever there is a significant change in the background, or instrument response.

**NOTE:** Do not subtract blank values when performing MDL calculations.

9.2.7 Minimum Reporting Level (MRL) – The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the MDL or at a concentration which would yield a response greater than a signal to noise ratio of five. Setting the MRL too low may cause repeated QC failure upon analysis of the ICCS. Although the lowest calibration standard may be below the MRL, the MRL must never be established at a concentration lower than the lowest calibration standard.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each analysis batch (Section 3.1). Data produced are used to assess

contamination from the laboratory environment. Values that exceed ½ the MRL indicate a laboratory or reagent contamination is present. If a method analyte is observed in the LRB it must not exceed ½ the MRL. Analytes that exceed this level will invalidate the analysis batch for that method analyte in all corresponding field samples.

9.3.1.1 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.

9.3.1.2 When the PCR method is used for low level bromate analysis on samples from public water systems (PWSs) which employ chlorine dioxide disinfection, the matrix must be pretreated to remove the potentially interferant chlorite anion (Section 11.1.4). When these types of pretreated samples, or any type of pretreatment is applied to field samples included as part of an analysis batch, a second LRB must be prepared, pretreated and analyzed to confirm no background effects of the pretreatment are present. If the analysis batch contains only pretreated samples, then only a pretreated LRB is required.

9.3.2 Laboratory Fortified Blank (LFB) – Prepare a secondary dilution stock using the same stock solutions used to prepare the calibration standards and the LFM fortification solution. Since calibration solutions are prepared in large volumes and can be used over an extended period of time, the integrity of the concentration of the solution used to fortify the LFM is checked by analyzing the LFB. The recovery of all analytes must fall in the acceptable recovery range, as indicated below, prior to analyzing samples. If the LRB recovery for an analysis batch does not meet these recovery criteria the data are considered invalid, and the source of the problem must be identified and resolved before continuing with analyses.

| LFB Fortified Concentration range | LFB Percent Recovery Limits |
|---|---|
| MRL to 5 x MRL | 75 - 125 % |
| 5 x MRL to highest calibration level | 85 - 115 % |

9.3.2.1 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.

9.3.3 Instrument Performance Check (IPC) – The Initial Calibration Check Standard (ICCS) is to be evaluated as the IPC solution in order to confirm proper

instrument performance. As specified in Section 10.3.1, this must be done using the lowest calibration standard or the standard level established as the MRL. This analysis confirms the MRL and demonstrates proper chromatographic performance at the beginning of each analysis batch. Chromatographic performance is judged 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. If these criteria are not met, corrective action must be performed prior to analyzing additional samples. Major maintenance like replacing columns require rerunning the IDC (Section 9.2).

9.3.3.1 Critically evaluate the surrogate peak in the initial calibration check standard, and calculate the PGF as follows:

$$PGF = \frac{1.83 \times W(½)}{W(^1/_{10})}$$

where, $W(½)$ is the peak width at half height, and
$W(^1/_{10})$ is the peak width at tenth height.

**NOTE:** Values for $W(½)$ and $W(^1/_{10})$ can be attained through most data acquisition software.

9.3.3.2 Small variations in retention time can be anticipated when a new solution of eluent is prepared but if sudden shifts of more than 5% 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 requires cleaning or replacement; especially if resolution problems are beginning to become common between previously resolved peaks. A laboratory should retain a historic record of retention times for the surrogate and all the target anions to provide evidence of an analytical columns vitality.

9.3.3.3 If a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, and no other analytes are being monitored on the conductivity detector, the surrogate may be omitted from the procedure. In this case, no measurement of PGF is required. However, the laboratory must carefully monitor the bromate retention time in the ICCS as an alternate to the surrogate retention time and, in the same manner, adhere to those specifications set forth in Section 9.3.3.2. During the course of the analysis, bromate retention times in the CCCS and ECCS must also be closely monitored to be certain they adhere to the QC requirements set forth in Section 10.3.2.2.

## 9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM) – The laboratory must add a known amount of each target analyte to a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. Additional LFM requirements, as described in Section 9.4.1.5, apply when the PCR system is used for low level bromate in chlorine dioxide disinfected waters. For a LFM to be valid, the target analyte concentrations must be greater than the native level and must adhere to the requirement outlined in Section 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 The fortified concentration must be equal to or greater than the native concentration. Fortified samples that exceed the calibration range must be diluted to be within the linear range. In the event that the fortified level is less than the observed native level 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 to fortified concentration ratio is greater than one.

9.4.1.2 The LFM should be prepared at concentrations no greater than ten times the highest concentration observed in any field sample and should be varied to reflect the range of concentrations observed in field samples. If no analytes are observed in any field sample, the LFM should be fortified near the MRL.

9.4.1.3 Calculate the percent recovery for each target analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should be calculated using the following equation:

$$\%REC = \frac{(C_s - C)}{s} \times 100$$

where, %REC = percent recovery,
$C_s$ = fortified sample concentration,
C = native sample concentration, and
s = concentration equivalent of analyte added to sample.

9.4.1.4 Recoveries may exhibit a matrix dependence. If the recovery of any analyte falls outside 75 - 125%, and the laboratory's performance for all other QC performance criteria are acceptable, the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample and the LFM must be labeled suspect/matrix to inform the data user that the result is suspect due to matrix effects. Repeated failure to meet suggested recovery criteria indicates potential problems with the procedure and should be investigated.

9.4.1.5 When the PCR method is used for low level bromate analysis on field samples from PWSs which employ chlorine dioxide disinfection and consequently contain chlorite, a LFM must be prepared, exclusively for trace bromate, for each of these field samples. Initially, the field sample is analyzed and chlorite, chlorate and bromide levels are determined. Then, a second aliquot of field sample is pretreated to remove chlorite, as described in Section 11.1.4, and analyzed to determine native bromate concentration. A third aliquot of the field sample then must be fortified with bromate, pretreated as described in Section 11.1.4 to remove chlorite, and analyzed to assess bromate recovery from that matrix. This additional QC is required to rule out matrix effects and to confirm that the laboratory performed the chlorite removal step (Section 11.1.4.1) appropriately. This LFM should be fortified with bromate at concentrations close to but greater than the level determined in the native sample. Recoveries are determined as described above (Section 9.4.1.3). Samples that fail the LFM percent recovery criteria of 75 - 125% must be reported as suspect/matrix.

9.4.2 SURROGATE RECOVERY – The surrogate is specific to the conductivity detector and shows no response on the postcolumn absorbance detector.

Calculate the surrogate recovery for the conductivity detector from all analyses using the following formula:

$$\%REC = \frac{SRC}{SFC} \times 100$$

where, %REC = percent recovery,
SRC = surrogate recovered concentration, and
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 range for the surrogate is extended to 115% to allow for the potential contribution of trace levels of dichloroacetate as a halogenated organic disinfection by-product (DBP) of 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, an analysis error is evident and sample reanalysis is required. Poor recoveries could be the result of imprecise sample injection or analyst fortification errors. If the second analysis also fails the recovery criterion, report all data for that sample as suspect.

9.4.2.3 If a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, and no other analytes are being monitored on the conductivity detector, the surrogate may be omitted from the procedure. In this situation, the laboratory MUST adopt the QC protocol outlined in Section 9.3.3.3.

9.4.3 FIELD OR LABORATORY DUPLICATES – The laboratory must analyze either a field or a laboratory duplicate for a minimum of 5% 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 repeated as a laboratory duplicate.

9.4.3.1 Calculate the relative percent difference (RPD) from the mean using the following formula:

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

where, RPD = relative percent difference
$I_C$ = the initial quantitated concentration, and
$D_C$ = the duplicate quantitated concentration

9.4.3.2 Duplicate analysis acceptance criteria.

| Concentration range | RPD Limits |
|---|---|
| MRL to 5 x MRL | ± 20 % |
| 5 x MRL to highest calibration level | ± 10 % |

9.4.3.3 If the RPD for any target analyte falls outside the acceptance criteria (Section 9.4.3.2) and if all other QC performance criteria are met for that analyte, the result for the sample and duplicate should be labeled as suspect/matrix to inform the data user that the result is suspect due to a potential matrix effect, which led to poor precision. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses), it indicates a problem with the instrument or analyst technique that must be corrected.

9.4.4 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 Section 9.2 and adhere to the condition of conductivity baseline stability found in Section 1.2.1.

9.4.5 It is recommended that the laboratory adopt additional quality assurance (QA) 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 standards and participate in relevant proficiency testing (PT) or performance evaluation (PE) sample studies.

