Laboratory Manager Approval: Kristy E. Hrehor / 08/19/2021

QA Manager Approval: Jeffrey Moore / 08/19/2021

EPA Method 300.0 – Common Anions in Water

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

1.1 This method may be used to determine chloride, fluoride and sulfate 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 Plan (see SOP reference 13.3) for Quality Control Definitions.

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.

3 Interferences

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

3.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 ml of concentrated eluent to 100 ml of each standard and sample. Note: If interference occurs, the column should be replaced.

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

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

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

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

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

3.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of

chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains. Note: This does not affect chloride, sulfate or fluoride analysis.

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision (See Section 13.8)

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- PN# 061830.
5.1.2 Anion suppressor device – Thermo Scientific ADRS 600 4 mm Suppressor –PN088666
5.1.3 Dionex CRD 4mm 200- P/N 062983
5.1.4 Thermo Gradient mixer 4mm P/N 042126
5.1.5 Anion separator column - Dionex AS18 Analytical Column – P/N 060549
5.1.6 Anion guard column - Dionex AG18 Guard Column – P/N 060551
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 500 KOH- Potassium Hydroxide- P/N 075778
5.1.10 Dionex AS-AP Auto-sampler
5.1.11 Dionex ICS-6000 DC Conductivity detector
5.1.12 Dionex ICS-6000 DP pump
5.1.13 Dionex ICS-6000 EG eluent generator
5.1.14 25 uL sample loop
5.1.15 Chromeleon 7 software
5.1.16 2 Plastic pressurized reservoirs; used for reagent water
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: half-gallon plastic container.
5.1.22 Air displacement pipettes of various volumes, auto- pipettors, bottle-top dispensers and 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 and bottle top dispensers 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- PN# 061830
5.2.2 Anion suppressor device -Thermo Scientific AERS 500 4 mm Suppressor – P/N 082540
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 AS18 Analytical Column – P/N 060549
5.2.6 Anion guard column - Dionex AG18 Guard Column – P/N 060551
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 Section6.2.2)
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 25 uL sample loop
5.2.15 Chromeleon 7 software
5.2.16 2 Plastic pressurized reservoirs; used for reagent water (See 6.2.1).
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: half-gallon plastic container.
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 and bottle-top dispensers 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 IC05 and IC04 (Dionex IC)

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]@ 25°C and a TOC of 50 ug/L or less).

6.1.2 Eluent Generator:
Dionex EGC III KOH- Potassium Hydroxide- PN# 074532 or Dionex EGC 500 KOH-Potassium Hydroxide-P/N 075778

6.2 Standards for use with both IC04 and IC05

6.3.1 Chloride Stock Standard(1000 mg/L) Primary Source(PS)
This standard is purchased from a commercially available source. This purchased standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner.

6.3.2 Sulfate Stock Standard(1000 mg/L) Primary Source(PS)
This standard is purchased from a commercially available source. This purchased standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner.

6.3.3 Fluoride Stock Standard A- (1000 mg/L)
This standard is purchased from a commercially available source. This purchased standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner. Only used when 100 mg/L is not available.

6.3.4 Fluoride Stock Standard B– (100 mg/L)
This standard is purchased from a commercially available source. This purchased standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner.

6.3.4.1 Fluoride Stock Standard B – (100 mg/L)
If not purchased per 6.3.4, use a 1L volumetric flask, add 100 ml of Fluoride Stock Standard A to 500 ml of reagent water, dilute to volume and mix thoroughly**.** This standard is stable for 6 months.

6.3.5 Working Mixed Standards-
Prepare the standards per Table 6.3.5.1 Dilute to volume using reagent water (See 6.1.1). Working standards should be prepared fresh weekly.

