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: **Total Kjeldahl Nitrogen**
Method: **SM 4500 N_{org} B-2011 (Aqueous)**
Determinative Method: **SM 4500 NH_3 C-2011 (Aqueous)**

EQUIPMENT:

	Digestion Apparatus **List:**		Heating Device (375 – 385 °C) **List:**
	Distillation Apparatus **List:**		pH meter
	Class A Volumetric Flasks		Burette
	Class A Volumetric Pipettes		

REAGENTS:

	Reagent water – ammonia free		Digestion Reagent **Circle:** (K_2SO_4, $CuSO_4$, H_2SO_4) or (K_2SO_4, $HgSO_4$, H_2SO_4)
	Sodium Hydroxide-Sodium Thiosulfate reagent		Borate buffer solution (recipe at the end of this checklist)
	Sulfuric Acid (H_2SO_4) Titrant, 0.02*N*		Indicating Boric Acid solution (recipe at the end of this checklist)
	Neutralization Reagent: H_2SO_4, 1*N*		Mixed indicator solution (recipe at the end of this checklist)
	Neutralization Reagent: NaOH, 1*N*		NaOH, 6*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 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.
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 Standard Operating Procedure documents.
3	Is there North Carolina data available for review?			If not, review PT data.
	PRESERVATION and STORAGE	**LAB**	**SOP**	**EXPLANATION**
4	Are samples collected and stored in polyethylene, Teflon®, or glass containers? [40 CFR 136.3 Table II]			
5	Are samples preserved within 15 minutes of collection with H_2SO_4 to pH of <2 S.U.? [40 CFR 136.3 Table II, Footnote 2]			
6	Is pH checked and documented to be <2 S.U. upon receipt in the laboratory? [40 CFR 136.3 Table II]			
7	What action is taken if pH is >2 S.U.? [15A NCAC 02H .0805 (a) (7) (M)]			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,