## 10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required prior to the IDC and before any samples are analyzed, is required intermittently throughout sample analysis to meet required QC performance criteria outlined in this method and is summarized in Tables 4 and 5. Initial calibration verification is performed using a QCS as well as with each analysis batch using an initial, continuing (when more than 10 field

samples are analyzed), and end calibration standards. The procedures for establishing the initial calibration curve are described in Section 10.2. The procedures to verify the calibration with each analysis batch is described in Section 10.3.

10.2 INITIAL CALIBRATION CURVE

10.2.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1 and configured as shown in Figure 1.

10.2.2 Estimate the Linear Calibration Range – The linear concentration range is the concentration range over which the instrument response is linear. On the conductivity detector for the four target analytes (chlorite, bromate, bromide and chlorate) the linear range should cover the expected concentration range of the field samples and should not extend over more than two orders of magnitude in concentration. The restriction of two orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

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

10.2.2.2 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. Because high concentrations of chlorite can interfere with the postcolumn analysis of low levels of bromate, the conductivity and absorbance detectors must be calibrated separately.

10.2.2.3 Since the concentration ranges in actual field samples by conductivity detection for chlorite, bromide and chlorate are expected to cover two orders of magnitude, the use of at least five calibration standards in the range 5 - 500 µg/L is recommended. Bromate concentrations are expected to be significantly lower. It is suggested that the conductivity detector be calibrated using at least five bromate calibration standard levels in the range 5 - 100 µg/L. Additionally, report values for bromate by conductivity ONLY when they are measured by the PCR above 15.0 ug/L. The conductivity detector will observe a response for bromate at concentration below 15.0 ug/L but concentrations between 5.0 and 15.0 ug/L are within the calibrated range for PCR detection and will reflect far better precision and accuracy.

10.2.2.4 Although the bromate calibration curve for the absorbance detector

extends over less than two orders of magnitude, the use of five calibration standards, containing only bromate in the range 0.5 - 15.0 µg/L, is recommended.

10.2.3 Prepare the calibration standards by carefully adding measured volumes of one or more stock standards (Section 7.3) to a volumetric flask and diluting to volume with reagent water. Prior to using mixed standards for calibration, it must be ensured that the individual calibration standards do not contain any appreciable concentrations of the other target analytes.

10.2.3.1 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 contributed by the addition of EDA to preserve the field samples.

10.2.3.2 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. This is done by adding 20 µL of the surrogate solution (Section 7.5) to a 20 mL disposable plastic micro beaker. Next, transfer 10.0 mL of calibration standard into the micro beaker and mix. These volumes may be adjusted to meet specific laboratory autosampler volume requirements provided the fortified surrogate concentration is at the prescribed concentration of 1.0 mg/L. The calibration standard is now ready for analysis. The same surrogate solution that has been employed for the standards should also be used in Section 11.1 for the field samples.

**NOTE**: This surrogate fortification procedure may be omitted if a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, and no other analytes are being monitored on the conductivity detector. In this situation, the laboratory must adopt the QC protocol outlined in Section 9.3.3.3.

10.2.4 Inject 225 µL of each calibration standard. Increased sensitivity for low level detection of bromate by PCR can be achieved by increasing the injected sample volume.[4] If the injection volume is increased special operating conditions must be used to insure proper chromatographic performance.[4]

10.2.5 Tabulate peak area responses against the concentration for the four target analytes, the surrogate from the conductivity detector and bromate from the postcolumn absorbance detector. The results are used to prepare calibration curves using linear regression analysis for each analyte on the conductivity detector and using a quadratic regression analysis for bromate on the absorbance

detector.

10.2.5.1 Use of 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 leading to peak broadening. 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.

10.2.6 After establishing or reestablishing calibration curves, the accuracy of this calibration must be verified through the analysis of a QCS or an externally prepared second source standard. The QCS should be prepared at a concentration near the middle of the calibration and is best to be analyzed in triplicate. As specified in Section 9.2.5, determined concentrations must fall within ± 15% of the stated values.

10.3 CONTINUING CALIBRATION VERIFICATION – Initial calibrations may be stable for extended periods of time. Once the calibration curves have been established for both the conductivity and absorbance detectors, they must be verified for each analysis batch, prior to conducting any field sample analyses using an Initial Calibration Check Standard. Continuing Calibration Check Standards and End Calibration Check Standards are also required as described in the sections below.

10.3.1 INITIAL CALIBRATION CHECK STANDARD (ICCS) – The initial calibration must be determined to be valid each day prior to analyzing any samples. Since two detectors are incorporated in this method, this must be accomplished by using a mixed calibration check standard for the four conductivity analytes and a separate low level bromate initial calibration check standard for the absorbance detector. In both cases, the lowest level standard used to prepare the calibration curve must be used. In cases where the analyst has chosen to set the MRL above the lowest standard, a standard at a concentration equal to or below the MRL is acceptable. Percent recovery for the ICCS must be in the range or 75 - 125% before the analyst is allowed to analyze samples.

10.3.2 CONTINUING CALIBRATION CHECK/END CALIBRATION CHECK STANDARDS (CCCS/ECCS) – Continuing calibration check standards must be analyzed after every tenth field sample analysis and at the end of the analysis batch as an end calibration check standard. For the reasons noted above, two separate continuing and end calibration check standards must be incorporated. If more than 10 field samples are included in an analysis batch, the analyst must

alternate between the middle and high continuing calibration check standard levels.

10.3.2.1 The percent recovery for the CCCS/ECCS must meet the following criteria:

| Concentration range | Percent Recovery Limits |
|---|---|
| MRL to 5 x MRL | 75 - 125 % |
| 5 x MRL to highest calibration level | 85 - 115 % |

10.3.2.2 If during the analysis batch, the measured concentration on either detector differs by more than the calibration verification criteria shown above, or the retention times shift more than ± 2% from the last acceptable initial or continuing calibration check standard for any analyte, all samples analyzed after the last acceptable calibration check standard are considered invalid and must be reanalyzed. The source of the problem must be identified and resolved before reanalyzing the samples or continuing with the analyses.

10.3.2.3 In the case where the end calibration failed to meet performance criteria, but the initial and middle calibration check standards were acceptable, the samples bracketed by the acceptable calibration check standards may be reported. However, all field samples between the middle and end calibration check standards must be reanalyzed.

## 11. PROCEDURE

### 11.1 SAMPLE PREPARATION

11.1.1 For refrigerated or field 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.

11.1.2 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. This is done by adding 20 µL of the surrogate solution (Section 7.5) to a 20 mL disposable plastic micro beaker. Next, place a 10.0 mL aliquot of sample into the micro beaker and mix. These volumes may be adjusted to meet specific laboratory autosampler volume requirements provided the fortified surrogate concentration is at the prescribed concentration of 1.0 mg/L. The sample is now ready for analysis.

**NOTE**: The less than 1% dilution error introduced by the addition of the

surrogate is considered insignificant. In addition, this surrogate fortification procedure may be omitted if a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, and no other analytes are being monitored on the conductivity detector. In this situation, the laboratory must adopt the QC protocol outlined in Section 9.3.3.3.

11.1.3 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 filtered, 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.

11.1.4 CHLORINE DIOXIDE - TREATED WATERS CONTAINING CHLORITE – Treatment plants that use chlorine dioxide as part of their treatment process can produce high levels of chlorite in samples. Since chlorite can interfere with the postcolumn quantitation of low levels of bromate as described in Section 4.6, chlorite must be removed from these samples prior to analysis.[12] The oxidation-reduction reaction between ferrous iron and chlorite[13] is used to remove chlorite without any adverse affects on the bromate concentration.[14] The EDA stabilized sample is acidified to a pH of 5-6 (verified using pH test strips), ferrous iron solution is added and allowed to react for 10 minutes. The sample is then filtered using a 0.45 micron membrane to remove precipitated ferric hydroxide and the excess soluble iron is removed by passing the filtered sample through a hydrogen cartridge [a solid phase extraction (SPE) clean-up cartridge in the H+ form, (Section 6.11)], prior to analysis. Prior to using any pretreatment, each lot of cartridges must be QC checked to insure proper analyte recoveries are maintained and laboratory reagent blanks are free from interferences. In addition, consistent lots of reagents, pretreatment cartridges, and membrane cartridges must be used throughout an entire analysis batch to maintain assured QC uniformity.

11.1.4.1 Place a 10 mL aliquot of sample in a 20 mL micro beaker and add 35 uL of 0.5 N sulfuric acid (Section 7.8). After mixing, verify the pH is between 5 and 6 using pH test strips, add 40 uL of ferrous iron solution (Section 7.7), mix and allow to react for 10 minutes. Filter the reaction mixture using a 0.45 micron particulate filter (Section 6.10) attached to a 10 mL syringe into the barrel of a second syringe to which a pre-conditioned hydrogen cartridge (Section 6.11) is attached. Pass the solution through a hydrogen cartridge at a flow rate of approximately 2 mL per minute. Discard the first 3 mL, and collect an appropriate volume (depending on autosampler vial size) for analysis.

