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 NO_3^- E- 2016**

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%
	Color reagent		Hydrochloric acid		Stock nitrate solution
					Stock nitrite 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	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	Is the sample preserved with H_2SO_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 2]			
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 2H .0805 (a) (7) (F) (vi)]			
8	Is the date of sample analysis documented? [15A NCAC 2H .0805 (a) (7) (F) (vii)]			
	PROCEDURE – Reduction Column Preparation	**LAB**	**SOP**	**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- 2016 (3) (b)]			Wash 25 g new or used 20- to 100-mesh Cd granules with 6N 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- 2016 (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 prevent entrapment of air. Wash column with 200 mL dilute NH_4Cl-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_4Cl-EDTA solution.
12	Is the column cleaned and stored per the method? [SM 4500 NO_3^- E- 2016 (3) (b) and (4) (b) (3)]			Pour 50 mL dilute NH_4Cl-EDTA solution on to the top and let it pass through the system. Store activated Cd covered with dilute ammonium chloride–EDTA solution and never let it dry.
	PROCEDURE – Meter Calibration	**LAB**	**SOP**	**EXPLANATION**
13	Is the meter calibrated with at least 5 non-zero standards? [SM 4500 NO_3^- E- 2016 (4) (c)] [15A NCAC 2H .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 2H .0805 (a) (7) (H) (v)]			
	PROCEDURE – Interferences	**LAB**	**SOP**	**EXPLANATION**
15	Is the sample filtered if turbid? [SM 4500 NO_3^- E-2016 (4) (b)]			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-2016 (1) (b)] [NC WW/GW LCB 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	**LAB**	**SOP**	**EXPLANATION**
17	Is the sample pH adjusted to 7-9 S.U.? [SM 4500 NO_3^- E-2016 (4) (b) (2)]			
18	Is 75 mL NH4Cl-EDTA solution added to 25 mL of sample? [SM 4500 NO_3^- E-2016 (4) (b) (3)]			
19	Is the sample poured into the column at rate of 7-10 mL per minute and the first 25 mL discarded? [SM 4500 NO_3^- E-2016 (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-2016 (4) (b) (4)]			
21	Is the sample analyzed against a distilled reagent water blank within			

	10 minutes to 2 hours of color reagent addition? [SM 4500 NO_3^- E-2016 (4) (b) (4)]			
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
22	Has a Method Detection Limit (MDL) been established? [SM 4500 NO_3^- A-2016 (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-2016 (3)] [SM 4020 B-2014 (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-2016 (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-2016 (3)] [15A NCAC 2H .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-2014 (1)] [SM 4500 NO_3^- A-2016 (3)] [15A NCAC 2H .0805 (a) (7) (A)] **Acceptance criteria:**			4020B: 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 NO_3^- A: For standards more than 10 times the MDL, the measured values must be 90% to 110% of the true values.
29	Is a second-source calibration-verification standard (CVS) analyzed immediately after the calibration? [SM 4500 NO_3^- A-2016 (3)] [15A NCAC 2H .0805 (a) (7) (H) (ii)]			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. Rule: Laboratories shall analyze one known second source standard to verify the accuracy of standard preparation if an initial calibration

				is performed and in accordance with the referenced method requirements thereafter.
30	Is the acceptance criterion for the second-source CVS recovery within ±10% of the true value? [SM 4500 NO_3^- A-2016 (3)] **True value:** **Acceptance criterion:**			See above
31	Is a standard at the lowest reporting concentration analyzed or back calculated each day samples are analyzed? [15A NCAC 2H .0805 (a) (7) (H)]			If the reporting limit is the same as one of the calibration standards, this will be covered by the curve back-calculation requirement.
32	What is the acceptance criterion for the lowest reporting concentration standard? [SM 4500 NO_3^- A-2016 (3)] [15A NCAC 2H .0805 (a) (7) (A)] **Acceptance criterion:**			4500 NO_3^- A: For standards more than 10 times the MDL, the measured values must be 90% to 110% of the true values. 4020B: If less than 10 times the MDL: For standards up to twice MRL, ±50%; between 3 and 5 times MRL, ±20%; greater than 5 times MRL ±10% of the true values.
33	Is a Laboratory Fortified Blank (LFB) analyzed with each sample set or on a 5% basis, whichever is more frequent? [SM 4020 B- 2014 (6)]			
34	Is the LFB filtered if any samples require filtration? [SM 4020 B-2014 (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.
35	Is Sodium thiosulfate added to the LFB if any samples must be treated for residual chlorine? [SM 4020 B-2014 (6)]			
36	What is the acceptance criterion for the LFB? [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.
37	Is a method blank analyzed with each sample set (batch) or on a 5% basis, whichever is more frequent? [SM 4020 B- 2014 (5)]			
38	Is the method blank filtered if any samples require filtration? [SM 4020 B-2011 (5)]			If there is a mix of filtered and unfiltered samples, you must have both a filtered and unfiltered method blank.
39	Is Sodium thiosulfate added to the method blank if any samples must be treated for residual chlorine? [SM 4020 B-2014 (5)]			
40	Is the acceptance criterion for the method blank ≤½ reporting limit? [15A NCAC 2H .0805 (a) (7) (H) (i)]			
41	Is a midpoint continuing calibration verification (CCV) analyzed prior to sample analysis, after every 10th sample, and at the end of each sample group? [15A NCAC 2H .0805 (a) (7) (H)] [SM 4500 NO_3^- A-2016 (3)] **True Value:**			
42	Is the acceptance criterion for the CCV recovery within ±10% of the true value? [SM 4500 NO_3^- A-2016 (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.
43	Is a calibration blank analyzed prior to sample analysis, after every 10th sample, and at the end of each sample group? [15A NCAC 2H .0805 (a) (7) (H)] [SM 4500 NO_3^- A-2016 (3)]			
44	Is the acceptance criterion for the calibration blank ≤ ½ reporting limit? [15A NCAC 2H .0805 (a) (7) (H) (i)]			
45	Is a matrix spike (MS) and matrix spike duplicate (MSD) pair analyzed with each sample set (batch of 20 samples or less) or on a 5% basis, whichever is more frequent? [SM 4020 B- 2014 (7)]			
46	How is the MS/MSD prepared?			See NC WW/GW LCB "Matrix Spiking Policy and Technical Assistance" document for volume and sample dilution requirements.

	Answer:			**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.
47	What is the acceptance criterion for the accuracy of the MS/MSD (recovery)? [SM 4020 B-2014 (7)] **Answer:**			**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.
48	What is the acceptance criterion for the precision of the duplicates? (RPD) [15A NCAC 2H .0805 (a) (7) (A)] **Answer:**			
49	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- 2014 (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.
50	What is the acceptance criterion for reduction efficiency? [SM 4500 NO_3^- E- 2016 (6)] **Answer:**			The efficiency must be 90% to 110%.
51	Are Cu-Cd granules reactivated if the reduction efficiency falls below 90%? [SM 4500 NO_3^- E-2016 (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.
52	Is the data qualified on the Discharge Monitoring Report (DMR) or client report if Quality Control (QC) requirements are not met? [15A NCAC 2H .0805 (a) (7) (B)]			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. If data qualifiers are used to qualify samples not meeting QC requirements, the data may not be useable for the intended purposes. It is the responsibility of the laboratory to provide

				the client or end-user of the data with sufficient information to determine the usability of the qualified data.

Additional Comments:

_____

_____

_____

_____

Inspector: _____Date:_____