NC DEQ/DWR WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION BRANCH

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

Parameter: Anions by IC
Method: SW-846 9056 A (Aqueous and Non-Aqueous)

Applicable to Chloride, Fluoride, Bromide, Nitrate, Nitrite, Orthophosphate and Sulfate

NOTE: To promote consistency with the use of SW-846 methods and to assure generation of data of known quality, the minimum recommended quality control benchmarks in the methods will be considered the minimum QA/QC requirements (i.e., **when the method says "should", we consider that to mean "must"**).

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: _____		Bomb with ≥ 300 mL capacity (SW-846 5050)

Reagents:

	Reagent water- should contain particles not larger than 0.20 µm		Regeneration solution (if using a micro membrane suppressor)		Sodium bicarbonate/sodium carbonate solution:
	Eluent solution:		Stock standard solutions, 1000 mg/L		White oil; refined (SW-846 5050)

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 review/revision dates and procedural edits 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? [SW-846 Chapter 3, Table 3-1] **Answer:**			Polytetrafluoroethylene (PTFE) or plastic must be used for Fluoride. PTFE, plastic or glass must be used for Bromide, Chloride, Nitrate, Nitrite, Orthophosphate, and Sulfate.
5	Are samples preserved at ≤6°C without evidence of freezing? [SW-846 9056A, Section 8.2]			Preserve samples at ≤ 6 °C.
6	Are Nitrate, Nitrite, and Orthophosphate samples analyzed within 48 hours of collection? [SW-846 9056A, Section 8.2]			

7	Are Bromide, Chloride, Fluoride and Sulfate samples analyzed within 28 days of collection? [SW-846 Chapter 3, Table 3-2]			
	INTERFERENCES	**LAB**	**SOP**	**EXPLANATION**
8	How are interference problems associated with retention times mitigated? [SW-846 9056A, Section 4.1] **Answer:**			Any species with a retention time similar to that of the desired anion will interfere. Large quantities of ions eluting close to the anion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present in industrial wastes. Two common species, formate and acetate, elute between fluoride and chloride.
9	If the water dip or negative peak is interfering with the fluoride peak, is the equivalent of 1 mL of concentrated eluent added to 100 mL of each standard and sample? [SW-846 9056A, Section 4.2]			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 (100 times more concentrated than the solution described in Sec. 7.3) to 100 mL of each standard and sample.
10	Are samples that contain particles larger than 0.45 µm and/or reagents that contain particles larger than 0.20 µm filtered prior to injection? [SW-846 9056A, Section 4.4]			Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems. The associated method blanks must also be filtered if any samples or reagents have undergone filtration.
	PROCEDURE – Solid Waste Sample Preparation	**LAB**	**SOP**	**EXPLANATION**
11	How are solid waste samples prepared? [SW-846 9056A, Section 1.1] **Answer:**			The method does not specify how the aqueous extract of solids are prepared. The SOP must describe a process that has been demonstrated to produce repeatable passing QC results. For guidance, and not required, EPA 300.0 does have instructions in Section 11.7- 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. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 µm membrane type filter. Alternatively, SW-846 5050 Bomb Preparation for Solid Waste may be used.
	PROCEDURE – Instrument Calibration	**LAB**	**SOP**	**EXPLANATION**
12	Are IC operating parameters equivalent to those listed in Table 1 of the method, or as recommended by the manufacturer? [SW-846 9056A, Section 10.1]			
13	Is a blank, and calibration standards at a minimum of 3 concentration levels, analyzed for each analyte of interest? [SW-846 9056A, Section 10.2]			For each analyte of interest, prepare a blank, and calibration standards at a minimum of three concentrations by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. A sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards must be representative of a concentration at or below the laboratory's lower reporting limit.

