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METHOD 326.0 DETERMINATION OF INORGANIC OXYHALIDE DISINFECTION BY-PRODUCTS IN DRINKING WATER USING ION CHROMATOGRAPHY INCORPORATING THE ADDITION OF A SUPPRESSOR ACIDIFIED POSTCOLUMN REAGENT FOR TRACE BROMATE ANALYSIS

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METHOD 326.0
DETERMINATION OF INORGANIC OXYHALIDE DISINFECTION BY-PRODUCTS IN DRINKING WATER USING ION CHROMATOGRAPHY INCORPORATING THE ADDITION OF A SUPPRESSOR ACIDIFIED 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 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	
Analyte	**Comments**
Bromate	report values > 15.0 ug/L *
Bromide	report values from source and raw waters only
Chorite	report values ≥Minimum Reporting Level in calibration range
Chloride	report values ≥Minimum Reporting Level in calibration range
Inorganic Disinfection By-products by Absorbance Detection	
Analyte	**Comments**
Bromate	report values ≥ Minimum Reporting Level to 15.0 ug/L *

* the concentrations reported for bromate assume both detectors to be running simultaneously.

1.2 The single laboratory reagent water Detection Limits (Sect. 3.15) for the above analytes are listed in Table 1. The Detection Limit is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[2] The Detection Limit differs from, and is lower than the Minimum Reporting Level (MRL) (Sect. 3.16). The Detection Limit 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.

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 9.8.

1.5 Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Section 9.

2. SUMMARY OF METHOD

2.1 The development of this method was based upon the work of several investigators as summarised elsewhere.[3] A volume of sample, approximately 225 µL (see Note), is introduced into an ion chromatograph (IC) which includes a guard column, analytical column, suppressor devices, conductivity detector, a postcolumn reagent delivery system (pneumatically controlled), a heated postcolumn reaction coil, and a ultraviolet/visible (UV/Vis) absorbance detector (see Figure 1). After separation and suppression of the eluent, the oxyhalide anions chlorite, chlorate, bromate >15.0 µg/L and bromide are measured using conductivity detection. To facilitate low-level detection of bromate, the suppressed effluent from the conductivity detector is combined with an acidic

solution of potassium iodide containing a catalytic amount of molybdenum VI. The mixture is heated at 80° C (to facilitate complete reaction) where the bromate reacts with iodide to form the tri-iodide ion which is measured by its UV absorption at 352 nm.

NOTE: A 225 uL sample loop can be made using approximately 111 cm (44 inches) of 0.02 inch i.d. PEEK tubing. 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)
- Continuing Calibration Check Standards (CCCs)
- Laboratory Fortified Blank (LFB)
- Laboratory Fortified Sample Matrix (LFSM), and
- Either a Field Duplicate (FD) or a Laboratory Fortified Sample Martix Duplicate (LFSMD).

3.2 SURROGATE ANALYTE (SUR) – A pure analyte, which chemically resembles target analytes and is extremely unlikely to be found in any sample. This analyte is added to a sample aliquot in known amount(s) before filtration or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SUR is to monitor method performance with each sample.

3.3 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents, sample preservatives, and surrogates that are used in the analysis batch. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water or other blank matrix to which known quantities of the method analytes and all the preservation compounds 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.

3.5 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – An aliquot of an environmental sample to which known quantities of the method analytes and all the preservation compounds are added in the laboratory. The LFSM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFSM corrected for background concentrations.

3.6 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A second aliquot of the field sample used to prepare the LFSM fortified, processed and analyzed identically. The LFSMD is used instead of the Field Duplicate to access method precision when the occurrence of target analytes is low.

3.7 LABORATORY DUPLICATES (LD1 and LD2) – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.8 FIELD DUPLICATES (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.9 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.

3.10 PRIMARY DILUTION STANDARD (PDS) SOLUTION – A solution containing the analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

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

3.12 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.

3.13 CONTINUING CALIBRATION CHECK (CCC) – A calibration standard containing the method analytes and surrogates (s), which is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

3.14 QUALITY CONTROL SAMPLE (QCS) – A solution of method analytes and surrogate(s) 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 standard integrity.

3.15 DETECTION LIMIT – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination of precision (Sect. 9.2.4), and accurate quantitation is not expected at this level. [2]

3.16 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 continuing calibration standard for that analyte and can only be used if acceptable quality control criteria for this standard are met.

3.17 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.

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 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 affect 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, 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 interfering 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 sparged 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 has not been precisely defined; each chemical compound should be treated as a potential health hazard, and exposure to these chemicals should be minimized. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of MSDSs should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.[4-7]

5.2 Pure standard materials and stock standards of these compounds should be handled with suitable protection to skin and eyes. Care should be taken not to breathe the vapors or ingest the materials.

5.3 The following chemical has the potential to be highly toxic or hazardous. The Material Safety Data Sheet (MSDS) should be consulted.

5.3.1 Sulfuric acid – used to prepare regenerant solution (Sect. 7.1.8) for the second suppressor (Dionex AMMS or Ultra ASRS-1 used in the chemical mode) and to for pretreatment of the samples for chlorite removal (Sect. 7.1.7, 11.1.4)

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, suppressors, conductivity detector, mixing "tee", postcolumn reagent delivery system, reaction coil, reaction coil heater, UV/Vis absorbance detector (Figure 1) and a computer-based data acquisition and control system.

NOTE: Because the KI PCR solution is susceptible to oxidation, resulting in a yellow colored solution, the PCR MUST be flushed from the suppressor, reaction coil and detector cell with reagent water 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 reagent water flush.

6.1.1 ANION GUARD COLUMN – Dionex AG9-HC 4 mm (Cat.#: 51791or 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 (Cat.#: 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 to accurately maintain the appropriate reduced flow rate for the PCR.

6.1.3 ANION SUPPRESSOR DEVICES – The data presented in this method were generated using a Dionex Ultra-1 Anion Self Regenerating Suppressor (4 mm ASRS, Cat.#: 53946) for electrolytic suppression of the eluent and a second Ultra -1 ASRS was used in the chemical mode to acidify the PCR just prior to addition to the mixing tee. Equivalent suppressor devices may be utilized providing comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 10 nS per minute over the background conductivity. Alternative suppressor evaluations subsequent to this method development work have indicated that improved detection limits and precision and accuracy can be obtained for bromate by conductivity detection [8]. If conductivity analytes below 10 ug/L are to be reported, the combined baseline drift/noise will be required to be no greater 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" port of the suppressor. The suppressor used to acidify the PCR must be capable of continuous operation using 150 mN sulfuric acid as the regenerant.

6.1.3.1 – The conductivity suppressor 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 an ASRS in recycle mode.

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

6.1.5 ABSORBANCE DETECTOR – Absorbance detector (Dionex AD20 or equivalent with 10-mm cell pathlength, equipped with a deuterium source bulb, or equivalent and capable of measuring absorbance at 352 nm) capable of providing data as required in Section 9.2.

6.1.6 POSTCOLUMN REAGENT DELIVERY SYSTEM –Delivery system (Dionex PC-10 or equivalent) capable of pneumatically delivering the postcolumn reagent to the "eluent in" port of the suppressor to acidify the PCR prior to entering the mixing tee (see Note). 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.

