NC DEQ/DWR WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION

LABORATORY NAME:		CERT #:	
PRIMARY ANALYST:		DATE:	
NAME OF PERSON COMPLETING CHECKLIST (PRINT):			
SIGNATURE OF PERSON COMPLETING CHECKLIST:			

Parameter: Anions by IC
Method: EPA 300.0, Rev. 2.1, 1993 (Aqueous and Non-Aqueous)

Equipment:

	Balance, capable of accurately weighing to the nearest 0.0001 g.		Anion separator column		Detector- Conductivity cell- approximately 1.25 µL internal volume
	Ion Chromatograph Analytical System including:		Anion analytical column:		Filters: 0.45 µm
	Anion guard column		Anion suppressor device		

Reagents: see recipes at the end of the checklist

	Reagent water- should contain particles not larger than 0.20 µm		Regeneration solution (if using a micro membrane suppressor)		
	Eluent solution		Stock standard solutions, 1000 mg/L		

PLEASE COMPLETE CHECKLIST IN INDELIBLE INK
Please mark Y, N or NA in the column labeled LAB to indicate the common lab practice and in the column labeled SOP to indicate whether it is addressed in the SOP.

	GENERAL	LAB	SOP	EXPLANATION
1	Is the SOP reviewed at least every 2 years? What is the most recent review/revision date of the SOP? [15A NCAC 2H .0805 (a) (7)] **Date:**			Quality assurance, quality control, and Standard Operating Procedure documentation shall indicate the effective date of the document and be reviewed every two years and updated if changes in procedures are made. Verify proper method reference. During review notate deviations from the approved method and SOP.
2	Are all revision dates and actions tracked and documented? [15A NCAC 2H .0805 (a) (7)]			Each laboratory shall have a formal process to track and document review dates and any revisions made in all quality assurance, quality control and SOP documents.
3	Is there North Carolina data available for review?			If not, review PT data
	PRESERVATION and STORAGE	**LAB**	**SOP**	**EXPLANATION**
4	What type of containers are used for sample collection? [40 CFR 136.3 Table II] **ANSWER:**			Polyethylene must be used for Fluoride Polyethylene, fluoropolymer, or glass must be used for Bromide, Chloride, Nitrate, Nitrite, Orthophosphate, and Sulfate
5	Are samples requiring the analysis of Nitrate, Nitrite, Orthophosphate, and Sulfate preserved at ≤6°C without evidence of freezing? [40 CFR 136.3 Table II]			Preservation not required if analyzed within 15 minutes. Bromide, Chloride and Fluoride do not require thermal preservation.
6	Are samples requiring the analysis of combined Nitrate+Nitrite, preserved to pH < 2 with H_2SO_4? [40 CFR 136.3 Table II]			
7	Are Orthophosphate samples filtered through a 0.45 µm filter within 15 minutes of collection? [40 CFR 136.3 Table II]			
8	Are Nitrate, Nitrite, and Orthophosphate samples analyzed within 48 hours of collection? [40 CFR 136.3 Table II]			

9	Are Bromide, Chloride, Fluoride, combined Nitrate+Nitrite, and Sulfate samples analyzed within 28 days of collection? [40 CFR 136.3 Table II]			
	INTERFERENCES	**LAB**	**SOP**	
10	Are sample dilution and/or fortification used to solve most interference problems associated with retention times? [EPA Method 300.0, Rev. 2.1 (1993), Section 4.1]			Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. 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.
11	If the water dip or negative peak is interfering with the fluoride peak, is the equivalent of 1 mL of concentrated eluent added to 100mL of each standard and sample? [EPA Method 300.0, Rev. 2.1 (1993), Section 4.2]			Concentration of 100X eluent recipe in the method.
12	Are samples that contain particles larger than 0.45 µm and reagents that contain particles larger than 0.20 µm filtered prior to injection? [EPA Method 300.0, Rev. 2.1 (1993), Section 4.4]			
	PROCEDURE – Instrument Calibration	**LAB**	**SOP**	**EXPLANATION**
13	Are IC operating parameters equivalent to those listed in Table 1A of the method established? [EPA Method 300.0, Rev. 2.1 (1993), Section 10.1]			See table at end of guide
14	Are calibration standards at a minimum of 3 concentration levels and a blank analyzed? [EPA Method 300.0, Rev. 2.1 (1993), Section 10.2]			
15	How are retention time windows determined? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.4] **ANSWER:**			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 the day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.
16	Are retention times recorded from the calibration curve? [EPA Method 300.0, Rev. 2.1 (1993), Section 10.3]			Using injections of 0.1-1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.
17	Does each standard curve have a correlation coefficient of greater than or equal to 0.995? [NC WW/GW LC Policy]			When linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified, then a minimum value of 0.995 (or a coefficient of determination, r^2, of 0.99) is required.

