Standard Operating Procedure for:

liquiTOCII High Temperature TOC/TN\textsubscript{b} Analyzer
(TIC/TOC R01.doc)

Missouri State University

and

Ozarks Environmental and Water Resources Institute (OEWRI)

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Approved by: __________________________ Date: _____________
OEWRI Director
Table of Contents
1  Identification of the method................................................................. 3
2  Applicable matrix or matrices.............................................................. 3
3  Detection Limit .................................................................................. 3
4  Scope of the method........................................................................... 3
5  Summary of method ........................................................................... 3
6  Definitions .......................................................................................... 3
7  Interferences ....................................................................................... 5
8  Health and safety ................................................................................ 6
9  Personnel qualifications ....................................................................... 6
10 Equipment and supplies ..................................................................... 6
11 Reagents and standards ....................................................................... 7
12 Quality control ................................................................................... 8
13 Calibration and standardization ......................................................... 9
14 Procedure .......................................................................................... 11
15 Data acquisition, calculations, and reporting ...................................... 16
16 Computer hardware and software ....................................................... 17
17 Method performance ........................................................................... 17
18 Pollution prevention ........................................................................... 17
19 Data assessment and acceptable criteria for quality control measures ... 18
20 Corrective actions for out-of-control or unacceptable data ................. 18
21 Waste management ............................................................................ 19
22 References ........................................................................................ 19
23 Tables, diagrams and flowcharts......................................................... 18
1 **Identification of the method**

liquiTOCII High Temperature TOC/TN<sub>b</sub> Analyzer

2 **Applicable matrix or matrices**

This instrument can be used for natural water samples.

3 **Detection Limit**

The operating modes for this instrument are Total Carbon (TC), Total Inorganically-bound Carbon (TIC), Total Organically-bound Carbon (TOC), Nonpurgable Organic Carbon (NPOC), and Purgable Organic Carbon (POC). The operating range for this instrument is 0 to 100,000 mg/l. The sample volume range is 0.05 ml to 4 ml. The method detection limit is 1.0 mg/l for all forms of carbon. Analysis requires 6 to 22 minutes for completion depending on the mode of operation.

4 **Scope of the method**

This standard operating procedure provides Missouri State University (MSU) laboratory personnel with guidance on the procedure for operation of the Elementar liquiTOCII High Temperature TOC/TN<sub>b</sub> Analyzer in TIC/NPOC and NPOC mode.

5 **Summary of method**

A sparger purges volatiles from the sample, then a high temperature catalytic oxidation occurs using a two-zone combustion reactor that separates the matrices and protects the catalyst, and then carrier gas delivers the gases to the detector.

A dosing syringe delivers the sample to the combustion system and the sample is warmed to 70°C to purge the POC. Acetous digestion of TIC occurs using 0.8% hydrochloric acid. The sample then undergoes a dynamic combustion at 850°C and catalytic post combustion at a maximum 800°C. Synthetic air is the carrier gas that transfers the CO<sub>2</sub> gas through a three-step drying process and then to the detector for measurement. The detector is a multi-channel non-dispersive infrared photometer with one channel dedicated to NO detection.

6 **Definitions**

6.1 Analytical batch: The set of samples processed at the same time.

6.2 Calibration standard: A solution prepared from the primary dilution standard solution or stock standard solutions. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

6.3 Chain of Custody (COC): Used to describe the written record of the collection, possession and handling of samples. Chain of custody forms should be completed as described in the Chain of Custody SOP # 1030R01. Chain of custody (COC) forms are located on a board in Temple Hall 125.

6.4 Daily factor calibration: Instrument calibration is performed before each batch using a stock standard solution which illustrates the instrument’s response to analyte concentration. Potassium phthalate (KHP) serves as TOC daily factor calibration standard when the instrument is programmed in NPOC mode. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) serves as the TIC daily factor calibration standard and is
combined with the TOC standard when the instrument is programmed in TIC/NPOC mode. The instrument is recalibrated when any of the daily factors are outside the range of 0.9 to 1.1. Fact1 is the TIC-factor, fact2 is the NPOC-factor, and fact3 is the TOC-factor in the final data sheet. These factors should be recorded with each data sheet to illustrate the quality of the data.