NOTE: Since KI is photosensitive, the KI/Mo PCR solution was observed to develop a light yellow color with time, even when stored under helium in the opaque plastic PC-10 delivery container inside the PC-10 pressurization vessel. Purging the KI/Mo solution with helium immediately after preparation to remove all oxygen did not completely eliminate the problem. Consequently, in order to facilitate overnight (24 hours) operation, the external wall of the PC-10 plastic pressurization vessel was wrapped with an opaque tape, or other light impervious material, to prevent any light exposure to the KI/Mo PCR (care must be exercised to leave about $1/16^{th}$ of an inch at both the top and bottom of the vessel free of tape to allow for proper sealing of the top and bottom. The generation of the tri-iodide ion is pH dependant and the second suppressor is used to acidify the PCR just before entering the reaction coil. Prior to initiating any analysis batch, to ensure that the pH of the reaction mixture is below 2, the effluent from the absorbance detector should be monitored using pH test strips.

6.1.7 REACTION COIL – 500-uL internal volume, knitted, potted and configured to fit securely in the postcolumn reaction coil heater. (Dionex Cat.#: 39349 or equivalent).

6.1.8 POSTCOLUMN REACTION COIL HEATER – Capable of maintaining a temperature of 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 Detection Limits, 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, used to weigh 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 – Opaque, high density polyethylene (HDPE) or amber glass, 30 mL, 125 mL, 250 mL - used for sample collection and storage of calibration solutions. Opaque 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 um (Cat.#: 4485 or equivalent) syringe filters. These cartridges are used to remove particulates and $[Fe(OH)_{3(s)}]$ which are formed during the oxidation-reduction reaction between Fe (II) and ClO_2^- (see Sect. 11.1.4).

6.11 HYDROGEN CARTRIDGES – Dionex OnGuard-H cartridges (Cat.#: 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 for trace levels of bromate (see Sect. 11.1.4).

7. REAGENTS AND STANDARDS

7.1 REAGENTS AND SOLVENTS – Reagent grade or better chemicals should be used. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the determination.

7.1.1 REAGENT WATER – Distilled or deionized water 18 M Ω or better, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.1.2 ELUENT SOLUTION – Sodium carbonate (CAS#: 497-19-8) 9.0 mM. Dissolve 1.91 g sodium carbonate (Na_2CO_3) in reagent water and dilute to 2 L.

7.12.1 This eluent solution must be sparged 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.

7.1.3 ETHYLENEDIAMINE (EDA) PRESERVATION SOLUTION (100 mg/mL) – Dilute 2.8 mL of ethylenediamine (99%) (CAS#: 107-15-3) to 25 mL with reagent water. Prepare fresh monthly.

7.1.4 AMMONIUM MOLYBDATE SOLUTION – A 2.0-mM solution of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, CAS#: 12027667, Fluka Cat.#: 09878 or equivalent] is prepared by dissolving 0.247 g in 100 mL of reagent water. This reagent is stored in an opaque plastic storage bottle and prepared fresh monthly.

7.1.5 POSTCOLUMN REAGENT (0.26 M KI, 43 uM ammonium molybdate heptahydrate) –The postcolumn reagent is prepared by adding 43.1 g of potassium iodide (KI, CAS#: 7681110, Fluka Cat.#: 60400 or equivalent) to a 1-L volumetric flask containing about 500 mL of reagent water. Two hundred and fifteen µL of the ammonium molybdate solution (Sect. 7.1.4) is added to the volumetric flask and diluted to volume with reagent water. The PCR is sparged with helium for 20 minutes to remove all traces of dissolved oxygen and immediately placed in the PC-10 delivery vessel and pressurized with helium. The reagent is stable for 24 hours if properly protected from light (Sect. 6.1.6).

7.1.6 FERROUS IRON SOLUTION [1000 mg/L Fe (II)] – Dissolve 0.124 g ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, CAS#: 7782630, Sigma Cat. #: F-7002 or equivalent) in approximately 15 mL reagent water containing 6 uL of 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.

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

7.1.8 SULFURIC ACID (0.15 N) – Dilute 8.5 mL of concentrated sulfuric acid (Fisher Scientific Certified ACS Plus, A 300-500) to 2000 mL.

7.2 STANDARD SOLUTIONS – Standard Solutions may be prepared from certified, commercially available solutions or from solid compounds. Compounds used to prepare solutions must be 96% pure or greater and the weight may be used without correction for purity to calculate the concentration of the stock standard. Solution concentrations listed in this section were used to develop this method and are included as an example. **Even though stability times for standard solutions are suggested in the following sections, laboratories should use standard QC practices to determine when Standard Solutions described in this section need to be replaced.**

7.2.1 ANALYTE STANDARD SOLUTIONS (1000 mg/L) – 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. Certified chlorite standard solutions are commercially available. If these are not used, chlorite requires careful consideration as outlined below in Section 7.2.1.1.4.

7.2.1.1 ANALYTE STOCK STANDARD SOLUTIONS – Individual Analyte Stock Standards Solutions are prepared as described below.

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

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

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

7.2.1.1.4 Chlorite (ClO_2^-) 1000 mg/L – Prepare from commercially available standards or as described below. If the amperometric titration of the technical grade sodium chlorite ($NaClO_2$), as specified in the Note below, had indicated the purity of the salt to be 80.0 % $NaClO_2$, the analyst would dissolve 0.1676 g of sodium chlorite ($NaClO_2$, CAS#: 7758-19-2) in reagent water and dilute to 100 mL in a volumetric flask.

Note: 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.[9] 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.

7.2.1.2 ANALYTE PRIMARY DILUTION STANDARD (Analyte PDS) SOLUTION – Prepare two Analyte PDSs by diluting the Analyte Stock Standard Solutions with reagent water containing EDA (at a final concentration of 50 mg/L) in volumetric glassware. The dilutions used to prepare these solutions during the method development studies are provided below as an example. Prior to using mixed standards for calibration or spiking solutions, ensure that the individual Analyte Stock Standard Solutions do not contain any appreciable concentrations of the other target analytes. Dilutions of these Analyte PDSs, referred to as Solution A and B below, are used to prepare the calibration solutions (Sect. 7.2.3) and the continuing calibration check solutions (Sect. 10.3) for both detectors.

Analyte PDS Solution A

Analyte	Initial Conc. (mg/L)	Volume (mL)	Final Volume (mL)	Final Conc. (mg/L)
Chlorite	1000	2.5	25	100
Bromide	10000	0.25	25	100
Chlorate	1000	2.5	25	100

Analyte PDS Solution B

Analyte	Initial Conc. (mg/L)	Volume (mL)	Final Volume (mL)	Final Conc. (mg/L)
Bromate	1000	1.0	100	10

7.2.2 SURROGATE ANALYTE (SUR) SOLUTION, DICHLOROACETATE (DCA, CAS#: 19559-59-2)

7.2.2.1 SURROGATE STOCK SOLUTION (0.50 mg/mL) – Prepare a surrogate stock solution by dissolving 0.065 g of dichloroacetic acid, potassium salt (Cl_2CHCO_2K) in reagent water and diluting to 100 mL in a volumetric flask. This solution is used to fortify all field samples, QC samples and calibration standards by adding a 20-uL aliquot of the Surrogate Stock Solution to 10 mL of the sample. This solution must be prepared fresh every 3 months or sooner if signs of degradation are present.

