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: **Ammonia Nitrogen**
Method: **Standard Methods 4500 NH_3 D – 2021 (Aqueous)**

Sample distillation is not required for this method. 40 CFR 136.3 Table IB footnote 6 states that manual distillation will be required to resolve any controversies.

EQUIPMENT:

	Ammonia Selective Electrode **Model:**		pH Meter/or Specific Ion Meter
	Magnetic stirrer, thermally insulated, with TFE-coated stirring bar		

ANALYSIS REAGENTS:

	Ammonia-free water
	Sodium hydroxide (NaOH), 10*N*
	NaOH/EDTA solution, 10*N*
	Stock ammonium chloride solution
	Standard ammonium chloride solutions
	ISA – Color indicator (see #30)

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 02H .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 02H .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	Are samples preserved at time of collection with H_2SO_4 to pH of <2 S.U.? [40 CFR 136.3 Table II]			Preservation not required if analyzed within 15 minutes.
5	Are samples checked for Total Residual Chlorine (TRC) at the time of collection and prior to pH preservation adjustment? [SM 4500-NH_3 A-2021 (2) and NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			Residual chlorine reacts with ammonia; remove by sample pretreatment. If a sample is likely to contain residual chlorine, immediately upon collection, treat with dechlorinating agent as in 4500-NH_3.B.3*d*. TRC strips or DPD powder may be used.
6	Is TRC neutralized at time of sample collection if necessary? [SM 4500-NH_3 A-2021 (2)]			4500-NH_3.B.3*d* : 3.5 g Sodium thiosulfate ($Na_2S_2O_3$ • $5H_2O$) in water and dilute to 1 L. Use 1 mL reagent to remove 1 mg/L residual chlorine in 500-mL sample.
7	Are samples checked for total residual chlorine upon receipt in the lab? [NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			Dechlorinating agents used at the time of sampling must be documented to have been effective (either by the sample collector or the receiving laboratory) by verifying a chlorine residual <0.5 mg/L at a neutral pH. If measuring chlorine

				concentration in an acidified sample, pour off a small portion of the sample and neutralize the pH prior to testing. Use sufficiently strong base to not dilute the sample. Discard that portion after testing.
8	What action is taken if chlorine is present? [15A NCAC 02H .0805 (a) (7) (M)] **Answer:**			If another sample cannot be collected, dechlorinate the sample and notify NC WW/GW Certification Branch that a non-compliant sample was received.
9	Is the residual chlorine check and any necessary mitigation documented? [NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			
10	Are samples iced to above freezing but ≤ 6 ºC during shipment? [40 CFR 136.3 Table II and footnote 18 and NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			40 CFR footnote 2 allows 15 minutes for sample preservation, including thermal. This means that if a sample is received in the lab within 15 minutes it is not required to be on ice. Document temperature downward trend for short transport samples. Note: sealed ice packs are not acceptable.
11	Is pH checked to document pH <2 S.U. upon receipt? [15A NCAC 02H .0805 (a) (7) (M)]			pH paper may be used
12	What action is taken if pH is >2 S.U.? [15A NCAC 02H .0805 (a) (7) (M)] **Answer:**			If another sample cannot be collected, analyze immediately or adjust pH to <2 S.U. and notify NC WW/GW Certification Branch that a non-compliant sample was received.
13	Are samples refrigerated above freezing to 6 °C during storage? [40 CFR 136.3 Table II and footnote 18]			
14	Are samples analyzed within 28 days of collection? [40 CFR 136.3 Table II]			
	PROCEDURE – Meter Calibration	**LAB**	**SOP**	**EXPLANATION**
15	What is the laboratory's reporting limit? [15A NCAC 02H .0805 (a) (7) (H)] **Answer:**			For analytical procedures requiring analysis of a series of standards, the concentrations of these standards shall bracket the range of the sample concentrations measured. One of the standards shall have a concentration equal to or less than the laboratory's lowest reporting concentration for the parameter involved. Generally, electrode methods are not accurate below 0.1 mg/L.
16	**List the values of standards used for the <u>daily</u> calibration:** [15A NCAC 02H .0805 (a) (7) (H) (iii)] **Answer:**			Rules: For electrode analyses, a series of two or more non-zero standards shall be used. Calibration must be performed each day samples are analyzed. Caution: If a two-point calibration is performed, the difference in concentration between the standards should not be greater than tenfold. A multipoint calibration is also acceptable. This can be either as a direct calibration, or the values obtained may be calculated in a linear regression formula to obtain the best fit straight line. Remember we certify for Ammonia as Nitrogen not Ammonia. Be sure to check the standards to be sure they are using the correct NH_3–N concentration not the NH_3 concentration. Preparation of standards in Standard Methods: all the methods refer back to SM 4500 NH_3 D section (3)(d) which states: stock ammonium chloride solution: Dissolve 3.819 g anhydrous NH_4Cl (dried at 100° C) in water and dilute to 1000 mL. **1.00 mL = 1.00 mg N = 1.22 mg NH_3** That solution equals a 1000 mg/L concentration of Ammonia as Nitrogen. The difference between the 1000 and 1220 can be calculated from the molecular weights, N = 14 and NH_3 = 17. So 17÷14 = 1.22. That is where you get a concentration

