

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: **Nitrogen, Nitrate + Nitrite**

Method: **SM 4500 NO₃⁻ E- 2019**

Equipment:

Colorimetric equipment (Circle one):
Spectrophotometer, for use at 543 nm, providing a light path of 1 cm or longer
Filter photometer with light path of 1 cm or longer and a filter whose maximum transmittance is near 540 nm
Reduction column

Reagents:

Cadmium granules	Ammonium chloride-EDTA solution	Copper sulfate solution, 2%	Stock nitrite solution
Color reagent	Hydrochloric acid	Stock nitrate solution	

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	L A B	S O P	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	L A B	S O P	EXPLANATION
4	Is the sample preserved with H ₂ SO ₄ to pH <2 S.U. within 15 minutes of collection? [40 CFR Part 136.3, Table II and footnote 2]			
5	Is sample transported and stored at ≤ 6°C without freezing? [40 CFR Part 136.3, Table II and footnote 18]			
6	Is the sample analyzed within 28 days of collection? [40 CFR Part 136.3, Table II]			
7	Are date and time of sample collection documented? [15A NCAC 02H .0805 (a) (7) (F) (vi)]			
8	Is the date of sample analysis documented? [15A NCAC 02H .0805 (a) (7) (F) (vii)]			
	PROCEDURE – Reduction Column Preparation	L A B	S O P	EXPLANATION
9	Is the reduction column purchased already packed? If yes, skip to next section for Meter Calibration			
10	Are the cadmium granules prepared as required by the method? [SM 4500 NO ₃ ⁻ E- 2019 (3) (b)]			Wash 25 g new or used 20- to 100-mesh Cd granules (≥ 99%) with 6 M HCl and rinse with water. Swirl Cd with 100 mL 2% CuSO ₄ solution for 5 min or until blue color partially fades. Decant and repeat with fresh CuSO ₄ until a brown colloidal precipitate begins to develop. Gently flush with ammonium chloride-EDTA solution to remove all precipitated Cu.
11	Is the column prepared as required by the method? [SM 4500 NO ₃ ⁻ E- 2019 (4) (a)]			Insert a glass wool plug into bottom of reduction column and fill with water. Add sufficient Cu–Cd granules to produce a column 18.5 cm long. Maintain water level above Cu–Cd granules to avoid entrapping air. Wash

				column with 200 mL dilute NH ₄ Cl-EDTA solution. Activate column by passing through it, at 7 to 10 mL/min, several 100 mL portions of a solution composed of one part 1.0 mg NO ₃ ⁻ N/L standard and 3 parts NH ₄ Cl-EDTA solution.
12	Is the column cleaned and stored per the method? [SM 4500 NO ₃ ⁻ E- 2019 (3) (b) and (4) (b) (3)]			Pour 50 mL dilute NH ₄ Cl-EDTA solution on to the top and let it pass through the system. Store Cu-Cd column in this solution and never let it dry. Store activated Cd covered with dilute ammonium chloride-EDTA solution.
	PROCEDURE – Meter Calibration	L A B	S O P	EXPLANATION
13	Is the meter calibrated with at least 5 non-zero standards? [SM 4500 NO ₃ ⁻ E- 2019 (4) (c)] [15A NCAC 02H .0805 (a) (7) (H) (v)] List standard concentrations:			The method requires 5 standards, so curves prepared daily must still analyze 5 standards.
14	If the curve is held, is it prepared every 12 months? [15A NCAC 02H .0805 (a) (7) (H) (v)]			
	PROCEDURE – Interferences	L A B	S O P	EXPLANATION
15	Is the sample filtered if turbid? [SM 4500 NO ₃ ⁻ E-2019 (4) (b) (1)]			Filter turbid sample through 0.45-µm membrane filter. Test filters for nitrate contamination (i.e., filter the reagent blank if any samples must be filtered)
16	Are aliquots of samples that are treated for residual chlorine in the field brought to a neutral pH and verified to be chlorine free when received in the lab?? [SM 4500 NO ₃ ⁻ E-2019 (1) (b)] [NC WW/GW LCB Sample Collection, Preservation and Receipt Requirements Policy]			NC WW/GW LCB Policy: Each chemically preserved sample must be checked for effectiveness and the results documented. 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.
	PROCEDURE – Sample Analysis	L A B	S O P	EXPLANATION
17	Is the sample pH adjusted to 7-9 S.U.? [SM 4500 NO ₃ ⁻ E-2019 (4) (b) (2)]			
18	Is 75 mL NH ₄ Cl-EDTA solution added to 25 mL of sample? [SM 4500 NO ₃ ⁻ E-2019 (4) (b) (3)]			
19	Is the sample poured into the column, collected at a rate of 7-10 mL per minute and the first 25 mL discarded? [SM 4500 NO ₃ ⁻ E-2019 (4) (b) (3)]			
20	Is 2.0 mL color reagent added to 50 mL sample within 15 minutes of reduction? [SM 4500 NO ₃ ⁻ E-2019 (4) (b) (4)]			
21	Is the sample analyzed against a distilled water-reagent blank between 10 minutes to 2 hours of color reagent addition? [SM 4500 NO ₃ ⁻ E-2019 (4) (b) (4)]			Zero spectrophotometer with reagent blank and measure samples at least 10 minutes after adding color reagent and no more than 2 hours after.
	QUALITY ASSURANCE	L A B	S O P	EXPLANATION
22	Has a Method Detection Limit (MDL) been established? [SM 4500 NO ₃ ⁻ A-2019 (3)] [40 CFR 136 Appendix B] State MDL value here: State determination date here:			The initial MDL determination must consist of minimum of 7 spikes and 7 method blanks. They must be divided among 3 separate prep batches on 3 separate days.

