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EPA Method 300.1 – Inorganic Disinfection By-product Anions in Water

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1 Scope and Application

1.1 This method may be used to determine chlorite and bromate anions in water samples. A small volume of sample is injected into the ion chromatograph, separated on the anion exchange separator column with a buffer eluent and then detected via conductivity with a chemical eluent suppressor.

1.2 Restricted Procedure:
This procedure is restricted to use by an analyst experienced in the operation of a Dionex ICS5000 and Dionex ICS6000 Ion Chromatographs and Automated Samplers. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions (see SOP reference 13.8).

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) - An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration.

2.6 Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), Method Detection Limit Blank (MDLB) or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7 MDLS (Method Detection Limit Spike) – MDLB spiked with analytes at the lowest calibration level to be used for the determination of MDL.

2.8 Instrument Performance Check Solution (IPC) or Low Level CCC – 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. This initial Calibration Check Standard is also referred to as a Low Level CCC and must be analyzed prior to sample analysis.

2.9 Peak Gaussian Factor (PGF) – a means to measure peak symmetry and monitoring retention time drift in the surrogate peak in the initial check standard. Refer to section 11.7 for calculation.

2.10 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3 **Interferences**

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

3.1.1 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 negatively affect performance by repeating and passing all the QC criteria.

3.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependent co-elution 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.

3.1.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. Prior to using any pretreatment, the analyst should be

aware that all instrument calibration standards must be pretreated in exactly the same manner as the pretreated unknown field samples. The need for these cartridges has been greatly reduced with recent advances in high capacity anion exchange columns.

3.2 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.

3.3 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.

3.4 Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

3.5 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, subsequent analysis. Normally, the elution of sulfate (retention time of 13.8 min) indicates the end of a chromatographic run, but, in the ozonated and chlorine dioxide matrices, which were included as part of the single operator accuracy and bias study, a small response (200 nS baseline rise) was observed for a very late eluting unknown peak at approximately 23 minutes. Consequently, a run time of 25 minutes is recommended to allow for the proper elution of any potentially inteferent 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.

3.6 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample must be purged with an inert gas (helium, argon or nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to ethylenediamine preservation and at time of sample collection.

4 Safety

4.1 Refer to Laboratory Safety/Chemical Hygiene Plan and Fire Safety Plan, online revision (SOP Reference 13.6).

5 Apparatus and Equipment

5.1 Apparatus and Equipment for IC05- (Dionex ICS-6000) P/N as listed or equivalent

5.1.1 Thermo Scientific Conductivity Detector-P/N 061830

5.1.2 Anion suppressor device--Thermo Scientific ADRS 600 2 mm Suppressor – P/N 088667
5.1.3 Dionex CRD 4mm 200- P/N 062983
5.1.4 Thermo Gradient mixer 2mm P/N 049135
5.1.5 Anion separator column - Dionex AS19-4µm Analytical Column – P/N 083223
5.1.6 Anion guard column - Dionex AG19-4µm Guard Column – P/N 083225
5.1.7 Dionex Regenerating Trap Column – P/N 088662
5.1.8 Thermo RFIC Eluent Degasser – P/N 062262-03
5.1.9 Dionex EGC III KOH- Potassium Hydroxide- P/N 075778(See Section 6.2.2)
5.1.10 Dionex AS-AP Auto-sampler
5.1.11 Dionex ICS-6000 DC Conductivity detector
5.1.12 Dionex ICS-6000 pump
5.1.13 Dionex ICS-6000 EG eluent generator
5.1.14 100 uL sample loop
5.1.15 Chromeleon 7 Software
5.1.16 2 Plastic pressurized reservoirs; used for reagent water (See 6.2.1).
5.1.17 1.5 mL vials with cap and septa – P/N 079812
5.1.18 Glassware – Class A volumetric flasks, graduated cylinders and pipettes.
5.1.19 Particulate filters – 0.45 micron syringe filters.
5.1.20 Balance: analytical, capable of accurately weighing to the nearest 0.0001g.
5.1.21 Sample Container: 250 ml HDPE opaque or glass amber bottles
5.1.22 Air displacement pipettes of various volumes, auto- pipettor, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.
5.1.22.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.
5.1.22.2 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Mechanical pipettes must be verified to be within ± 2.5% of the expected weight.
5.1.22.3 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ± 2.5 percent of the nominal volume.
5.1.22.4 Mechanical pipettes must be professionally calibrated every 6 months.

5.2 Apparatus and Equipment for IC04- (Dionex ICS-5000) P/N as listed or equivalent
5.2.1 Thermo Scientific Conductivity Detector- P/N 061830
5.2.2 Anion suppressor device -Thermo Scientific ADRS 600 2 mm Suppressor – P/N 088667
5.2.3 Dionex CRD 4mm 200- P/N 062983
5.2.4 Thermo Gradient mixer 2mm P/N 049135
5.2.5 Anion separator column - Dionex AS19 Analytical Column – P/N 062886
5.2.6 Anion guard column - Dionex AG19 Guard Column – P/N 062888

5.2.7 Dionex Regenerating Trap Column – P/N 060477
5.2.8 Thermo RFIC Eluent Degasser – P/N 062262-03
5.2.9 Dionex EGC III KOH- Potassium Hydroxide- P/N 074532(See Section 6.1.2)
5.2.10 Dionex AS-AP Auto-sampler
5.2.11 Dionex ICS-5000 DC Conductivity detector
5.2.12 Dionex ICS-5000 DP pump
5.2.13 Dionex ICS-5000 EG eluent generator
5.2.14 100 uL sample loop
5.2.15 Chromeleon 7 software
5.2.16 2 Plastic pressurized reservoirs; used for reagent water (See 6.1.1).
5.2.17 1.5 mL vials with cap and septa – P/N 079812
5.2.18 Glassware – Class A volumetric flasks, graduated cylinders and pipettes.
5.2.19 Particulate filters – 0.45 micron syringe filters.
5.2.20 Balance: analytical, capable of accurately weighing to the nearest 0.0001g.
5.2.21 Sample Container: 250 ml HDPE opaque or glass amber bottles
5.2.22 Air displacement pipettes of various volumes, auto- pipettor, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.
5.2.22.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.
5.2.22.2 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Mechanical pipettes must be verified to be within ± 2.5% of the expected weight.
5.2.22.3 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ± 2.5 percent of the nominal volume.
5.2.22.4 Mechanical pipettes must be professionally calibrated every 6 months.

