Laboratory Manager Approval: Kristy E. Hrehor / 08/19/2021

QA Manager Approval: Jeffrey Moore / 08/19/2021

SM 5310B - Total Organic Carbon in Water and Wastewater

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

1.1 This high temperature combustion method covers the determination of Total Organic Carbon in drinking waters, surface waters, domestic and industrial wastes. The CO2 from the oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a non-dispersive infrared analyzer. Because total carbon is measured, inorganic carbon must be removed by acidification and sparging.

1.2 Restricted Procedure
This procedure is restricted to use by an analyst experienced in the operation of a TOC-L Shimadzu Combustion TOC Analyzer. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples (SOP reference 13.3). Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method (SOP reference 13.7).

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.2) for Quality Control Definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration. The CCC is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.6 Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), MDLB or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7 MDLS (Method Detection Limit Spike) – MDLB spiked with analytes at the lowest calibration level to be used for the determination of MDL.

2.8 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3 Interferences

3.1 Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise.

3.2 Loss can also occur if large carbon-containing particles fail to enter the needle used for injection.

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision (See Section 13.7)

5 Apparatus and Equipment

5.1 Sample Container: 250 ml HDPE bottles, containing 2.5 ml of 10% sulfuric acid (preservative), for sampling

5.2 Analytical Balance, capable of accurately weighing to the nearest 0.0001 g

5.3 Glassware -- Class “A” volumetric flasks, graduated cylinders, and pipettes.

5.4 Shimadzu TOC-L TOC Analyzer

5.5 Auto-Sampler

5.5.1 Auto-sampler vials, glass, 40 ml

5.5.2 Auto-Sampler rack

5.6 Ultra-High Purity Compressed Air Tank

5.7 Air displacement pipettes of various volumes, auto-pipettors, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.

5.7.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.

5.7.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1g. Mechanical pipettes must be verified to be within ± 2.5 percent of the nominal volume.

5.7.1.2 Mechanical pipettes must be professionally calibrated every 6 months.

5.7.1.3 Auto-pipettors may be verified by measuring the volume dispensed with a Class “A” graduated cylinder. The volume dispensed must be within ± 2.5 percent of the nominal volume.

5.8 HDPE bottles, various sizes, for storage of reagents.

5.9 Glass bottles, dark amber in color, for storage of reagents and standards.

5.10 Disposal pipette tips, 101-1000 µl - Fisher PN# 02-707-507 or equivalent.
5.11 Disposable transfer pipettes:
5.11.1 Plastic - VWR® Disposable Transfer Pipets PN# 16001-190 or Fisherbrand™ Standard Disposable Transfer Pipettes PN# 13-711-7M.

6 Reagents

6.1 Compressed Ultra Pure Air
6.2 Reagent Water:
6.2.1 Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest (Deionized, HPLC, Milli-Q water, or equivalent. Milli-Q water has a resistivity of 18.2[MΩ.cm] @ 25oC and a TOC of 50 ug/L or less).
6.3 10% Sulfuric Acid Solution:
6.3.1 Purchased from VWR, Part # BDH3358-4 or equivalent.
6.3.2 This solution is used for preservation of standards and blanks.
6.3.3 This purchased chemical is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner. Store at room temperature.
6.4 1N HCl Solution:
6.4.1 Measure 250 ml of reagent water and pour into the designated plastic HCL Solution reagent bottle. Next add 20 ml of ACS grade Hydrochloric Acid. Mix well.
6.4.2 Reagent has been modified from Standard Methods per Shimadzu methodology.
6.4.3 Prepare fresh monthly.
6.5 Primary Source (PS) Stock standard, 1000 mg organic carbon/L:
6.5.1 2.1254 grams of dried ACS grade KHP is dissolved and brought to volume in a 1000 ml volumetric flask with reagent water. Keep under refrigeration.
6.5.2 Prepare every 6 months.
6.6 Calibration standards:
6.6.1 Using the Primary Source (PS) Stock standard, 1000 mg organic carbon/L, prepare calibration standards at five concentrations in reagent water.
6.6.2 The calibration standards range from 1.00 to 50.0 mg of organic carbon/L.
6.6.3 After the standards are brought to volume with reagent water, 10 ml of 10% sulfuric acid per 1000ml of standard is added for preservation.
6.6.4 Prepare every three months or when new stock standard is made.
6.6.5 Keep standards under refrigeration.