23	Are at least two spikes at the same concentration as the initial MDL study analyzed in separate batches each quarter that samples are analyzed? [40 CFR 136 Appendix B]		Must have at least two per quarter, however if additional standard at that concentration are analyzed, they must be included in the ongoing recalculation of the MDL.
24	Is the MDL evaluated at least every 13 months and updated if required? [40 CFR 136 Appendix B]		
25	Has each new analyst completed an Initial Demonstration of Capability (IDC) before analyzing any samples? [SM 4500 NO ₃ ⁻ A-2019 (3)] [SM 4020 B-2022 (3)] Attach a copy of each analyst's IDC to this checklist.		At a minimum, include 1 reagent blank and at least 4 LFBs at a concentration between 1 and 4 times the MRL (or other level specified in the method). Run the IDC after analyzing all required calibration To establish laboratory-generated accuracy and precision limits, calculate the upper and lower control limits from the mean and standard deviation of percent recovery for ≥20 data points: Upper control limit = Mean + 3(Standard deviation) Lower control limit = Mean - 3(Standard deviation)
26	Is the correlation coefficient of the calibration curve ≥0.995? [SM 4500 NO ₃ ⁻ A-2019 (3)]		Using a calculator, electronic spreadsheet, or instrument software, calculate the slope, intercept, and correlation coefficient (r) or coefficient of determination (r ²) of the calibration curve. The r value must be at least 0.995 (r ² = 0.99).
27	Are the standard values back-calculated with each calibration? [SM 4500 NO ₃ ⁻ A-2019 (3)] [15A NCAC 02H .0805 (a) (7) (H)]		Back-calculate the apparent concentrations of the standards.
28	What are the acceptance criteria for the back-calculated standards? [SM 4020 B-2022 (1)] [SM 4500 NO ₃ ⁻ A-2019 (3)] [15A NCAC 02H .0805 (a) (7) (A)] Acceptance criteria:		4020 B: 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 the individual methods, identify the source of any outlier(s) and correct before sample quantitation. 4500 NO₃⁻ A: For standards more than 10 times the MDL, the measured values must be 90% to 110% of the true values.
29	If a calibration curve is not analyzed each day of analysis, is a lower reporting limit standard analyzed? [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.
30	Is a second-source calibration-verification standard (CVS) analyzed immediately after the calibration? [SM 4500 NO ₃ ⁻ A-2019 (3)]		Prepare a calibration-verification standard (CVS) from a stock solution separate from that used to prepare the calibration standards. The CVS's NO ₃ ⁻ -N concentration should be 30% to 70% of the highest calibration standard; however, some QA/QC programs may require different concentrations. Run the CVS immediately after calibration; the result must be 90% to 110% of the expected value.
31	Is the acceptance criterion for the second-source CVS recovery within ±10% of the true value? [SM 4500 NO ₃ ⁻ A-2019 (3)] True value: Acceptance criterion:		See above
32	If a calibration curve is not analyzed each day of analysis, is a lower reporting limit standard analyzed? [15A NCAC 02H .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.
33	What is the acceptance criterion for the lowest reporting concentration standard? [SM 4500 NO ₃ ⁻ A-2019 (3)] [15A NCAC 02H .0805 (a) (7) (A)] Acceptance criterion:		4500 NO₃⁻ A: For standards more than 10 times the MDL, the measured values must be 90% to 110% of the true values. Rules: Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.