				of 1.0 mg/L for Ammonia as Nitrogen (N) and 1.22 mg/L for Ammonia (NH_3).
17	Are standards analyzed from lowest to highest? [SM 4500 NH_3 D-2021 (4) (b)]			
18	For concentrations ≤1 mg/L NH_3-N, are readings allowed to stabilize for at least 2 to 3 minutes? [SM 4500 NH_3 D-2021 (4) (b)]			
19	Are curves plotted using Ammonia concentration versus potential (mV) developed? [SM 4500 NH_3 D-2021 (4) (c)]			No is an acceptable answer - either plot a curve or **use a direct reading from the meter if available.** A millivolt vs. concentration plot is made on semi-logarithmic graph paper or a spreadsheet. It is more preferable to calculate a manual linear regression of the log of the standard conc. versus mV response to obtain the slope and intercept. Sample results are then converted to mg/L using the following equation: Conc. = antilog of [sample mV x slope + intercept]
20	Is the slope documented? [15A NCAC 02H .0805 (a) (7)]			For Ammonia, a true curve is not created. Instead, it creates a point-to-point straight line between the calibration standards. And **since it is not a true curve, calculation of the correlation coefficient is not required because there isn't one**. Instead, we require calculation and documentation of the slope because it is a straight line rather than a curve.
21	What is the acceptable slope range? [Manufacturer's instruction manual and [SM 4500 NH_3 D-2021 (4) (c)] **Answer:**			If the electrode is functioning properly a tenfold change of NH3-N concentration produces a potential change of about 59 mV. Slope of tenfold millivolt change (i.e., difference in millivolt readings between one standard and another with a concentration ten times greater than the first standard) should be within manufacturer's requirement (generally -54 to -60 mV). The millivolt change may vary from the given ranges depending on the concentration of the standards used. It is harder to achieve with 0.1 and 1.0 mg/L standards, should be routine for 1 and 10 mg/L. If the calibration range is two decades (e.g., 0.1 to 10 mg/L), the difference in mV between the upper and lower standard should be 108 to 120 mV.
	PROCEDURE – Sample Analysis	**LAB**	**SOP**	**EXPLANATION**
22	What sample volume is analyzed? [SM 4500 NH_3 D-2021 (4) (e)] **Answer:**			100 mL - if necessary, dilute sample to bring into the range of the calibration curve. Use same low speed stirring rate for standard solutions and samples.
23	Are samples allowed to come to room temperature before analysis? [SM 4500 NH_3 D-2021 (4) (b)]			Use standard solutions and samples that have the same temperature (about 25°C).
24	Is the stirring speed limited to minimize loss of ammonia and maintained at the same rate during calibration and sample analyses? [SM 4500 NH_3 D-2021 (4) (b)]			Limit the stirring speed to minimize a possible loss of ammonia from the solution. Maintain the same stirring rate and a temperature of about 25 °C throughout calibration and testing procedures.
25	Is 10*N* NaOH added to all blanks, standards, and samples to raise the pH above 11 S.U. **after** immersing the electrode? [SM 4500 NH_3 D-2021 (4) (b)]			Add NaOH after immersing the electrode because ammonia may be lost from a basic solution. NH_3 is in a gaseous state at pH>11 S.U.
26	Is 10*N* NaOH/EDTA used in place of the NaOH if the presence of silver or mercury is possible? [SM 4500 NH_3 D-2021 (4) (b)]			If historical data shows the presence of silver or mercury is possible, NaOH/EDTA must be used to elevate the pH. However, compilation of this data is not required.
27	Is the volume of 10*N* NaOH or NaOH/EDTA solution added to the blanks, standards, and samples documented? [SM 4500 NH_3 D-2021 (4) (e)]			1 mL is usually sufficient. Orion's ISA solution (Ionic Strength Adjuster) states to use 2 mL.
28	If a different volume of NaOH is added to the sample than to the calibration standards, is a correction made to the result? [SM 4500-NH_3 D-2021 (5)]			If a different volume of pH adjuster is needed for the sample, the following formula is used: mg NH_3–N/L = A x B x $\frac{(100 + D)}{(100 + C)}$ A = Dilution Factor

