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: **Chemical Oxygen Demand (COD)**
Closed Reflux, Colorimetric Method
Method: **Hach 8000 (1979)**

Chemical Oxygen Demand is considered a method-defined parameter per the definition in the Code of Federal Regulations, Part 136.6, Section (a) (5). This means that the method may not be modified per Part 136.6, Section (b) (3).

Equipment:

	Block heater, 150 ± 2°C **Model:**		Commercially supplied digestion vessels with premixed reagents* o High range (HR): 20 to 1500 mg/L o Low range (LR): 3 to 150 mg/L
	Hach Spectrophotometer, 620 nm [20 to 1500 mg/L] and/or 420 nm [3 to 150 mg/L] **Model:**		Volumetric Pipette, Class A
	Blender (for samples with large amounts of solids)		Spectrophotometer light shield for Hach instrument models: DR 3900, DR 3800, DR 2800 and DR 2700

*COD2 reagents are not approved for USEPA reporting purposes. Because COD2 reagents do not contain mercury as a masking agent, they exhibit a positive interference from chloride.

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)] **ANSWER:**			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 revision dates and actions 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	Are samples preserved at the time of collection with H_2SO_4 to pH of <2? [40 CFR Part 136.3, Table II]			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.
5	Are samples iced to above freezing but ≤ 6°C during shipment? [40 CFR Part 136.3, Table II and footnote 18]			
6	Is pH checked to document pH <2 S.U. upon receipt? [40 CFR Part 136.3, Table II]			pH indicator strips may be used.
7	What action is taken if pH is >2 S.U.? [15A NCAC 2H .0805 (a) (7) (M)] **ANSWER:**			If another sample cannot be collected, analyze immediately or adjust pH to <2, and notify NC WW/GW Laboratory Certification that a non-compliant sample was received and analyzed.

8	Are samples refrigerated above freezing to 6°C during storage? [40 CFR Part 136.3, Table II and footnote 18]			
9	Are samples analyzed within 28 days of collection? [40 CFR Part 136.3, Table II]			
	PROCEDURE – Meter Calibration	**LAB**	**SOP**	**EXPLANATION**
10	What is your laboratory's reporting limit? [15A NCAC 2H .0805 (a) (7) (H)] **ANSWER:**			Greater than or equal to the lowest calibration or calibration verification standard.
11	If a factory-set curve is used, is that curve verified at least every 12 months with 5 standards or daily with 3 standards (for each wavelength)? [15A NCAC 2H .0805 (a) (7) (H) (v)] **List the concentrations of the standards used.**			A manufacturer's factory-set calibration (internal curve) shall be verified with the same number of standards and frequency as a prepared curve. Later versions of this method discuss a standard adjust option. The approved 1979 version does not mention this and it is not allowed.
12	What are the acceptance criteria of the verified standards? [15A NCAC 2H .0805 (a) (7) A)] **ANSWER:**			Unless specified by the method or this Rule, 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. When the method of choice specifies performance acceptance criteria for precision and accuracy, and the laboratory chooses to develop laboratory-specific limits, the laboratory-specific limits shall not be less stringent than the criteria stated in the approved method.
13	If the laboratory prepares its own calibration curve for each wavelength, how often is it prepared? [15A NCAC 2H .0805 (a) (7) (H) (v)] **ANSWER:**			For colorimetric analyses, a series of five or more non-zero standards for a curve prepared every 12 months or three or more non-zero standards for curves established each day, or standards as set forth in the analytical procedure, shall be analyzed to establish a calibration curve.
14	What is the acceptance criterion for linearity for the laboratory-prepared curve? [NC WW/GW LC Policy] **ANSWER:**			When linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified, then a minimum value of 0.995 (or a coefficient of determination, r^2, of 0.99) is required.
	PROCEDURE – Sample Preparation	**LAB**	**SOP**	**EXPLANATION**
15	Is traceability documented for the COD digestion vial lot numbers? [15A NCAC 2H .0805 (a) (7) (K) and NC WW/GW LC Policy]			The laboratory shall have a documented system of traceability for the purchase, preparation, and use of all chemicals, reagents, standards, and consumables. All chemicals, reagents, standards and consumables used by the laboratory must have the following information documented: Date received, Date Opened (in use), Vendor, Lot Number, and Expiration Date (where specified). This information as well as the vendor and/or manufacturer, lot number, and expiration date must be retained for primary standards, chemicals, reagents, and materials used for a period of five years. **Consumable materials such as pH buffers, lots of pre-made standards and/or media, solids and bacteria filters, etc. are included in this**