7.2.2.1.1 Dichloroacetate is potentially present in treated drinking waters as the acetate of the organic disinfection byproduct, dichloroacetic acid (DCAA). Typical concentrations of DCAA rarely exceed 50 µg/L, which would represent only a five percent increase in the observed response over the fortified concentration of 1.00 mg/L. Consequently, the upper recovery limit for the surrogate (90% to 115%) has been increased to allow for this potential background.

7.2.2.1.2 If the analyst is exclusively interested in monitoring trace bromate using the PCR and the UV/VIS absorbance detector, suppression of the eluent prior to reaction with the PCR MUST be incorporated. In addition, the surrogate must also be included and meet the QC requirements as outlined in Section 9.7.1.

7.2.2.2 SURROGATE PRIMARY DILUTION STANDARD – A Surrogate PDS is not prepared since the Surrogate Stock (Sect 7.2.2.1) is used to fortify samples.

7.2.3 CALIBRATION STANDARDS (CAL) – At least 5 calibration concentrations are required to prepare the initial calibration curve (Sect. 10.2) for each detector. Prepare the calibration standards over the concentration range of interest from dilutions of the Analyte PDSs A and B in reagent water containing EDA (50 mg/L). The lowest concentration calibration standard must be at or below the MRL, which may depend upon system sensitivity. The calibration standards for the development of this method were prepared by adding aliquots of the two Analyte PDSs (Analyte PDS Solution A and B described above in Sect. 7.2.1.2) as shown in the tables below to a volumetric flask, containing the listed volume of

EDA solution, and diluting to volume with reagent water. These standards may be also be used as CCCs.

Conductivity Detector CAL and CCC Standards

Cal Std.	Stock A (µL)	Stock B (µL)	EDA Volume (uL)	Final Volume (mL)	ClO_2, Br, ClO_3 Final Conc. (µg/L)	Bromate Final Conc. (µg/L)
1*	10	100	50	100	10	10
2	25	250	50	100	25	25
3*	75	500	50	100	75	50
4	200	750	50	100	200	75
5*	500	1000	50	100	500	100

*Prepared in larger volume and used as CCCs

Absorbance Detector CAL and CCC Standards

Cal Std.	Stock B (µL)	EDA Volume (uL)	Final Volume (mL)	Bromate Final Conc. (µg/L)
1*	5	50	100	0.5
2	10	50	100	1.0
3	20	50	100	2.0
4*	50	50	100	5.0
5	100	50	100	10.0
6*	150	50	100	15.0

*Prepared in larger volume and used as CCCs

7.2.3.1 Fortify each CAL or CCC standard by adding a 20 uL aliquot of the Surrogate Stock Standard Solution (Sect. 7.2.2.1) to a 20 mL disposable plastic micro beaker containing 10.0 mL of the calibration standard (or CCC) and mix. These volumes may be adjusted to meet specific laboratory autosampler volume requirements.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 SAMPLE COLLECTION

8.1.1 Samples should be collected in opaque plastic or amber glass bottles. All bottles must be thoroughly cleaned and the volume collected should be sufficient to ensure a representative sample, allow for replicate analysis and laboratory fortified matrix analysis, if required, while minimizing waste disposal.

8.1.2 When collecting a field sample from a treatment plant employing chlorine dioxide, the field sample must be sparged with an inert gas (helium or nitrogen) prior to addition of the EDA preservative at time of sample collection. The sample should be collected in a clean wide mouth flask (such as an Erlenmeyer flask). The sparging gas can be obtained by using a lecture bottle of nitrogen or helium fitted with a regulator and connected to a disposable glass Pasteur pipette with PVC tubing. The gas flow should be adjusted to produce a steady flow of bubbles. After 10-15 minutes of sparging, all traces of chlorine dioxide should be removed from the sample. It can then be poured from the flask into the sample bottle that contains the ethylenediamine (EDA) preservative. In order to eliminate potential cross contamination problems, it is recommended that a clean Erlenmeyer flask and a new disposable pipette be used at each sampling point.

8.1.3 Add a sufficient volume of the EDA preservation solution (Sect. 7.1.3) 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.

8.2 SPECIAL SAMPLING REQUIREMENTS AND PRECAUTIONS FOR CHLORITE

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

8.2.2 When preparing the LFSM, 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 LFSM, EDA preservation will not control this demand and reduced chlorite recoveries may be observed.

8.2.3 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.[10] 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.

8.3 SAMPLE SHIPMENT AND STORAGE – All samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Samples must be confirmed to be at or below 10 °C when they are received at the laboratory. Samples stored in the lab must be held at or below 6 °C and protected from light until analysis. Samples should not be frozen. Sample preservation and holding times for the anions are as follows:

Analyte	Preservation	Holding Time
Bromate	50 mg/L EDA, store at < 6 °C	28 days
Chlorate	50 mg/L EDA, store at < 6 °C	28 days
Chlorite	50 mg/L EDA, store at <6 °C	14 days
Bromide*	50 mg/L EDA, store at <6 °C	28 days

*Source and raw water only.

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 (Sect. 3.1) of a Laboratory Reagent Blank (LRB), Continuing Calibration Check Standards (CCCs), Laboratory Fortified Blank (LFB), Instrument Performance Check Standard (IPC), Laboratory Fortified Sample Matrix (LFSM) and either Laboratory Fortified Sample Matrix Duplicate (LFSMD) or a Field Duplicate (FD) Sample. This section details the specific

requirements for each of these QC parameters for both the conductivity and absorbance detectors used in this application. Although the Detection Limits and MRLs may differ, 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. These criteria are considered the minimum acceptable QC criteria, and laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – Requirements for the Initial Demonstration of Capability are described in the following sections and summarized in Section 17, Table 4.

9.2.1 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND – Before any field samples are analyzed, and any time a new set of reagents is used, it must be demonstrated that a laboratory reagent blank is reasonably free of contamination and that the criteria in Section 9.4 are met.

9.2.2 INITIAL DEMONSTRATION OF ACCURACY – Prior to the analysis of the IDC samples, verify calibration accuracy with the preparation and analysis of a mid-level QCS as defined in Section 9.11. If the analyte recovery is not $\pm$ 15% of the true value, the accuracy of the method is unacceptable. The source of the problem must be identified and corrected. After the accuracy of the calibration has been verified, prepare and analyze 7 replicate LFBs fortified at a recommended concentration of 20 ug/L for the conductivity detector or near the mid-range of the initial calibration curve. For the absorbance detector, prepare 7 replicate LFBs fortified at a recommended concentration of 2.0 ug/L bromate. Sample preservatives as described in Section 8.1.3 must be added to all LFBs. The average recovery of the replicate values must be within ± 15% of the true value.