6 Reagents

6.1 Reagents for use with both the IC04 (Dionex ICS-5000) and IC05 (Dionex-6000)

6.1.1 Reagent Water:
Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest. (Deionized, HPLC, Milli-Q water or equivalent. Milli-Q water has a resistivity of 18.2[MΩ.cm]@ 25oC and a TOC of 50 ug/L or less).

6.1.2 Eluent Generator:
Dionex EGC III KOH- Potassium Hydroxide- P/N 074532 or Dionex EGC III KOH- Potassium Hydroxide- P/N 075778.

6.2 Standards for use with both IC05 and IC04

6.2.1 Bromate and Chlorite Stock Standards(1000 mg/L) Primary Source (PS)

6.2.1.1 Purchased from a commercially available source at the 1000 mg/L concentration.

6.2.2 Bromate Intermediate Stock Standard, 1000 µg/L:

6.2.2.1 Pipette 0.5 ml of Bromate stock standard (1000 mg/L) into a 500 ml volumetric flask and dilute to volume with reagent water. This standard is stable for 6 months.

6.2.3 Chlorite Intermediate Stock Standard, 10 mg/L:

6.2.3.1 Pipette 5 ml of Chlorite stock standard (1000 mg/L) into a 500 ml volumetric flask and dilute to volume with reagent water. Stable for two weeks when stored protected from light at 4ºC.

6.2.4 Ethylenediamine (EDA) preservation solution, 100 mg/ml:

6.2.4.1 Dilute 2.8 ml of ethylenediamine (99%) (CASRN 107-15-3) to 25 ml with reagent water. Prepare fresh monthly.

6.2.4.2 EDA is primarily used as a preservative for chlorite. EDA also preserves the integrity of bromate concentrations by binding with hypobromous acid/hypobromite which is an intermediate formed as a by-product of the reaction of either ozone or hypochlorous acid/hypochlorite with bromide ion. If hypobromous acid/hypobromite is not removed from the matrix further reactions may form bromate ion.

6.2.4.3 EDA must be added to all blanks, LCS/LCSD pairs, MS/MSD pairs, ICV's, CCCs, etc. Every sample analyzed must be preserved with EDA at the concentration level of 50 mg/L, including standards. Adding 0.1 ml of EDA preservation solution (100 mg/ml) to 200 ml of each standard/blank will bring the EDA concentration to the required level of 50 mg/L. Field samples must have 0.125 ml of EDA preservation since they are collected in 250 ml sample bottles. Field samples must be preserved in field. Record the amount and concentration of E.D.A. added on the Bromate/Chlorite EPA 300.1 DCA/EDA Form

6.3 Surrogate Solution:

6.3.1 0.50 mg/ml dichloroacetate (DCA) is prepared by dissolving 0.065g dichloroacetic acid, potassium salt (Cl_2CHCO_2K, CASRN 19559-59-2) in reagent water and dilute to 100 ml in a volumetric flask. Commercially prepared DCA Surrogate Solution may also be purchased and used. Ex: DCA solution from Inorganic Ventures Cat # ICDCA-S.

6.3.2 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.

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

6.3.4 The surrogate solution must be added to all blanks, LCS/LCSD pairs, MS/MSD pairs, ICVs, CCCs, etc. Every sample analyzed must be spiked with this surrogate solution at the 1000 µg/L level. Adding 0.4 ml of 0.50 mg/ml (DCA) to 200 ml of standard/blank will bring the DCA concentration to the required level of 1000 µg/L. Since field samples are collected in 250

ml sample containers, adding 0.5 ml of 0.50 mg/ml (DCA) to 250 ml of sample will bring the DCA concentration to the required level of 1000 µg/L.

6.4 Working Standards:

6.4.1 Prepare the standards per tables 6.5a and 6.5b and dilute to volume using reagent water. EDA must be added to the calibration standards at the 50 mg/L. Chlorite working standards should be prepared fresh daily. Bromate working standards should be prepared fresh monthly.

6.4.1.1 Preservation: Add 0.1 ml of EDA preservation solution (100 mg/ml) to each standard after they have been diluted to the final volume of 200 ml. This will bring the EDA concentration of each standard to the required concentration of 50 mg/L. See tables 6.5a and 6.5b.

6.4.1.2 Surrogate fortification: Add 0.4 ml of 0.50 mg/ml (DCA) surrogate solution to each standard after they have been diluted to the final volume of 200ml. This will bring the DCA concentration of each standard to the required concentration of 1000 µg/L. See tables 6.5a and 6.5b.

Table 6.5a – Bromate Calibration Standards

Bromate Intermediate Stock Standard (1000 µg/L) (ml)	Final Volume (reagent water) (ml)	Bromate Concentration (µg/L)	EDA Preservation Solution (100mg/ml) (ml)	Surrogate Solution (DCA) (0.50 mg/ml) (ml)	EDA/Surrogate Concentration
1	200	5	0.1	0.4	50 µg/L / 1000 µg/L
1.5	200	7.5	0.1	0.4	50 µg/L / 1000 µg/L
2	200	10	0.1	0.4	50 µg/L / 1000 µg/L
3	200	15	0.1	0.4	50 µg/L / 1000 µg/L
5	200	25	0.1	0.4	50 µg/L / 1000 µg/L
10	200	50	0.1	0.4	50 µg/L / 1000 µg/L

Table 6.5b – Chlorite Calibration Standards

Chlorite Intermediate Stock Standard (10 mg/L) (ml)	Final Volume (reagent water) (ml)	Chlorite Concentration (µg/L)	EDA Preservation Solution (100mg/ml) (ml)	Surrogate Solution (DCA) 0.50 mg/ml (ml)	EDA/Surrogate Concentration
0.4	200	20	0.1	0.4	50 µg/L / 1000 µg/L

1	200	50	0.1	0.4	50 µg/L / 1000 µg/L
2	200	100	0.1	0.4	50 µg/L / 1000 µg/L
5	200	250	0.1	0.4	50 µg/L / 1000 µg/L
10	200	500	0.1	0.4	50 µg/L / 1000 µg/L
15	200	750	0.1	0.4	50 µg/L / 1000 µg/L
20	200	1000	0.1	0.4	50 µg/L / 1000 µg/L

6.5 Spiking Solution:

6.5.1 Chlorite LCS/LCSD and MS/MSD Solutions:

6.5.1.1 Add 1.25 ml of Chlorite Intermediate Stock Standard (10 mg/L) to 25 ml volumetric flask and bring to volume with sample or blank for a spike amount of 500µg/L for Chlorite. The Method Blank is prepared with EDA therefore preparing the LCS and LCSD using the Blank as a diluent incorporates EDA in those QC samples.