				requirement.
16	How are the unused COD digestion vials stored? [Hach Method 8000, 1979, Reactor Digestion Method Step 3] **ANSWER:**			The reagent mixture is light sensitive. Keep unused vials in the opaque shipping container, in a refrigerator if possible.
17	Is 2 mL of the sample, standard or blank added into the digestion vial while holding at a 45° angle? [Hach Method 8000, 1979, Reactor Digestion Method Step 4]			Hold the vial at a 45° angle. Pipet 2.00 mL of sample, standard or deionized water into the vial.
18	Are samples with chloride concentrations greater than 2000 mg/L dilute to reduce chloride concentrations to below 1000 mg/L? [Hach Method 8000, 1979, Reactor Digestion Method Interferences Section]			Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to level specified in column 1. Samples with higher chloride concentrations should be diluted. Dilute the sample enough to reduce the chloride concentration to the level given in column 2.
19	If noticeable suspended solids are observed, is 500 ml of sample homogenized for 2 minutes in a blender? [Hach Method 8000, 1979, Reactor Digestion Method Step 1]			Hach technical support stated that the blender homogenization step was only needed if suspended solids were observed in the sample.
20	Is the vial discarded if any reagent has spilled? [Hach Method 8000, 1979, Reactor Digestion Method Step 4]			Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Do not run tests with vials that have been spilled
21	Is the vial held by the cap and gently inverted several times? [Hach Method 8000, 1979, Reactor Digestion Method Step 6]			
22	Is the block heater verified and documented to be 150°C during digestion? [Hach Method 8000, 1979, Reactor Digestion Method Step 1] [15A NCAC 2H .0805 (a) (7) (E)]			Preheat to 150°C. It is recommended that the thermometer be rotated through the entire digestion block to ensure even temperatures. Rules: All analytical records, including original observations and information necessary to facilitate historical reconstruction of the calculated results, shall be maintained for five years. All analytical data and records pertinent to each certified analysis shall be available for inspection upon request.
23	Are the vials heated for 2 hours? [Hach Method 8000, 1979, Reactor Digestion Method Step 8]			
24	After cooling for about 20 minutes, are the vials inverted several times while still warm after digestion? [Hach Method 8000, 1979, Reactor Digestion Method Step 10]			Wait about 20 minutes for the vials to cool to 120 °C or less. Invert each vial several times while still warm.
	PROCEDURE – Sample Analysis	**LAB**	**SOP**	**EXPLANATION**
25	Is the light shield in place before readings are observed? [Hach Method 8000, 1979, Colorimetric Determination Step 9]			
26	Are the vials analyzed after they have reached room temperature? [Hach Method 8000, 1979, Reactor Digestion Method Step 10]			Wait until the vials have cooled to room temperature.
27	Is a wavelength of 420 nm used for low range (0-150 mg/L) analysis? [Hach Method 8000, 1979, Colorimetric Determination, 0 to 150 mg/L COD Step 2]			
28	Is a wavelength of 620 nm used for high range (0-1500 mg/L) analysis? [Hach Method 8000, 1979, Colorimetric Determination, 0 to 1500 mg/L COD Step 2]			
29	Is the meter zeroed with a digested blank? [Hach Method 8000, 1979, Instrument Setup]			HACH technical support verified in an email on 9/18/18 that the meter is zeroed with a digested blank.
30	Are over-range samples diluted to fall within the range of the calibration curve/verified portion of the curve? [15A NCAC 2H .0805 (a) (7) (I)]			For analytical procedures requiring analysis of a series of standards, the concentrations of these standards shall bracket the range of the