6.5 Dissolved Organic Carbon (DOC): organic carbon remaining in a sample after the sample has been filtered using a 0.45μm filter.

6.6 Field blank (FB): An aliquot of deionized water treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

6.7 Field duplicate (FD): Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

6.8 Instrument calibration: A 5-point instrument calibration occurs monthly and potassium hydrogen phthalate (KHP) is used when the instrument is in NPOC mode. Sodium carbonate (Na₂CO₃) is used in addition to KHP when the instrument is in TIC/NPOC mode.

6.9 Instrument drift: Gradual change in some operating characteristic of a circuit, tube, or other electronic device in a laboratory instrument. This can be measured during a brief period as an effect of warming up or during a long period as an effect of continued use.

6.10 Laboratory duplicate (LD): Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

6.11 Laboratory reagent blank (LRB): An aliquot of HPLC water that is used to calibrate the instrument at the beginning of the analyses and is used within the batch analysis sequence for QA/QC. The LRB’s purpose is to determine if analytes or interferences are present in the laboratory environment or the apparatus.

6.12 Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

a. To calculate the MDL:

b. Prepare triplicates of two water samples with low concentrations of non-purgeable organic carbon. The laboratory director or supervisor will choose appropriate samples to use to determine MDL.
c. Analyze all samples.
d. Include all sample processing steps in the determination.
e. Calculate the standard deviation ($s$).
f. From a table of the one-sided $t$ distribution select the value of $t$ for $7 - 1 = 6$ degrees of freedom at the 99% level. This value is 3.14
g. The product 3.14 times $s$ is the desired MDL.

6.13 Minimum Quantification Interval: The lowest level that can be quantitated accurately and is generally defined as four times the method detection limit = $4(\text{MDL})$.


6.15 Purgeable Organic Carbon (POC): volatile organic carbon that has been sparged from a sample.

6.16 Relative Percent Difference (RPD): calculated as the difference between a sample and duplicate results, divided by the average of the sample and duplicate results, multiplied by 100%.

6.17 Suspended Organic Carbon: particulate organic carbon (PtOC) that is too large to pass through a 0.45μm filter.

6.18 Total Carbon (TC): both inorganic and organic carbon in a sample.

6.19 Total Inorganic Carbon (TIC): carbonate, bicarbonate, and dissolved carbon dioxide derived from non-living or artificial sources.

6.20 Total Organic Carbon (TOC): material derived from decaying vegetation, bacterial growth, metabolic activities of living organisms, and from synthetic sources such as detergents, pesticides, fertilizers, and industrial chemicals. Natural organic matter produces humic acid, amines, and urea. TOC is a non-specific indicator of water quality.

7 Interferences

7.1 Sample acidification invalidates any inorganic carbon determination.

7.2 The removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic carbon or POC.

7.3 Some turbid samples may need to be filtered through a 1.5 μm pore diameter membrane filter to remove organic matter from the sample due to the small sample tube diameter associate with the instrument. A 0.45μm pore diameter membrane filter may also be used to determine the dissolved fraction.

7.4 The instrument is calibrated by the manufacturer and certified by the installer.
8 Health and safety

8.1 These analyses involve handling freshwater samples that may contain live microorganisms and therefore pose some threat of infection. Laboratory personnel who are routinely exposed to such water samples are encouraged to protect themselves from water borne illnesses by wearing clean disposable gloves and washing their hands frequently.

8.2 Use protective gloves to handle all of the chemical substances necessary for operation of this instrument. Review the MSDS for additional information and safety concerns regarding the chemical substances used throughout these procedures.

8.3 The combustion tube within the instrument is routinely at temperatures exceeding 850°C. Do not remove the left instrument panel. All maintenance will be performed by authorized personnel only.