6.5.1.2 When preparing the LCS/LCSD, the blank must be poured from a 250 ml sample collection bottle into the 25 ml flask before spiking. Record lot # of bottle.

6.5.2 Bromate LCS/LCSD and MS/MSD solutions:

6.5.2.1 Add 0.625 ml of Bromate Intermediate Stock Standard (1000 µg/L) to a 25 ml volumetric flask and bring to volume with sample or blank for a spike amount of 25 µg/L. The Method Blank is prepared with EDA therefore preparing the LCS and LCSD using the Blank as a diluent incorporates EDA in those QC samples.

6.5.2.2 When preparing the LCS/LCSD, the blank must be poured from a 250 ml sample collection bottle into the 25 ml flask before spiking. Record lot # of bottle.

6.5.3 Continuing Calibration Check (CCC):

6.5.3.1 Bromate CCC levels must alternate between 25 µg/L and 50 µg/L. and highest calibration level.

6.5.3.2 Chlorite CCC levels must alternate between 500 µg/L and 1000 µg/L.

6.5.4 ICB, CCC, MBLK, MDLB and Dilution Water:

6.5.4.1 Reagent water preserved with 50 mg/L of EDA preservation solution and spiked with 1000 µg/L of DCA surrogate solution.

6.5.4.2 Adding 0.4 ml of 0.50 mg/ml (DCA) and 0.1 ml of EDA preservation solution (100 mg/ml) to 200 ml of reagent water will bring the DCA concentration to the required level of 1000 µg/L and the EDA concentration to the required level of 50 mg/L. Pour into a 250 ml sample collection bottle before pouring into the sample vial. Record lot # of sample bottle.

6.5.5 Initial Calibration Check Standard (IPC)/Low level CCC:

6.5.5.1 IPC for Bromate is analyzed at the 5.0 µg/L level and the IPC for Chlorite is analyzed at the 20 µg/L level. See Tables 6.5a and 6.5b for how to prepare these standards.

6.5.6 Method Detection Limit Spike(MDLS):

6.5.6.1 To prepare MDLS for Bromate, spike reagent water with 5.0 µg/L of Bromate, 50 mg/L of EDA preservation solution and 1000 µg/L of DCA

surrogate solution. Pour MDLS into a sample 250 ml collection bottle before pouring into a sample vial. Record lot # of bottle.

6.5.6.2 To prepare MDLS for Chlorite, spike reagent water with 20 µg/L of Chlorite, 50 mg/L of EDA preservation solution and 1000 µg/L of DCA surrogate solution. Pour MDLS into a 250 ml sample collection bottle before pouring into a sample vial. Record lot # of bottle.

7 Sample Collection

7.1 Samples are to be collected in 250 ml glass amber or HDPE opaque bottles.

7.2 Add 0.125 ml of EDA preservation solution per 250 ml of sample for both Bromate and Chlorite analysis (Final concentration must be 50 mg/L).

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

7.4 Chlorite samples must be cooled and stored at 0 - 6° C (not frozen).

7.5 Chlorite holding time is 14 days when preserved with EDA.

7.6 Bromate holding time is 28 days when preserved with EDA.

8 Calibration

8.1 Calibration Curve

8.1.1 The Dionex Ion Chromatograph is calibrated every six months or as needed when the Initial Quality Control Sample does not meet acceptance criteria of +/- 15% of true value. 6 bromate standards are used to construct the calibration curve for the bromate analysis, and 7 chlorite standards are used to construct the calibration curve for the chlorite analysis. Minimum acceptable correlation coefficient, r, is 0.995 using a linear regression. The origin is set to be ignored when calculating the linearity of the calibration. This is necessary due to limitations of the software that do not allow for incorporating a blank (CCB) as one of the curve standards.

8.2 Calibration Standards

8.2.1 The Bromate calibration curve consists of six standards at the following concentrations: 5.0 µg/L, 7.5 µg/L, 10 µg/L, 15 µg/L, 25 µg/L, and 50 µg/L. The Chlorite calibration curve consists of seven standards at the following concentrations: 20 µg/L, 50 µg/L, 100 µg/L, 250 µg/L, 500 µg/L, 750 µg/L, and 1000 µg/L. Both Chlorite and Bromate standards are fortified with a surrogate solution at a concentration of 1000 µg/L. Both Chlorite and Bromate standards are preserved with EDA at a concentration of 50 µg/L.

8.3 Calibration Verification

8.3.1 Initial calibrations are performed at a minimum of once every 6 months or whenever needed. An initial calibration verification standard (ICV), an initial calibration check standard (IPC) and an initial calibration blank (ICB) must be analyzed prior to conducting sample analysis.

8.3.2 The initial calibration verification standard must be prepared with a stock from a different source than the standards used in the calibration

of the instrument. The ICV value must be within 15% of its true value or the run will have to be repeated.

8.3.3 The verification of linearity must use a minimum three standards. A 5.0 µg/L, 25 µg/L and 50 µg/L standard are used for Bromate. A 20 µg/L, 500 µg/L and 1000 µg/L standard are used for Chlorite. The linearity study must be analyzed following initial calibrations, every 6 months or whenever a significant change to the instrument is made. The standards must have an area response within ± 10 % of the area of the initial calibration standard responses for Bromate and Chlorite. The three standard levels should be analyzed twice over 2 workdays.