				The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector.
14	Are calibration standards analyzed in order of increasing concentration? [SW-846 9056A, Section 10.4]			After a stable baseline is obtained (approximately 30 min), begin to inject standards starting with the lowest concentration standard and increasing in concentration to the highest standard. Use a fixed injection volume between 25 and 100 µL (determined by injection loop volume) for each calibration standard. Record the peak area responses and retention times for each analyte.
15	Are peak area responses and retention times recorded for each analyte? [SW-846 9056A, Section 10.4]			See explanation above.
16	How are retention time windows determined? [SW-846 9056A, Section 11.2.4] **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 and may include concentrations from both ends of the calibration range. 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.
17	Does each standard curve have a correlation coefficient of greater than or equal to 0.995? [SW-846 9056A, Section 10.5]			Establish the individual analyte calibration curves by plotting the peak area responses for each standard against the corresponding concentrations. Use a least squares linear regression to calculate the calibration curve formula. The linear correlation coefficient should be equal to or greater than 0.995. A weighted least squares regression may also be performed using 1/concentration or $1/(concentration)^2$ as the weighting factor. The acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher. Refer to Method 8000 for additional guidance on calibration procedures.
18	Is the initial calibration curve verified with an Initial Calibration Verification (ICV) standard? [SW-846 9056A, Section 10.6]			Verify the accuracy of the initial calibration curve by analyzing an initial calibration verification (ICV) standard.
19	Is the ICV standard prepared from a second source at a concentration at or near the mid-range of the calibration curve? [SW-846 9056A, Section 10.6]			The ICV standard must be prepared from an independent (second source) material at or near the mid-range of the calibration curve.
20	What is the acceptance criterion for ICV standard? [SW-846 9056A, Section 10.6] **Answer:**			The acceptance criteria for the ICV standard must be no greater than ± 10% of its true value.
21	What corrective action is taken if the ICV standard recovery is outside of established acceptance criterion? [15A NCAC 2H .0805 (a) (7) (B)] [SW-846 9056A, Section 10.6] **Answer:**			Rule: 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. 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. 90506A: If the calibration curve cannot be verified within the specified limits, the cause must be determined, and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file

				with the sample analysis data.
	PROCEDURE – Sample Analysis	**LAB**	**SOP**	**EXPLANATION**
22	What is done if more resolution is needed between peaks? [SW-846 9056A, Section 4.1] **Answer:**			Separation can be improved by adjusting the eluent concentration and/or flow rate.
23	Are sample dilutions made with eluent? [SW-846 9056A, Sections 11.1.3 and 11.2.5]			Aqueous extracts of solids and oils from the bomb would be diluted with water and all other aqueous samples would be diluted with eluent. 11.1.3 - Any dilutions required in analyzing other water samples should be made with the eluent solution. 11.2.5 - If the peak area response exceeds the working calibration range, then dilute the sample with an appropriate amount of reagent water (for extracts from bomb combustion) or eluent (for straight aqueous samples) and reanalyze.
24	If the water dip or negative peak is interfering with the fluoride peak, is the equivalent of 1 mL of concentrated eluent (100 times more concentrated than the solution described in Section 7.3) added to 100mL of each standard and sample? [SW-846 9056A, Section 4.2]			
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
25	Does the lab perform IDOCs for new staff or when significant instrumentation changes are made? [SW-846 9056A, Section 9.2]			Each laboratory must demonstrate initial proficiency with the sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 D Section 9.3 for information on how to accomplish an initial demonstration of proficiency.
26	What is the Lower Limit of Quantitation for each analyte? [SW-846 9056A, Section 10.2] **Answer:**			The laboratory should establish the LLOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements.
27	Are recoveries for LLOQ standards analyzed or back-calculated within 50% of their true values? [SW-846 9056A, Section 10.2]			Analysis of a standard prepared at the LLOQ concentration levels or use of the LLOQ concentration as the lowest point calibration standard and then back-calculated against the curve provides confirmation of the established sensitivity of the method. The LLOQ recoveries must be within 50% of the true values to verify the data reporting limit.
28	Is a Continuing Calibration Verification (CCV) standard prepared from the same source as the calibration standards			Verify the accuracy of the working calibration curve on each working day, or whenever the