8.4 Keep all loose clothing away from mechanical moving parts associated with the carousel and sample tubes.

9 Personnel qualifications

Samples will be analyzed by Missouri State University (MSU) laboratory personnel who have received appropriate training from experienced personnel, prior coursework, and laboratory experience regarding the analyses, and who are familiar with all of MSU's sample handling and labeling procedures and appropriate SOPs.

10 Equipment and supplies

10.1 Carousel: loads samples into the instrument.

10.2 Chain of Custody Forms: used to describe the written record of the collection, possession and handling of samples. Chain of custody (COC) forms are located on a board in Temple Hall 125. Chain of custody forms should be completed as described in the Chain of Custody SOP # 1030R01.

10.3 Protective Gloves: for protection against chemicals.

10.4 Stir bars: 8-agon, 0.31" x 0.5", Fisherbrand catalog number: 14-512-145

10.5 Vials: 18ml plastic, Elementar Part Number: 05 001 342

10.6 Filters, Glass microfiber: 47 mm diameter, 1.5 µm nominal pore size, such as Whatman 934-AH (catalog number: 1827 047) or equivalent. And/or a 47 mm diameter, 0.45µm nominal pore size, such as Millipore Corp RW0304700(Fisher catalog number: RW03 047 00).

10.7 Filtration apparatus
   a. Filter pump
   b. 1-L receiving flasks with tubulation
   c. Filter funnel manifold, 3 positions
d. Glass vacuum filter holders, 47mm, 300 mL

e. Vacuum tubing, ¼” inside diameter

10.8 Tongs.

11 Reagents and standards

11.1 Copper wire: Elementar 05 000 699.

11.2 0.8% Hydrochloric Acid: Add 22 ml concentrated HCl to 500 ml of HPLC water under a fume hood and dilute to 1 liter.


11.4 Magnesium Perchlorate: Elementar 05 001 059. Must wear safety goggles and protective gloves.

11.5 TIC/NPOC mode Solutions

a. Standard Stock Solution (500mg/l TOC and 500mg/l TIC): Dissolve 1062.7 mg KHP and 4412.1 mg Na₂CO₃ in 1 liter HPLC-grade water and store within a brown bottle. This solution is stable for approximately 28 days.

b. Monthly Calibration Standard: Dilute 12.5ml of the Standard Stock Solution prepared in 11.5a to 250ml using HPLC-grade water within a 250ml volumetric flask. The instrument automatically dilutes this monthly calibration standard so only one solution is prepared. Prepare fresh and use immediately.

c. Daily Factor Calibration Solutions. Prepare fresh daily. Prepare the LRB by filling a clean sample vial with HPLC-grade water. Prepare standard check for the daily factor calibration solution by diluting 12.5ml of the Standard Stock Solution prepared in 11.5a to 250ml using HPLC-grade water within a 250ml volumetric flask. Prepare fresh and use immediately.

11.6 NPOC mode Solutions

a. Standard Stock Solution (500mg/l TOC): Dissolve 1062.7 mg KHP in 1 liter HPLC grade water and store within a brown bottle. This solution is stable for approximately 28 days.

b. Monthly Calibration Standard: Dilute 12.5ml of the Standard Stock Solution prepared in 11.6a to 250ml using HPLC-grade water within a 250ml volumetric flask. The instrument automatically dilutes this monthly calibration standard so only one solution is prepared. Prepare fresh and use immediately.

c. Daily Factor Calibration Solutions. Prepare fresh daily. Prepare the LRB by filling a clean sample vial with HPLC-grade water. Prepare the standard check (the software recognizes this solution as the “Test” so that
is what it is called in the template) for the daily factor calibration solution by diluting 12.5ml of the Standard Stock Solution prepared in 11.6a to 250ml using HPLC-grade water within a 250ml volumetric flask. Prepare fresh and use immediately.