8.3.4 The ICB value for Bromate or Chlorite must be less than the method RL or the run will have to be repeated.

8.3.5 As a mandatory requirement of the calibration verification, the laboratory must verify calibration using the lowest calibration standard as the Initial Calibration Check Standard (IPC). The IPC must be within the required 75-125% recovery limits. The retention time shift of the IPC window must be no more than +/- 2% from the expected value.

8.3.6 Proper chromatographic performance must be demonstrated on The IPC by calculating the Peak Gaussian Factor (PGF), which measures peaks symmetry and monitors retention time drift in the surrogate peak over time. See section 11.7 for calculation formula. The PGF of the Initial Calibration Check Standard (IPC) must be between 0.80 and 1.15.

8.3.7 A continuing calibration check standard (CCC) and a continuing calibration blank (CCB) must be analyzed after every tenth sample and at the end of the sample run. The continuing calibration check may come from the same source as the calibration standards. The levels selected for the calibration check standards (CCC's) should be varied between a middle calibration level and the highest calibration level. The response for the initial, continuing and end calibration check must satisfy the criteria listed in 8.3.7.1. The CCB must be less than the reporting limit. If the CCC or CCB does not meet acceptance criteria, then all samples affected by the out of control CCC or CCB are to be rerun.

8.3.7.1 Control limits for calibration verification

Concentration range	Percent Recovery Limits
MRL to 10x MRL	75-125%
10xMRL to highest calibration level	85-115%
Retention Time(s)	± 5% of Absolute Retention Times

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

8.4 Retention Time Windows

8.4.1 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a

retention time can be used to calculate a suggested window size for each analyte.

8.4.2 Each time the analytical system is calibrated, the software sets the Absolute Retention Time of the analyte based on the last standard analyzed for the calibration curve. The response for the Initial Calibration Verification Standards(ICVs) and Continuing Calibration Standards(CCCs) must not shift more than +/- 5% from the expected values for any analyte or the test must be repeated, using fresh calibration standards.

8.4.3 After the Absolute Retention Times in Section 8.4.2 above are determined, the retention time windows for samples are calculated as the Absolute Retention Time (each analyte) +/- 3 times the standard deviation determined in 8.4.2 above for that analyte. Any sample peak found outside of these windows are considered to be non-detects.

8.4.4 As it is possible for a window of zero width to be determined should the standard deviation calculated in 8.4.3 be very small or zero, a minimum window of +/-5% of the Absolute Retention Time may be established. In no case may a retention time window for samples greater then +/-10% of the Absolute Retention Time.

8.5 Sample Concentration

8.5.1 Sample results are expressed in µg/L.

8.5.2 Sample dilution will alter your RL by a proportion equivalent to that of the dilution.

8.5.3 If sample is filtered, a blank and LCS/LCSD pair must also be filtered to show that filter does not affect result.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RLs), Appendix A for Quality Assurance criteria and Table 14.2 for a summary of Quality Control procedures associated with this method.

9.2 A method detection limit study must be performed twice per year. Refer to reference 13.5.

9.3 Refer to SOP reference 13.2 for training and certification procedures.

9.4 Refer to SOP reference 13.3 for control charting procedures.

9.5 Default control limits for recovery for LCS/LCSD pairs are based on Section 9.3.2 of EPA Method 300.1 (reference 13.1) as noted in Table 9.5.1 below. By default, the EPD laboratory sets LCS/LCSD precision control limits to 0-20% RPD. Default control limits for recovery for MS/MSD pairs are based on Section 9.4.1.4 of EPA Method 300.1 Precision limit defaults are based on Section 9.4.3.2 of EPA Method 300.1. In-house limits based on control charts may never exceed the default limits. The default control limits are presented to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

9.6 LCS control limits are used to monitor LCSD recovery. LCSD recovery is not used to validate batch data.

9.7 MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.7.1 The actual MDL varies depending on instrument and matrix.

9.7.2 The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.7.3 The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.7.4 The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blank.

9.7.5 A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.7.6 The results of the MDLBlank will be entered into Labworks using the Method Blank test code, B_Chlorite or B_Bromate. The MDLSpike result will be entered using the MLChlorite or MLBromate. The MDL Spiked Amount will be entered into the test code MAChlorite or MABromate. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-Chlorite or INSTR-Bromate.

9.7.7 MDL study must be performed twice per year and before the MDL for the instrument expires.

Table 9.5.1 Default Quality Assurance Criteria for Method EPA 300.1

QC Type	Analyte	Accuracy(%R) LCL UCL	Precision (%RPD)
LCS/LCSD	Bromate/Chlorite	75 – 125[1] 85 – 115[1]	20[4]
MS/MSD	Bromate/Chlorite	75 – 125[2]	0 - 10 or 0 – 20[5]
Surrogate	Dichloroacetate (DCA)	90 – 115[3]	NA

[1]EPA 300.1 specifies initially for the LCS/LCSD a 75 - 125% recovery range for all analytes in the concentration range of MRL to 10x MRL and 85 - 115% for recovery range for all analytes in the concentration range of 10x MRL to highest calibration level.

[2]EPA 300.1 specifies initially for the MS/MSD a 75 – 125% recovery range for all analytes.

[3]EPA 300.1 specifies surrogate a surrogate recovery range of 75 – 125%. Surrogate recovery limits are static.
[4]By default, the EPD laboratory sets LCS/LCSD precision control limits to 0-20% RPD. Precision limits are static.
[5]EPA 300.1 sets MS/MSD precision control limits to 0-20% when the concentration range is MRL to 10xMRL and 0-10% for a concentration range of 10xMRL to highest calibration range. Precision limits are static.

10 Procedure

10.1 Procedure for Dionex IC05 – See Appendix B

10.2 Procedure for Dionex IC04 – See Appendix C

11 Calculations

11.1 The weighted external standard calibration is calculated by the instrument software and is documented in the instrument software.