	and at a concentration at or near the mid-range of the calibration curve? [SW-846 9056A, Section 10.7]			anion eluent composition or strength is changed, and for every batch of 10 or less samples, through the analysis of a continuing calibration verification (CCV) standard. The CCV should be made from the same material as the initial calibration standards at or near mid-range.
29	Is a CCV standard analyzed after every tenth sample and at the end of the sample group? [15A NCAC 2H .0805 (a) (7) (H)]			A calibration blank and calibration verification standard shall be analyzed prior to sample analysis, after every tenth sample, and at the end of each sample group, unless otherwise specified by the method, to check for carryover and calibration drift.
30	Is a CCV standard analyzed whenever eluent composition or strength is changed? [SW-846 9056A, Section 10.7]			See explanation from Question 28.
31	Is a method blank analyzed with each batch of samples? [SW-846 9056A, Section 9.3] [SW-846 Chapter 3, Section 3.1]			9056A: At a minimum, the laboratory should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch. Any method blanks, matrix spike samples, replicate samples and LCSs should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples. Chapter 3: Method blank: A volume of reagent water equal to that used for aqueous samples, or, otherwise, a clean, empty container, equivalent to that used for actual solid samples, processed through each sample preparation and determinative procedure. Analysis of a method blank is used to assess contamination from the laboratory environment, sample processing equipment, and/or reagents.
32	If any samples were filtered to address interferences, is a filtered method blank analyzed? [SW-846 9056A, Section 9.3] [SW-846 Chapter 3, Section 3.1]			See explanation above.
33	What is the acceptance criterion of the method blank? [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.
34	What corrective action is taken if the blanks do 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.
35	Is a Laboratory Control Sample (LCS) analyzed daily? [SW-846 9056A, Section 9.3.2]			A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume.
36	How is the LCS prepared? [SW-846 9056A, Section 9.3.2] **Answer:**			The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate.
37	What is the acceptance criterion for the LCS? [SW-846 9056A, Section 9.3.2] **Answer:**			In the absence of historical data or well-defined MQOs/DQOs, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data must be no wider that ± 20%.
38	What corrective action is taken if the acceptance criterion is			If the LCS result is not acceptable, then the LCS must be reanalyzed once. If the results

	not met for the LCS? [SW-846 9056A, Section 9.3.2] **Answer:**			are still unacceptable, then all samples analyzed after the last acceptable LCS must be reprepared and reanalyzed.
39	Is a Calibration Blank analyzed immediately following daily calibration, after every 10 samples, and at the end of analysis? [15A NCAC 2H .0805 (a) (7) (H)]			A calibration blank and calibration verification standard shall be analyzed prior to sample analysis, after every tenth sample, and at the end of each sample group, unless otherwise specified by the method, to check for carryover and calibration drift.
40	What is the acceptance criterion for the Calibration Blank? [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.
41	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. 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.
42	Is a Matrix Spike (MS) analyzed with each batch of samples? [SW-846 9056A, Section 9.3.3]			Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.
43	How is the MS prepared? [NC WW/GW LCB Matrix Spike Technical Assistance.] **Answer:**			See Matrix Spike Technical Assistance document.
44	Is the volume of spike solution added to the sample ≤ 5% of the total volume? [NC WW/GW LCB Matrix Spike Policy]			The volume of spike solution used in MS preparation must in all cases be ≤ 5% of the total MS volume.
45	If the volume of spike solution added to the sample is greater than 1% of the total volume, is the recovery calculation adjusted? [NC WW/GW LCB Matrix Spike Policy]			It is preferable that the spike solution constitutes < 1% of the total MS volume so that the MS can be considered a whole volume sample with no adjustment (i.e., volume correction) by calculation necessary. If the spike solution volume constitutes >1% of the total sample volume, the sample concentration must be adjusted by calculation.
46	What is the acceptance criterion for the MS? [SW-846 9056A, Section 9.3.3.2]			The method control limits for % Recovery are 80 - 120. Alternate limits may be used provided that they meet the data quality objectives of the specific project.

	Answer:			
47	What corrective action does the laboratory take if the MS results are outside of established control limits for **accuracy**? [15A NCAC 2H .0805 (a) (7) (B)] [SW-846 9056A, Section 9.3.3.2] **Answer:**			Rule: 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. 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. 9056A: Failure to meet the MS % Recovery criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem. If %R is outside the control limits and all other QC data is within limits, a matrix effect is suspected. The associated data should be flagged according to project specifications or noted in the comments section of the report.
48	Is a sample duplicate or matrix spike duplicate analyzed with each batch of 20 or fewer samples? [SW-846 9056A, Section 9.3.3.3] [15A NCAC 2H .0805 (a) (7) (C)]			A duplicate or matrix spike duplicate (MSD) should be analyzed within every analytical batch in order to establish the precision of the method. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair. 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. NOTE: A matrix spike duplicate can satisfy our Rule requirement for a sample duplicate but should be analyzed at the same frequency as the MS.
49	What is the acceptance criterion **for precision** between sample duplicates or MS/MSD (i.e., relative percent difference)? [SW-846 9056A, Section 9.3.3.3] **Answer:**			The method control limit for RPD is 15% for all sample concentrations that are near or above the mid-range of the calibration curve. The method control limit for RPD is 50% for sample concentrations that are near the low-range of the calibration curve. Alternate limits may be used provided that they meet the data quality objectives of the specific project.
50	When is manual integration used? [NC WW/GW LCB Manual Integration Policy] **Answer:**			Under no circumstances will manual integration be performed solely for the purpose of meeting quality control criteria, nor is it to be used as a substitute for proper sample preparation (e.g., cleanup), proper instrument optimization or maintenance on the chromatographic system. Corrective actions, with regard to the instrumentation for computer software, must be taken if manual integrations become common for an analysis or an instrument that normally uses automated peak integration. Examples of inappropriate manual integration may include the following: • Peak trimming, shaving or clipping

