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 C-2011 (Aqueous)**

Equipment:

	Burette
	pH Meter
	All Borosilcate Glass Distillation Equipment

Titration Reagents:

	Mixed Indicator Solution
	Indicating Boric Acid Solution
	H_2SO_4 Titrant, 0.02*N*

Distillation Reagents:

	Ammonia-Free Water
	Borate Buffer
	NaOH, 6*N*
	Dechlorinating Reagent: 3.5 g Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) per L.
	Neutralization Reagent: NaOH, 1*N*
	Neutralization Reagent: H_2SO_4, 1*N*

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 iced to above freezing but ≤ 6 º C during shipment? [40 CFR 136.3 Table II and footnote 18]			
5	Are samples checked for Residual Chlorine at the time of collection and prior to pH preservation adjustment? [SM 4500 NH_3 B-2011 (4) (b)] [NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			Testing for residual chlorine must be performed at a neutral pH (i.e., before pH preservation adjustment). DPD screening and test strips are not reliable at extreme pHs.
6	Is residual chlorine neutralized at time of sample collection? [SM 4500 NH_3 B-2011 (4) (b)] [NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			Remove residual chlorine by adding, at the time of collection, dechlorinating agent equivalent to the chlorine residual. If necessary, neutralize to approximately pH 7 with dilute acid or base, using a pH meter. 1ml of dechlorinating agent will neutralize 1 mg/L residual chlorine in 500 ml sample.
7	Are samples preserved with H_2SO_4 to pH of <2 S.U. at time of			Preservation not required if analyzed

	collection, but after chlorine check? [40 CFR 136.3 Table II]			within 15 minutes.
8	Is dechlorination verified upon receipt in the lab? [15A NCAC 02H .0805 (a) (7) (M)]			Testing with chlorine strips after the sample has been pH preserved will likely not produce reliable results. Sample must be neutralized before dechlorination is verified.
9	What action is taken if chlorine is present? [15A NCAC 02H .0805 (a) (7) (M)]			If another sample cannot be collected, dechlorinate the sample and notify NC WW/GW Certification group that a non-compliant sample was received.
10	Is pH checked and documented to be <2 S.U. upon receipt in the laboratory? [40 CFR 136.3 Table II]			
11	What action is taken if pH is >2 S.U.? [15A NCAC 02H .0805 (a) (7) (M)] **Answer:**			Sample preservation shall be verified and documented. If a laboratory receives a sample subject to G.S. 143-215.1 and 143-215.63 that does not meet sample collection, holding time, or preservation requirements, the laboratory shall document the incident, notify the sample collector or client, and secure another sample that meets the regulatory requirements, if possible. If another viable sample cannot be secured, the original sample may be analyzed but the results reported shall be qualified with the nature of the sample collection, holding time, or preservation infractions and the laboratory shall notify the State Laboratory of the infractions. The notification shall include a statement indicating corrective action taken to prevent future infractions.
12	Are samples refrigerated above freezing to 6°C during storage? [40 CFR 136.3 Table II and footnote 18]			
13	Are samples analyzed within 28 days of collection? [40 CFR 136.3 Table II]			
	PROCEDURE	**LAB**	**SOP**	**EXPLANATION**
14	Is the manual distillation at pH 9.5 S.U used? [40 CFR 136.3 Table 1B] [SM 4500 NH_3 C-2011 (1)]			**REQUIRED** The titrimetric method is used only on samples that have been carried through preliminary distillation (see 4500-NH_3.B).
15	How is the distillation equipment cleaned? [SM 4500 NH3 B-2011 (4) (a)] **Answer:**			Add 500 ml water and 20 ml borate buffer, adjust pH to 9.5 with 6N NaOH solution, and add to distillation flask. Add a few glass beads or boiling chips and use this mixture to steam out the distillation apparatus until distillate shows no traces of ammonia. To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation.
16	What sample volume is distilled? [SM 4500 NH_3 B-2011 (4) (b)] **Answer:**			Check sample volume distilled versus reporting limit. Method calls for 500 mL original sample volume to be distilled and at least 200 mL to be collected. See calculation for # 23. Must distill original volume of at least 250 mL to reach reporting level of approximately 0.1 mg/L. That is 0.1 X 280 / 250 mL = 0.112 mg/l. (The 0.1 value is the smallest A-B value you can obtain) An original sample volume distilled of 100 mL will yield a reporting level of approximately 0.3 mg/L. That is 0.1 X 280 / 100 mL = 0.28 mg/L
17	Is 25 mL of borate buffer solution added to the sample? [SM 4500 NH_3 B-2011 (4) (b)]			Based on 500 mL total volume in flask

