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 Organic Carbon (TOC)**
Persulfate-Ultraviolet or Heated Persulfate Method
Method: **Standard Methods 5310 C-2014 (Aqueous)**

Total Organic Carbon 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 and reagents:

	Total organic carbon analyzer **Model:** **Detector Type:**		Peroxydisulfate (*as recommended by instrument manufacturer*) **Form and concentration:**		Inorganic carbon removal check solution (see end of checklist for prep directions)
	Sampling and injection accessories (*as specified by the instrument manufacturer*)		Organic carbon stock 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 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 preserved at the time of collection with H_2SO_4, or H_3PO_4 to pH of <2 S.U.? [40 CFR Part 136.3, Table II] [SM 5310 C-2014 (1) (b)]			**SM states:** Chloride interferes with persulfate oxidation, so HCl must not be used to acidify samples for this method (see 5310 B.1). Insufficient acidification or sparging results in incomplete removal of IC (see 5310 A.5*b*10).
5	Is pH verified and documented to be <2 S.U. upon receipt? [15A NCAC 02H .0805 (a) (7) (M)]			pH indicator strips may be used. If a meter is used, confirm it is properly calibrated.
6	What action is taken if pH is >2 S.U.? [15A NCAC 02H .0805 (a) (7) (M)] **Answer:**			If another sample cannot be collected, analyze immediately or adjust pH to <2 S.U. and notify NC WW/GW Laboratory Certification that a non-compliant sample was received and analyzed.
7	Are samples iced to above freezing but ≤ 6°C during shipment? [40 CFR Part 136.3, Table II and footnote 18]			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.
8	Are samples analyzed within 28 days of collection? [40 CFR Part 136.3, Table II]			

	PROCEDURE – Calibration	LAB	SOP	EXPLANATION
9	What is the laboratory's reporting limit? [15A NCAC 02H .0805 (a) (7) (H)] [SM 5310 C-2014 (1) (c)] **Answer:**			Must be greater than or equal to the lowest calibration or calibration verification standard. Concentrations <0.1 mg TOC/L can be measured by some instruments if scrupulous attention is given to minimizing sample contamination and method background.
10	Is the TOC analyzer calibrated properly? [SM 5310 C-2014 (4) (a) and (d)]			Follow manufacturer's instructions for assembling, testing, calibrating, and operating analyzer. Prepare an organic carbon standard series that spans the range of organic carbon concentrations in samples. Run standards and blanks and record the analyzer's response. Determine instrument response for each standard and blank. To confirm proper instrument operation, analyze standards with concentrations above and below those determined in the samples (preferably prepared in a similar matrix).
11	List the concentrations of the calibration or calibration verification standards. **Answer:**			
12	If the calibration standards are prepared in-house, is the TOC of the reagent water determined and subtracted from the standard? [SM 5310 A-2014 (3)]			Determine the background TOC level in the reagent water used to prepare standards. Handle this water similarly to the standards and subtract the background TOC level from the TOC level of the standards. **5310 C-2014 (4) (d) states:** Correct the instrument response to standards by subtracting reagent water blank and plotting organic carbon concentration in milligrams per liter against corrected instrument response. (This is unnecessary for instruments that digitally compute concentration).
13	How often is the TOC analyzer calibrated? [SM 5310 C-2014 (4) (a)] **Answer:**			Follow manufacturer's instructions for assembling, testing, calibrating, and operating analyzer.
14	Is each calibration point compared to the curve and its concentration recalculated? [SM 5020 B-2017 (1) (b)]			
15	What are the acceptance criteria for the recalculated concentrations? [SM 5020 B-2017 (1) (b)] **Answer**:			If any recalculated values are not within the method's acceptance criteria- ≤3 times the MRL ±50%; between 3 and 5 times the MRL ±20%; or >5 times the MRL ±10%, unless otherwise specified in individual methods
16	What corrective action is performed if the acceptance criteria are not met? [SM 5020 B-2017 (1) (b)] **Answer**:			Identify the source of any outliers and correct before sample quantitation
17	Is the correlation coefficient of the calibration curve ≥ 0.995? [NC WW/GW LCB Correlation Coefficient for Linear Calibration Curves Policy]			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
18	Are samples that contain gross solids or insoluble matter homogenized? [SM 5310 C-2014 (4) (b)]			If a sample contains particulates, homogenize until a representative portion can be withdrawn through the syringe needle, autosampler tubing, or sample inlet system of continuous on-line monitor.
	PROCEDURE – Sample Analysis	**LAB**	**SOP**	**EXPLANATION**
19	Are manufacturer's instructions followed for sample and standard injection? [SM 5310 C-2014 (4) (c)] [SM 5310 B-2014 (4) (c)]			
20	Are 3 replicates analyzed until measurement is reproducible to within ±10% RSD? [SM 5310 B-2014 (4) (c)]			Repeat injection until at least three replicate measurements are reproducible to within ±10% RSD.
21	Is the reagent blank subtracted only from diluted samples? [SM 5310 C-2014 (5)] [SM 5310 B-2014 (5)]			See 5310B.5 or use instrument manufacturer's procedure. Calculate the corrected instrument response to standards and samples by subtracting the instrument-blank results from those of the standard and sample. Only subtract **reagent water blank** from standards prepared in reagent water or from the portion of diluted samples containing reagent water.
	QUALITY ASSURANCE	**LAB**	**SOP**	**EXPLANATION**
22	Is an ongoing inorganic carbon (IC) check performed? [SM 5310 A-2014 (5) (b) (10)]			Confirm on a frequency that corresponds to the laboratories' routine periodic maintenance schedule, or when maintenance has been conducted on an instrument that may affect the tool/technique for inorganic carbon removal, that inorganic carbon is sufficiently removed from the samples.
23	Is the IC check result <½ the minimum reporting level (MRL)? [SM 5310 A-2014 (5) (b) (10)]			Prepare a 102.5 mg/L IC test solution (based on bicarbonate calculations and impurities) and analyze the solution to confirm that the result is <1/2 MRL. The IC removal check may be performed on a different matrix, but the IC level in the check sample should be higher than those in the unknown samples.
24	What corrective action is taken if the IC check is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] **Answer:**			
25	Is a TOC carryover check performed at the beginning of each analytical day? [SM 5310 A-2014 (5) (a) (4)]			Immediately following the analysis of the highest calibration standard, analyze a blank. Analyze the high calibration point/blank pair at the beginning of every analytical day to verify that carryover is not occurring.
26	Is the TOC carryover check acceptance criterion <½ MRL? [SM 5310 A-2014 (5) (a) (4)]			The concentration of the blank must be <½ MRL.
27	What corrective action is taken if the TOC carryover check is not acceptable? [SM 5310 A-2014 (5) (a) (4)] **Answer:**			If the blank has a value >½ of the MRL, then the highest calibration point must be lowered until the blank immediately following the point has a value <½ MRL.
28	Is an initial instrument blank analyzed daily? [SM 5310 A-2014 (5) (b) (4)]			Analyze a blank consisting of recycled water or low TOC water. The purpose is to determine if there is any TOC present in the instrument that may contaminate the system.
29	Is the instrument blank <½ the concentration of the lowest calibration standard? [SM 5310 A-2014 (5) (b) (4)]			Instrument blank results should be <½ MRL and not affect the linearity of the calibration curve.