Table 6.3.5.1 Working Mixed Standards for Dionex IC02 and Dionex IC04

Fluoride Stock B (100 mg/L) (mL)	Cl- Stock (1000 mg/L) (mL)	SO_4^{2-} Stock (1000 mg/L) (mL)	Final Volume (reagent water) (mL)	Fluoride Standard Concentration (mg/L)	Cl- & SO_4^{2-} Mixed Standard Concentration (mg/L)
NA	0.5	0.5	100	NA	5
0.50	2.5	2.5	250	0.20	10
0.50	2.5	2.5	100	0.50	25
1.0	5.0	5.0	100	1.00	50
2.0	8.0	8.0	100	2.0	80
5.0	10	10	100	5.00	100

6.4 ICV Fluoride, Chloride and Sulfate of Second Source Stock Standard Solution(SS):
A 100 mg/L Fluoride Stock standard solution, a 1000 mg/L Chloride Stock Standard Solution and a 1000 mg/L Sulfate Stock Standard solution are purchased from a second source vendor. A different lot from the same vendor as the calibration standards for each analyte is also acceptable. These purchased stock standards are stable until expiration date on bottle or within 6 months of opening date, whichever is sooner. Store at ≤ 6 ºC.

6.4.1 ICV Fluoride, Chloride and Sulfate Solution:
Pipette 2 mL of the Fluoride Stock Standard B (100 mg/L) ICV Stock Standard solution, 5 mL of the Chloride ICV 1000 mg/L Stock Standard solution and 5 mL of the Sulfate ICV 1000 mg/L Stock Standard Solution into a 100 ml volumetric flask and dilute to volume with reagent water. The working ICV should be prepared fresh weekly. This solution is used for both Fluoride and Anion analysis.

6.5 LCS/LCSD solutions:
For Fluoride (T.V of 2.00 mg/L), pipette .2 ml of Fluoride Stock Standard B (100 mg/L) in a 10 mL volumetric flask and dilute to volume with reagent water that was stored in a ½ gallon sample container. Record the lot# of bottle used. For Anion (T.V. of 50.0 mg/L Chloride/Sulfate) analysis, pipette .5 mL each of the Chloride Stock Standard(1000 mg/L) and the Sulfate Stock Standard(1000 mg/L) into a 10 mL volumetric flask and dilute to volume with reagent water that was stored in a ½ gallon sample container. Record the lot# of bottle used. Make sure that auto-pipettor volume has been verified and recorded prior to use.

6.6 MS/MSD solutions:
For Fluoride analysis (amount spiked of 2.00 mg/l), pipette .2 ml of Fluoride Stock Standard B(100 mg/L) in a 10 mL volumetric flask and dilute to volume with QC sample. For Anions(amount spiked of 50.0 mg/l each of Chloride/Sulfate), pipette .5 mL each of the Chloride Stock Standard(1000 mg/L) and the Sulfate Stock Standard(1000 mg/L) into a 10 mL volumetric flask and dilute to volume with QC sample. Make sure that auto-pipettor volume has been verified and recorded prior to use.

6.7 Continuing Calibration Check(CCC):
A mixed Fluoride/Chloride/Sulfate standard at the levels of 2.0/50/50 mg/L respectively is used for the CCC.

6.7.1 Pipette 2 ml of Fluoride Stock Standard B (100 mg/L), 5 mL each of the Chloride Stock Standard (1000 mg/L) and the Sulfate Stock Standard(1000 mg/L) into a 100 mL volumetric flask and dilute to volume with reagent water. Make sure that auto-pipettor volume has been verified and recorded prior to use.

6.8 ICB, CCB, MBLK, MDLB and Dilution Water:
Reagent water is used for the ICB and CCB. Before pouring the ICB, CCB, MBLK or MDLB into the sample vial, make sure to pour reagent water into a ½ gallon sample container and record the lot #. See section 6.1

6.9 Low Level Calibration Check standard (Low Level CCC):
A low level calibration check standard (CCC) at a concentration of 0.20 mg/L for Fluoride and 10.0 mg/L for Chloride and Sulfate must be analyzed once per analytical run. Recovery of the low level calibration check standard must be ±50%.