11.2 Mean ($\bar{X}$):

$$\bar{X} = \frac{X_1 + X_2 + \cdots X_n}{n}$$

11.2.1 Where:

$X_1 + X_2 + \cdots X_n$ = The sum of a set of values X_i, i = 1 to n

n = The number of values in the set

11.3 Standard Deviation (n – 1) (σ_{n-1}):

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \bar{X})^2}{n-1}}$$

11.3.1 Where:

$\bar{X}$ = Mean of the values

X_i = Individual values 1 through i

n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{\sigma_{n-1}}{\bar{X}} * 100$$

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation

$\overline{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

$$\%\text{RPD} = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} * 100$$

11.5.1 Where:

$|X_1 - X_2|$ = Absolute difference between two values

$\frac{(X_1 + X_2)}{2}$ = Average of two values

11.6 Percent Drift, %Drift:

$$\%\text{Drift} = \frac{(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}})}{\text{Concentration}_{\text{Expected}}} * 100$$

11.6.1 Where:

$\text{Concentration}_{\text{Calculated}}$ = Concentration calculated from result

$\text{Concentration}_{\text{Expected}}$ = Theoretical concentration of the standard

11.7 Peak Gaussian Factor (PGF):

$$\text{PFG} = \frac{1.83 \text{ x } W_{\frac{1}{2}}}{W_{\frac{1}{10}}}$$

where:

$W_{1/2}$ is the peak width at half height

$W_{1/10}$ is the peak width at one tenth height

11.8 Percent Recovery:

11.8.1 *LCS/LCSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.1.1 Where:

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample
$\text{Conc}_{\text{expected}}$ = Expected concentration

11.8.2 *MS/MSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}} - \text{Conc}_{\text{unspiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.2.1 Where:

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample
$\text{Conc}_{\text{unspiked}}$ = Concentration found in unspiked sample
$\text{Conc}_{\text{expected}}$ = Expected concentration

11.9 Calculation of Dilution Factors

$$C \times D = F$$

11.9.1 Where:

C = concentration from instrument in mg/L
D = dilution factor, if any
F = final concentration in mg/L

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating Procedures (SOP Reference 13.4).

13 References

13.1 National Exposure Research Laboratory, Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio. Method 300.1, Revision 1.0 (1997) with errata (April 1999).
13.2 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision and Continuing Demonstration of Capability SOP 6-002, online revision.

13.3 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.
13.4 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.5 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP MDL 6-007, online revision.
13.6 GA EPD Laboratory Safety Plan – EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.
13.7 Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005.
13.8 EPD Laboratory Quality Assurance Plan, online revision.

14 Reporting Limits (RLs) and Quality Control Approach

Table 14.1 RL's for EPA 300.1

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
EPA 300.1	Bromate	5.0	µg/L
EPA 300.1	Chlorite	20	µg/l

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 300.1

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 300.1	Bromate and Chlorite	Initial calibration for Bromate or Chlorite	Calibration every 6 months or as needed.	Correlation coefficient $\geq$ 0.995 for linear regression	Correct problem then repeat initial calibration	
		Retention time window calculated for each analyte	Each initial calibration and calibration verifications	+/- 3 times standard deviation for 3 standard levels over 2 work days	Correct problem then reanalyze all samples analyzed since the last retention time check	
		Linearity Study	After every calibration, run 3 levels of standards for each analyte (low, middle and high) over 2 work days	Area of linearity standards must not differ more than 10% of initial calibration standard area.	Correct problem and rerun linearity study or repeat initial calibration.	
		Second Source Calibration Verification (ICV)	Before sample analysis and at least quarterly whichever is sooner	All analytes within 15% of expected value	Correct problem then repeat initial calibration	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 300.1

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 300.1	Bromate and Chlorite	Initial Calibration Check Standard(IPC) *Low level CCC	Prior to sample analysis	*Must use lowest calibration standard. *%Recovery limit is 75-125%. *< 5% shift in retention time or Bromate or Chlorite *≤ 2% shift in retention time for surrogate *PGF (0.80 -1.15)	Correct problem and repeat initial calibration.	
		Initial Calibration Blank (ICB)	Once per analytical run.	Value must be < RL.	Correct problem and repeat initial calibration.	
		Continuing Calibration Check (CCC)	Prior to sample analysis, and after every 10 samples and at the end of the sample run.	% Recovery limit of 75-125% (MRL to 10x MRL) and 85-115% (10xMRL to highest calibration level) . CCC levels must be varied between middle and highest calibration level	Correct problem then reanalyze CCC and all samples in the affected batch	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of the sample run.	Result must be < RL	Correct problem then reanalyze CCB and all samples in affected batch	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank, a blind sample, and an MDL study. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria SOP 3-015 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.2)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria.	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria SOP 3-015 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.2)		

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 300.1

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 300.1	Bromate and Chlorite	Method Blank	One per batch	Result must be < RL	Correct problem then analyze method blank and all samples processed with the contaminated blank	If unable to reanalyze, flag with "B"
		Laboratory Control Sample (LCS/LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table A.1, Appendix A	Correct problem then reanalyze the LCS/LCSD and all samples in the affected batch	If unable to reanalyze, flag with "J"
		Matrix spike (MS/MSD)	Two MS/MSD per analytical batch	QC Acceptance Criteria Table A.1, Appendix A	Evaluate out of control event, reanalyze or flag data	
		Surrogate spike	Every sample, spiked sample, QC sample, standard and blank	QC acceptance criteria Table A.1, Appendix A	Evaluate out of control event, reanalyze or flag data	
		MDL Low Level Spike (MDLS) 5.0 ug/L Bromate 20 ug/L Chlorite	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL Blank (MDLB)	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL study	Twice per year or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	

Appendix A: Quality Assurance Criteria for - EPA Method 300.1 – Inorganic Disinfection By-product Anions in Water

Table A.1 Quality Assurance Criteria for Method EPA 300.1			
QC Type	Analyte	Accuracy(%R) LCL UCL	Precision (%RPD)
IDC	Bromate/Chlorite	See default limits SOP3-015 Table 9.5.1	
LCS/LCSD	Bromate/Chlorite	75 – 125[1] 85 – 115[1]	20[3]
MS/MSD	Bromate/Chlorite	75 – 125[1]	0 - 10 or 0 – 20[4]
Surrogate	Dichloroacetate (DCA)	90 – 115[2]	NA

[1]***Insufficient data points to chart; Default limits in use until sufficient data points collected. Control chart data generated from 01/01/2018– 01/01/2021.***

[2]*EPA 300.1 specifies surrogate a surrogate recovery range of 75 – 125%. Surrogate recovery limits are static.*

[3]*By default, the EPD laboratory sets LCS/LCSD precision control limits to 0-20% RPD. Precision limits are static.*

[4]*EPA 300.1 sets MS/MSD precision control limits to 0-20% when the concentration range is MRL to 10xMRL and 0-10% for a concentration range of 10xMRL to highest calibration range. Precision limits are static.*

Appendix B – Procedure for ICS 6000(IC05) for EPA Method 300.1 Inorganic Disinfection By-Product Anions in Water

1 IC05 Instrument Start-Up Procedure

1.1 Fill auto-sampler and eluent reservoir with reagent water.

1.2 Inspect the KOH reservoir visually for leakage. Check the level of KOH (EGC % Remaining) by clicking on “Instruments” icon in the bottom left corner and then choosing “ Eluent Generator” tab at the top of the screen. The level should be 15% or greater. If not, install a new one (refer to manufacturer’s instructions for installation).