9.2.3 INITIAL DEMONSTRATION OF PRECISION – Using the same set of replicate data generated for Section 9.2.2, calculate the standard deviation and percent relative standard deviation of the replicate recoveries. The percent relative standard deviation (%RSD) of the results of the replicate analyses must be $\leq$ 20%.

9.2.4 DETECTION LIMIT DETERMINATION – Prepare and analyze at least 7 replicate LFBs at a concentration estimated to be near the Detection Limit over at least 3 days using the procedure described in Section 11. This fortification level may be estimated by selecting a concentration with a signal of 2 to 5 times the noise level. The appropriate concentration will be dependent upon the sensitivity of the IC system being used. Sample

preservatives as described in Section 8.1.3 must be added to these samples. Calculate the Detection Limit using the equation

$$\text{Detection Limit} = St_{(n-1,\ 1-\text{alpha}\ =\ 0.99)}$$

where
$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,
n = number of replicates, and
S = standard deviation of replicate analyses.

NOTE: Calculated Detection Limits need only be less than $^1/_3$ of the laboratory's MRL to be considered acceptable. Do not subtract blank values when performing Detection Limit calculations. The Detection Limit is a statistical determination of precision only.[2] No precision and accuracy criteria are specified.

9.3 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 not be established at an analyte concentration that is less than either three times the Detection Limit or a concentration which would yield a response less than a signal-to-noise (S/N) ratio of five. Depending upon the study's data quality objectives it may be set at a higher concentration. **The lowest calibration standard must be at or below the MRL and therefore, the MRL must never be established at a concentration lower than the lowest calibration standard**.

9.4 LABORATORY REAGENT BLANK (LRB) – A LRB is required with each Analysis Batch (Sect. 3.1) of samples to determine any background system contamination. If within the retention time window of any analyte, the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or contaminants that interfere with the measurement of method analytes must be below 1/3 the MRL. If the target analytes are detected in the LRB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples in the analysis batch.

9.4.1. EDA must be added to the LRB at 50 mg/L. By including EDA in the LRB, any potential background contamination from the EDA will be identified.

9.4.2 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 interfering chlorite anion (Sect. 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.

9.5 CONTINUING CALIBRATION CHECK (CCC) – CCCs are prepared in the same manner as the Calibration Standards (Sect. 7.2.3), using reagent water and EDA as described in Section 8.1.3. They are analyzed during an analysis batch at a required frequency to confirm that the instrument meets initial calibration criteria. See Section 10.3 for concentration requirements, frequency requirements, and acceptance criteria.

9.6 LABORATORY FORTIFIED BLANK (LFB) - A LFB is required with each analysis batch to confirm acceptable method accuracy. 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 LFSM is checked by preparing the LFB using the same Analyte Stock Standard Solutions used to prepare the LFSM fortification solution. The fortified concentration of the LFB should be rotated between, low, medium, and high concentrations from batch to batch. The low concentration LFB must be as near as practical to, but no more than two times the MRL. Similarly, the high concentration should be near the high end of the calibration range established during the initial calibration (Sect. 10.2). The recovery of all analytes fortified at the low concentration must be 75-125% of the true value, and 85-115% when fortified at the medium and high concentrations. If the LFB 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 Recovery Limits**
MRL to 2 x MRL	75 - 125 %
2 x MRL to highest calibration level	85 - 115 %

9.7 SURROGATE RECOVERY – The surrogate standard is fortified into all samples, blanks, CCCs, QDCSs, LRBs, and LFSMs and LFSMDs prior to analysis. It is

also added to the calibration curve and calibration check standards. The surrogate is a means of assessing chromatographic method performance.

9.7.1 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.

9.7.2 When surrogate recovery from a sample, blank, or CCC is less than 90% or greater than 115%, check (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the sample.

9.7.3 If the reanalysis meets the surrogate recovery criteria, report only data for the reanalyzed sample.

9.7.4 If the sample reanalysis fails the 90-115% surrogate recovery criteria, the analyst should check the calibration by re-injecting the most recently acceptable calibration standard. If the calibration standard fails the criteria of Section 10.3, recalibrate as described in Section 10.2. If the calibration standard is acceptable, preparation and analysis of the sample should be repeated provided the sample is still within the holding time. If this sample reanalysis also fails the recovery criteria, report all data for that sample as suspect due to surrogate recovery.

9.7.5 If a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, suppression of the eluent MUST be used and the surrogate added and monitored on the conductivity detector and the appropriate QC criteria for the surrogate as outlined in Section 9.7.1 must be met.

9.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – Analysis of LFSMs are required in each analysis batch and are used to determine that the sample matrix does not adversely affect method accuracy. Additional LFSM requirements, as described in Section 9.8.4, apply when the PCR system is used for low level bromate in waters disinfected with chlorine dioxide. If the occurrence of target analytes in the samples is infrequent, or if historical trends are

unavailable, a second LFSM, or LFSMD (Sect. 9.9), must be prepared, and analyzed from a duplicate of the field sample used to prepare the LFSM to assess method precision. Analytical batches that contain LFSMDs will not require the analysis of a Field Duplicate (Sect. 9.9). If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, LFSM data should be documented for all routine sample sources for the laboratory.

9.8.1 Within each analysis batch, a minimum of one field sample is fortified as a LFSM for every 20 samples processed. The LFSM is prepared by spiking a sample with an appropriate amount of the appropriate Analyte PDS (Sect. 7.2.1.2). Select a spiking concentration at least twice the matrix background concentration, if known. Use historical data or rotate through a range of concentrations when selecting a fortifying concentration. Selecting a duplicate bottle of a sample that has already been analyzed aids in the selection of appropriate spiking levels.

9.8.2 Calculate the percent recovery (%R) for each analyte using the equation

$$\%R = \frac{(A - B)}{C} * 100$$

where
A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample, and
C = fortification concentration.

9.8.3 Analyte recoveries may exhibit a matrix bias. For samples fortified at or above their native concentration, recoveries should range between 75 - 125%. If the accuracy of any analyte falls outside the designated range, and the CCC performance for that analyte is shown to meet the acceptance criteria, the recovery is judged to be matrix-biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.8.4 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 LFSM 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 (Sect. 11.1.4) appropriately. This LFSM 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 (Sect. 9.8.2). Samples that fail the LFSM percent recovery criteria of 75 - 125% must be reported as suspect/matrix.

9.9 FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD or LFSMD) – Within each analysis batch, a minimum of one Field Duplicate (FD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD) must be analyzed. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If target analytes are not routinely observed in field samples, a LFSMD should be analyzed rather than a FD.

9.9.1 Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2) using the equation

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} * 100$$

9.9.2 If a LFSMD is analyzed instead of a Field Duplicate, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation

$$RPD = \frac{|LFSM - LFSMD|}{(LFSM + LFSMD)/2} * 100$$

9.9.3 RPDs for FDs and duplicate LFSMs should fall in the range presented in the table below for samples fortified at or above their native concentration. Greater variability may be observed when LFSMs are spiked near the MRL.