11.7 Platinum catalyst: Elementar 05 001 380.


11.9 Sodium Carbonate (Na₂CO₃): anhydrous, Fisher S263-500.

12 Quality control
12.1 Quality control program: The minimum requirements of the quality control program for this analysis consist of an initial demonstration of laboratory capability and the periodic analysis of laboratory reagent blanks and other laboratory solutions as a continuing check on performance. The laboratory must maintain performance records that define the quality of the data that are generated.

a. Analyses of laboratory blanks are required to demonstrate freedom from contamination. One LRB is analyzed for every 15 samples analyzed.

b. The laboratory will, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.

c. The laboratory will maintain records to define the quality of data that is generated.

12.2 Initial demonstration of performance. The following must be satisfied before the analytical procedure may be used for samples and before a new analyst may analyze samples.

a. Method Detection Limit (MDL) – To establish the ability to detect the analyte, the analyst shall determine the MDL by carrying through 7 or more separately prepared blanks through the analytical procedures. The average value, X, and the standard deviation of the values, s, shall be calculated. The MDL is equal to 3s (3 x standard deviation). The MDL should ≤ 0.5 mg/l for all forms of carbon.

b. Initial Precision and Accuracy– Initial instrument calibration, monthly instrument calibration, individual batch calibration with daily factor generation establishes the ability of operators to generate acceptably precise and accurate results. The manufacturer performed an initial 5-point calibration of the instrument. Additional 5-point calibrations are performed monthly. The measured values must be within 10% of the true value of the standards. The instrument calibration remains stable for a
month. Batch calibrations provide daily factors that must be within the range of 0.9 to 1.1.

12.3 The LRB is measured along with the standards at the start of the analytical cycle. The LRB must be less than or equal to the required method detection limit to pass the quality control program. A set including the LRB, the laboratory duplicate (LD), and a check standard (Check) will be analyzed after every 15 samples. The criteria for these checks are noted in Table 1.

Table 1. Quality control samples and acceptance criteria.

<table>
<thead>
<tr>
<th>Check</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRB</td>
<td>≤ MDL</td>
</tr>
<tr>
<td>LD</td>
<td>± 20% of the true value</td>
</tr>
<tr>
<td>Check</td>
<td>± 20% of the true value</td>
</tr>
</tbody>
</table>

13 Calibration and standardization

13.1 Calibration employs an equation to represent the relationship between the detector signal and its concentration. The liquiTOCII software automatically computes the calibration function and illustrates the calibration plot as well as the calibration coefficients.

\[ c = \frac{a + b I_k}{IV} \]

where: 
- \( a \) = represents the offsets
- \( b \) = slope of the line
- \( IV \) = injection volume
- \( I_k \) = peak areas corrected by the blank value of the flushing volume.

13.2 Based on this equation, the detector signal of each standard should predict the concentration of the standard to within ±20% accuracy. The correlation coefficient, \( R^2 \) value of the equation, should be ≥0.995 in order for the equation to be used to predict concentration although the manufacturer recommends >0.990. The liquiTOCII software lists the \( R^2 \) value as “r” under the calibration plot.

13.3 If a peak maximum lies below the saturation concentration of the detector, the data will be saved. If the peak is out of range, the peak will not be saved.

13.4 The manufacturer indicates that the instrument calibration remains stable for at least one month.

13.5 Monthly calibration procedures are as follows:

a. Use the solution prepared in Section 11.5b if the instrument is in TIC/NPOC mode. Use the solution prepare in Section 11.6b if the instrument is in NPOC mode.
b. The liquiTOC software includes a calibration wizard that will be followed to perform the calibration. Once a calibration is complete the software will automatically create a calibration plot.

c. Open the liquiTOC software by double clicking on the liquiTOC icon on the desktop screen.

d. Choose Wizards from the menu bar then choose Calibration. Define the calibration as follows:
   1. Number of measurements per sample: 3
   2. Number of run-in samples: 3
   3. Number of blank samples: 3
   4. Concentration Range: 20 ppm
   5. Number of calibration points: 5
   6. Choose the option: Different volumes, unique parent solution
   7. Input the concentration of the standards prepared: 25 ppm TOC.