6.9.1 Pipette 0.5 ml of Fluoride Stock Standard B (100 mg/L), 2.5 mL each of the Chloride Stock Standard (1000 mg/L) and the Sulfate Stock Standard (1000 mg/L) into a 250 mL volumetric flask and dilute to volume with reagent water. Make sure that auto-pipettor or bottle-top dispenser volume has been verified and recorded prior to use.

6.10 Method Detection Limit Spike(MDLS)

6.10.1 Reagent water spiked with 0.20 mg/L of Fluoride, 5.0 mg/L of Chloride and 5.0 mg/L of Sulfate.

6.10.2 Pipette 1 ml of Fluoride Stock Standard B (100 mg/L), 2.5 mL each of the Chloride Stock Standard (1000 mg/L) and the Sulfate Stock Standard (1000 mg/L) into a 500 mL volumetric flask and dilute to volume with reagent water. Pour the MDLS into a ½ gallon standard container before pouring into the sample vial. Record lot # of bottle used. Make sure that auto-pipettor volume has been verified and recorded prior to use.

7 Sample Collection

7.1 Samples should be collected in plastic bottles

7.2 Samples should be stored at ≤ 6.0° C (not frozen) except for Fluoride only samples (IOC samples) which do not require refrigeration.

7.3 Preservation is not required.

7.4 Holding time is 28 days.

8 Calibration

8.1 Calibration Standards

The calibration curve consists of standards containing Chloride and Sulfate at the following concentrations: 5.0 mg/L, 10 mg/L, 25 mg/L, 50 mg/L, 80 mg/L and 100 mg/L and Fluoride at the following concentrations: 0.2 mg/L, 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 5.0 mg/L.

8.2 Calibration Curve

The Dionex Ion Chromatograph is calibrated every six months or as needed when the initial Quality Control Sample does not meet acceptance criteria of +/- 10% of true value. Six mixed chloride/sulfate/fluoride standards are used to construct the anion calibration curve and five mixed chloride/sulfate/fluoride standards are used to construct the fluoride curve. For IC05 and IC04, 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. Minimum acceptable correlation coefficient, r, is 0.995 using a linear regression.

8.3 Calibration Verification

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

8.3.1 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 10% of its true value and the ICB area count must be less than ½ of the area of the lowest standard for each analyte or the run will have to be repeated.

8.3.2 The verification of linearity must use a minimum three standards. A 0.2 mg/L, 1.0 mg/L and 5.0 mg/L standard are used for Fluoride. A 10 mg/L, 50 mg/L and 100 mg/L standard are used for both Chloride and Sulfate. 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 Fluoride, Chloride and Sulfate. The three standard levels should be analyzed twice over 2 workdays.

8.3.3 The ICB/CCB must have an area count of less than 50% of the area of the lowest standard in the curve.

8.3.4 A continuing calibration check (CCC) and a continuing calibration blank (CCB) must be analyzed at the beginning of sample analysis, every 10 samples and at the end of the sample run and must meet the same criteria as the ICV and ICB. The continuing calibration check may come from the same source as the calibration standards. 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.

8.3.5 A low level calibration check standard at a concentration of 0.20 mg/L for Fluoride and 10 mg/L for Chloride and Sulfate must be analyzed once per analytical run. Recovery of the standard must be ± 50%.

8.3.6 A MDLS (low level mdl spike) at the concentration of 2.0 mg/L F, 5.0 mg/L Chloride and 5.0 mg/L Sulfate must be analyzed with each batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

8.3.7 A MDLB (MDL blank) must be analyzed once per analytical batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

8.4 Retention Time Windows

8.4.1 Once per year or whenever a change is made to the system that can affect retention times. Three levels of standards (low, middle and high) should be analyzed twice over two working days. The population standard deviation (n-1) is calculated for the retention times of the injections for each analyte (Refer to Section 11.3). The Retention Time Window for an analyte is defined as 3 times the standard deviation.