TOC Calibration Standards

Primary Source (PS) Stock standard 1000 mg/L	Final volume (ml)	Concentration (mg/L)
1	1000	1.00
5	1000	5.00
10	1000	10.0
25	1000	25.0
50	1000	50.0

6.7 0.00 mg/L Standard, ICB, CCB, MBLK, MDLB and Dilution water):
To prepare an ICB/CCB, Pipette 10ml of 10% H2SO4 into a 1L volumetric flask that already contains 1L of reagent water. This solution is stable for 28 days. The volume of the reagent may be altered if the final concentration remains the same. Keep under refrigeration. The ICB/CCB/MBLK/MDLB must be poured into a 250 ml sample collection bottle before it is poured into the appropriate vials. Record lot # of bottle used.

6.8 Continuing Calibration Check (CCC) 25.0 mg/L Standard:
To prepare the CCC, pipette 25 ml of the (PS) 1000 mg/L Stock standard Solution into a 1L volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 10 ml of 10% Sulfuric Acid Solution.

6.8.1 This solution is stable for 3 months. Keep under refrigeration.

6.9 Method Detection Limit Spike (MDLS) 1.00 mg/L Standard
To prepare the MDLS, pipette 1.0 ml of the (PS) 1000 mg/L Stock standard Solution into a 1L volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 10 ml of 10% Sulfuric Acid Solution.

6.9.1 This solution is stable for 3 months. Keep under refrigeration.

6.9.2 The (MDLS) 1.00 mg/L standard must be poured into a 250 ml sample collection bottle before it is poured into the appropriate vial. Record lot # of bottle used.

6.10 LCS's should be analyzed at the 25.0 mg/l concentration.

6.10.1 Prepare the LCS and LCSD by pipetting 0.625 ml of the Primary Source (PS) Stock standard, 1000 mg organic carbon/L into a 25ml volumetric flask and bring to volume with dilution water that was stored in a 250 ml sample collection bottle (See Section 6.7). Record lot # of bottle used.

6.11 The matrix spike should be prepared at the 25.0 mg/l concentration. To prepare the matrix spike and matrix spike duplicate, pipette 0.625 ml of the Primary Source (PS) Stock standard, 1000 mg organic carbon/L into a 25ml volumetric flask and bring to volume with sample chosen as the spike.

6.12 ICV Stock Standard Solution, 1000 mg organic carbon/L or Second Source (SS)

6.12.1 The ICV stock standard is used as a second source standard.

6.12.2 This stock standard must be from a different source than the stock standard used to make the calibration standards.

6.12.3 The prepared standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner. Keep under refrigeration.

6.13 ICV Solution 25.0 mg organic carbon/L(SS)

6.13.1 A 25 ml aliquot of the ICV Stock Standard Solution (1000 mg organic carbon/L), is pipetted into a 1L volumetric flask and diluted to volume with reagent water. Once the ICV is diluted to volume with reagent water, preserve the solution using 10 ml of 10% Sulfuric Acid Solution.

6.13.2 The ICV solution must be prepared fresh every 3 months. Keep under refrigeration.

6.14 Volumes and amounts of reagents, chemicals and standards may be altered if the final concentrations remain the same. Sample volumes and injection amounts may be altered if the required detection limits can be met and sample/reagent ratios remain the same.

7 Sample Collection

7.1 Samples are collected in 250 ml HDPE bottles.
7.2 The sample bottles are pre-preserved with 2.5ml of 10% Sulfuric Acid to a pH of < 2 in the field.
7.3 Sample preservation is checked in the receiving lab at time of receipt.
7.4 Samples are cooled and stored at 0-6° C (not frozen).
7.5 Sample holding time is 28 days.

8 Calibration

8.1 Calibration Standards:
The calibration curve consists of calibration standards at the following concentrations: 0.00 mg/L C, 1.00 mg/L C, 5.00 mg/L C, 10.0 mg/L C, 25.0 mg/L C, and 50.0 mg/L C.