Add the respective volume of surrogate solution, depending on the volume collected, and the sample is ready for analysis.

**NOTE:** Pretreated samples can be held for no more than 30 hours after initial pretreatment. If this time has expired, the pretreatment steps must be repeated on a second aliquot of both the field sample matrix and the respective LFM.

11.1.4.2 In order to ensure data quality, all samples from PWSs which utilize chlorine dioxide which have been pretreated to remove chlorite, MUST also be used to prepare a pretreated LFM specific to trace bromate. This LFM should be fortified with bromate at concentrations close to but greater than the level determined in the native sample. Initially, the field sample is analyzed and chlorite, chlorate and bromide levels are determined. Then, a second aliquot of field sample is pretreated to remove chlorite, as described above and analyzed to determine native bromate concentrations. A third aliquot of the field sample then must be fortified with bromate, pretreated to remove chlorite, and analyzed to assess bromate recovery from that matrix. This additional QC is required to rule out matrix effects and to confirm that the laboratory performed the chlorite removal step appropriately. If the bromate recovery falls outside the acceptance range of 75 - 125% (Section 9.4.1.5), that particular sample should be reported as suspect/matrix.

11.1.4.3 Suppressor devices which have had long term exposure to iron cations may have reduced method performance in other applications, such as the determination of certain common inorganic anions. If reduced peak response is observed, particularly for fluoride or phosphate, the ASRS should be cleaned according to the manufacturer's recommendations.

11.2 SAMPLE ANALYSIS

11.2.1 Table 1 summarizes the recommended operating conditions for the ion chromatograph and delivery of the postcolumn reagent. Included in this table is estimated retention times that can be achieved by this method. Other columns or chromatographic conditions may be used if the requirements of Section 9.2 are met.

11.2.2 Establish a valid initial calibration as described in Section 10.2 and complete the IDC (Section 9.2). Check system calibration by analyzing an ICCS (Section 10.3.1) as part of the initial QC for the analysis batch and, if required, recalibrate as described in Section 10.3.

11.2.3 Inject 225 µL of each sample. Use the same size loop for standards and samples. An automated constant volume injection system may also be used.

11.2.3.1 Increased sensitivity for low level detection of bromate by PCR can be achieved by increasing the injected sample volume.[4] If the injection volume is increased (Section 10.2.4) special operating conditions must be used to insure proper chromatographic performance.[4]

11.2.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of 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.

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

11.2.6 Should more complete resolution be needed between any two coeluting peaks, the eluent (Section 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 verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9, and by reestablishing a valid initial calibration curve (Section 10.2). As a specific precaution, upon dilution of the carbonate eluent, a peak for bicarbonate may be observed by conductivity within the retention time window for bromate which will negatively impact the analysis.

11.2.6.1 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.

11.3 AUTOMATED ANALYSIS WITH METHOD 317.0

11.3.1 Laboratories conducting analyses on large numbers of samples often prepare

large analysis batches that are run in an automated manner. When conducting automated analyses, careful attention must be paid to all reservoirs to be certain sufficient volumes are available to sustain extended operation. Laboratories must ensure that all QC performance criteria are met as described in preceding sections to ensure their data are of acceptable quality.

11.3.1.1 Special attention must be made when the PCR reservoir is refilled. Since this is a pneumatically driven system, the baseline will require a minimum of ten minutes to restabilize after the reservoir has been refilled and the bottle repressurized.

11.3.2 Because this method has two detectors that require independent calibration, analysis sequences must be carefully constructed to meet required QC specifications and frequency (Table 5). To help with this task, an acceptable sequence for a sample analysis batch, with all the method-required QC, is shown in Table 6. This schedule is included only as an example of a hypothetical analysis batch where the analyst desires to collect data using both detectors. Within the analysis batch, references to exact concentrations for the ICCS, CCCS and ECCS are for illustrative purposes only. The analyses for sample #14 provides an example of the QC requirements for a complete conductivity and trace bromate PCR analysis of a sample from a PWS employing chlorine dioxide disinfection.

11.3.3 Table 6 may be used as a guide when preparing analysis batches.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify the method analytes in the sample chromatogram by comparing the retention time of the suspected analyte peak to the retention time of a known analyte peak in a calibration standard. If analyte retention times have shifted (generally towards shorter times) since the initial calibration, but are still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibrations to confirm the presence or absence of target analytes.

12.2 Compute sample concentration using the initial calibration curve generated in Section 10.2.

12.3 Report ONLY those values that fall between the MRL and the highest calibration standards. Samples with target analyte responses exceeding the highest standard must be diluted and reanalyzed. When this is not possible the alternate calibration procedures described in Section 11.2.5 must be followed. Samples with target analytes identified but quantitated below the concentration established by the lowest calibration standard may be reported as present, but below the minimum reporting limit (MRL), and consequently not quantitated.

12.3.1 Report bromate concentrations using the postcolumn UV/VIS absorbance detector when they fall between the MRL and 15.0 ug/L. When bromate concentrations exceed 15.0 ug/L, as detected by UV/VIS absorbance, either report by conductivity, calibrate the postcolumn UV/VIS absorbance detector to a higher bromate concentration, or dilute the sample.

12.4 Report results in µg/L.

12.5 Software filtering of the postcolumn UV/VIS absorbance signal is required to improve the precision of peak measurements, minimize non-random noise and improve peak appearance. Olympic smoothing (25 points, 5 seconds with 1 iteration) was chosen using peak area for quantitation because it was determined to have minimal effect on peak height and/or area.[2,15] The use of alternate smoothing routines is acceptable providing all QC criteria are met.

## 13. METHOD PERFORMANCE

13.1 Table 1 gives the standard conditions, typical retention times and single laboratory MDLs in reagent water, as determined for each of the inorganic oxyhalide DBPs and bromide. Included in this table is a comparison of the MDLs determined by conductivity both with and without the postcolumn UV/VIS absorbance system on-line. These data indicate that the postcolumn UV/VIS detector system has no effect on conductivity detector performance (careful attention must however be paid to insure backpressure on the suppressor is kept below 120 psi).

13.2 Table 2 shows the precision and accuracy of the trace bromate measurement, evaluated on both detectors, at two fortified concentrations, in chlorinated surface water, a simulated high ionic strength water (HIW) and a simulated high organic (HOW) content water. The mean bromate recovered concentration (accuracy relative to the fortified level) and the precision (expressed as %RSD of the replicate analyses) are tabulated. The HIW was designed to simulate a high ionic strength field sample and the HOW designed to simulate a high organic content field sample. The HIW 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.[1] The HOW was prepared from reagent water fortified with 1.0 mg/L fulvic acid.[1]

13.3 Table 3 gives the single laboratory standard deviation and precision (% RSD) for each anion included in the method in a variety of waters for the standard conditions identified in Table 1.[1,2]

13.4 Table 3A shows the stability data for the inorganic oxyhalide DBPs. Each data point in these tables represent the mean percent recovery following triplicate analyses. These

data were used to formulate the holding times shown in Section 8.3.[1]

## 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 feasiblely 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 Section 14.3.

## 16. REFERENCES

1. U.S. EPA Method 300.1. EPA Document number: EPA/600/R-98/118. NTIS number PB98-169196 INZ.

2. Wagner, H.P., Pepich, B.V., Hautman, D.P. and Munch, D.J. "Analysis of 500 ng/L Levels of Bromate in Drinking Water by Direct Injection and Suppressed Ion Chromatography Coupled with a Single, Pneumatically Delivered Postcolumn Reagent." Journal Chromatography A, 850 (1999), 119-129.

3. Wagner, H.P., Alig, A.E., Pepich, B.V., Frebis, C.P., Hautman, D.P. and Munch, D.J. "A Study of Ion Chromatographic Methods for Trace Level Bromate Analysis in Drinking Water Comparing the Selective Anion Concentration (SAC) Method, U.S. EPA 300.1 and a Postcolumn Reagent Procedure." AWWA WQTC Proceedings, 4D-1, San Diego, CA, (November 1998).

4. Wagner, H.P., Pepich, B.V., Hautman, D.P. and Munch, D.J. "Performance Evaluation of a Method for the Determination of Bromate in Drinking Water by Ion Chromatography (EPA 317.0) and validation of EPA Method 324.0 " Presented at the International Ion Chromatography Symposium, San Jose, CA, September, 1999. Accepted for publication Journal of Chromatography A, (anticipated) June 2000.

5. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L. "Trace Analyses for Wastewater," Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

6. "OSHA Safety and Health Standards, General Industry," (29CFR1910). Occupational Safety and Health Administration, OSHA 2206, (Revised, Jan. 1976).

7. ASTM Annual Book of Standards, Part II, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986.

8. "Carcinogens-Working with Carcinogens," Publication No. 77-206, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Atlanta, Georgia, August 1977.

9. "Safety In Academic Chemistry Laboratories," 3rd Edition, American Chemical Society Publication, Committee on Chemical Safety, Washington, D.C., 1979.

10. 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).

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

12. Wagner, H.P., Pepich, B.V., Hautman, D.P. and Munch, D.J. "The Use of EPA Method 300.1 with the Addition of a Postcolumn Reagent for the Analysis of Ultra Trace Levels of Bromate in Drinking Water and the Analysis of Bromate in Bottled Waters." Presented at Pittcon 99, Orlando FL, paper 1414, (March 1999).

13. Iatrou, A. and Knocke, W.R. Removing Chlorite by the Addition of Ferrous Iron. Journal of the AWWA, Research and Technology, (November, 1992), 63-68.

14. Wagner, H.P., Pepich, B.V., Hautman, D.P. and Munch, D.J. "Eliminating the Chlorite Interference in US Environmental Protection Agency Method 317.0 Permits the Analysis of Bromate in all Drinking Water Matrices." Accepted for publication in Journal of Chromatography A, (anticipated) Fall 2000.

15. Schibler, J.A. American Laboratory, (December, 1997), 63-64.

16. Dixon, W.J. "Processing Data Outliers." Biometrics, BIOMA, 9 (No.1):74-89 (1953).

## 17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

### TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE INORGANIC OXYHALIDE DISINFECTION BY-PRODUCTS AND BROMIDE.

### Standard Conditions and Equipment[a]:

| | |
|---|---|
| Ion Chromatograph: | Dionex DX500 |
| Sample Loop: | 225 µL |
| Eluent: | 9.0 mM $Na_2CO_3$ |
| Eluent Flow: | 1.3 mL/min |
| Columns : | Dionex AG9-HC / AS9-HC, 4 mm |
| Typical System Backpressure: | 2300 psi |
| Suppressor: | ASRS-I, external water mode, 100 mA current |
| Detectors: | Suppressed Conductivity Detector, Dionex CD20<br>Background Conductivity: 24 µS<br>Absorbance Detector, Dionex AD20 (10 mm cell path)<br>Set for absorbance at 450 nm (Tungsten lamp) |
| Postcolumn Reagent Flow: | 0.7 mL/min |
| Postcolumn Reactor Coil: | knitted, potted for heater, 500 uL internal volume |
| Postcolumn Heater: | 80 °C |
| Recommended method total analysis time: | 25 minutes |

### Analyte Retention Times and Method Detection Limits (MDLs):

| | | MDL DETERMINATION | | |
|---|---|---|---|---|
| Analyte | Retention Time [b] (min.) | Fortified Conc. (µg/L) | # of Reps. | MDL (µg/L) |
| Chlorite[c] | 4.20 | 2.0 | 8 | 0.45 |
| Chlorite[d] | 4.20 | 2.0 | 8 | 0.89 |
| Bromate[c] | 4.85 | 2.0 | 8 | 0.98 |
| Bromate[d] | 4.85 | 2.0 | 8 | 0.71 |
| Bromate[e] | 5.35 | 0.50 | 7 | 0.12 |
| Surrogate: DCA[d] | 8.50 | | | |
| Bromide[c] | 10.0 | 2.0 | 8 | 0.54 |
| Bromide[d] | 10.0 | 2.0 | 8 | 0.69 |
| Chlorate[c] | 11.0 | 2.0 | 8 | 0.92 |
| Chlorate[d] | 11.0 | 2.0 | 8 | 0.62 |

(a) Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
(b) Reference to chromatograms in Figure 2 and 3.
(c) Method 317.0 conductivity detection without PCR online.
(d) Method 317.0 conductivity detection with PCR online.
(e) Method 317.0 ONLY bromate by postcolumn UV/VIS absorbance detection.

**TABLE 2. SINGLE LABORATORY PRECISION IN VARIOUS MATRICES FOR BROMATE BY CONDUCTIVITY AND ABSORBANCE DETECTION.**

| | | PRECISION | | | | |
|---|---|---|---|---|---|---|
| Matrix | Detection | Fortified Conc. (µg/L) | # of Reps. | Mean (µg/L) | SD (n-1) | % RSD |
| Reagent Water | Conductivity | 0.50 | 8 | < MRL[a] | | < MRL |
| | Conductivity | 5.0 | 8 | 4.8 | 0.420 | 8.83 |
| | Absorbance | 0.50 | 8 | 0.50 | 0.054 | 10.8 |
| | Absorbance | 5.0 | 8 | 5.4 | 0.110 | 2.10 |
| Chlorinated Drinking Water | Conductivity | 0.50 | 8 | < MRL | | < MRL |
| | Conductivity | 5.0 | 7[b] | 4.1 | 0.650 | 15.7 |
| | Absorbance | 0.50 | 8 | 0.53 | 0.050 | 2.77 |
| | Absorbance | 5.0 | 8 | 5.2 | 0.098 | 1.87 |
| High Ionic Water | Conductivity | 0.50 | 8 | < MRL | | < MRL |
| | Conductivity | 5.0 | 8 | 4.5 | 0.960 | 21.4 |
| | Absorbance | 0.50 | 8 | 0.52 | 0.430 | 8.20 |
| | Absorbance | 5.0 | 8 | 5.1 | 0.199 | 3.90 |
| High Organic Water | Conductivity | 0.50 | 8 | < MRL | | < MRL |
| | Conductivity | 5.0 | 8 | 5.1 | 0.199 | 3.90 |
| | Absorbance | 0.50 | 8 | 0.50 | 0.044 | 8.81 |
| | Absorbance | 5.0 | 8 | 5.2 | 0.014 | 2.61 |

[a] <MRL = analyte was not detected at or above the minimum reporting level.
[b] n = 8 one outlier reject using Dixon's Outlier Test.[16]

Standard Conditions: Same as listed in Table 1.

**TABLE 3. SINGLE-LABORATORY PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS AND BROMIDE.[1,2]**

| Analyte | Matrix | Unfortified Conc. (µg/L) | Fortified Conc. (µg/L) | # of Reps. | Mean (µg/L) | Mean %REC | SD(n-1) | %RSD |
|---|---|---|---|---|---|---|---|---|
| Chlorite | RW | <MRL[a] | 100 | 9 | 96.2 | 96.2 | 0.95 | 0.99 |
| | | | 500 | 9 | 520 | 105 | 3.13 | 0.60 |
| | HIW | <MRL | 100 | 9 | 102 | 102 | 2.19 | 2.15 |
| | | | 500 | 9 | 520 | 104 | 3.64 | 0.70 |
| | SW | <MRL | 100 | 9 | 91.4 | 91.4 | 1.22 | 1.33 |
| | | | 500 | 9 | 500 | 99.0 | 7.54 | 1.52 |
| | GW | <MRL | 100 | 9 | 92.9 | 92.9 | 1.65 | 1.77 |
| | | | 500 | 9 | 490 | 98.1 | 3.40 | 0.69 |
| | ClW | <MRL | 100 | 9 | 87.4 | 87.4 | 0.59 | 0.68 |
| | | | 500 | 9 | 490 | 97.1 | 6.36 | 1.31 |
| | CDW | 292 | 100 | 9 | 400 | NC[b] | 1.64 | 0.41 |
| | | | 500 | 9 | 810 | 104 | 4.00 | 0.49 |
| | O3W | <MRL | 100 | 9 | 84.4 | 84.4 | 0.46 | 0.54 |
| | | | 500 | 9 | 480 | 96.1 | 3.24 | 0.67 |
| Bromate by Conductivity | RW | <MRL | 5.0 | 9 | 5.05 | 101 | 0.45 | 8.86 |
| | | | 25 | 9 | 26.5 | 106 | 1.71 | 6.47 |
| | HIW | <MRL | 5.0 | 9 | 4.88 | 97.5 | 0.95 | 19.5 |
| | | | 25 | 9 | 25.5 | 102 | 1.37 | 5.37 |
| | SW | <MRL | 5.0 | 9 | 4.46 | 89.2 | 0.58 | 13.0 |
| | | | 25 | 9 | 26.3 | 105 | 1.10 | 4.18 |
| | GW | <MRL | 5.0 | 9 | 5.10 | 102 | 0.50 | 9.75 |
| | | | 25 | 9 | 22.2 | 88.9 | 1.29 | 5.81 |
| | ClW | <MRL | 5.0 | 9 | 4.63 | 92.6 | 0.77 | 16.7 |
| | | | 25 | 9 | 25.0 | 100. | 1.64 | 6.55 |
| | CDW | <MRL | 5.0 | 9 | 4.14 | 82.7 | 0.62 | 15.1 |
| | | | 25 | 9 | 25.3 | 101 | 1.28 | 5.09 |
| | O3W | 1.45 | 5.0 | 9 | 5.50 | 80.9 | 0.61 | 11.1 |
| | | | 25 | 9 | 24.1 | 90.6 | 1.13 | 4.69 |

RW = Reagent Water
HIW = High Ionic Strength Water
SW = Surface Water
GW = Groundwater
ClW = Chlorinated Drinking Water
CDW = Chlorine Dioxide Treated Drinking Water
O3W = Ozonated Drinking Water

[a] <MRL = analyte was not detected at or above the minimum reporting level.
[b] NC = Not calculated since amount fortified was less than unfortified native matrix concentration (Section 9.4.1.1.).