				B = Concentration of NH_3-N/L, mg/L, from calibration curve C = Volume of 10*N* NaOH added to the calibration standards, mL D = Volume of 10*N* NaOH added to sample, mL
29	Is the adjusted pH verified and documented? [SM 4500 NH_3 D-2021 (4) (b) and 15A NCAC 2H .0805 (a) (7)]			The pH must be raised above 11 S.U. If the purchased ISA is used, the sample will turn blue when the pH is greater than 11. No further verification is required, but the pH > 11 must be documented. If the lab uses 10*N* NaOH (made or bought) without color indicator, the pH must be verified to be greater than 11 with either a pH meter or pH strips. This must also be documented. In either case, a check box indicating the pH is > 11 S.U. may be used.
30	How is the adjusted pH verified? **Answer:**			Color indicator, pH meter (calibrated with buffer >11 S.U.), pH strips. Phenolphthalein is not a suitable color indicator since the color is pink from 8.3 to 10 S.U., but slowly disappears until colorless at pH 13 S.U. Thymolphthalein is the indicator Orion uses.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
	Skip to 34 if point-to-point calibration is performed			
31	Is each calibration standard back-calculated and evaluated each time a standard curve is prepared? [SM 4020 B-2022 (1) (b)]			Compare each calibration point to the curve and recalculate its concentration.
32	What are the acceptance criteria for the back-calculated standards? [SM 4020 B-2022 (1) (b)] **Answer:**			If any recalculated values are not within the method's acceptance criteria—up to twice the MRL ±50%; between 3 and 5 times the MRL ±20%; or greater than 5 times the MRL ±10%—unless otherwise specified in individual methods, identify the source of any outlier(s) and correct before sample quantitation.
33	What corrective action is taken if any back-calculated result exceeds the acceptance criterion? [15A NCAC 02H .0805 (a) (7) (B)] **Answer:**			
34	Does the laboratory analyze a standard at the reporting limit each day samples are analyzed? [15A NCAC 02H .0805 (a) (7) (H) and SM 4020 B-2022 (9)]			The reporting limit is the lowest standard concentration.
35	What is the acceptance criterion of the reporting limit standard? [15A 02H NCAC .0805 (a) (7) (A)] **Answer:**			
36	What corrective action is taken if the reporting limit standard recovery is outside of established control limits? [15A NCAC 02H .0805 (a) (7) (B) and SM 4020 B-2022 (9)] **Answer:**			**SM states:** With each analytical batch, analyze a reagent-water sample spiked at MRL and ensure that it meets MRL acceptance criteria (generally ±50%). If not, reanalyze the entire batch or flag results for all samples in the batch. If the MRL is biased high, nondetect (ND) samples can be reported with flags if the method or regulation allows.