8.2 Calibration Curve:
The TOC-L Shimadzu Combustion TOC Analyzer are calibrated per manufacturer's instructions at least every six months or as needed when the ICV does not meet acceptance criteria of ± 10% of true value or when new stock standard used. Six standards are used to calibrate the instrument. Minimum acceptable correlation coefficient is 0.995 using a linear regression. Dilute all samples with a response greater than 50.0 mg/L.

8.3 Calibration Verification:
8.3.1 An Initial Calibration Verification standard (ICV), a Continuing Calibration Check (CCC) and an Initial Calibration Blank (ICB) must be analyzed immediately after the calibration standards.
8.3.1 The initial calibration verification standard must be prepared with a stock from a different source than the standards used in the calibration of the instrument.
8.3.1.1 The ICV value must be within 10% of its true value.
8.3.1.2 The %Drift (see calculation 11.6) of the ICV from the true value must be within ±10%. Repeat once if it fails. If it fails the second attempt, determine the source of the problem, correct and recalibrate.
8.3.2 The ICB, CCB, MDLB and MBLK values must be less than the method RL or the run will have to be repeated.
8.3.3 A CCC and a Continuing Calibration Blank (CCB) must be analyzed every 10 samples and at the end of the sample run and must meet the same criteria as the ICV and ICB respectively.
8.3.3.1 The CCC may be from the same source as the calibration standards.
8.3.3.2 If the CCC or CCB do not meet acceptance criteria, then all samples affected by the out of control CCC or CCB are to be rerun.
8.3.4 A MDLS (low level spike) at the concentration of 1.00 mg/L must be analyzed with each batch to perform ongoing MDL study. All batch QC must be valid to report this result.
8.3.5 A MDLB (MDLB) must be analyzed once per analytical batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RL's), Table 14.2 for Quality Control

Acceptance Criteria. Table 14.3 for Quality Control Procedures associated with this method and the Standard Operating Procedures for Control Charts and Control Limits.

9.1.1 The default control limits from SM5310B are 90 – 110% recovery for TOC for LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.1.2 By default, the EPD Laboratory sets LCS/LCSD precision control limits for this method to be 0 – 15% RPD.

9.1.3 LCS/LCSD recovery and precision limits are static by EPA/Method/EPD Lab default.

9.1.4 5% of all routine samples must be spiked. The EPD Laboratory requires recovery control limits of 90 – 110% for matrix spikes. The EPD Laboratory applies MS recovery limits to MSDs.

9.1.5 By default, the EPD Laboratory sets default sample precision control limits to be 0 – 15% RPD.

9.1.6 MS/MSD recovery and precision limits are monitored and adjusted using control charts every 6 months.

9.1.7 See Administrative SOP for Control Charting and Control Limits for further details (SOP Reference 13.4).

9.2 Batch samples in groups of 20. For each batch, analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for a minimum of 5% of routine samples.

9.3 MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.3. 1 The actual MDL varies depending on instrument and matrix.

9.3. 2 The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.3.3 The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.3.4 The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial “pairs” are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blank.

9.3.5 A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.3.6 The results of the MDLBlank will be entered into Labworks using the Method Blank test code, B_TOC. The MDLSpike result will be entered using the MLTOC. The MDL Spiked Amount will be entered into the test code MATOC. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-TOC.

9.3.7 MDL study must be performed every six months and before the MDL for the

instrument expires.

10 Procedure

10.1 Procedure for the TOC-L Shimadzu Combustion TOC Analyzers – TOC07 and TOC09.

10.1.1 Remove sample bottles, standards and reagents from cold storage and allow to equilibrate to room temperature prior to sample preparation and/or analysis.

10.1.2 Perform a backlog of pending TOC samples. Batch in groups of 20. For each batch select one sample to use as a matrix spike and a matrix spike duplicate.

10.1.3 Check the Ultra-Pure Air gas cylinder and make sure there is at least 500 psi to do the run. The Ultra-Pure Air gas tank should remain open so that the instrument can remain on standby when not in use. If the instrument is not going to be used for a long period of time the furnace and the air can be turned off to conserve the air.