Concentration Range	RPD Limits
MRL to 5 x MRL	± 20 %
5 x MRL to highest calibration level	± 10 %

If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to meet the acceptance criteria in the LFB, the recovery for that analyte is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects

9.10 INSTRUMENT PERFORMANCE CHECK – The low-level CCC Standard is evaluated in each analytical batch in order to confirm proper instrument performance (Sect. 10.3). 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 monitor retention time drift in the surrogate peak over time. The PGF, as determined below, must fall between 0.80 and 1.15, and the retention time for the surrogate must be at least 80% of the initial retention time when the IC column was new. If these criteria are not met, corrective action must be performed prior to analyzing additional samples. Major maintenance such as replacing columns requires repeating the IDC determination (Sect. 9.2).

9.10.1 The PGF is calculated using the equation

$$PGF = \frac{1.83 x W(½)}{W(1/10)}$$

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 ($^1/_{10}$) for each peak can be attained through most data acquisition software packages.

9.10.2 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 should be

suspected. Potential problems include improperly prepared eluent, erroneous method parameters 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 resemble 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 occur 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 column's efficiency.

9.10.3 If a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, suppression of the eluent MUST be used and the surrogate added and monitored on the conductivity detector and the appropriate QC criteria for the surrogate as outlined in Section 9.7.1 must be met.

9.11 QUALITY CONTROL SAMPLE (QCS) – Each time new Calibration Standards (Sect. 7.2.3) are prepared, or at least quarterly, analyze a QCS from a source different from the source of the calibration standards. The acceptance criteria for the QCS is 85-115% of the true value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration of acceptable initial calibration is required prior to performing the IDC and before any samples are analyzed. It is also required intermittently throughout sample analysis to meet required QC performance criteria summarized in Tables 4 and 5. Initial calibration verification is performed using a QCS (Sect. 9.11) as well as with each analysis batch using Continuing Calibration Check Standards. The procedure for establishing the initial calibration curve is described in Section 10.2. The procedure to verify the calibration with each analysis batch is described in Section 10.3.

10.2 INITIAL CALIBRATION

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

10.2.2 Estimate the calibration 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 method development data were collected on single linear calibrations that spanned 5 to 500 ug/L for chlorite, bromide and chlorate and 5 to 100 ug/L bromate for the conductivity detector and 0.5 to 15.0 ug/L for bromate on the absorbance detector.

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

10.2.2.2 A minimum of five Calibration Standards (Sect. 7.2.3) should be prepared for each calibration. It is recommended that at least four of the Calibration Standards are at a concentration ≥ the MRL. 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 When quantitated using the initial calibration curve, each calibration point, except the lowest point, for each analyte should calculate to be 85-115% of its true value. The lowest point should calculate to be 75-125% of its true value. Failure to meet this criteria may indicate future difficulty in meeting CCC QC requirements during the analysis batch.

10.2.2.4 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 calibration standards in the range 5 - 500 µg/L is recommended.

10.2.2.5 Bromate concentrations are expected to be significantly lower. It is suggested that the conductivity detector be calibrated using 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 may exhibit a response for bromate at concentrations below 15.0 ug/L, but these should not be reported. When using both detectors, PCR results for bromate in this range (5 - 15 ug/L) will have far better precision and accuracy.

10.2.3 Prepare a set of at least 5 calibration standards as described in Section 7.2.3. The lowest concentration calibration standard must be at or below the MRL, which may depend on system sensitivity.

10.2.4 Inject 225 µL of each calibration standard and 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. Prepare calibration curves using linear regression analysis for each analyte on the conductivity detector and using a quadratic polynomial function for bromate on the absorbance detector.

10.2.4.1 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. However, poorly drawn baselines can have a more significant influence on peak areas than peak heights. It is the analyst's responsibility to review all chromatograms to ensure accurate baseline integration of target analyte peaks.

10.2.5 After establishing (or re-establishing) 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 range. As specified in Section 9.11, determined concentrations must fall within ± 15% of the stated values.

10.3 CONTINUING CALIBRATION CHECK (CCC) – 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 CCCs. The first CCC each day must be at or below the MRL in order to verify instrument sensitivity prior to any analyses. Subsequent CCCs must be run after every 10 field samples and should alternate between a mid- and high-level CCC. LRBs, CCCs, LFSMs and LFSMDs are not counted as field samples.

10.3.1 A low-level CCC must be determined to be valid each day prior to analyzing any samples by injecting an aliquot of the appropriate CCC under the same instrumental conditions used to collect the initial calibration. 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 CCC for the

absorbance detector. The low-level CCC for both detectors must be at or below the MRL. Percent recovery for the low-level CCC must be in the range of 75 - 125% before the analyst is allowed to analyze samples.

10.3.2 Additional CCC standards must be analyzed after every tenth field sample and at the end of the analysis batch. If more than 10 field samples are included in an analysis batch, the analyst should alternate between the mid- and high-level CCC Standards. Percent recovery for the mid- and high-level CCCs must be in the range of 85 - 115%.

10.3.3 If the calibration verification criteria listed above are not met, or the retention times shift more than ± 2% from the last acceptable initial or continuing calibration check standard for any analyte, then 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.

10.3.2.1 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 at 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 (Sect. 7.2.2) to a 20-mL disposable plastic micro beaker. Next, place a 10.0-mL aliquot of sample in 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. If a laboratory chooses to monitor exclusively for trace bromate using PCR and the UV/VIS absorbance detector, suppression of the eluent MUST be used and the surrogate added and monitored on the conductivity detector and the appropriate QC criteria for the surrogate as outlined in Section 9.7.1 must be met.

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.[11] The oxidation-reduction reaction between ferrous iron and chlorite[12] is used to remove chlorite without any adverse affects on the bromate concentration.[13]

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 (Sect. 7.1.7). After mixing, verify the pH is between 5 and 6 using pH test strips, add 40 uL of ferrous iron solution (Sect. 7.1.6), mix and allow to react for 10 minutes. Filter the reaction mixture using a 0.45 micron particulate filter (Sect. 6.10) attached to a 10-mL syringe into the barrel of a second syringe to which a pre-conditioned hydrogen cartridge (Sect. 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. The sample is ready for analysis (Sect. 11.2).

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 LFSM.

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 LFSM specific to trace bromate. This LFSM 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% (Sect. 9.8), that particular sample should be reported as suspect/matrix.

11.1.4.3 All samples from PWSs that utilize chlorine dioxide, which have been pretreated to remove chlorite, MUST also include an additional pretreated LRB in the analytical batch (Sect. 9.4.2).

11.1.4.4 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 suppressor 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 are the actual retention times and Detection Limits that were determined during the development of this method. Other columns or chromatographic conditions may be used if the requirements of Section 9 are met.

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

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.

11.2.4 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.

11.2.6 Should more complete resolution be needed between any two coeluting peaks, the eluent (Sect. 7.1.2) can be diluted. This will extend 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 the IDC (Sect. 9.2), and by reestablishing a valid initial calibration curve (Sect. 10.2). As a specific precaution, upon dilution of the carbonate eluent, a peak for bicarbonate may be observed on the conductivity detector 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 Detection Limit for each analyte.

11.3 AUTOMATED ANALYSIS WITH METHOD 326.0

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 paid when the PCR reservoir is refilled. The PCR is stable for only 24 hours and consequently the reservoir must be regularly filled with freshly prepared reagent. 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 (Sect. 17, 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 CCCs 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.