8.4.2 Each time the analytical system is calibrated, the Absolute Retention Time of each analyte is based on the average response of the standards used for the calibration curve. This value must be manually entered as an integration parameter for IC04 and IC05. All Initial Calibration Verification Standards (ICVs) and Continuing Calibration Standards (CCCs) must be within 5 % of the Absolute Retention Time for Fluoride and Chloride and 10% of the Absolute Retention Time for Sulfate. Although the retention time study for Sulfate may yield a standard deviation close to zero, the study does not account for the faster elution as concentration increases. If an ICV or CCC retention time(s) falls outside of these windows, analysis must be stopped, and the cause of the drift determined and corrected. After correction, recalibration of the system may be required.

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 * the standard deviation determined in 8.4.1 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 8.4.1 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 be greater than ± 10% of the Absolute Retention Time. (See 8.4.2)

8.5 Sample Concentration

8.5.1 Sample results are expressed in mg/L.

8.5.2 If the response of any sample or QC sample is greater than the high standard, those samples must be diluted and rerun in a valid sequence. Dilution ratios should be determined, as nearly as possible, so that the response is near the mid-point of the calibration range. Note: 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, Table A.1 for Quality Control Acceptance Criteria, and Table 14.2 for Quality Control Procedures associated with this method.

9.2 See reference 13.5. for control charting procedures.

9.3 See reference 13.4. for training and certification procedures.

9.3.1. For Initial Demonstrations of Capability (IDC), Method 300.0 requires a recovery range of 90% - 110% (see calculation 11.8.).

9.3.1.1. The EPD Laboratory sets a 15% RSD requirement for IDC replicates (see calculation 11.4.).

9.3.2. The EPD Laboratory uses the most current accuracy and precision control ranges in use for samples for Continuing Demonstrations of Capability (CDC). If 4 replicates are performed (as opposed to two LCS/LCSD pairs) a 15% RSD is required (see calculation 11.4.).

9.4. Control Limits:

9.4.1. Method 300.0 requires control limits to be adjusted through the use of control charts.

9.4.2. Default control limits for recovery for LCS/LCSD pairs are based on Section 9.3.3 of EPA Method 300.0(SOP reference 13.1.) as noted in Table 9.4.1. The default limits are 90% - 110% recovery.

9.4.3. The EPD laboratory sets default LCS/LCSD precision control limits to 0-15% RPD.

9.4.4. Default control limits for recovery for MS/MSD pairs are based on Section 9.4.2 of EPA Method 300.0. The default limits are 90% - 110% recovery.

9.4.4.1. Method 300.0 section 9.4.1 requires that 10% of all routine samples must be spiked.

9.4.5. MS/MSD default precision limit are set by the EPD lab as 0 – 15% RPD.

9.4.6. In-house limits based on control charts may never exceed the default limits.

9.4.7. See Administrative SOP for Control Charting and Control Limits, SOP reference 13.5. for further details.

Note: The default control limits are presented to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

Table 9.4.1 Default Quality Assurance Criteria for Method EPA 300.0

QC Type	Analyte	Accuracy(%R) LCL UCL	Precision (%RPD)
LCS/LCSD	Chloride/Sulfate/Fluoride	90 - 110	15
MS/MSD	Chloride/Sulfate/Fluoride	90 - 110	15

9.5. Batching:

9.5.1. Batch samples 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.

9.5.2. 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.

9.5.3. Each batch must have an LCS, LCSD, Method Blank, MDLB and MDLS.

9.6. 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.

9.6. 1 The actual MDL varies depending on instrument and matrix.

9.6. 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.

9.6.3 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.

9.6.4 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 blanks.

9.6.5 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.

9.6.6 For Chloride and Sulfate, the results of the MDLBlank will be entered into Labworks using the Method Blank test code, $B_ANION. The MDLSpike result will be entered using the $MLANION. The MDL Spiked Amount will be entered into the test code $MAANION. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-ANION.