10.1.1 Turn on computer and screen adjacent Shimadzu TOC-L instrument.

10.2.5 Locate and click on "**TOC-Control L**" application to open. A new window provides three options. Click on the **SAMPLE TABLE EDITOR** button. Enter initials into the box and click on the **OK** button. If this button is not visible, make sure the MEASUREMENT tab is selected, not the ADMINISTRATIVE tab in the application window.

10.2.6 TOC-L SAMPLE TABLE EDITOR opens and should be empty. Locate the **NEW** button above the sample table column on left and click on it. A new window should pop up prompting the selection of the table type. The system should be set to **Shimadzu TOC** and the table type should be set to **Normal**. If a different system or table type is set, use the drop-down menu to find and select Shimadzu TOC and Normal. Click on the **OK** button.

10.2.7 When the open table window appears, expand the spreadsheet by clicking on the box located at top right corner of the window. Right click on the first row. Select the **"Insert – Multiple Samples"** option from the menu. In the SAMPLE GROUP WIZARD (PAGE 1) SAMPLE SOURCE window select **"Calibration Curve"** by clicking in the circle on left. Find and click on the button with three dots past the white typing.

10.2.8 Another window opens prompting the selection of the calibration curve. Locate FILES OF TYPE towards the bottom of the window and access the drop-down menu to select the **"ALL CAL. CURVE FILES"**. Once this is completed, several calibration curves will appear in the center of the window. Click on the most recent calibration curve. This is done by clicking on the DATE menu until the dates descend from most recent to oldest files. Click on the correct calibration curve file beginning with "npoc" followed by the date and ending in ".cal". Click the **OPEN** button. Click the **NEXT** button.

10.2.9 The second window called SAMPLE GROUP WIZARD (PAGE 2) SAMPLE PARAMETERS opens prompting the quantity of samples to be analyzed. Enter the number of samples in the appropriate box and click the **FINISH** button. The VIEW VIAL window will open displaying blue colored vials in the circular tray corresponding to the number of vials entered. Click on **OK** button. Locate and click VIEW VIAL SETTINGS, the button resembling a cake and candles, to view samples after the window closes.

10.2.10 The spreadsheet will now have some columns and rows with information. "NPOC" should show in the rows below the ANALYSIS column. "Undefined" should show in the rows below the SAMPLE ID column. "Defined" should show in the rows below the STATUS column. The RESULTS column and DATE/TIME column should be empty until the analysis begins. The VIAL column should be numbered in chronological order ascending from "1" to the last sample number. The maximum number is "68". Only sixty-eight (68) samples will fit on the auto-sampler vial tray for Shimadzu TOC-L instrument.

10.2.11 To enter the batch sheet samples and quality control samples names, click each row/box below the SAMPLES ID column. Replace "Undefined" by typing the name of samples into each line corresponding to the batch sheets position. For instance, the first-row sample ID name should correspond with the sample listed in the first position of the batch sheet. Compare the spreadsheet to the batch once all the samples and QCs are entered to check for errors. Click on the **SAVE** button. Another method to save the spreadsheet is to select the "SAVE" option from the FILE menu.

10.2.12 Saving the editor table will prompt a name for the spreadsheet. Enter the name of the file in the FILE NAME box. Begin the title of the file with "T" and follow it with the date using two-digit month, day and year, i.e. MMDDYY. An example is "T040116". Click on the **SAVE** button. Confirm the file has saved by looking at the top of the editor table and see the title is what you named it following *TOC-L Sample Table Editor*.

10.2.13 Print out the worksheet by printing the table. Find the PRINT menu. Select options "SAMPLE TABLE" for results in portrait format, double sided. Hole-punch and place worksheet into the Run Log binder with appropriate placement of analysis name (TOC), batch numbers, initials, date and proper pagination written on each page.

10.2.14 Perform maintenance check and remember to place drain tubes into the waste drum. Replace the rinse water with reagent water.

10.2.15 Begin preparing the LCS, LCSD, MS, and MSD for the batches.

10.2.16 Turn on the Shimadzu TOC-L instrument by pushing the power button located on the front face of the instrument. Click on the **CONNECT** button towards the top of the editor window. A new window, SEQUENCE, should pop up showing that the port is opened. The instrument will begin to initialize and provide the

progress as percentage values. The window will close upon completion of initialization.