1.3 The expiration date of the Eluent generator cartridge is 1 year from the date of opening, or manufacturer expiration date, or 15% remaining, whichever comes first.

1.4 Turn on computer and the main power to the following: pump, column compartment, auto-sampler and detector

1.5 Start communication with instrument by clicking the yellow lizard in left corner. Click *start instrument controller.*

1.6 Click the green lizard in the left corner of the screen

1.7 Click the instrument category in the bottom left corner.

1.8 Select System 2. Then select Home tab.

1.9 Turn on pump by clicking the slider bar. Set flow to 0.250 mL/min. Make sure pressure is building.

1.10 Turn on the eluent generator labeled "EGC KOH." Change setting to 20.0 mM.

1.11 In same box, turn on CR-TC

1.12 Turn on the detector by clicking the slider bar labeled CD Tot right.

1.13 Turn on the Suppressor by clicking the slider bar labeled Suppressor right. Change to 13 mA.

1.14 Change compartment temperature to 25.0 C. Turn on heater by clicking the column slider bar. Change column temperature to 25.0 C. Click the monitor baseline icon on the top of the screen.

1.15 Allow the instrument to run for an hour or until baseline is stable. Click Monitor Baseline in upper center bar.

1.16 While baseline is stabilizing, generate a backlog of pending samples in Labworks. Batch in groups of 20. For each batch, analyze a matrix spike (MS) and a matrix spike duplicate (MSD) for a minimum of 10% of routine samples.

1.17 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair.

1.18 Once baseline is stable, record background conductivity, system pressure and any maintenance performed on instrument.

2 IC05 Quick Start

2.1 Click data category in bottom left corner.

2.2 Click on sequence file of last calibration, labeled "cal date."

2.3 Once the calibration run is displayed, click "File" and "Save As." Check the "Save Raw Data" box and save as follows: Bromate and today's date or Chlorite and today's date.

2.4 Click "Insert Row" and add lines by increments of 3, 5 or 10.

2.5 Delete the contents of the name column of the added rows by highlighting them. Then right click and choose delete.

2.6 Change the Column type of added lines to “unknown” by changing the first line to “unknown” then clicking F9.

2.7 Change the Position for the 1st added line to GA1. “G” stands for green section, “A” stands for row, “1” stands for column. Click F9 and select renumber (make sure the start position is GA1, increment is 1 and injection/vial is 1). Instrument will automatically assign the positions with the following section order: G-green, B-blue, and R-red.

2.8 Enter dilution factor for samples that require dilutions.

2.9 Click on the processing method on the bottom, this will open the studio.

2.10 Click on calibration tab. Make sure mode is total, curve fitting is normal. Ignore the origin of the fixed standards.

2.11 Click “Save.”

2.12 Click resume run on top of screen. Refer to section 3 for “Full instruction.”

3 IC05 Full Instruction

3.1 Click “Create.” Then click on sequence.

3.2 Select system 2. Then click next.

3.3 Set number of vials to 1, injection per vial to 1, injection volume to 100 uL. Start position should be set to Auto-sampler number GA1.

3.4 Click next.

3.5 Select browse for instrument method, then select “Bromate IC05” for Bromate or “Chlorite IC05” for Chlorite.

3.6 Select browse for processing method, then select “BROMATE IC05” for Bromate or “Chlorite IC05” for Chlorite.

3.7 Select browse for report template, then select, “Bromate-Chlorite with PGF.”

3.8 Channel should be CD_2.

3.9 Click Finish.

3.10 Save sequence. Name sequence either “Bromate” with date or “Chlorite” with date. Click Save. Add injections by clicking down arrow to match #in batch.

3.11 Add additional rows by clicking the insert icon. Type sample IDs in the “name” column.

3.12 Change type to unknown if default is not set to unknown.

3.13 Click on the auto-sampler number, click F9 and re-number (make sure the start position is GA1, increment is 1 and “injection vial” is 1).

3.14 Volume should be 100 µL. Instrument method should be "Bromate IC05" or "Chlorite IC05." Processing Method should be "BROMATE IC05" or "Chlorite IC05." Weight should be 1.00.

3.15 Click Save. Close screen and click scroll arrow button by print icon. Click injection list.

3.16 Advance autosampler position to correct color by clicking system 2 and click sampler. Load samples according to assigned auto-sampler positions.

3.17 Place tray in correct color section in auto-sampler.

3.18 Once sequence has completed, Click Studio. Inspect chromatograms for proper integration and detections. Refer to SOP 6-020 – Standard Operation Procedure for Manual Integration if manual integration needs to be performed.

3.18.1 If any manual integrations are performed, initial and date next to the peak that was modified.

3.18.2 Make sure to print both the original chromatogram and updated chromatogram and include both in the data packet. Write "not reported" on the original chromatogram.

3.19 Make sure the area count for the blanks is less than half the low standard.

3.20 Exit out of studio.

3.21 Click Print icon on top of the "Data" screen, then click "Report." Select integration and Calibration for printing, then click OK.

3.22 Print out the sequence by clicking print icon on top, then click injection list.

3.23 If a sample needs a dilution; you can run the dilution the next day along with an ICV, ICB, CCC and CCB as long as it in within 24 hours of the start of the original run. If a diluted sample is reanalyzed the next day, make sure to flag the affected result with a D to show that the analysis date may differ from the QC data. A corrective action should be completed so a comment can be added to the sample.