34	Is a Laboratory Fortified Blank (LFB) analyzed with each sample set or on a 5% basis, whichever is more frequent? [SM 4020 B- 2022 (6)]			
35	Is the LFB filtered if any samples require filtration? [SM 4020 B-2022 (6)]			Process the LFB through all sample preparation and analysis steps. If there are a mix of both filtered and unfiltered samples, you must have both a filtered and unfiltered LFB.
36	Is Sodium thiosulfate added to the LFB if any samples must be treated for residual chlorine? [SM 4020 B-2022 (6)]			
37	What is the acceptance criterion for the LFB? [SM 4020 B- 2022 (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.
38	Is a method blank analyzed with each sample set (batch) or on a 5% basis, whichever is more frequent? [SM 4020 B- 2022 (5)]			
39	Is the method blank filtered if any samples require filtration? [SM 4020 B-2022 (5)]			If there is a mix of filtered and unfiltered samples, you must have both a filtered and unfiltered method blank.
40	Is Sodium thiosulfate added to the method blank if any samples must be treated for residual chlorine? [SM 4020 B-2022 (5)]			
41	Is the acceptance criterion for the method blank $\leq \frac{1}{2}$ reporting limit? [15A NCAC 2H .0805 (a) (7) (H) (i)]			
42	Is a midpoint continuing calibration verification (CCV) analyzed prior to sample analysis, after every 10 th sample, and at the end of each sample group? [15A NCAC 02H .0805 (a) (7) (H)] [SM 4500 NO ₃ ⁻ A-2019 (3)] True Value:			Note that the method requires the standard to be midpoint
43	Is the acceptance criterion for the CCV recovery within $\pm 10\%$ of the true value? [SM 4500 NO ₃ ⁻ A-2019 (3)]			If the measured NO ₃ ⁻ - N concentration in the CCV is not 90 to 110% of the expected value, recalibrate and rerun all samples read since the last good CCV reading.
44	Is a calibration blank analyzed prior to sample analysis, after every 10 th sample, and at the end of each sample group? [15A NCAC 02H .0805 (a) (7) (H)] [SM 4500 NO ₃ ⁻ A-2019 (3)]			
45	Is the acceptance criterion for the calibration blank $\leq \frac{1}{2}$ reporting limit? [15A NCAC 2H .0805 (a) (7) (H) (i)]			
46	Is a Laboratory Fortified Matrix (LFM) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (7) and Table 4020:1]			
47	How is the LFM prepared? [NC WW/GW LCB Matrix Spike Technical Assistance Policy] [SM 4020 B-2022 (7)] Answer:			See NC WW/GW LCB "Matrix Spiking Policy and Technical Assistance" document for volume and sample dilution requirements. 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.
48	Is a Laboratory Fortified Matrix Duplicate (LFMD) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2022 (8) and Table 4020:1]			SM 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.
49	What is the acceptance criterion for the accuracy of the LFM/LFMD (recovery)? [15A NCAC 02H .0805 (a) (7) (A)] Answer:		Each laboratory shall establish performance acceptance criteria for all quality control analyses. Each laboratory shall calculate and document the precision and accuracy of all quality control analyses with each sample set.
50	What corrective action does the laboratory take if the LFM/LFMD results are outside of established control limits for accuracy ? [15A NCAC 02H .0805 (a) (7) (B)] Answer:		Our Rule requires corrective action any time quality control results indicate a problem.
51	What is the acceptance criterion for the precision of the duplicates? (RPD) [15A NCAC 02H .0805 (a) (7) (A)] Answer:		Each laboratory shall establish performance acceptance criteria for all quality control analyses. Each laboratory shall calculate and document the precision and accuracy of all quality control analyses with each sample set.
52	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)] Answer:		Our Rule requires corrective action any time quality control results indicate a problem.
53	Is at least one mid-level NO ₂ ⁻ standard compared to a NO ₃ ⁻ standard at the same concentration to verify reduction column efficiency? [SM 4500 NO ₃ ⁻ E- 2019 (6)]		Run a mid-level NO ₃ ⁻ -N standard followed immediately by a NO ₂ ⁻ -N standard of the same concentration. Calculate reduction efficiency as follows: Efficiency = (NO ₃ ⁻ -N response ÷ NO ₂ ⁻ -N response) × 100.
54	What is the acceptance criterion for reduction efficiency? [SM 4500 NO ₃ ⁻ E- 2019 (6)] Answer:		The efficiency must be 90% to 110%.
55	Are Cu-Cd granules reactivated if the reduction efficiency falls below 90%? [SM 4500 NO ₃ ⁻ E-2019 (6)]		If not, stop and correct the problem by either following the manufacturer's instructions or passing 6 M HCl through the column followed by rinsing with dilute ammonium chloride-EDTA solution. Prepare or, if it cannot be reactivated, purchase a new column according to 4500-NO3 E.3 b and activate according to 4500-NO3 E.4 a.
56	Is the data qualified on the Discharge Monitoring Report (DMR) or client report if Quality Control (QC) requirements are not met? [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:

Inspector: _____ Date: _____