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 standard. 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.

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 analyte concentrations in µg/L (usually with two significant figures).

12.5 Software filtering of the postcolumn UV/Vis absorbance signal is recommended to improve the precision of peak measurements, minimize non-random noise and

improve peak appearance, ensuring that all QC requirements for the method are met. 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.[14] The use of alternate smoothing routines is acceptable providing all QC criteria are met.

13. METHOD PERFORMANCE

13.1 Table 1 lists the standard conditions, typical retention times and single laboratory Detection Limits in reagent water, as determined for each of the inorganic oxyhalide DBPs and bromide.

13.2 Table 2 shows the precision and accuracy of the trace bromate measurement, evaluated on both detectors, at two fortified concentrations, in reagent water (RW), a simulated high ionic strength water (HIW) and a simulated high organic (HOW) content water. The mean recovered bromate 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 humic acid.[1]

13.3 Table 3 summarizes the single laboratory accuracy (%Recovery) and precision (% RSD) for each anion included in the method in a variety of waters for the standard conditions identified in Table 1.

14. POLLUTION PREVENTION

14.1 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 analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents are used. The matrices of concern are finished drinking water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and

controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and 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" also available from the American Chemical Society at the address in Section 14.1.

16. REFERENCES

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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
Conductivity Suppressor:	ASRS-1, external water mode, 100 mA current for conductivity
PCR Suppressor:	ASRS-1 used with sulfuric acid regenrant to acidify the PCR
Detectors:	Dionex CD20 suppressed conductivity detector, background conductivity: 24 µS Dionex AD20 Absorbance Detector, 10 mm cell path length, set at 352 nm (deuterium lamp)
Postcolumn Reagent Flow:	0.4 mL/min
Postcolumn Reactor Coil:	knitted, potted for heater, 500 uL internal volume
Postcolumn Heater:	80 ° C
Postcolumn Regenerant	150 mN H_2SO_4, 2.5 mL/min, effluent pH < 2
Total analysis time:	25 minutes

Analyte Retention Times and Detection Limits :

Analyte	Retention Time [(b)] (min.)	Fortified Conc. (µg/L)	# of Reps.	Detection Limit (µg/L)
Chlorite	4.11	5.0	8	2.0
Bromate (c) **Bromate (d)**	4.73 5.28	5.0 0.50	8 8	1.2 0.17
Surrogate: DCA	8.01			
Bromide	9.18	5.0	8	1.7
Chlorate	10.07	5.0	8	1.7

(a) Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
(b) Refer to chromatograms in Figures 2 and 3.
(c) Bromate by conductivity detection
(d) Bromate by absorbance detection

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

Matrix	Detection	PRECISION			
		Fortified Conc. (μg/L)	# of Reps.	Mean (μg/L)	% RSD
Reagent Water	Absorbance	1.0	8	1.1	4.4
	Absorbance	5.0	8	5.2	2.1
High Ionic Water	Absorbance	1.0	8	1.1	4.2
	Absorbance	5.0	8	5.2	2.0
High Organic Water	Absorbance	1.0	7	1.1	3.4
	Absorbance	5.0	8	5.2	3.2

Standard Conditions: Same as listed in Table 1.

TABLE 3. SINGLE-LABORATORY PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS, BROMIDE AND SURROGATE.

Analyte	Matrix	Fortified Conc. (ug/L)	# of Replicates	Mean % Recovery	%RSD
Chlorite	RW	100 500	8 8	107 108	3.0 1.2
	HIW	100 500	8 8	102 106	2.0 0.71
	HOW	100 500	8 8	99.3 107	2.7 0.49
Bromate by Conductivity	RW	10.0 25.0	8 8	102 99.8	4.6 4.3
	HIW	10.0 25.0	8 8	103 92.9	3.8 11
	HOW	10.0 25.0	8 8	101 97.6	8.1 5.9
Bromide	RW	10.0 25.0	8 8	97.5 104	5.3 5.1
	HIW	10.0 25.0	8 8	108 104	4.8 5.0
	HOW	10.0 25.0	8 8	104 99.7	6.1 3.7
Chlorate	RW	100 500	8 8	111 104	1.7 0.97
	HIW	100 500	8 8	99.0 100	2.3 0.66
	HOW	100 500	8 8	101 105	2.8 1.1
Surrogate	RW	1.00	8 8	108 106	6.1 4.7
	HIW	1.00	8 8	103 105	1.3 2.1
	HOW	1.00	8 8	108 108	4.4 4.0

RW = Reagent Water; HIW = High Ionic Strength Water; HOW = High Organic Water

TABLE 4. INITIAL DEMONSTRATION OF CAPABILITY QC REQUIREMENTS.

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.1 and 9.4	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 ≤ 1/3 of the proposed MRL
Sect. 9.2.2	Initial Demonstration of Accuracy (IDA)	Run mid-level QCS and determine recovery. Conductivity: analyze 7 replicate LFBs recommend fortify at 20 ug/L Absorbance: analyze 7 replicate LFBs recommend fortify with bromate at 2.0 ug/L Calculate average recovery of IDA replicates	QCS recovery must be ± 15% of true value. Mean % recovery for IDA replicates must be ± 15% of true value.
Sect. 9.2.3	Initial Demonstration of Precision (IDP)	Calculate the %RSD of the IDA replicates.	%RSD must be ≤ 20%
Sect. 9.2.6	Detection Limit 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 over at least 3 days using equation in Section 9.2.6 - do not subtract blank	Detection Limit must be < 1/3 the MRL

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 Bromide 28 days, EDA Permitted Chlorate 28 days, refrig. at <6 °C / EDA Preservation Chlorite 14 days, refrig. at <6 °C / EDA Preservation	Holding time and temperature must not be exceeded. EDA added to all samples
Sect. 9.4	Laboratory Reagent Blank (LRB)	Include LRB with every analysis batch (up to 20 samples) Analyze prior to analyzing field samples	All analytes must be ≤ 1/3 MRL
Sect. 9.4.2 (specific to PCR)	PRETREATED Laboratory Reagent Blank	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 < 1/3 MRL
Sect. 9.6	Laboratory Fortified Blank (LFB)	Laboratory must analyze LFB in each analysis batch following the first CCC. Calculate %REC prior to analyzing samples	LFB recovery fortified at: ≥MRL to 5X MRL = 75 - 125% ≥5X MRL to highest CCC = 85 - 115% Sample results from batches that fail LFB are invalid
Sect. 10.2	Initial Calibration	Conductivity: generate calibration curve using at least 5 standards Absorbance: generate calibration curve using at least 5 bromate standards	The lowest calibration standard MUST be at or below the MRL 4 CAL standards should be above the MRL
Sect. 9.5 and Sect. 10.3	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a low level CCC prior to analyzing samples. CCCs are then injected after every 10 samples and after the last sample, rotating concentrations to cover the calibrated range of the instrument.	Recovery for each analyte must be 85-115% of the true value for all but the lowest level of calibration. The lowest calibration level CCC must be 75-125% of the true value All acceptable data MUST be bracketed by valid CCCs

TABLE 5. QUALITY CONTROL REQUIREMENTS (SUMMARY CONTINUED).