3.24 Dilute all samples with a response greater than the high standard (50 µg/L for Bromate and 1000 µ/L for Chlorite).

3.25 Use reagent water (See 6.1.1) to dilute samples. To prepare dilutions, use either Class A volumetric glass pipettes or use a verified auto-pipettor.

3.26 If using an auto-pipettor, make sure that the volume has been verified and recorded prior to use. Record verification in the laboratory pipette calibration log book.

3.27 Volumes and amounts of reagents, chemicals and standards may be altered as long as final concentrations remain the same. Sample volumes and injection amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.

3.28 Attach the Retention Time Study and Linearity Study to the data package. The calibration will be printed automatically in the beginning of the report.

4 **IC05 Calibration Procedure** (without previous "Calibration Template")

4.1 Fill DI reservoir for auto-sampler and eluent.
4.2 Turn on computer.
4.3 Start communication with instrument by selecting the local instrument controller in the bottom right corner in task bar. Click start instrument controller.
4.4 You are now in the console.
4.5 Click the instrument category in the bottom left corner
4.6 Select System 2. Click, "Create" on top left corner. Then select "sequence" and "system 2."
4.7 Set number of vials to 1, injection per vial to 1, injection volume to 100 uL. Start position should be set to Auto-sampler number GA1. Note: This number will be changed later.
4.8 Click next.
4.9 Select Instrument Method, "Bromate IC05" or "Chlorite IC05".
4.10 Select "BROMATE IC05" or "Chlorite IC05" under processing method.
4.11 Select Bromate-Chlorite with PGF, under report template.
4.12 Channel should be CD_2.
4.13 Click "Next" and "Finish."
4.14 Name sequence with either Bromate or Chlorite, then month, date and year. Save in sequences folder.
4.15 Type up calibration Schedule.
4.16 Change type to calibration and assign correct level (01- 07).
4.17 Click on data category tab.
4.18 Click processing folder on bottom of spreadsheet.
4.19 Select Processing Method "BROMATE IC05" for Bromate or "Chlorite IC05" for Chlorite.
4.20 Select Calibration Tab.
4.21 Change mode to Total.
4.22 Save changes and close screen. Print out sequence.
4.23 Load samples according to assigned Auto-sampler positions.
4.24 Place tray in correct color section in auto-sampler.
4.25 Click start. Once the run is finished, select studio.

4.26 Inspect chromatograms for proper integration and detections. Refer to SOP 6- 020 – Standard Operating Procedure for Manual Integration if manual integration needs to be performed.
4.27 Once all integration is checked, close screen but "don't save."
4.28 Click print, "do not scroll down" then select calibration and integration. Click OK.
4.29 Review the components and make sure the correlation coefficient is 0.995 or greater.
4.30 Once the calibration is verified and is acceptable, click the processing method "BROMATE IC05" for Bromate or "Chlorite IC05" for Chlorite.
4.31 Click the calibration tab.
4.32 Change the mode to total and make sure curve fitting is normal.
4.33 Initial and date calibration, then place in maintenance log book.
4.34 Retention time windows must also be calculated. Refer to Section 8.4 in SOP 3-015.
4.35 A low, middle and high standard should be analyzed to confirm linearity. Refer to section 8.3.3 in SOP 3-015.

Appendix C – Procedure for ICS 5000(IC04) for EPA Method 300.1 Inorganic Disinfection By-Product Anions in Water

1 IC04 Instrument Start-Up Procedure

1.0 Fill auto-sampler and eluent reservoir with reagent water.

1.1 Inspect the KOH reservoir visually for leakage. Check the level of KOH(EGC % Remaining) by clicking on "Instruments" icon in the bottom left corner and then choosing " Eluent Generator" tab at the top of the screen. The level should be 15% or greater. If not, install a new one (refer to manufacturer's instructions for installation).
1.2 The expiration date of the Eluent generator cartridge is 1 year from the date of opening, or manufacturer expiration date, or 15% remaining, whichever comes first.
1.3 Turn on computer and the main power to the following: pump, column compartment, auto-sampler and detector
1.4 Start communication with instrument by clicking the yellow lizard in left corner. Click *start instrument controller.*
1.5 Click the green lizard in the left corner of the screen
1.6 Click the instrument category in the bottom left corner.

1.7 Select System 2. Then select Home tab.
1.8 Turn on pump by clicking the slider bar. Set flow to 0.250 mL/min. Make sure pressure is building.
1.9 Turn on the eluent generator labeled "EGC KOH." Change setting to 20.0 mM.
1.10 In same box, turn on CR-TC
1.11 Turn on the detector by clicking the slider bar labeled CD Tot right.
1.12 Turn on the Suppressor by clicking the slider bar labeled Suppressor right. Change to 13 mA.
1.13 Change compartment temperature to 25.0 C. Turn on heater by clicking the column slider bar. Change column temperature to 25.0 C. Click the monitor baseline icon on the top of the screen.
1.14 Allow the instrument to run for an hour or until baseline is stable. Click Monitor Baseline in upper center bar.
1.15 While baseline is stabilizing, generate a backlog of pending samples in Labworks. Batch in groups of 20. For each batch, analyze a matrix spike (MS) and a matrix spike duplicate (MSD) for a minimum of 10% of routine samples.
1.16 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair.
1.17 Once baseline is stable, record background conductivity, system pressure and any maintenance performed on instrument.

2 IC04 Quick Start

2.1 Click data category in bottom left corner.
2.2 Click on sequence file of last calibration, labeled "cal date."
2.3 Once the calibration run is displayed, click "File" and "Save As." Check the "Save Raw Data" box and save as follows: Bromate and today's date or Chlorite and today's date.
2.4 Click "Insert Row" and add lines by increments of 3, 5 or 10.
2.5 Delete the contents of the name column of the added rows by highlighting them. Then right click and choose delete.
2.6 Change the Column type of added lines to "unknown" by changing the first line to "unknown" then clicking F9.
2.7 Change the Position for the 1st added line to GA1. "G" stands for green section, "A" stands for row, "1" stands for column. Click F9 and select renumber (make sure the start position is GA1, increment is 1 and

injection/vial is 1). Instrument will automatically assign the positions with the following section order: G-green, B-blue, and R-red.