For Fluoride, the results of the MDLBlank will be entered into Labworks using the Method Blank test code, $B_FLUORIDE. The MDLSpike result will be entered using the $MLFLUORIDE. The MDL Spiked Amount will be entered into the test code $MAFLUORIDE. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-FLUORIDE.

9.6.7 MDL study must be performed every six months and before the MDL for the instrument expires.

9.6.8 MDL data is pulled from a two year period.

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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 ($\overline{X}$):

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

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}):

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

11.3.1 Where:

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

X_i = Individual values 1 through i

n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

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

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 Extract Concentration:

11.7.1 The extract concentration is calculated relative to the calibration curve by the instrument software.

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:

$Conc_{spiked}$ = Concentration found in the spiked sample

$Conc_{unspiked}$ = Concentration found in unspiked sample

$Conc_{expected}$ = Expected concentration

11.9.3 Calculation of Dilution Factors

$$C \times D = F$$

11.9.3.1 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 13.6).

13 References

13.1 EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Rev. 2.1, August 1993

13.2 Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005.

13.3 EPD Laboratory Quality Assurance Plan, online revision.

13.4 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.

13.5 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.

13.6 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.7 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP, SOP 6-007, online revision.

13.8 GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 RL's for EPA 300.0

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
EPA 300.0	Chloride	10	mg/L
EPA 300.0	Sulfate	10	mg/L
EPA 300.0	Fluoride	0.20	mg/L

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 300.0

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 300.0	Chloride, Sulfate and Fluoride	Initial calibration for chloride, sulfate and fluoride	Calibration every 6 months or as needed.	Correlation coefficient (r) $\geq$ 0.995 linear regression	Correct problem then repeat initial calibration	
		Second source calibration Verification (ICV)	Prior to sample analysis or quarterly, whichever is sooner	All analytes within 10% of expected value	Correct problem then repeat initial calibration	
		Initial Calibration Blank (ICB)	Once per analytical run.	Area must be < 50% of the area of lowest standard.	Correct problem and 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 workdays	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 workdays	Area of linearity standards must not differ more than 10% from area of initial calibration standard area.	Correct problem and rerun linearity study or repeat initial calibration.	
		Low level CCC at reporting limit	Once per analytical run	Concentration within 50-150% of expected value	Correct problem then repeat initial calibration	
		Continuing Calibration Check (CCC)	Prior to sample analysis and after every 10 samples and at the end of the sample run.	Concentration within 10% of expected value	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.	Area must be < 50% of the area of lowest standard.	Correct problem then reanalyze CCB and all samples in affected batch	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 300.0

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 300.0	Chloride, Sulfate and Fluoride	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 3-009 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.4)	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 3-009 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.4)		
		Method Blank	One per batch	Area must be < 50% of the area of lowest standard.	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)	10% of all routine samples	QC Acceptance Criteria Table A.1, Appendix A	Evaluate out of control event, reanalyze or flag data	
		MDL Low level Spike (MDLS) 0.2 mg/L Fluoride 5.0 mg/L Sulfate 5.0 mg/L Chloride	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	Every six months 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	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 300.0

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 300.0	Chloride, Sulfate and Fluoride	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 for EPA Method 300.0- Common Anions in Water

Table A.1 – Current Control Limits – EPA 300.0

QC Type	Analyte	Accuracy (%R) LCL	UCL	Precision (%RPD)
LCS/LCSD				
	Chloride	90	110	15
	Sulfate	90	110	15
	Fluoride	90	110	15
MS/MSD				
	Chloride	90	110	15
	Sulfate	90	110	15
	Fluoride	90	110	15

***MS/MSD Control limits are static by EPA Method/EPD Lab default.**
***Control chart data generated from 01/01/2019-01/01/2021**

Appendix B – Procedure for ICS 6000(IC05) for EPA Method 300.0 Common 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 1.00 mL/min. Make sure pressure is building.

1.10 Turn on the eluent generator labeled "EGC KOH." Change setting to 23 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 3.1 V.