10.2.17 At the very top right corner of the editor window will be an orange circle stating NOT READY. Adjacent this circle find the **MONITOR** button and click it. A window will present parameters for Background and NDIR. Red boxes with "x" encircled indicate parameters are not ready for analysis. The parameters will continue to prepare for the analysis and indicate readiness by the boxes changing to green with check marks when the furnace warms up to the appropriate temperature of 680ºC.

10.2.18 While the instrument warms up, pour samples and QC into vials. Place these vials in auto-sampler rack according to their placement in the numbered batch sheet.

10.2.19 Load the auto-sampler tray with the vials from the silver trays according to the appropriate positions recorded on the batch sheet. When the lid is taken off the auto-sampler to access the tray, the computer will show a notice window. After all the vials are loaded into the auto-sampler tray and the lid is placed back on, click on the **OK** button in the notice window. (Analyst may need to click ok earlier in order to view Monitor.)

10.2.20 The NOT READY orange circle should be replaced with a green **READY** circle in the top right corner of the editor window. Once the READY is indicated and the furnace is at a steady 680ºC, the instrument can begin the analysis.

10.2.21 Click on the **START** button to initiate the analysis. Measurement Start window will appear. Confirm selection of "Shut down instrument" before clicking the **START** button**.** When the instrument begins the analysis, the green READY circle will change to a blue **RUN**. This indicates the instrument is analyzing. The rows in the editor spreadsheet will change to pink and the STATUS column will change to "Measuring". Note the DATE/TIME and RESULTS column will begin to enter information. The date and time of the analysis should show as well as the results from the measurements analyzed by the instrument. At this point no changes can be made to the editor's spreadsheet.

10.2.22 After the analysis is completed, the blue RUN will change back to the green READY. All the results, time, and date will be entered under the appropriate column corresponding to the samples. STATUS column should now say "completed" for each sample as well. Find the **SHUTDOWN** button located between the STOP and the MONITOR buttons. Click on **SHUTDOWN** and be sure to click **OK** in the window when prompted to for the system to begin shutting down. This takes thirty (30) minutes.

10.2.23 Print results. Find the PRINT menu. Select options "SAMPLE TABLE" for result worksheet in landscape format and "SAMPLE REPORT – ALL" for detailed report in portrait format.

10.2.24 Close the editor window by clicking the white "x" in the red box located in the top right corner.

10.2.25 Close the "**TOC – CONTROL L**" application window by clicking the black x in the top right corner.

10.2.26 Select the **SHUTDOWN** option from the Window's Home Menu and confirm. Turn off the monitor screen. Verify that the instrument is off after an hour. Pull out waste lines out of drum and secure cap onto the drum until next run.

10.2.27 Dilute and reanalyze all samples with a response greater than 50.0 mg/L.

11 Calculations

11.1 The linearized signal which is proportional to the instantaneous concentration of CO_2 is integrated and referred to stored calibration data and the carbon concentration in the sample is calculated to display carbon concentration in parts-per-million (ppm).

11.2 Mean ($\overline{X}$):

$$\overline{X} = \frac{X_1 + X_2 + \cdots X_n}{n}$$

11.2.1 Where:

$X_1 + X_2 + \cdots X_n$ = The sum of a set of values X_i, i = 1 to n

n = The number of values in the set

11.3 Standard Deviation (n – 1) (σ_{n-1}):

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{n-1}}$$

11.3.1 Where:

$\overline{X}$ = Mean of the values

X_i = Individual values 1 through i

n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{\sigma_{n-1}}{\overline{X}} * 100$$

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation

$\overline{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

$$\%RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} * 100$$

11.5.1 Where:

$|X_1 - X_2|$ = Absolute difference between two values

$\frac{(X_1 + X_2)}{2}$ = Average of two values

11.6 Percent Drift, %Drift:

$$\%\text{Drift} = \frac{(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}})}{\text{Concentration}_{\text{Expected}}} * 100$$

11.6.1 Where:

$\text{Concentration}_{\text{Calculated}}$ = Concentration calculated from result
$\text{Concentration}_{\text{Expected}}$ = Theoretical concentration of the standard