	PROCEDURE – Solid Sample Preparation	LAB	SOP	EXPLANATION
18	Is an amount of reagent water equal to 10X the dry sample weight added to the sample? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.7]			Section 11.7 states the following extraction should be used for solid materials. Add an amount of reagent water equal to 10 times the weight of dry solid material taken as a sample.
19	Is the slurry mixed for 10 minutes using a magnetic stirring device? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.7]			
20	Is the slurry filtered using a 0.45 µm membrane type filter? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.7]			
	PROCEDURE – Sample Analysis	**LAB**	**SOP**	**EXPLANATION**
21	Is the sample well mixed before injection? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.3]			
22	Is the same size loop used for standards and samples? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.3]			
23	Is the injection loop flushed thoroughly with each new sample? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.3]			
24	If the chromatogram fails to produce adequate resolution or if identification of a specific anion is questionable, is the sample fortified with standard and reanalyzed? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.6]			Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration may produce poor resolution or identification.
25	Is the sample analyzed at a dilution if the peak response exceeds the working range of the calibration curve? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.5]			If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.
26	If the determined value for the combined nitrate+nitrite exceeds 0.5 mg/L as N^-, is a resample analyzed for the individual concentrations of nitrate and nitrite? [EPA Method 300.0, Rev. 2.1 (1993), Section 8.2] **NOT REQUIRED.**			NC data receivers do not require any monitoring or reporting of Nitrite. If Nitrate reporting is required, the facility will have a separate monitoring requirement for it.
27	If more resolution is needed between peaks, is the eluent diluted? [EPA Method 300.0, Rev. 2.1 (1993), Section 11.9]			This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
28	Is a Method Detection Limit (MDL) established for all analytes? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.2.4]			MDLs must be established for all analytes.
29	How often is the MDL determined? [40 CFR 136 Appendix B] **ANSWER:**			Ongoing data accumulation and annual verification is required with the 2017 MUR that was made effective September 27, 2017
30	Is a Laboratory Fortified Blank (LFB) analyzed with each batch of samples? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.3.2]			LFB - An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine

				whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The method does not specify if the LFB is primary or second source. It is recommended that the LFB be prepared from a second source standard to satisfy NC WW/GW policy and sections 9.2.3 of the method. If prepared from a Primary source: a QCS (which is second source) will also be required each day samples are analyzed per NC WW/GW policy [see question #30]
31	What is the acceptance criterion for the LFB? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.3.2] **ANSWER:**			Method requires 90 - 110 % recovery
32	What corrective action is taken if the acceptance criterion is not met for the LFB? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.2.3] **ANSWER:**			If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.
33	Is a Quality Control Sample (QCS- second source standard) analyzed after each initial calibration prior to sample analysis? [15A NCAC 2H .0805 (a) (7) (H) (ii) and EPA Method 300.0, Rev 2.1 (1993), Section 3.12]			Laboratories shall analyze one known second source standard to verify the accuracy of standard preparation if an initial calibration is performed and in accordance with the referenced method requirements thereafter. If the LFB is prepared from a second source, the requirement is satisfied.
34	What is the acceptance criterion for the QCS? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.2.3.] **ANSWER:**			Method requires 90 - 110 % recovery
35	What corrective action is taken if the acceptance criterion is not met for the QCS? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.2.3] **ANSWER:**			If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.
36	Is a lower reporting limit standard analyzed or back-calculated with each analysis? [15A NCAC 2H .0805 (a) (7) (H)]			Laboratories shall analyze or back-calculate a standard at the same concentration as the lowest reporting concentration each day samples are analyzed.
37	What is the acceptance criterion for the lower reporting limit standard? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
38	What corrective action does the laboratory take if the lower reporting limit standard does not meet the acceptance criterion? [15A NCAC 2H .0805 (a) (7) (B)] **ANSWER:**			If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible. Recalibrate/re-verify the curve.