**TABLE 3. SINGLE-LABORATORY PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS AND BROMIDE (cont.).[1,2]**

| Analyte | Matrix | Unfortified Conc. (µg/L) | Fortified Conc. (µg/L) | # of Reps. | Mean (µg/L) | Mean %REC | SD(n-1) | %RSD |
|---|---|---|---|---|---|---|---|---|
| Bromide | RW | <MRL[a] | 20.0 | 9 | 20.8 | 104 | 0.80 | 3.82 |
| | | | 100 | 9 | 110 | 107 | 0.60 | 0.56 |
| | HIW | 3.2 | 20.0 | 9 | 21.7 | 92.5 | 0.79 | 3.63 |
| | | | 100 | 9 | 110 | 102 | 1.05 | 1.00 |
| | SW | 31 | 20.0 | 9 | 51.0 | NC[b] | 0.97 | 1.90 |
| | | | 100 | 9 | 140 | 109 | 1.88 | 1.35 |
| | GW | 150 | 20.0 | 9 | 170 | NC | 0.78 | 0.45 |
| | | | 100 | 9 | 260 | NC | 218 | 0.82 |
| | ClW | 16 | 20.0 | 9 | 39.0 | 115 | 0.64 | 1.62 |
| | | | 100 | 9 | 130 | 109 | 2.00 | 1.60 |
| | CDW | 12 | 20.0 | 9 | 35.0 | 115 | 0.76 | 2.22 |
| | | | 100 | 9 | 130 | 113 | 1.24 | 0.99 |
| | O3W | 40. | 20.0 | 9 | 65.0 | NC | 3.67 | 5.61 |
| | | | 100 | 9 | 150 | 113 | 1.00 | 0.65 |
| Chlorate | RW | <MRL | 100 | 9 | 98.3 | 98.3 | 0.80 | 0.82 |
| | | | 500 | 9 | 520 | 104 | 4.15 | 0.80 |
| | HIW | <MRL | 100 | 9 | 86.1 | 86.1 | 1.47 | 1.70 |
| | | | 500 | 9 | 500 | 100. | 4.52 | 0.90 |
| | SW | 3.2 | 100 | 9 | 100 | 98.3 | 1.57 | 1.55 |
| | | | 500 | 9 | 510 | 102 | 7.11 | 1.39 |
| | GW | <MRL | 100 | 9 | 93.5 | 93.5 | 2.00 | 2.14 |
| | | | 500 | 9 | 510 | 102 | 3.84 | 0.75 |
| | ClW | 34 | 100 | 9 | 140 | 102 | 1.01 | 0.74 |
| | | | 500 | 9 | 550 | 103 | 3.11 | 0.57 |
| | CDW | 120 | 100 | 9 | 220 | NC | 3.20 | 1.44 |
| | | | 500 | 9 | 650 | 106 | 3.50 | 0.54 |
| | O3W | 6.2 | 100 | 9 | 110 | 100. | 1.20 | 1.13 |
| | | | 500 | 9 | 520 | 103 | 2.45 | 0.47 |

RW = Reagent Water
HIW = High Ionic Strength Water
SW = Surface Water
GW = Groundwater
ClW = Chlorinated Drinking Water
CDW = Chlorine Dioxide Treated Drinking Water
O3W = Ozonated Drinking Water

[a] <MRL = analyte was not detected at or above the minimum reporting level.
[b] NC = Not calculated since amount fortified was less than unfortified native matrix concentration (Section 9.4.1.1.).

**TABLE 3. SINGLE-LABORATORY PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS AND BROMIDE (cont.).[1,2]**

| Analyte | Matrix | Fortified Conc. (mg/L) | # of Reps. | Mean (mg/L) | Mean %REC | SD(n-1) | %RSD |
|---|---|---|---|---|---|---|---|
| Surrogate: DCA | RW | 5.0 | 9 | 5.1 | 102 | 0.93 | 0.91 |
| (see Note) | | | | 5.0 | 99.5 | 0.69 | 0.69 |
| | HIW | 5.0 | 9 | 5.0 | 100. | 0.79 | 0.79 |
| | | | | 5.0 | 99.2 | 1.76 | 1.78 |
| | SW | 5.0 | 9 | 4.9 | 98.9 | 0.70 | 0.7 |
| | | | | 5.0 | 99.8 | 1.60 | 1.61 |
| | GW | 5.0 | 9 | 5.1 | 102 | 0.50 | 0.49 |
| | | | | 5.1 | 103 | 0.50 | 0.49 |
| | ClW | 5.0 | 9 | 5.2 | 103 | 1.73 | 1.68 |
| | | | | 5.1 | 103 | 1.12 | 1.09 |
| | CDW | 5.0 | 9 | 5.0 | 100. | 1.02 | 1.02 |
| | | | | 5.0 | 101 | 1.08 | 1.07 |
| | O3W | 5.0 | 9 | 5.0 | 99.8 | 0.70 | 0.7 |
| | | | | 5.1 | 101 | 0.53 | 0.52 |

RW = Reagent Water
HIW = High Ionic Strength Water
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 INORGANIC DISINFECTION BY-PRODUCTS AND BROMIDE.[1]**

| Analyte | Preservative | Matrix | Unfortified Conc. (µg/L) | Fortified Conc. (µg/L) | Analyte % Recovery Day 0 | Day 3 | Day 10 | Day 30 | See Note |
|---|---|---|---|---|---|---|---|---|---|
| Chlorite | None | RW | <MRL | 500 | 99.8 | 100 | 104 | 94.3 | |
| | | HIW | <MRL | 500 | 99.3 | 98.5 | 106 | 89.3 | |
| | | SW | <MRL | 500 | 92.0 | 88.5 | 82.3 | 75.1 | (a) |
| | | GW | <MRL | 500 | 93.9 | 94.5 | 96.1 | 91.7 | |
| | | ClW | <MRL | 500 | 93.7 | NA[(a)] | 90.3 | 84.7 | (b,c) |
| | | CDW | 290 | 500 | 98.6 | 101 | 91.7 | 77.5 | (a,c) |
| | | O3W | <MRL | 500 | 10.0 | NA | 82.5 | 90.5 | (b) |
| Chlorite | EDA | RW | <MRL | 500 | 101 | 101 | 104 | 95.3 | |
| | | HIW | <MRL | 500 | 98.4 | 98.7 | 104 | 95.4 | |
| | | SW | <MRL | 500 | 98.3 | 97.3 | 97.8 | 92.7 | |
| | | GW | <MRL | 500 | 97.7 | 97.1 | 97.5 | 92.6 | |
| | | ClW | <MRL | 500 | 98.9 | NA | 96.9 | 92.6 | (b) |
| | | CDW | 300 | 500 | 103 | 107 | 102 | 94.5 | |
| | | O3W | <MRL | 500 | 105 | NA | 96.3 | 91.9 | (b) |
| Bromate | None | RW | <MRL | 25.0 | 93.6 | 94.1 | 110 | 96.1 | |
| | | HIW | <MRL | 25.0 | 100. | 86.0 | 105 | 87.7 | |
| | | SW | <MRL | 25.0 | 98.7 | 95.1 | 105 | 102 | |
| | | GW | <MRL | 25.0 | 79.4 | 92.4 | 77.8 | 82.2 | |
| | | ClW | <MRL | 25.0 | 102 | NA | 101 | 103 | (b) |
| | | CDW | <MRL | 25.0 | 104 | 96.8 | 98.9 | 92.1 | |
| | | O3W | 2.3 | 25.0 | 87.3 | NA | 84.3 | 99.9 | (b) |
| Bromate | EDA | RW | <MRL | 25.0 | 97.3 | 95.3 | 99.5 | 102 | |
| | | HIW | <MRL | 25.0 | 86.9 | 86.1 | 107 | 91.2 | |
| | | SW | <MRL | 25.0 | 100. | 104 | 103 | 94.9 | |
| | | GW | <MRL | 25.0 | 83.2 | 101 | 88.4 | 88.3 | |
| | | ClW | <MRL | 25.0 | 105 | NA | 101 | 102 | (b) |
| | | CDW | <MRL | 25.0 | 117 | 97.3 | 98.1 | 83.9 | |
| | | O3W | 2.3 | 25.0 | 92.6 | NA | 84.5 | 88.9 | (b) |

NOTES:
(a) Degradation in the unpreserved matrix is apparent.
(b) NA indicates "NOT ANALYZED"
(c) Analyte recovery will be adversely effected by reactions with free chlorine.