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: "A" for Anions and today's date of "F" for Fluoride 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 1. Then click next.
3.3 Set number of vials to 1, injection per vial to 1, injection volume to 25 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 “ANION-F Processing Method”.
3.7 Select browse for report template, then select, “ron hooper report temp (2)”.
3.8 Channel should be CD_1.
3.9 Click Finish.
3.10 Save sequence. Name sequence either “A” for Anions or “F” for Fluoride. Then add 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 25 µL. Instrument method should be “EPA 300.0”. Processing Method should be “ANION-F Processing Method”. 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 1 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 if 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 100 mg/L for Sulfate and Chloride and 5 mg/L for Fluoride.

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 logbook.

3.27 Volumes and amounts of reagents, chemicals and standards may be altered if final concentrations remain the same. Sample volumes and injection amounts may be altered if 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 1. Click, "Create" on top left corner. Then select "sequence" and "system 1."
4.7 Set number of vials to 1, injection per vial to 1, injection volume to 25 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, "EPA 300.0".
4.10 Select "ANION-F Processing Method" under processing method.
4.11 Select "ron hooper report temp (2)", under report template.
4.12 Channel should be CD_1.
4.13 Click "Next" and "Finish."
4.14 Name sequence with prefix "A" for Anions or "F" for Fluoride, 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- 06).
4.17 Click on data category tab.
4.18 Click processing folder on bottom of spreadsheet.
4.19 Select Processing Method "ANION-F Processing Method".
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 "ANION-F Processing Method".

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 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 Dionex IC04 for EPA Method 300.0- Common Anions in Water

1 Dionex IC04 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 department, 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 1. Then select Home tab.
1.9 Turn on pump by clicking the slider bar. Set flow to1.00 mL/min. Make sure pressure is building.
1.10 Turn on the eluent generator labeled "EGC KOH." Change setting to 23 mM.
1.11 In same box, turn on CR-TC
1.12 Turn on the detector by clicking the slider bar labeled CD Tot left.
1.13 Turn on the Suppressor by clicking the slider bar labeled Suppressor left. Change to 57 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 Dionex 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: "A" for Anions and today's date or "F" for Fluoride 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 (See 3.23).

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 10.4 for "Full instruction."

3 Dionex IC04 Full Instruction

3.1 Click "Create." Then click on sequence.

3.2 Select system 1. Then click next.

3.3 Set number of vials to 1, injection per vial to 1, injection volume to 25.0 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_1.

3.9 Click Finish.

3.10 Save sequence. Name sequence with prefix "A" for Anions or "F" for Fluoride. Then add 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 25 uL. Instrument method should be "EPA 300.0". Processing Method should be "Anions Processing Method 082913." 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 1 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 original chromatograms 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 if it is within 24 hours of the start of the original run. For Chloride and Sulfate analysis, 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 for the Chloride and/or Sulfate may differ from each other or 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 100 mg/L for Sulfate and Chloride and 5 mg/L for Fluoride.

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 **Dionex 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 1. Click, "Create" on top left corner. Then select "sequence" and "system 1."

4.7 Set number of vials to 1, injection per vial to 1, injection volume to 25 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 EPA 300.0.

4.10 Select Anions Processing Method 082913, under processing method.

4.11 Select Ron Hooper report temp 2, under report template.

4.12 Channel should be CD_1.

4.13 Click "Next" and "Finish."

4.14 Name sequence with prefix "A" for Anions or "F" for Fluoride, 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- 06).

4.17 Click on data category tab.

4.18 Click processing folder on bottom of spreadsheet.

4.19 Select Anion Processing Method 082913.

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 Operation 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 082913.
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 3-009.
4.35 A low, middle, and high standard should be analyzed to confirm linearity. Refer to section 8.3.2 in SOP 3-009.

Updates to Previous Version:
Appendices A, B & C added.
Updated for online revision.
Section 9
Table A.1
Table 14.3