e. Check flows, pressure, and maintenance levels before starting a continuous run. The pressure and flows will change throughout the run, the analysis should begin with the following parameters.
   1. The gas pressure should be approximately 1.0 - 1.2 bar at the bottle pressure reducing valve on the zero air generator.
   2. The pressure display on the PC should read 0.95 – 1.0 bar.
   3. The MFC (Mass Flow Controller) representing the current gas flow directly at the entrance of the IR detector should be 200 mL/min.
   4. The FM (Flow Meter) representing the current carrier gas flow at the carrier gas entrance of the analysis instrument should be 200 ± 10 mL/min.
   5. The furnace should have the catalyst portion at approximately 800°C and the reactor portion at approximately 90°C and not >90°C.
   6. The water and acid bottles next to the instrument should be stocked.

f. Place the run-in, blank, and “test” (standards) into the autosampler according to the hole position that is labeled in the sample pane provided by the wizard.

g. Add two drops of 6M HCl from the dropper bottle labeled “TIC/TOC 6M HCL” to each vial if the instrument is in NPOC mode. Do not add acid to vials if the instrument is in TIC/NPOC mode.

h. Place a clean stir bar in each vial.

i. Click the [ ] on the toolbar to begin the continuous run.
j. After the calibration analysis is complete, click on Math from the menu bar, then click on calibrate to display the calibration information in the Statistics pane.

k. The value of $r$ should be >0.995. If that is not the case inform the laboratory director.

l. Click View/Next until the calibration coefficients dialog box is displayed.

m. Click OK to save the coefficients.

13.6 Calibration standards ("test") and check standards ("check") are analyzed with each batch to monitor instrument shift and combustion tube performance.

14 Procedure
14.1 Pre-analysis Procedures
a. Some samples will have to be filtered prior to analysis. The laboratory director and project manager will have determined whether filtration is necessary prior to analysis. To filter samples:
   1. Set up the filtration apparatus, insert a filter, and apply vacuum.
   2. Wet the filter with a small volume of deionized water to seat it allowing the DI water to pass into a waste collection flask.
   3. Remove the waste collection flask and replace it with a clean sample collection flask.
   4. Filter approximately 20ml of sample and collect the filtrate in the sample collection flask.
   5. Transfer the filtered sample into a clean vial and proceed with the remaining samples using clean sample collection flasks for each sample. The filter can be reused if flushed with 50ml of DI water in between samples. Verify with the laboratory director prior to reusing filters.

b. Turn on the PC and printer and wait for the booting procedure to end.

c. Turn on the autosampler by flipping the switch located on the right side near the back just above the plug and wait for the reference run to end.

d. Turn on the liquiTOC’s main switch located on the right side of the instrument. Wait for the instrument to initialize. You will hear the syringe located inside the left panel of the instrument move up and then down. When the syringe stops moving the instrument has been initialized.

e. Open the liquiTOC software by double clicking on the liquiTOC icon, on the desktop screen. Click Enter when asked for a user name and password.
f. Turn the gas supply on by turning the switch on the top of the zero-air generator (ZAG) to ‘auto’.

g. Check gas flow by viewing the flow meter displays on the screen. The gas pressure should be approximately 1.0 – 1.2 bar at the bottle pressure reducing valve on the ZAG. The pressure display on the PC should read 0.95 – 1.0 bar. Adjust the regulator on the ZAG if necessary.

h. When the program is ready, the status field will turn from red to green.