37	Is a reagent/method blank analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (5)]			The reagent/method blank contains the same acid used to preserve samples and is carried through all sample preparatory steps (this would include the distillation step when applicable). **SM states:** As a minimum, include one reagent blank with each sample set (batch) or on a 5% basis, whichever is more frequent.
38	Is the reagent/method blank concentration less than or equal to ½ the lowest reporting concentration? [15A NCAC 02H .0805 (a) (7) (H) (i)]			**Rule:** 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. **Note:** The meter must be allowed to stabilize until the reading is ≤ ½ the reporting limit. Documenting <RL does not demonstrate the acceptance criterion has been met. **SM states:** Any constituent(s) recovered must generally be less than or equal to one-half the reporting level (unless the method specified otherwise).
39	What corrective action is taken if the reagent/method blank is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] **Answer:**			Our Rule requires corrective action any time quality control results indicate a problem.
40	Is the calibration verified by analyzing a calibration verification standard (CVS) or Continuing Calibration Verification (CCV) prior to sample analysis, after every ten samples and at the end of the run? [SM 4020 B-2022 (1) (c) and 15A NCAC 02H .0805 (a) (7) (H)] **List value(s) of standard used:**			**Rules state:** 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. **SM states:** Verify calibration by analyzing one standard whose concentration is near the midpoint of the calibration range.
41	What is the acceptance criterion for the calibration standard? [15A NCAC 02H .0805 (a) (7) (A) and SM 4020 B-2022 (1) (c)] **Answer:**			The results must be within allowable deviations from either initial-calibration values or specific points on the calibration curve.
42	Does the laboratory take appropriate corrective action if the calibration standard does not meet the acceptance criterion? [SM 4020 B-2022 (1) (c)]			If the CCV is out of control, then take corrective action – including re-analysis of any samples analyzed since the last acceptable CCV.
43	Is the calibration verified by analyzing a calibration blank prior to sample analysis, after each batch of ten samples and at the end of the run? [15A NCAC 02H .0805 (a) (7) (H)]			The calibration blank is equivalent to the reagent/method blank unless samples are distilled. If samples are distilled, the method blank is distilled, but the calibration blank is not. **Rules state:** 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.
44	What is the acceptance criterion for the calibration blank? [15A NCAC 02H .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.

45	Does the laboratory take appropriate corrective action if the calibration blank results are greater than one-half the lowest reporting concentration? [15A NCAC 02H .0805 (a) (7) (B)]			
46	Does the laboratory analyze a second source standard to verify standard preparation? [SM 4020 B-2022 (1) (b) and 15A NCAC 02H .0805 (a) (7) (H) (ii)] **True value of standard:**			A second source standard must be analyzed at least initially to confirm the accuracy of the standard preparation. The required Laboratory Fortified Blank (LFB) may serve as the second source standard (refer to question #49) **SM states:** Verify the initial calibration by analyzing a standard prepared from a different stock standard than that used to create the calibration curve; its concentration should be near the midpoint of the calibration range. The analytical results for this second-source midrange standard must be within 10% of its true value.
47	What is the acceptance criterion for the second source standard? [SM 4020 B-2022 (1) (b)]? **Answer:**			The analytical results for this second source mid-range standard must be within 10% of its true value.
48	What corrective action is taken if the second source standard recovery is outside of established control limits? [15A NCAC 02H .0805 (a) (7) (B) and SM 4020 B-2022 (1) (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. **SM states:** If not, determine the cause of the error, take corrective action and re-verify the calibration. If the re-verification passes, continue the analyses; otherwise, repeat the initial calibration.
49	Does the laboratory analyze a laboratory-fortified blank (LFB) at least daily or per batch of 20 or fewer samples? [SM 4020 B-2022 (6)] **True value:**			As a minimum, include one LFB with each sample set (batch) or on a 5% basis, whichever is more frequent. Depending on method requirements, prepare the addition solution from either the same reference source used for calibration or an independent source. The LFB is a reagent blank (i.e., treated just like a sample including addition of the preservation acid) fortified with the analyte. If the LFB is **primary source**, it may be equivalent to the CVS (refer to question #40). Analyze at least one daily or per batch of 20 or fewer samples. Use control charts to establish limits or default to the CVS acceptance criterion. If the LFB is **secondary source**, it may be equivalent to the second source standard (refer to question #46). Analyze one daily or per batch of 20 or fewer samples. The acceptance criterion must be recovery within ± 10% of true value.
50	What is the acceptance criterion of the LFB? [15A NCAC 02H .0805 (a) (7) (A) and SM 4020 B-2022 (1) (b) and (6)] **Answer:**			If used as the second source verification, the acceptance criterion must be recovery within ± 10% of true value. Otherwise, evaluate the LFB for percent recovery of the added analytes by comparing results to method-specified limits, control charts, or other approved criteria.
51	What corrective action is taken if the LFB recovery is outside established control limits? [15A NCAC 02H .0805 (a) (7) (B) and SM 4020 B-2022 (6)] **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.