				• Peak enhancement • Baseline elevated above the signal • Baseline dropped below the signal • Improper peak identification • Selectively adjusting integration events • Insufficient sensitivity Problematic compounds must be specifically addressed in the method Standard Operating Procedure (SOP) and have detailed quantitation instructions. Supporting data (i.e., duplicates, dilutions, second column confirmation or second method confirmation) may be required to settle borderline cases. In some instances, the affected data may have to be reported as estimated.
51	Are manually integrated anions clearly identified? [NC WW/GW LCB Manual Integration Policy]			When manual integration is employed, the laboratory must clearly identify manually integrated compounds, document the reason the manual integration was performed, the date performed and who completed the work.
52	Is the date performed and analyst performing the manual integration documented? [NC WW/GW LCB Manual Integration Policy]			See above.
53	Is the reason for manual integration documented? [NC WW/GW LCB Manual Integration Policy]			A flag or qualifier code may suffice for simple manual integrations.
54	Are both the original and manually integrated instrument printouts, of similar scale, retained in the data package? [NC WW/GW LCB Manual Integration Policy]			In addition, a hardcopy printout of the data displaying the manual integration shall be included in the raw data package (i.e., both the original and manually integrated chromatograms, of similar scale, must be present in the data package). All information necessary for the historical reconstruction of data must be maintained by the lab.
55	Does the laboratory have a data validation procedure in place to assure manual integrations are technically sound? [NC WW/GW LCB Manual Integration Policy]			Additionally, the laboratory must employ a systematic data validation procedure to check manual integrations to assure integrations are technically sound and representative of the response.
56	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 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. 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.

Additional Comments:

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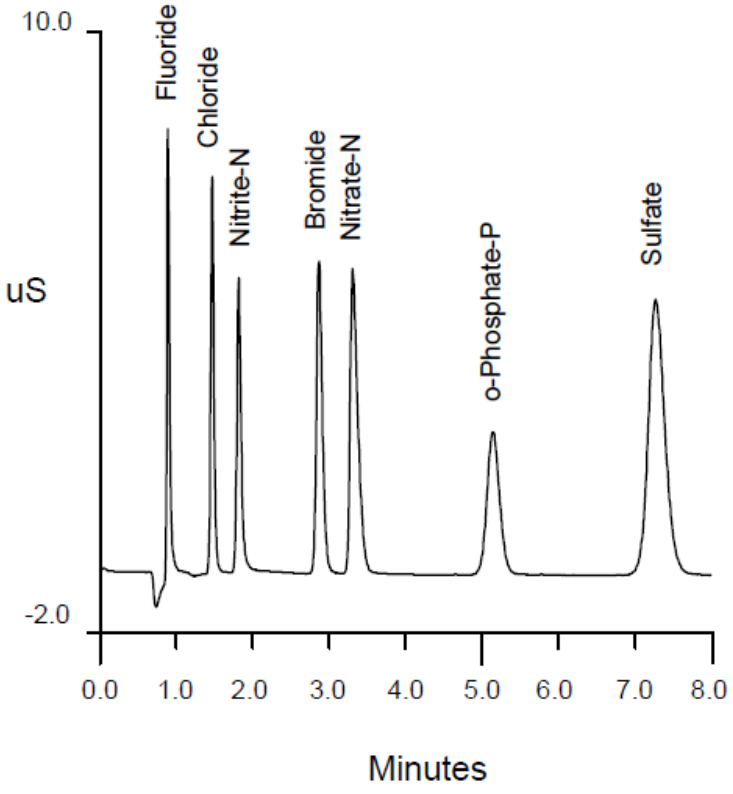
Inspector: _____Date:_____

FIGURE 2

EXAMPLE ANION PROFILE



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