**TABLE 3A. STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS AND BROMIDE (cont.).[1,2]**

| Analyte | Preservative | Matrix | Unfortified Conc. (µg/L) | Fortified Conc. (µg/L) | Analyte % Recovery Day 0 | Day 3 | Day 10 | Day 30 | See Note |
|---|---|---|---|---|---|---|---|---|---|
| Bromide | None | RW | <MRL | 100 | 99.4 | 97.2 | 107 | 101 | |
| | | HIW | <MRL | 100 | 102 | 103 | 105 | 105 | |
| | | SW | 31 | 100 | 102 | 97.1 | 107 | 99.1 | |
| | | GW | 150 | 100 | 97.7 | 95.3 | 109 | 100. | |
| | | ClW | 4.7 | 100 | 8.90 | NA[(a)] | 37.0 | 11.4 | (b,c,d) |
| | | CDW | <MRL | 100 | 5.78 | 23.1 | 39.0 | 51.3 | (c,d) |
| | | O3W | 30 | 100 | 98.3 | NA | 120 | 108 | (b,d) |
| Bromide | EDA | RW | <MRL | 100 | 98.4 | 98.6 | 107 | 100. | |
| | | HIW | <MRL | 100 | 104 | 103 | 106 | 105 | |
| | | SW | 31 | 100 | 99.5 | 98.2 | 107 | 100. | |
| | | GW | 150 | 100 | 100. | 97.0 | 114 | 97.7 | |
| | | ClW | 12 | 100 | 101 | NA | 115 | 97.4 | (b,c) |
| | | CDW | 6.1 | 100 | 101 | 96.5 | 119 | 110 | (c) |
| | | O3W | 31 | 100 | 97.3 | NA | 122 | 102 | (b) |
| Chlorate | None | RW | <MRL | 500 | 102 | 102 | 105 | 97.4 | |
| | | HIW | <MRL | 500 | 97.0 | 97.8 | 101 | 95.4 | |
| | | SW | 5.8 | 500 | 100. | 97.8 | 100. | 96.0 | |
| | | GW | <MRL | 500 | 100. | 98.7 | 101 | 99.8 | |
| | | ClW | 38 | 500 | 102 | NA | 104 | 98.2 | (b) |
| | | CDW | 130 | 500 | 102 | 99.9 | 104 | 99.6 | |
| | | O3W | 8.3 | 500 | 100. | NA | 103 | 97.3 | (b) |
| Chlorate | EDA | RW | <MRL | 500 | 104 | 98.6 | 103 | 97.3 | |
| | | HIW | <MRL | 500 | 97.0 | 103 | 100. | 95.0 | |
| | | SW | 6.7 | 500 | 100. | 98.2 | 100. | 95.6 | |
| | | GW | <MRL | 500 | 102 | 97.0 | 101 | 99.3 | |
| | | ClW | 38 | 500 | 101 | NA | 102 | 96.1 | (b) |
| | | CDW | 120 | 500 | 102 | 96.5 | 105 | 97.7 | |
| | | O3W | 8.6 | 500 | 98.0 | NA | 103 | 96.4 | (b) |

NOTES:
(a) Degradation in the unpreserved matrix is apparent.
(b) NA indicates "NOT ANALYZED"
(c) Analyte recovery will be adversely effected by reactions with free chlorine.
(d) Measurement of $Br^-$ is not in the scope (source/raw water only)

**TABLE 4. INITIAL DEMONSTRATION OF CAPABILITY QC REQUIREMENTS.**

| Reference | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 9.2.2<br>9.3.1 | Initial Demonstration of Low System Background | Analyze a method blank (LRB) and determine that all target analytes are below ½ of the proposed MRL prior to performing the IDC | The LRB concentration must be ≤ ½ of the proposed MRL |
| Sect. 9.2.3 | Initial Demonstration of Precision (IDP) | Conductivity: analyze 7 replicate LFBs recommend fortify at 20 ug/L<br>Absorbance: analyze 7 replicate LFBs recommend fortify with bromate at 2.0 ug/L | %RSD must be ≤ 20% |
| Sect. 9.2.4 | Initial Demonstration of Accuracy (IDA) | Calculate average recovery of IDP replicates | Mean % recovery must be ± 15% of true value. |
| Sect. 9.2.5 | Quality Control Sample (QCS) | Initially and at least quarterly analyze a QCS from an external/second source | QCS must be ± 20% of the true value |
| Sect. 9.2.6 | Method Detection Limit (MDL) Determination | Select a fortifying level at 3-5 times the estimated instrument detection limit at or lower than the MRL. Analyze 7 replicate LFBs Calculate MDL using equation in Section 9.2.6 - do not subtract blank | |
| Sect. 9.2.7 | Minimum Reporting Level (MRL) | MRLs MUST be established for all analytes during the IDC. | The low CAL standard can be lower than the MRL, but the MRL MUST be no lower than the low CAL standard |

**TABLE 5. QUALITY CONTROL REQUIREMENTS (SUMMARY).**

| Reference | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 8.3 | Sample Holding Time / Preservation | Bromate 28 days, refrig. at <6°C / EDA Preservation<br>Bromide 28 days, EDA Permitted<br>Chlorate 28 days, refrig. at <6°C / EDA Preservation<br>Chlorite 14 days, refrig. at <6°C / EDA Preservation | Holding time and temperature must not be exceeded. EDA added to all samples |
| Sect. 11.1.4.1 (specific to PCR) | Pretreated Sample (acidified/ Fe [II] added to remove chlorite) Holding Time | ONLY REQUIRED when samples containing chlorite are pretreated and PCR is employed to measure trace bromate in samples.<br>MAXIMUM PRETREATED SAMPLE HOLDING TIME: 30 hours | Pretreated sample holding time must not be exceeded |
| Sect. 10.2 | Initial Calibration | Conductivity: generate calibration curve using at least 5 standards<br>Absorbance: generate calibration curve using at least 5 bromate standards | MRL MUST be no lower than the lowest calibration standard |
| Sect. 10.3.1 | Initial Calibration Check | Daily, verify calibration of conductivity detector at the MRL by analyzing an initial low-level continuing calibration check standard (ICCS) and a separate low-level ICCS for the absorbance detector at the MRL. | Recovery must be 75- 125% of the true value on both detectors |
| Sect. 10.3.2 | Continuing Calibration and End Calibration Checks | Alternately analyze separate mid and high level CCCS/ECCS after every 10 samples and after the last sample | MRL to 5 x MRL must have 75 - 125% recovery on both detectors<br>For 5 x MRL to highest CCCS must have 85 - 115% recovery on both detectors |
| Sect. 9.3.1 | Laboratory Reagent Blank (LRB) | Include LRB with every analysis batch (up to 20 samples)<br>Analyze prior to analyzing field samples | All analytes must be ≤ ½ MRL |
| Sect. 9.3.1.2 (specific to PCR) | PRETREATED Laboratory Reagent Blank (LRB) | REQUIRED in any analysis batch which includes samples which have been pretreated to remove chlorite prior to PCR measurement of trace bromate. | PCR measured bromate < ½ MRL |
| Sect. 9.3.2 | Laboratory Fortified Blank (LFB) | Laboratory must analyze LFB in each analysis batch following the ICCS. Calculate %REC prior to analyzing samples | LFB recovery if fortified at conc. from MRL to 5X MRL must be 75 - 125%. For 5X MRL to highest CCCS must be 85 - 115%. Must have acceptable recoveries prior to analyzing samples. Sample results from batches that fail LFB are invalid |