2.8 Enter dilution factor for samples that require dilutions.

2.9 Click on the processing method on the bottom, this will open the studio.

2.10 Click on calibration tab. Make sure mode is total, curve fitting is normal. Ignore the origin of the fixed standards.

2.11 Click "Save."

2.12 Click resume run on top of screen. Refer to section 3 for "Full instruction."

3 IC04 Full Instruction

3.1 Click "Create." Then click on sequence.

3.2 Select system 2. Then click next.

3.3 Set number of vials to 1, injection per vial to 1, injection volume to 100 uL. Start position should be set to Auto-sampler number GA1.

3.4 Click next.

3.5 Select browse for instrument method, then select "EPA 300.0"

3.6 Select browse for processing method, then select "processing method."

3.7 Select browse for report template, then select, "Ron Hooper report temp."

3.8 Channel should be CD_2.

3.9 Click Finish.

3.10 Save sequence. Name sequence either "Bromate" with date or "Chlorite" with date. Click Save. Add injections by clicking down arrow to match #in batch.

3.11 Add additional rows by clicking the insert icon. Type sample IDs in the "name" column.

3.12 Change type to unknown if default is not set to unknown.

3.13 Click on the auto-sampler number, click F9 and re-number (make sure the start position is GA1, increment is 1 and "injection vial" is 1).

3.14 Volume should be 100 µL. Instrument method should be "test-Bromate" or "test-Chlorite." Processing Method should be "Bromate" or "Chlorite." Weight should be 1.00.

3.15 Click Save. Close screen and click scroll arrow button by print icon. Click injection list.

3.16 Advance autosampler position to correct color by clicking system 2 and click sampler. Load samples according to assigned auto-sampler positions.

3.17 Place tray in correct color section in auto-sampler.

3.18 Once sequence has completed, Click Studio. Inspect chromatograms for proper integration and detections. Refer to SOP 6-020 – Standard Operation

Procedure for Manual Integration if manual integration needs to be performed.

3.18.1 If any manual integrations are performed, initial and date next to the peak that was modified.

3.18.2 Make sure to print both the original chromatogram and updated chromatogram and include both in the data packet. Write "not reported" on the original chromatogram.

3.19 Make sure the area count for the blanks is less than half the low standard.

3.20 Exit out of studio.

3.21 Click Print icon on top of the "Data" screen, then click "Report." Select integration and Calibration for printing, then click OK.

3.22 Print out the sequence by clicking print icon on top, then click injection list.

3.23 If a sample needs a dilution; you can run the dilution the next day along with an ICV, ICB, CCC and CCB as long as it analyzed within 24 hours of the start of the original run. If a diluted sample is reanalyzed the next day, make sure to flag the affected result with a D to show that the analysis date may differ from the QC data. A corrective action should be completed so a comment can be added to the sample.

3.24 Dilute all samples with a response greater than the high standard (50 µg/L for Bromate and 1000 µ/L for Chlorite).

3.25 Use reagent water (See 6.1.1) to dilute samples. To prepare dilutions, use either Class A volumetric glass pipettes or use a verified auto-pipettor.

3.26 If using an auto-pipettor, make sure that the volume has been verified and recorded prior to use. Record verification in the laboratory pipette calibration lo book.

3.27 Volumes and amounts of reagents, chemicals and standards may be altered as long as the final concentrations remain the same. Sample volumes and injection amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.

3.28 Attach the Retention Time Study and Linearity Study to the data package. The calibration will be printed automatically in the beginning of the report.

4 **IC04 Calibration Procedure** (without previous "Calibration Template")

4.1 Fill DI reservoir for auto-sampler and eluent.

4.2 Turn on computer.

4.3 Start communication with instrument by selecting the local instrument controller in the bottom right corner in task bar. Click start instrument controller.

4.4 You are now in the console.
4.5 Click the instrument category in the bottom left corner
4.6 Select System 2. Click, “Create” on top left corner. Then select “sequence” and “system 2.”
4.7 Set number of vials to 1, injection per vial to 1, injection volume to 100 uL. Start position should be set to Auto-sampler number GA1. Note: This number will be changed later.
4.8 Click next.
4.9 Select Instrument Method, “test-Bromate” or “test-Chlorite”.
4.10 Select “Bromate” or “Chlorite” under processing method.
4.11 Select Ron Hooper report temp 2, under report template.
4.12 Channel should be CD_2.
4.13 Click “Next” and “Finish.”
4.14 Name sequence with either Bromate or Chlorite, then month, date and year. Save in sequences folder.
4.15 Type up calibration Schedule.
4.16 Change type to calibration and assign correct level (01- 07).
4.17 Click on data category tab.
4.18 Click processing folder on bottom of spreadsheet.
4.19 Select Processing Method “Bromate” for Bromate or “Chlorite” for Chlorite.
4.20 Select Calibration Tab.
4.21 Change mode to Total.
4.22 Save changes and close screen. Print out sequence.
4.23 Load samples according to assigned Auto-sampler positions.
4.24 Place tray in correct color section in auto-sampler.
4.25 Click start. Once the run is finished, select studio.
4.26 Inspect chromatograms for proper integration and detections. Refer to SOP 6- 020 – Standard Operating Procedure for Manual Integration if manual integration needs to be performed.
4.27 Once all integration is checked, close screen but “don’t save.”
4.28 Click print, “do not scroll down” then select calibration and integration. Click OK.
4.29 Review the components and make sure the correlation coefficient is 0.995 or greater.
4.30 Once the calibration is verified and is acceptable, click the processing method “Bromate” for Bromate or “Chlorite” for Chlorite.
4.31 Click the calibration tab.
4.32 Change the mode to total and make sure curve fitting is normal.

4.33 Initial and date calibration, then place in maintenance logbook.

4.34 Retention time windows must also be calculated. Refer Section 8.4 in SOP 3-015.

4.35 A low, middle and high standard should be analyzed to confirm linearity. Refer to section 8.3.3 in SOP 3-015.

Updates to Previous Version:

Section 2
Section 4
Section 6
Section 9
Table A.1
Table 14.2