30	What corrective action is taken if the instrument blank is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] [SM 5310 A-2014 (5) (b) (4)] **Answer:**			**SM states:** If the result is higher, analyze several blanks to clear the system.
31	Is a method blank (reagent blank) analyzed daily or with each batch of 20 or fewer samples, whichever is more frequent? [SM 5310 A-2014 (5) (b) (5)]			**SM 5310 A states:** After the initial calibration or after an existing calibration has been verified, and prior to sample analysis, a method blank must be analyzed. The method blank consists of low TOC water as well as any reagents (including preservatives) that have been added to samples.
32	Is the method blank concentration less than ½ the concentration of the MRL? [SM 5310 A-2014 (5) (b) (5)]			**SM states:** The value of the method blank must be <½ of the MRL.
33	What corrective action is taken if the method blank is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] [SM 5310 A-2014 (5) (c) (1)] **Answer:**			**Rules state:** If QC 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 process documented, and any samples involved shall be reanalyzed, if possible. If the sample cannot be reanalyzed, or if the QC results continue to fall outside established limits or show an analytical problem, the results shall be qualified as such. **SM 5310 A states:** Consult instrument manual. Check for contamination of reagents, sample containers, and equipment. Both high inorganic-matrix samples and high-TOC samples may cause an ongoing elevated blank. Diluting samples may help. Higher MRLs may be required.
34	Is a second source mid-range calibration check standard analyzed daily? [15A NCAC 02H .0805 (a) (7) (H) (ii)] [SM 5310 A-2014 (5) (b) (3)] **List concentration of second-source standard:**			**Rules state:** Laboratories shall analyze one known second source standard to verify the accuracy of the standard preparation if an initial calibration is performed and in accordance with the referenced method requirements thereafter. **SM states:** At least once per analytical day, analyze a mid-range calibration check sample prepared from a different source than that used for the initial calibration.
35	Is the acceptance criterion of the second-source calibration check sample ±10% [SM 5020 B-2017 (1) (b)]			The results must be within 10% of the theoretical.
36	What corrective action is taken if the second-source calibration check sample is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] **Answer:**			
37	Is a lower reporting limit standard analyzed or back-calculated with each analysis? [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. On days when an initial calibration is being performed, then this requirement has been met (see question #14).
38	What is the acceptance criterion for the lower reporting limit standard? [15A NCAC 02H .0805 (a) (7) (A)] [SM 5310 A-2014 (5) (b) (7)] **Answer:**			The low-range standard should agree within 50% of the true value.
39	What corrective action is taken if the lower reporting limit standard is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] [5310 A-2014 (5) (c) (2)] **Answer:**			**SM states:** Consult instrument manual. The instrument may need to be recalibrated.