	Answer:			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.
8	Are samples iced to above freezing but ≤ 6 º C during shipment? [40 CFR 136.3 Table II]			
9	Are samples refrigerated above freezing but ≤ 6 º C during storage? [40 CFR 136.3 Table II]			
10	Are samples analyzed within 28 days of collection? [40 CFR 136.3 Table II]			
	DIGESTION PROCEDURE	**LAB**	**SOP**	**EXPLANATION**
11	What sample volume is digested? [SM 4500 N_{org} B-2011 (4) (a)] **Answer:**			Select sample size based on expected organic nitrogen in sample per the table in SM. If necessary, dilute the sample to 300 mL, neutralize sample to pH 7 S.U. and dechlorinate as described in Section 4500-NH3.B.4b. Organic Nitrogen in Sample *mg/L* / Sample size *mL* 0-1 / 500 1-10 / 250 10-20 / 100 20-50 / 50.0 50-100 / 25.0
12	Is 50 mL digestion reagent added to the flask? [SM 4500 N_{org} B-2011 (4) (c)]			Cool and add carefully 50 mL digestion reagent (or substitute 6.7 mL conc H_2SO_4, 6.7 g K_2SO_4, and 0.365 g $CuSO_4$) to distillation flask.
13	Is sample heated at a temperature range of approximately 375 – 385 ºC and boiled briskly until the sample has been reduced to about 25-50mL? [SM 4500 N_{org} B-2011 (4) (c)]			Boil briskly until the volume is greatly reduced (to about 25 to 50 mL) and copious white fumes are observed (fumes may be dark for samples high in organic matter).
14	Once reduced, is the sample digested for an additional 30 minutes? [SM 4500 N_{org} B-2011 (4) (c)]			Continue to digest for an additional 30 min. As digestion continues, colored or turbid samples will become transparent and pale green.
15	Is the digested sample allowed to cool and diluted to 300 mL with water? [SM 4500 N_{org} B-2011 (4) (c)]			After digestion, let cool, dilute to 300 mL with water, and mix.
16	Is 50 mL of sodium hydroxide-thiosulfate reagent added to the sample? [SM 4500 N_{org} B-2011 (4) (c)]			Tilt flask away from personnel and carefully add 50 mL sodium hydroxide-thiosulfate reagent to form an alkaline layer at flask bottom.
17	Is flask swirled to ensure complete mixing and connected to a steamed-out distillation apparatus, as described in the explanation for question # 24? [SM 4500 Norg B-2011 (4) (c)]			Connect flask to a steamed-out distillation apparatus and swirl flask to ensure complete mixing.
18	Is the pH of the solution > 11.0 S.U.? [SM 4500 N_{org} B-2011 (4) (c)]			Checking the pH of the solution is recommended but not required.
	DISTILLATION PROCEDURE	**LAB**	**SOP**	**EXPLANATION**
19	How is the distillation equipment cleaned? [SM 4500 NH_3 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.
20	Is sample distilled and 200 mL of distillate collected? [SM 4500 N_{org} B-2011 (4) (d)]			Distill and collect 200 mL distillate.
21	Is the distillate collected in 50 ml of indicating boric acid solution? [SM 4500 N_{org} B-2011 (4) (d)]			Use 50 mL indicating boric acid as absorbent solution when ammonia is to be determined by titration.
22	Is the condenser outlet tip submerged below the surface of the receiving acid solution? [SM 4500 N_{org} B-2011 (4) (d)]			Extend tip of condenser well below level of absorbent solution and do not let temperature in condenser rise above 29°C.
23	Is the temperature in the condenser kept from rising above 29 ºC? [SM 4500 N_{org} B-2011 (4) (d)]			
24	Is the collected distillate lowered free of the condenser and distillation allowed to continue for an additional 1 to 2 minutes to cleanse the condenser? [SM 4500 N_{org} B-2011 (4) (d)]			Lower collected distillate free of contact with condenser tip and continue distillation during last 1 to 2 minutes to cleanse the condenser.
	TITRATION PROCEDURE	**LAB**	**SOP**	**EXPLANATION**
25	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.
26	How is the normality of H_2SO_4 titrant calculated? [SM 4500 NH_3 C-2011 (3) (c)] [SM 2320 B-2011 (3) (b)] **Answer:**			Normality, $N = \frac{A \times B}{53.00 \times C}$ where: A= g Na_2CO_3 weighed into 1-L flask B= mL Na_2CO_3 solution taken for titration, and C= mL acid used. For greatest accuracy, standardize titrant against an amount of Na_2CO_3 that has been incorporated in the indicating boric acid solution to reproduce the actual conditions of sample titration.
27	Is a reagent blank carried through all steps of the digestion and distillation procedure? [SM 4500 Norg B-2011 (4) (f)] [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. 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.
28	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.
29	Are values calculated properly? [SM 4500 NH_3 C-2011 (3)(c) and (5) (a)]			Calculation: mg TKN/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 digested (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)
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
30	What is the laboratory's lower reporting limit? **Answer**:			Based on lowest buret increment
31	Is a Laboratory-Fortified Blank (LFB) analyzed at least daily or per batch of 20 or fewer samples? [SM 4020 B-2014 (6) and Table 4020:I] **List concentration(s) of standard(s) used:**			As a minimum, include one LFB with each sample set (batch) or on a 5% basis, whichever is more frequent.
32	What is the source of the LFB standard? **Answer:**			Glutamic acid may be used for the LFB. 1.0504 g GA/L = 100 ppm solution.
33	Is the LFB carried through all steps of the procedure? [SM 4500 N_{org} B-2011 (4) (f)] [SM 4020 B-2014 (6)]			**SM 4020 B:** A laboratory-fortified blank [laboratory control standard (LCS)] is a reagent water sample (with associated preservatives) to which a known concentration of the analyte(s) of interest has been added. **SM 4500 Norg:** Carry a reagent blank and standards through all steps of the procedure.
34	What is the acceptance criterion for the LFB recovery? [SM 4020 B-2014 (6)] **Answer:**			Evaluate the LFB for percent recovery of the added analytes by comparing results to method-specified limits, control charts, or other approved criteria.
35	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. 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 LFB results are out of control, take corrective action, including re-preparation and re-analysis of associated samples if required.
36	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.
37	What compound is used in the spiking solution? **Answer:**			Must be an organically bound nitrogen compound.
38	How is the LFM prepared? [NC WW/GW LCB Matrix Spiking Policy]			See Spiking Technical Assistance document for guidance

	Answer:			
39	Is the spike concentration rotated to verify performance at various levels? [SM 4020 B-2014 (7)]			Rotating the concentration is recommended but not required.
40	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.
41	What is the acceptance criterion for the LFM/LFMD recovery? [15 A 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.
42	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:**			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.
43	What is the acceptance criterion for the LFM/LFMD precision (relative percent difference)? [15 A 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.
44	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.
45	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.

Dates of data reviewed:

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Additional Comments:

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Inspector: _____Date:_____

Reagent Recipes:

Mixed indicator solution: 200 mg methyl red dissolved in 100 mL 95% ethyl or isopropyl alcohol combined with 100 mg methyl blue dissolved in 50 mL 95% ethyl or isopropyl alcohol.

Indicating boric acid solution: 20 g H_3BO_3 dissolved in water, 10 mL mixed indicator solution, dilute to 1 L.

Borate buffer solution: 88 mL 0.1*N* NaOH added to 500 mL 0.025*M* sodium tetraborate and dilute to 1 L.