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.7	Surrogate	Dichloroacetate is added to all blanks, samples and standards	Surrogate recovery must be 90 - 115%. Samples that fail surrogate recovery must be reanalyzed. If second analysis fails label result as suspect/matrix
Sect. 9.8 Sect. 11.1.4.3	Laboratory Fortified Sample Matrix (LFSM)	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 LFSM must be fortified above the native level and at no greater than 5 x the highest field sample concentration Calculate target analyte recovery using formula (Sect. 9.8.2) When field samples from chlorine dioxide plants which contain chlorite are pretreated prior to the PCR measurement of trace bromate, an additional LFSM must be prepared for each pretreated field sample (Sect. 9.8.4)	Recovery should be 75 - 125% If fortified sample fails the recovery criteria, label both as suspect/matrix.
Sect. 9.9	Field Duplicate (FD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD)	Analyze either a FD or LFSMD for a minimum of 5% of field samples or at least one within each analysis batch for both detectors. Calculate the relative percent difference (RPD) using formula in Section 9.9.1	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
Sect. 9.10	Instrument Performance Check (IPC)	Calculate Peak Gaussian Factor (PGF) using equation (Sect. 9.10.1) and monitor retention time for surrogate in the initial CCC each day	PGF must fall between 0.80 and 1.15 Ret. Time (RT) for surrogate must remain 80% of initial RT when column was new

TABLE 6. EXAMPLE SAMPLE ANALYSIS BATCH WITH QUALITY CONTROL REQUIREMENTS

Injection #	Sample Description	Acceptance Criteria
1	Laboratory reagent blank (LRB)	≤ 1/3 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 Sample Matrix (LFSM) [(a)] at concentrations specific for conductivity detector	± 25% fortified level
10	Field sample 2 - LFSM 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	Pretreate (Sect. 9.3.1.2) using the acid/Fe(II) chlorite removal procedure (Sect. 11.1.4)	≤ 1/3 MRL
26	Field sample 14 [(b)] - (finished water from PWS using chlorine dioxide) pretreated with acid/Fe(II) (Sect. 11.1.4)	
27	Field sample 14 - (finished water from PWS using chlorine dioxide) LFSM specific for trace bromate on the absorbance detector, pretreated with acid/Fe(II) (Sect. 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 LFSM can be selected and reanalyzed as the laboratory matrix 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 (Sect. 3.1).

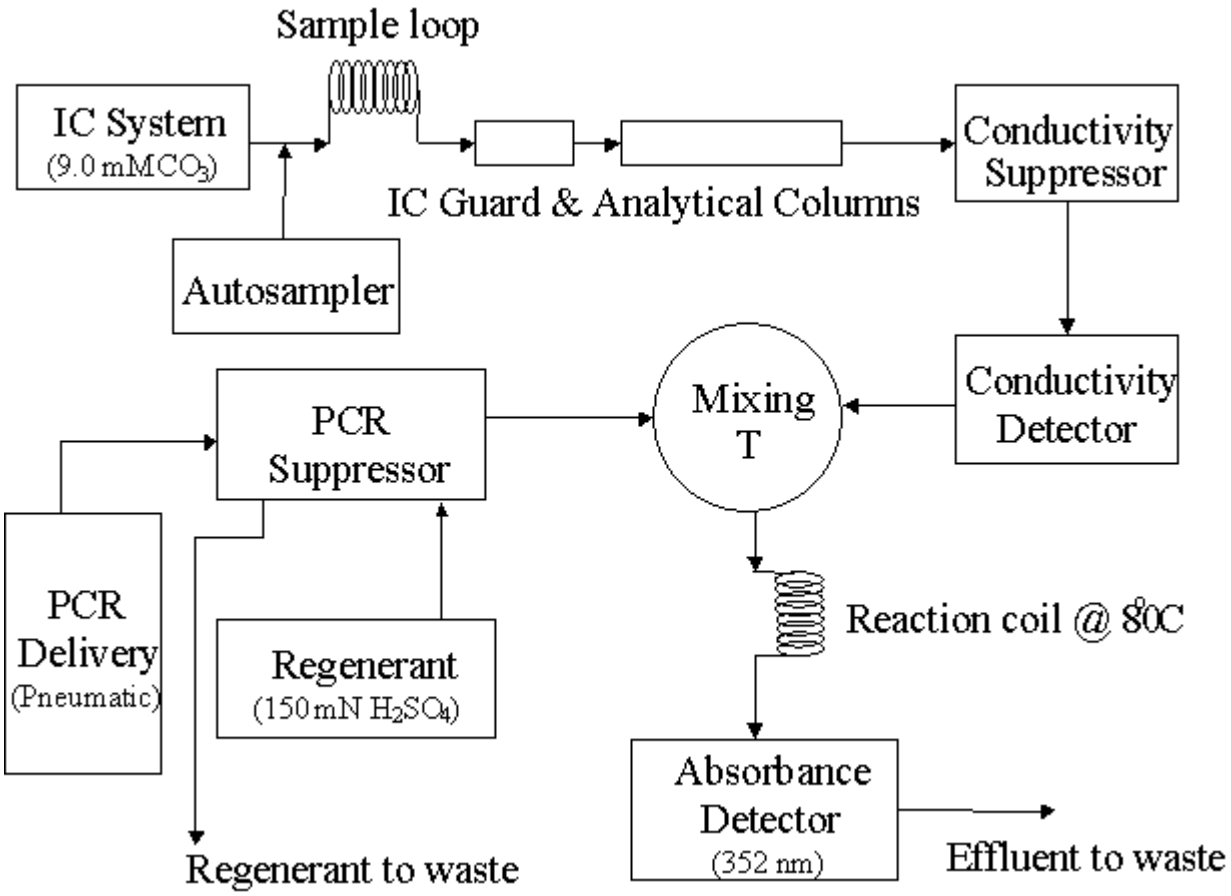

Figure 1: Schematic detailing the configuration of postcolumn hardware addition to an ion chromatograph. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. If the requirements found in Section 9 are met, equivalent products or hardware can be employed.

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 manufacture's equipment is used. These backpressure coils are not required when the Method 326.0 instrument configuration is employed since the additional PCR system components, placed in-line, function in the same capacity and provide sufficient backpressure.