39	Is a Laboratory Reagent Blank (LRB) analyzed with each batch of samples? [EPA Method 300.0, Rev. 2.1 (1993), Sections 3.7 and 9.3.1]			An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
40	What is the acceptance criterion for the LRB? [15A NCAC 2H .0805 (a) (7) (H) (i)] **ANSWER:**			The concentration of reagent, method, and calibration blanks shall not exceed 50 percent of the lowest reporting concentration or as otherwise specified by the reference method. EPA Method 300.0, Rev. 2.1 (1993), Section 9.3.1 states that corrective actions must be taken for values that exceed the MDL. This is more stringent than the rule and is not required.
41	What corrective action is taken if the LRB does not meet acceptance criterion? [15A NCAC 2H .0805 (a) (7) (B)] **ANSWER:**			If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible.
42	Is a mid-range Instrument Performance Check (IPC) analyzed immediately following daily calibration, after every 10 samples, and at the end of analysis, and whenever the anion eluent is changed? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.3.4 and 10.4]			IPC - A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria. The method does not specify if the IPC is primary or second source. It is recommended the IPC be prepared from a primary source to satisfy NC WW/GW Policy. If the IPC is prepared from a secondary source, is the laboratory also analyzing a primary source verification standard after calibration and after every 10 samples? Also known as a Calibration Verification Standard per NC WW/GW LC Policy.
43	What is the acceptance criterion for the IPC? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.3.4] **ANSWER:**			±10% of true values
44	What corrective action is taken if the IPC does not meet acceptance criterion? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.3.4] **ANSWER:**			If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed.
45	Is a Calibration Blank analyzed immediately following daily calibration, after every 10 samples, and at the end of analysis? [EPA Method 300.0, Rev. 2.1 (1993), Sections 3.1 and 9.3.4]			Calibration Blank - A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.
46	What is the acceptance criterion for the Calibration Blank? [NC WW/GW Policy]			NC WW/GW LC Policy states: For analyses requiring a calibration curve, the concentration of reagent, method and calibration blanks must not exceed 50% of the reporting limit or as

	ANSWER:			otherwise specified by the reference method.
47	What corrective action is taken if the Calibration Blank does not meet acceptance criterion? [15A NCAC 2H .0805 (a) (7) (B)] **ANSWER:**			If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible.
48	Is a Laboratory Fortified Matrix (LFM) analyzed at a minimum frequency of 10% of samples? [EPA Method 300.0, Rev. 2.1 (1993), Sections 3.6 and 9.4.1]			LFM - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. Also known as a Matrix Spike per NC WW/GW LC Policy.
49	How is the LFM prepared? [NC WW/GW LC Policy and EPA Method 300.0, Rev. 2.1 (1993), Section 9.4.1] **ANSWER:**			The concentration must be high enough to be detected above the original sample and should not be less than 4 times the MDL. The added analyte concentration should be the same as that used in the LFB.
50	What is the acceptance criterion for the LFM? [EPA Method 300.0, Rev. 2.1 (1993), Section 9.4.3] **ANSWER:**			Use 80-120% until sufficient data becomes available to develop control limits. (Laboratory established limits must be within method limits) Note: guidance from EPA acknowledges that there is a typo in 9.4.2 that states the LFM range is 90-110%, that should refer to the LFB
51	What corrective action is taken if the LFM does not meet acceptance criterion? [EPA Method 300.0, Rev. 2.1 (1993), Sections 9.4.2 and 9.4.4] **ANSWER:**			If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.
52	Are five percent of samples analyzed in duplicate? [15A NCAC 2H .0805 (a) (7) (C)]			Except where otherwise specified in an analytical method, laboratories shall analyze five percent of all samples in duplicate to document precision. Laboratories analyzing fewer than 20 samples per month shall analyze one duplicate during each month that samples are analyzed. Analysis of a LFM duplicate may also fulfill this requirement.
53	What is the acceptance criterion for the duplicates? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses. Limits set by the laboratory