**TABLE 5. QUALITY CONTROL REQUIREMENTS (SUMMARY CONTINUED).**

| Reference | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 9.3.3 | Instrument Performance Check (IPC) | Calculate Peak Gaussian Factor (PGF) using equation (Sect. 9.3.3.1) and monitor retention time for surrogate in Initial Calibration Check Standard (ICCS) each day | PGF must fall between 0.80 and 1.15<br>Ret. Time (RT) for surrogate must remain 80% of initial RT when column was new |
| Sect. 9.4.1<br><br><br><br><br><br><br>Sect. 11.1.4.2 | Laboratory Fortified Sample Matrix (LFM) | Must add known amount of each target analyte to a minimum of 5% of field samples or at least one within each analysis batch for both detectors<br>LFM must be fortified above the native level and at no greater than 5 x the highest field sample concentration<br>Calculate target analyte recovery using formula (Sect. 9.4.1.3)<br>When field samples from chlorine dioxide plants which contain chlorite are pretreated prior to the PCR measurement of trace bromate, an additional LFM must be prepared for each pretreated field sample (Sect. 9.4.1.5) | Recovery should be 75 - 125%<br><br>If fortified sample fails the recovery criteria, label both as suspect/matrix. |
| Sect. 9.4.2 | Surrogate | Dichloroacetate is added to all blanks, samples and standards (if measuring by conductivity and absorbance)<br>Calculate recovery using formula in Section 9.4.2 | Surrogate recovery must be 90 - 115%.<br>Samples that fail surrogate recovery must be reanalyzed. If second analysis fails label result as suspect/matrix |
| Sect. 9.4.3 | Field or Laboratory Duplicates | Analyze either a field or laboratory duplicate for a minimum of 5% of field samples or at least one within each analysis batch for both detectors<br>Calculate the relative percent difference (RPD) using formula in Section 9.4.3.1 | The RPD for concentrations at MRL to 5 x MRL should be ± 20% on both detectors, and ± 10% on both detectors for concentrations at 5 x MRL to highest CCCS. If this range is exceeded, label both as suspect/matrix |

**TABLE 6. EXAMPLE SAMPLE ANALYSIS BATCH WITH QUALITY CONTROL REQUIREMENTS**

| Injection # | Sample Description | Acceptance Criteria |
|---|---|---|
| 1 | Laboratory reagent blank (LRB) | ≤ ½ MRL |
| 2 | ICCS conductivity detector (5.0 µg/L) | 3.75 to 6.25 µg/L |
| 3 | ICCS absorbance detector (0.5 µg/L) | 0.375 to 0.625 µg/L |
| 4 | Laboratory Fortified Blank (LFB) - conductivity detector | ± 25 % fortified level |
| 5 | LFB - absorbance detector | ± 25 % fortified level |
| 6 | Field sample 1 | |
| 7 | Field sample 1 - Laboratory Duplicate (LD) [(a)] | ± 15 % RPD |
| 8 | Field sample 2 | |
| 9 | Field sample 2 - Laboratory Fortified Matrix (LFM) [(a)] at concentrations specific for conductivity detector | ± 25% fortified level |
| 10 | Field sample 2 - LFM specific for trace bromate on the absorbance detector | ± 25% fortified level |
| 11 | Field sample 3 | |
| 12 | Field sample 4 | |
| 13 | Field sample 5 | |
| 14 | Field sample 6 | |
| 15 | Field sample 7 | |
| 16 | Field sample 8 | |
| 17 | Field sample 9 | |
| 18 | Field sample 10 | |
| 19 | CCCS conductivity detector (75.0 µg/L) | 63.8 to 86.3 µg/L |
| 20 | CCCS absorbance detector (5.0 µg/L) | 4.25 to 5.75 µg/L |
| 21 | Field sample 11 | |
| 22 | Field sample 12 | |

| | | |
|---|---|---|
| 23 | Field sample 13 | |
| 24 | Field sample 14 - (finished water from PWS using chlorine dioxide) | |
| 25 | Pretreated LRB (Section 9.3.1.2) using the acid/Fe(II) chlorite removal procedure (Section 11.1.4) | ≤ ½ MRL |
| 26 | Field sample 14 [(b)] - (finished water from PWS using chlorine dioxide) pretreated with acid/Fe(II) (Section 11.1.4) | |
| 27 | Field sample 14 - (finished water from PWS using chlorine dioxide) LFM specific for trace bromate on the absorbance detector, pretreated with acid/Fe(II) (Section 11.1.4.2) | ± 25% fortified level |
| 28 | Field sample 15 | |
| 29 | Field sample 16 | |
| 30 | Field sample 17 | |
| 31 | Field sample 18 | |
| 32 | Field sample 19[(b)] | |
| 33 | ECCS conductivity detector (500.0 µg/L) | 425 to 575 µg/L |
| 34 | ECCS absorbance detector (15.0 µg/L) | 12.8 to 17.3 µg/L |

[(a)] If no analytes are observed above the MRL for a sample, an alternate sample which contains reportable values should be selected as the laboratory duplicate. Alternately, the LFM can be selected and reanalyzed as the laboratory duplicate ensuring the collection of QC data for precision.

[(b)] Field sample #19 was the final field sample permitted in this batch but 20 total field samples were analyzed.
Field sample #14 was analyzed both initially and as a acid/Fe (II) pretreated sample, therefore, it accounted for two "field sample analyses" toward the maximum of twenty in an analysis batch (Section 3.1).

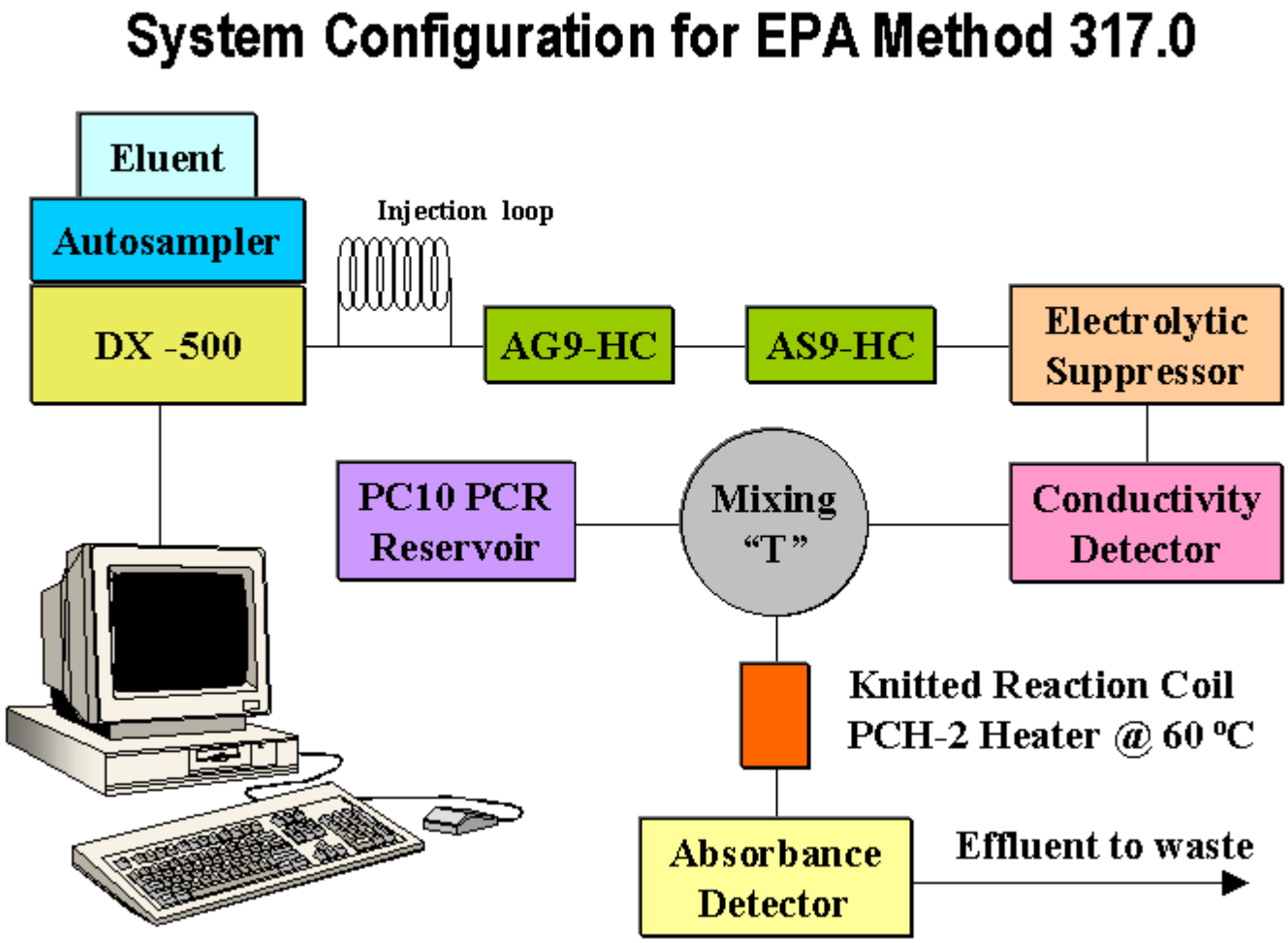


Figure 1: Schematic detailing the configuration of postcolumn hardware addition to an ion chromatograph. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. If the requirements found in Section 9 are met, equivalent products or hardware can be employed.