40	Is a **continuing calibration check** standard (CCC) analyzed after every 10th sample and at the end of the run? [15A NCAC 02H .0805 (a) (7) (H)] [SM 5310 A-2014 (5) (b) (7)] **List concentrations of standards used:**			**SM states:** After every 10 samples, analyze one of three calibration check samples – low-range, mid-range, and high-range standard concentrations – on a rotating basis. The low-range standard should be at or below the minimum reporting level. NC WW/GW LCB Rules state that a calibration check standard must also be analyzed at the end of the set of samples.
41	Is the CCC concentration rotated between low-, mid- and high-range concentrations? [SM 5310 A-2014 (5) (b) (7)]			The lab must set a rotational frequency and include this in the SOP.
42	What acceptance criteria are used to evaluate the CCC? [SM 5310 A-2014 (5) (b) (7)] **List acceptance criteria for each CCC standard:**			The low-range standard should agree within 50% of the true value, and the mid- and high-range samples should agree within 15%.
43	What corrective action is taken if the CCC is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] [SM 5310 A-2014 (5) (c) (2)] **Answer:**			**SM states:** Consult instrument manual. The instrument may need to be recalibrated.
44	Is a **continuing blank check** (CBC) analyzed after every 10th sample and at the end of the run? [15A NCAC 02H .0805 (a) (7) (H)] [SM 5310 A-2014 (5) (b) (6)]			**SM states:** After every 10 samples, analyze a blank preferably consisting of recycled combusted water or low-TOC water. The blank must contain any reagents that have been added to the samples. With some instruments, this is difficult to do regularly. If so, monitor a given lot of reagent water throughout the day's run. NC WW/GW LCB Rules state that a blank must also be analyzed at the end of the run.
45	Is the CBC <½ the concentration of the MRL? [SM 5310 A-2014 (5) (b) (6)]			The results for subsequent reagent-water blanks must be <½ MRL.
46	What corrective action is taken if the CBC is not acceptable? [15A NCAC 02H .0805 (a) (7) (B)] [SM 5310 A-2014 (5) (c) (1)] **Answer:**			**SM 5310 A states:** Consult instrument manual. Check for contamination of reagents, sample containers, and equipment. Both high inorganic-matrix samples and high-TOC samples may cause an ongoing elevated blank. Diluting samples may help. Higher MRLs may be required.
47	Is a Laboratory Fortified Matrix (LFM analyzed with each batch of 10 or fewer samples? [SM 5310 A-2014 (5) (b) (9)]			Spike one sample per every 10 samples analyzed or part thereof.
48	How is the LFM (spike) prepared? [SM 5310 A-2014 (5) (b) (9)] **Answer:**			**SM 5310 A states:** The spike level should be greater than 5 times the MRL and generally within 50 – 200% of the expected concentration. **SM 5020 B 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 to allow analysts to separate the matrix's effect from laboratory performance. Prepare LFM form 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). 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.

49	What is the acceptance criterion for the LFM/LFMD recovery? [SM 5310 A-2014 (5) (b) (9)] **Answer:**			The recovery should be between 85-115%.
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)] [SM 5310 A-2014 (5) (c) (3)] **Answer:**			**SM states:** This suggests a matrix problem, or it may be caused by non-homogenous suspended particulates in the sample. Consult instruction manual. Diluting samples may help.
51	Is a sample duplicate or Laboratory Fortified Matrix Duplicate (LFMD) analyzed with each batch of 10 or fewer samples? [SM 5310 A-2014 (5) (b) (8)]			Perform a duplicate analysis for every 10 samples (or part thereof) analyzed. The duplicate analysis can be a duplicated fortified sample.
52	What acceptance criterion is used to evaluate **precision**? [SM 5310 A-2014 (5) (b) (8)] **Answer:**			The RPD (relative percent difference) should be less than 15%.
53	What corrective action does the laboratory take if the duplicate results are outside of established control limits for **precision**? [15A NCAC 02H .0805 (a) (7) (B)] [SM 5310 A-2014 (5) (c) (3)] **Answer:**			**SM states:** This suggests a matrix problem, or it may be caused by non-homogenous suspended particulates in the sample. Consult instruction manual. Diluting samples may help.
54	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.

Additional Comments:

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Inspector: _____Date:_____

IC-removal check solution: Because inorganic salts are not soluble in a single concentrated solution, prepare four separate stock solutions (A–D). Prepare Solution A by adding 2.565 g magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$ to 1 L of low-TOC water. Prepare Solution B by adding 0.594 g ammonium chloride (NH_4Cl), 2.050 g calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$), 0.248 g calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], 0.283 g potassium chloride (KCl), and 0.281 g sodium chloride (NaCl) to 1 L of low-TOC water. Prepare Solution C by adding 2.806 g sodium bicarbonate ($NaHCO_3$) and 0.705 g sodium phosphate dibasic heptahydrate ($NaHPO_4 \cdot 7H_2O$) to 1 L of low-TOC water. Prepare Solution D by adding 1.862 g sodium-meta silicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) to 1 L of low-TOC water. Take a 10-mL aliquot from each solution (A–D) and add it to a 40-mL vial. Acidify with 40 µL of an appropriate acid; use the same acid sample preservation.