				SM states: If LFB results are out of control, take corrective action, including re-preparation and re-analysis of associated samples if required.
52	Is a Laboratory Fortified Matrix (LFM) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (7) and Table 4020:I]			**SM (7) states:** If an LFM is feasible and the method does not specify LFM frequency requirements, then include at least one LFM with each sample set (batch) or on a 5% basis, whichever is more frequent. Laboratory fortified matrix is the same as a matrix spike; that is, a spiked sample.
53	Is a Laboratory Fortified Matrix Duplicate (LFMD) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (8) and Table 4020:I]			**SM (8) states:** As a minimum, include one duplicate sample or one LFM duplicate with each sample set (batch) or on a 5% basis, whichever is more frequent, and process it independently through the entire sample preparation and analysis Laboratory fortified matrix is the same as a matrix spike; that is, a spiked sample. **Note: Based on Table 4020:I, no option to perform an environmental sample duplicate and then spike separately – must perform MS/MSD for this method.**
54	How is the LFM (spike) prepared? [SM 4020 B-2022 (7) and NC WW/GW LCB Matrix Spiking Policy] **Answer:**			See Matrix Spike Technical Assistance document. **SM states:** Add a concentration that is at least 10 x MRL, less than or equal to the midpoint of the calibration curve, or method-specified level to the selected sample(s). The analyst should use the same concentration as for LFB (4020 B.6) to allow analysts to separate the matrix's effect from laboratory performance. **Prepare LFM from the same reference source used for LFB.** Make the addition such that sample background levels do not adversely affect recovery (preferably adjust LFM concentrations if the known sample is more than 5 times the background level). At a minimum, the spike must at least equal the background concentration, unless the method specifies otherwise. For example, if the sample contains the analyte of interest, then add approximately as much analyte to the LFM sample as the concentration found in the known sample. **NC Policy states**: The volume of spike solution used in MS preparation must in all cases be ≤5% of the total MS volume. 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.
55	What is the acceptance criterion for LFM/LFMD recovery? [SM 4020 B-2022 (7)] **Answer:**			There will be two % recovery calculations for accuracy from spike recoveries and one RPD calculation for precision from duplicate calculation. **SM states:** Evaluate LFM results for percent recovery; if they are not within control limits, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported. See method for specific LFM acceptance criteria until the laboratory develops statistically valid, laboratory-specific performance criteria. If the method does not provide limits, use the calculated preliminary limits from the IDC (4020 B.3). LFM control limits may be wider than for LFB or LCS, and batch acceptance generally is not contingent upon LFM results.
56	What corrective action does the laboratory take if the LFM/LFMD results are outside of established control limits for **accuracy**? [SM 4020 B-2022 (7) and 15A NCAC 02H .0805 (a) (7) (B)]			**Rules state:** 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

	Answer:			reanalyzed, if possible. Compare to LFB result and other QC. Reanalyze LFM. If it still fails, qualify the spiked sample result. **SM states**: Evaluate LFM results for percent recovery; if they are not within control limits, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported.
57	What is the acceptance criterion for the precision of the LFM/LFMD? [SM 4020 B-2022 (8)] **Answer:**			**SM states:** See method for specific acceptance criteria for LFM duplicates or duplicate samples until the laboratory develops statistically valid, laboratory-specific performance criteria. If the method does not provide limits, use the calculated preliminary limits from the IDC.
58	What corrective action does the laboratory take if the LFM/LFMD results are outside of established control limits for **precision**? [15A NCAC 02H .0805 (a) (7) (B) and SM 4020 B-2022 (8)] **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. **SM states:** If duplicate results are out of control, then re-prepare and re-analyze the sample and take additional corrective action, as needed.
59	Are results qualified to indicate quality control failures or sample anomalies when reporting results? [15A NCAC 02H .0805 (e) (5)]			Reported data associated with quality control failures, improper sample collection, holding time exceedances, or improper preservation shall be qualified as such.

Additional Comments:

Stock Standard – Dissolve 3.819 g anhydrous NH_4CL (dried at 100 ºC) in ammonia-free water and dilute to 1000 mL.
1.00mL = 1.00 mg N = 1.22 mg NH_3.

NOTE: Data is reported as NH_3–N, that is Ammonia as Nitrogen, so 1.00 mL of stock standard equals 1 mg of Ammonia nitrogen

Additional Comments:

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Inspector: _____Date: _____