				sample concentrations measured.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
31	Is all required QC analyzed with each analytical range?			Low and high-range programs are separate, and each range requires its own set of QC.
32	Is a digested blank analyzed with each set of samples? [Hach Method 8000, 1979, Reactor Digestion Method, Step 7]			One blank must be run with each set of samples. All tests (samples and blank) should be run with the same lot of vials.
33	If the digested blank is reused, how is it stored and checked for acceptability? [Hach Method 8000, 1979, Blanks for Colorimetric Determination] **ANSWER:**			The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark. Monitor decomposition by measuring the absorbance at the appropriate wavelength (420 or 620 nm). Zero the instrument is the absorbance mode using a vial containing deionized water and measure the absorbance of the blank. Record the value. Prepare a blank when the absorbance has changed by about 0.01 absorbance units.
34	After initially zeroing the instrument, is a calibration blank analyzed before sample analysis, after every 10 samples and at the end of analysis? [15A NCAC 2H .0805 (a) (7) (H)]			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. Note: The same blank used to zero the instrument may be used. Analyze this blank to get a mg/L result. **If tube lot numbers change in the middle of an analytical run, analyze a blank and check standard from each lot number.**
35	Is the acceptance criterion for the blank ≤50% of the reporting limit? [15A NCAC 2H .0805 (a) (7) (H) (i)]			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.
36	What corrective action is taken if the blank does not meet the acceptance criterion? [15A NCAC 2H .0805 (a) (7) (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.
37	Is the calibration verified by analyzing a **calibration verification standard** initially, after every 10th sample and at the end of the run? [15A NCAC 2H .0805 (a) (7) (H)]			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. The standard only needs to be prepped once per batch. It can be read multiple time to satisfy this requirement.
38	What is the calibration verification standard acceptance criterion for recovery? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
39	What corrective action is taken if the standard does not meet the acceptance criterion? [15A NCAC 2H .0805 (a) (7) (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
40	Is a lower reporting limit standard analyzed or back-calculated with each analysis? [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.
41	What is the acceptance criterion of the lower reporting limit standard? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Establish laboratory control limits
42	Are duplicates analyzed on a 5% basis? [15A NCAC 2H .0805 (a) (7) (C)]			Except where otherwise specified in an analytical method, laboratories shall analyze five percent of all samples in duplicate to document precision. Laboratories analyzing fewer than 20 samples per month shall analyze one duplicate during each month that samples are analyzed.
43	What is the acceptance criterion for the duplicates? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Establish laboratory control limits.
44	What corrective action is taken if the duplicates do not meet the laboratory's acceptance criterion? [15A NCAC 2H .0805 (a) (7) (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
45	Are matrix spikes analyzed on a 5% basis? [15A NCAC 2H .0805 (a) (7) (D)]			Unless the referenced method states a greater frequency or the parameter is not amenable to spiking, laboratories shall spike five percent of samples monthly. Laboratories analyzing fewer than 20 samples per month shall analyze one Matrix Spike during each month that samples are analyzed.
46	How is the matrix spike prepared? [NC WW/GW LC Matrix Spike Technical Assistance] **ANSWER:**			Because sample volume added to the digestion vial is limited to 2 ml, it is suggested that the matrix spike be prepared in a separate flask with a larger sample volume in order to not exceed the maximum allowable sample dilution of 5%. It is preferable to not exceed a sample dilution of 1% so as to not have to adjust the spike recovery calculation. See the bottom of this checklist and/or Matrix Spike Technical Assistance document for additional guidance.
47	How is recovery of the matrix spike calculated? [NC WW/GW LC Matrix Spike Technical Assistance] **ANSWER:**			See Matrix Spike Technical Assistance document. If the spike solution volume constitutes >1% of the total sample volume, the sample concentration must be adjusted by calculation.
48	What is the acceptance criterion for the matrix spike recovery? [15A NCAC 2H .0805 (a) (7) (A)] **ANSWER:**			Unless specified by the method or this Rule, each laboratory shall establish performance acceptance criteria for all quality control analyses.
49	What corrective action is taken if the matrix spike does not meet the laboratory's acceptance criterion? [15A NCAC 2H .0805 (a) (7) (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
50	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.

Program 430 (LR). Program 435 (HR).

Additional Comments:

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Inspector: _____Date:_____

It's not easy to prepare a matrix spike for COD due to the 2 mL sample volume so it's recommended that the matrix spike be prepared using a larger volume prior to analysis. Two examples of this are listed below, but refer to the NC WW/GW LC Matrix Spiking Policy and Technical Assistance document for further information.

Example 1: Add 1 mL of 5000 mg/L COD standard to 100 mL of sample. Analyze 2 mL of this solution for the matrix spike. This creates a matrix spike with a theoretical concentration of 50 mg/L. Since the spiked volume is not greater than 1% of the overall volume, no adjustment to the percent recovery must be calculated.

Example 2: Bring 5 mL of 5000 mg/L COD standard to 100 mL with sample. Analyze 2 mL of this solution for the matrix spike. This results in a theoretical matrix spike concentration of 250 mg/L. Since the spiking solution is greater than 1% but not greater than 5% of the overall volume, the percent recovery must be adjusted using the following formula:

$$\% R = \frac{A - (B \times C) \times 100}{D}$$

Where:
(A) The spiked sample result
(B) Unspiked sample result
(C) % sample expressed as a decimal (sample volume used divided by final volume)
(D) Theoretical spike concentration