NOTE: In a typical Method 300.1 hardware configuration, a backpressure coil is included after the conductivity cell as part of the waste stream when this manufacturer's equipment is used. These backpressure coils are not required when the Method 317.0 instrument configuration is employed since the additional PCR system components, placed in-line, function in the same capacity and provide sufficient backpressure.

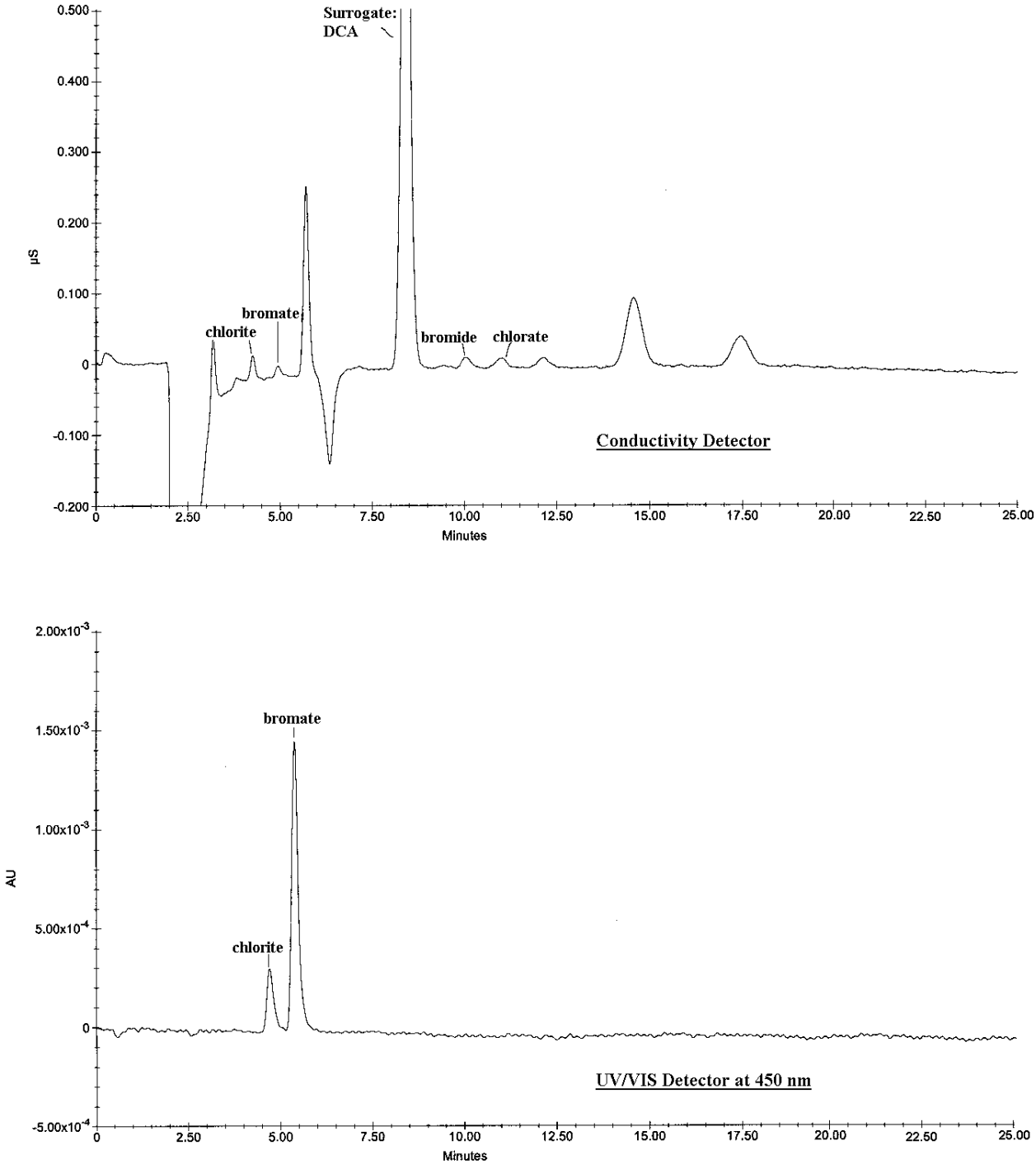


Figure 2: Reagent water fortified with inorganic disinfection by-products and bromide at 10 ug/L.

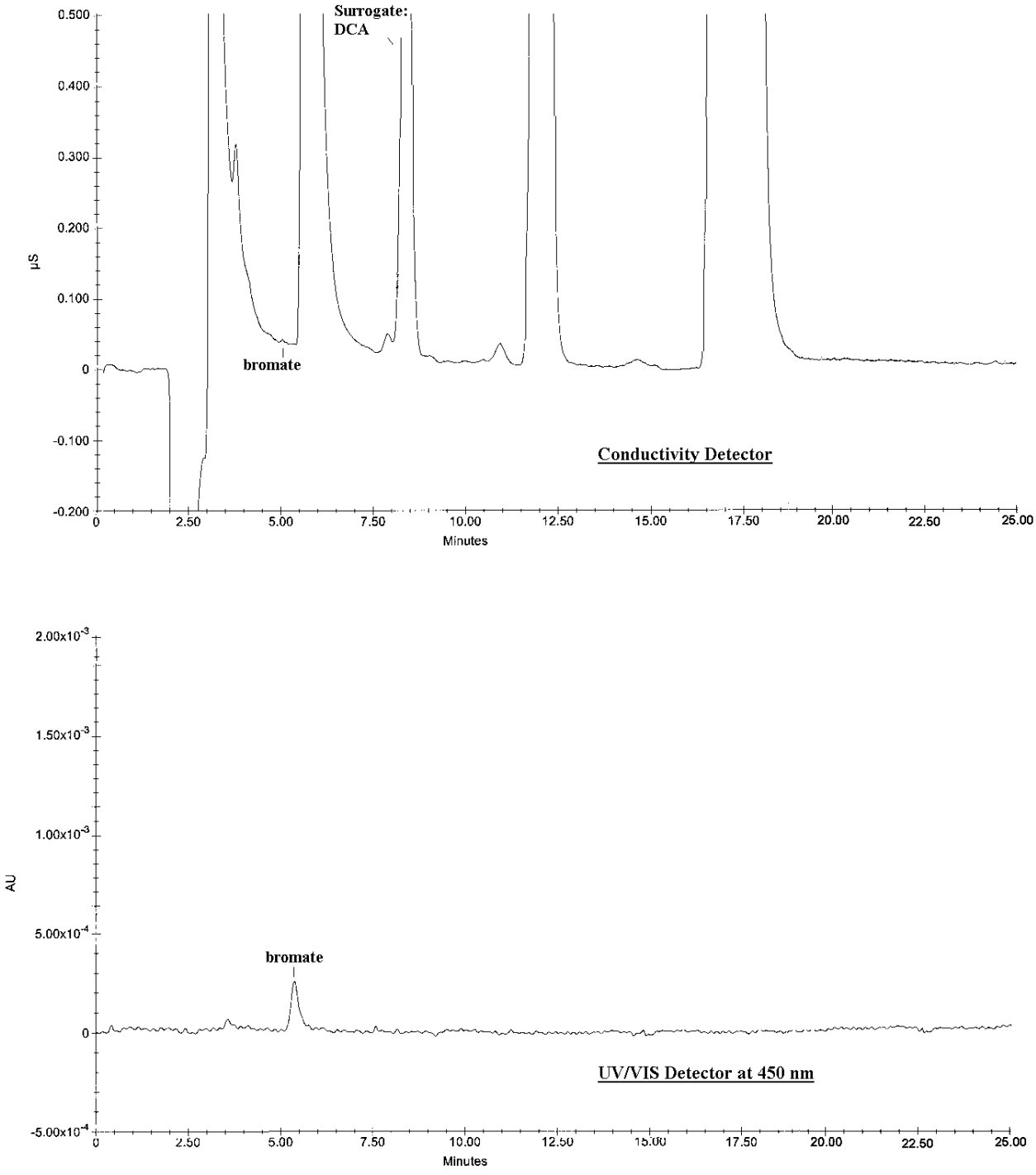


Figure 3: Chlorinated tap water fortified with bromate at 2.0 ug/L.