18	After adding the borate buffer solution, is the sample pH adjusted to 9.5 S.U. with 6*N* NaOH using a pH meter? [SM 4500 NH_3 B-2011 (4) (b)]			
19	Is the distillate collected in 50 mL of indicating boric acid solution? [SM 4500 NH_3 B-2011 (4) (c)]			Indicating boric acid contains borate buffer and mixed indicator solution. Preparation is in SM 4500 NH_3 C-2011 (3) (a) and (b)]. Mixed indicator and indicating boric acid must be prepared monthly
20	Is the condenser outlet tip submerged below the surface of the receiving acid solution? [SM 4500 NH_3 B-2011 (4) (b)]			
21	Is the distillate collected diluted to the original volume in the flask? [SM 4500 NH_3 B-2011 (4) (c)]			
22	Is sample titrated with 0.02 *N* H_2SO_4? [SM 4500 NH_3 C-2011 (4) (c)]			End point of titration is pale lavender color.
23	Is the Sulfuric Acid titrant standardized initially (if prepared in house) and monthly thereafter? [SM 4500 NH_3 C-2011 (3) (c)] [NC WW/GW LCB Titrant Standardization Policy]			Titrants prepared in the laboratory must be standardized initially and monthly thereafter. All certified titrants which are purchased, may be used initially without standardization. The Certificate of Analysis must be kept on file. The certified titrant must be standardized monthly thereafter, for as long as it is used. If the normality changes, a new titrant at the specified normality must be used, or the sample results must be calculated using the newly determined normality. Quality control standards do not take the place of titrant standardization.
24	How is the normality of H2SO4 titrant calculated? [SM 4500 NH3 C-2011 (3) (c)] [SM 2320 B-2011 (3) (b)] **Answer:**			Normality, N = $\frac{A \times B}{53.00 \times C}$ where: A= g Na2CO3 weighed into 1-L flask B= mL Na2CO3 solution taken for titration, and C= mL acid used. For greatest accuracy, standardize titrant against an amount of Na2CO3 that has been incorporated in the indicating boric acid solution to reproduce the actual conditions of sample titration.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
25	Is a reagent blank carried through all steps of the distillation procedure? [SM 4500 NH_3 C-2011 (4) (d)] [SM 1020 B-2014 (5)]			**SM 4500 NH_3:** Carry a blank through all steps of the procedure and apply the necessary correction to the results. **SM 1020 B:** A reagent blank (method blank) consists of reagent water (see Section 1080) and all reagents (**including preservatives**) that normally are in contact with a sample during the entire analytical procedure. The reagent blank is used to determine whether, and how much, reagents and the preparative analytical steps contribute to measurement uncertainty.
26	Are values calculated properly? [SM 4500 NH_3 C-2011 (5) (a)]			Calculation: mg NH_3-N/L = $\frac{(A-B) \times C}{\text{mL sample}}$

				where: A= volume H_2SO_4 titrated for sample, mL, and B= volume of H_2SO_4 titrated for blank, mL. mL sample = original sample volume distilled (not amount caught in flask) C= 14 x normality of H_2SO_4 titrant x 1000 µg N (For 0.02 *N*, 1.00 mL = 280 µg N) (For 0.023 *N*, 1.00 mL = 322 µg N)
27	What is the laboratory's lower reporting limit? **Answer**:			Based on lowest buret increment
28	Does the laboratory distill and analyze a laboratory-fortified blank (LFB) at least daily or per batch of 20 or fewer samples? [SM 4020 B-2014 (6)] **List value(s) and acceptance criterion of standard used.**			Standard concentration should be close to majority of sample concentrations. May want to vary concentration. Remember we certify for Ammonia as Nitrogen not Ammonia (see calculation above). Be sure to check the standard 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. **1.0 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 NH3 = 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 (NH3)
29	What is the acceptance criterion for the LFB recovery? [SM 4020 B-2014 (6)] **Answer:**			Must establish acceptance criterion. Evaluate the LFB for percent recovery of the added analytes by comparing results to method-specified limits, control charts, or other approved criteria.
30	What corrective action is taken if the LFB recovery is outside established control limits? [15A NCAC 02H .0805 (a) (7) (B)] [SM 4020 B-2014 (6)] **Answer:**			**Rules:** 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. Use LFB results to evaluate batch performance, calculate recovery limits, and plot control charts.
31	Is a Laboratory Fortified Matrix (LFM) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2014 (7) and Table 4020:I]			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.
32	How is the LFM prepared? [NC WW/GW LCB Matrix Spiking Policy] **Answer:**			See Spiking Technical Assistance document for guidance
33	Is the spike concentration rotated to verify performance at various levels? [SM 4020 B-2014 (7)]			Rotating the concentration is recommended but not required.
34	Is a Laboratory Fortified Matrix Duplicate (LFMD) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2014 (8) and Table 4020:I]			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. Note: Per Table 4020:I, an LFMD must be analyzed to demonstrate precision. A sample duplicate will not fulfill this requirement.
35	What is the acceptance criterion for the LFM/LFMD recovery? [15A NCAC 02H .0805 (a) (7) (A)] [SM 4020 B-2014 (7)] **Answer:**			**Rules:** Each laboratory shall establish performance acceptance criteria for all quality control analyses. **SM 4020 B:** Evaluate LFM results for percent recovery.
36	What corrective action does the laboratory take if the LFM/LFMD results are outside of the established control limits for accuracy (percent recovery)? [15A NCAC 02H .0805 (a) (7) (B)] [SM 4020 B-2014 (7)] **Answer:**			**Rules:** 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. **SM 4020 B:** 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. Possible corrective action for low spike recoveries may be to change the catalyst.
37	What is the acceptance criterion for the LFM/LFMD precision (relative percent difference)? [15A NCAC 02H .0805 (a) (7) (A)] [SM 4020 B-2014 (8)] **Answer:**			**Rules:** Each laboratory shall establish performance acceptance criteria for all quality control analyses. **SM 4020 B:** Evaluate LFM duplicate results for precision and accuracy.
38	What corrective action does the laboratory take if the LFM/LFMD results are outside of the established control limits for precision? [15A NCAC 02H .0805 (a) (7) (B)] [SM 4020 B-2014 (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. 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. SM 4020 B: If LFM duplicate results are out of control, then take corrective action to rectify the matrix effect, use another method, use the method of standard addition, or flag the data if reported.
39	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.

Stock Standard – Dissolve 3.819 g anhydrous NH_4Cl (dried at 100 °C) in water and dilute to 1000 mL.
1.00mL = 1000 mg N = 1220 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: _____