11.7 Extract Concentration:

11.7.1 The extract concentration is calculated relative to the calibration curve by the instrument software.

11.8 Percent Recovery:

11.8.1 LCS/LCSD:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.1.1 Where:

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample
$\text{Conc}_{\text{expected}}$ = Expected concentration

11.8.2 MS/MSD:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}} - \text{Conc}_{\text{unspiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.2.1 Where:

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample
$\text{Conc}_{\text{unspiked}}$ = Concentration found in unspiked sample
$\text{Conc}_{\text{expected}}$ = Expected concentration

11.9 Calculation of Dilution Factors

$$C \times D = F$$

11.9.1 Where:

C = concentration from instrument in mg/L
D = dilution factor, if any
F = final concentration in mg/L

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP reference 13.5.

13 References

13.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 5-19, 5-20, Method 5310 B. High-Temperature Combustion Method (2000).
13.2 EPD Laboratory Quality Assurance Plan, Revision 11, September 2018, or later.
13.3 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.
13.4 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.
13.5 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.6 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.
13.7 GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 RL for Method SM 5310B

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
SM 5310B	Total Organic Carbon	1.0	mg/L

Table 14.2 Acceptance Criteria for Method SM 5310B			
Method	**Analyte**	**LCS, LCSD, MS Accuracy Water (%R)**	**LCSD, MSD Precision Water (RPD)**
SM 5310B	Total Organic Carbon	90-110	15

Table 14.3 Summary of Calibration and QC Procedures for Method SM 5310B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM 5310B	Total Organic Carbon	Initial calibration for all analytes	Once per initial calibration or quarterly, whichever is sooner.	Correlation coefficient ≥ 0.995 linear regression	Correct problem then repeat initial calibration	
		Second source calibration verification (ICV)	Prior to sample analysis	TOC concentration within 10% of expected value	Correct problem then repeat initial calibration	
		Initial Calibration Blank (ICB)	Once per analytical run	Value mist be < RL.	Correct problem and repeat initial calibration	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria Table, SOP 3-032 Appendix A and Initial Demonstration SOP (SOP Reference 13.3)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
SM 5310B	Total Organic Carbon	Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table, SOP 3-032 Appendix A and Continuing Demonstration of Capability SOP (SOP Reference 13.3)	Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	
		Initial Calibration Blank (ICB)	Once per analytical run	TOC value < 1.00 mg/L	Correct problem and repeat initial calibration	
		Method Blank (MBLK)	One per analytical batch	TOC value must be < RL	Correct problem then analyze method blank and all samples processed with the contaminated blank	If unable to re-analyze, flag with a "B"

Table 14.3 Summary of Calibration and QC Procedures for Method SM 5310B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
		Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table, SOP 3-032 Appendix A	Correct problem then reanalyze the LCS/LCSD and all samples in the affected batch	If unable to re-analyze, flag with a "J"
		Matrix Spike (MS/MSD)	5% of samples	QC Acceptance Criteria Table, SOP 3-032 Appendix A	Evaluate out of control event, reanalyze or flag data	
		Continuing Calibration Check (CCC)	After every 10 samples and at the end of the sample run	TOC concentration within 10% of expected value	Correct problem then reanalyze all samples associated with out of control CCC.	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of the sample run	TOC concentration must be < RL	Correct problem then reanalyze all samples associated with out of control CCB.	
		MDL Low level Spike (MDLS) 1.00 mg/L	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL Blank (MDLB)	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL study	Every six months or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall	Re-do MDL Study	
SM 5310B	Total Organic Carbon	MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	

Appendix A – Quality Assurance Criteria for Method SM5310B

Table A.1 Quality Assurance Criteria for Method SM5310B					
QC Type	Analyte	Accuracy(%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	TOC	90	-	110	15
MS/MSD	TOC	90*	-	110*	15
*MS/MSD Control limits are static by EPD Lab default. Control Chart data generated from 01/01/2019 -01/01/2021					

Updates to Previous Version:
Appendix A added. Updated for online revision.
Section 2
Section 4
Section 9
Table 14.3
Table A.1