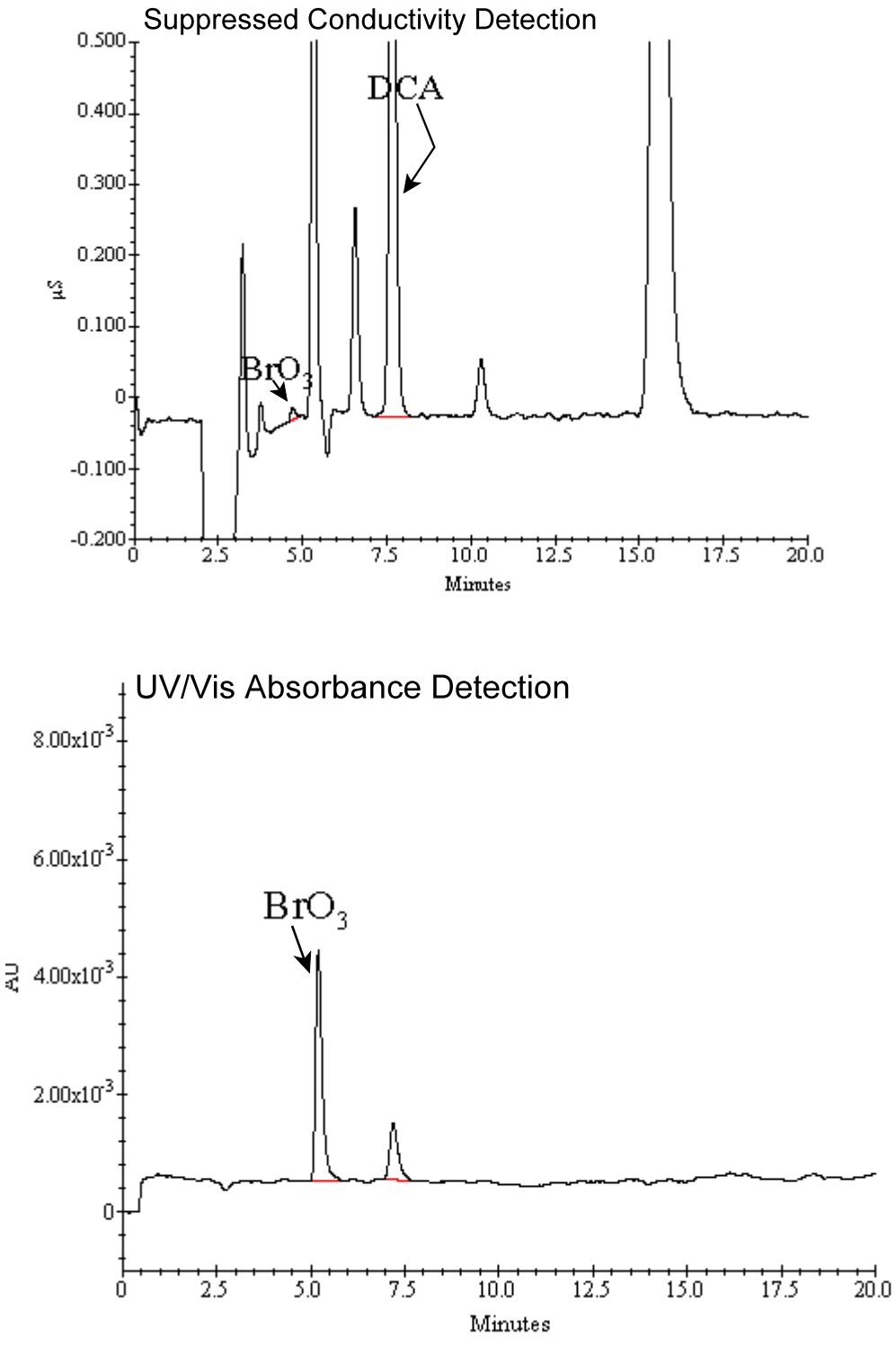

Figure 2: Reaent water fortified with bromate at 10 ug/L on both detectors.

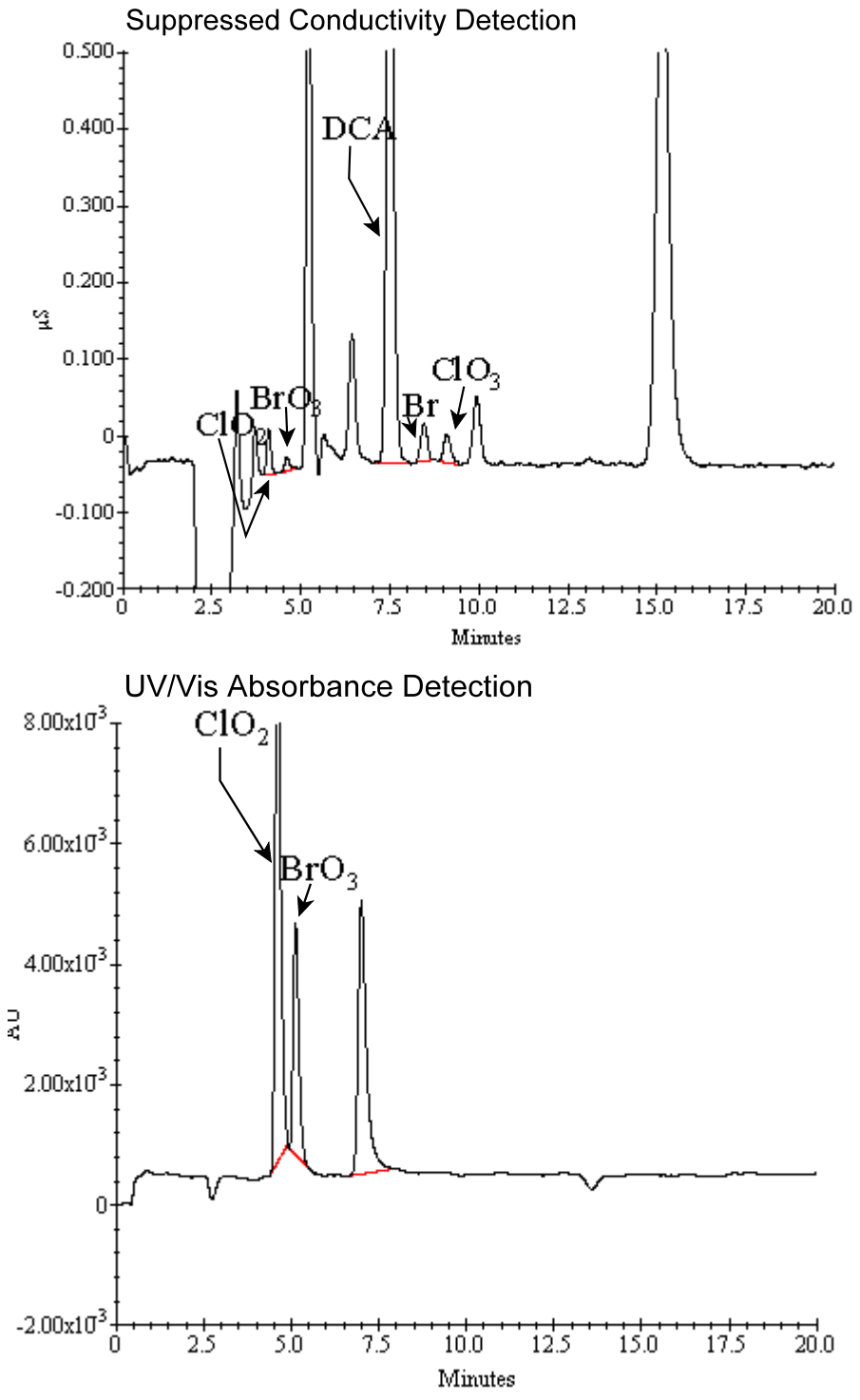

Figure 3: Reagent water fortified with inorganic oxyhalide disinfection by-products and bromide at 20.0 ug/L and bromate at 10 ug/L on both detectors.