54	What corrective action is taken if the acceptance criterion for the duplicates is not met? [15A NCAC 2H .0805 (a) (7) (B)] **ANSWER:**			Any time quality control results indicate an analytical problem, the problem must be resolved and any samples involved must be rerun if the holding time has not expired.
55	Is the data qualified on the electronic Discharge Monitoring Report (eDMR) or client report if Quality Control (QC) requirements are not met? [15A NCAC 2H .0805 (a) (7) (B)]			If the sample cannot be reanalyzed, or if the quality control results continue to fall outside established limits or show an analytical problem, the results shall be qualified as such. If data qualifiers are used to qualify samples not meeting QC requirements, the data may not be useable for the intended purposes. It is the responsibility of the laboratory to provide the client or end-user of the data with sufficient information to determine the usability of the qualified data.
56	Is manual integration used? [NC WW/GW LC Policy]			
57	Are manually integrated anions clearly identified? [NC WW/GW LC Policy]			
58	Is the date performed and analyst performing the manual integration documented? [NC WW/GW LC Policy]			
59	Is the reason for manual integration documented? [NC WW/GW LC Policy]			A flag or qualifier code may suffice for simple manual integrations.
60	Are both the original and manually integrated instrument printouts, of similar scale, retained in the data package? [NC WW/GW LC Policy]			
61	Does the laboratory have a data validation procedure in place to assure manual integrations are technically sound? [NC WW/GW LC Policy]			

Eluent Solution: Sodium bicarbonate 1.7 mM, sodium carbonate 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium carbonate (Na_2CO_3) in reagent water and dilute to 2 L.

Regeneration solution (for a micro membrane suppressor): Sulfuric acid 0.025N. Dilute 2.8 mL conc. Sulfuric acid (H_2SO_4) to 4 L with reagent water.

Stock Standard Solutions 1000 mg/L: May be purchased or prepared using ACS reagent grade materials (dried at 105°C for 30 minutes).

Bromide 1000mg/L: Dissolve 1.2876 g sodium bromide (NaBr) in reagent water and dilute to 1 L.

Chloride 1000mg/L: Dissolve 1.6485 g sodium chlorate (NaCl) in reagent water and dilute to 1 L.

Fluoride 1000mg/L: Dissolve 2.2100 g sodium fluoride (NaF) in reagent water and dilute to 1 L.

Nitrate 1000mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$) in reagent water and dilute to 1 L.

Nitrite 1000mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$) in reagent water and dilute to 1 L.

Phosphate 1000mg/L: Dissolve 4.3937 g potassium phosphate (KH_2PO_4) in reagent water and dilute to 1 L.

Sulfate 1000mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4) in reagent water and dilute to 1 L

Stock standards are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

Additional Comments:

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Inspector: _____Date:_____

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART A)

Analyte	Peak #*	Retention Time (min)	MDL (mg/L)
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate-P	6	5.4	0.003
Sulfate	7	6.9	0.02

Standard Conditions:

Columns: as specified in Sesction 6.2.2.1
Detector: as specified in Section 6.2.4
Eluent: as specified in Section 7.3
Pump Rate: 2.0 mL/min.
Sample Loop: 50 µL

MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1 uMHO full scale.
*See Figure 1