14.2 Software Setup

a. Mode Selection
   1. Make sure the status field displays the desired mode of analysis.
   2. To change the mode of analysis select system on the menu bar and then choose mode. The document that is open on the screen must be blank to change modes.
   3. For NPOC mode, select NPOC (external strip-out of TIC necessary!) For TIC/NPOC mode select TIC/NPOC, TC=TIC + NPOC.

b. Open the standard template by clicking on the open folder hot button, scrolling down to either “oweri Template” for NPOC mode or “OEWRI Template (TIC/NPOC mode)” for TIC/NPOC mode, and clicking ok. The standard template has the correct analysis sequence and number of duplicates, blanks, and “test” (standards) required of the analyses. The template will look like this:

![OEWRI Template](image)

Figure 1. OEWRI Template

Other specific project templates may be used.
c. Make sure that the conc. range column reads “20 ppm”. If the conc. range column does not read “20 ppm”, double click on the cell located below the conc. range title cell and select **20 ppm**.

14.3 Sample Preparation

a. Organize the project sample bottles to minimize confusion when preparing samples and entering sample information into the template.

b. Fill a sample vial with the standard check solution prepared in Section 11.5c or 11.6c depending on the mode of operation (TIC/NPOC or NPOC). Place the vial in the No. 1 position in the carousel. This vial will be used for the “Run In” portion of the calibration and will be sampled 3 times to complete the triplicate determination. So the vial in position No. 1 will provide the source of sample no. 1, 2, and 3 on the template.

c. Fill another sample vial with HPLC water and place the vial in the No. 2 position in the carousel. This vial will be used for the “Blank” portion of the calibration and will be sampled 3 times to complete the triplicate determination. So the vial in position No. 2 will provide the source of sample no. 4, 5, and 6 on the template.

d. Fill a third sample vial with the standard check solution prepared in Section 11.5c or 11.6c depending on the mode of operation (TIC/NPOC or NPOC). Place the vial in the No. 3 position in the carousel. This vial will be used for the “Test” portion of the calibration and will be sampled 3 times to complete the triplicate determination. So the vial in position No. 3 will provide the source of sample no. 7, 8, and 9 on the template.

e. Fill a fourth vial with a water sample and place the vial in the No. 4 position in the carousel. Enter the sample ID in the name column of the template by double clicking the empty cell in the name column. Type the correct sample ID in the sample pane window and click **OK**.

f. Continue to fill vials with water samples, place them in the appropriate position in the carousel, and enter the sample IDs accordingly.

g. A laboratory duplicate (LD), a laboratory reagent blank (LRB), and a standard check (called “check”) will be analyzed after every 15 water samples. So choose a water sample at random, fill a vial with the water sample chosen, and place the vial in the No. 19 position in the carousel. Type “-LD” after the sample ID when entering the sample ID into the name cell for No. 19. Fill another vial with HPLC water and place the vial in the No. 20 position in the carousel. Type “LRB” into the name cell for No. 20. Fill a different vial with the standard check solution used in 14.3d and place the vial in the No. 21 position in the carousel. Type “Check” into the name cell for No. 21.
h. Continue filling vials with water samples adding the LD, LRB, and check
to the analysis sequence after every 15 water samples to determine
instrument drift and precision.

i. When finished or when the carousel is full, add 2 drops of 6M HCl to each
vial if the instrument is in NPOC mode. Do not add acid to vials if the
instrument is in TIC/NPOC mode. Then add a clean stir bar to each vial.

14.4 Sample Analysis
a. Check all maintenance intervals including pressure and flow rates
   1. MFC flow should be 200ml/min.
   2. FM flow should be 200 ±10ml/min.
   3. The pressure display should be 0.95 - 1.0bar.

b. Check water and acid stock bottle volumes.

c. Check the waste bottle for free board volume and dispose of waste
   properly if the bottle is already ¾ full.

d. Click on from the toolbar to begin a continuous analysis.

e. When the instrument is analyzing a sample the sample line in the
   database setup screen will turn yellow.

f. Check daily factor calibration by viewing the “Dil.Factor” column on the
   template after the first water sample has been analyzed. Recalibrate and
   reanalyze when any of the daily factors are outside the range of 0.9 to
   1.1. If the factor is out of range, stop the analyses by selecting system on
   the main toolbar then selecting the stop tag sub category. A window
   displaying “set stop tag at desired No.” will be displayed. Change the
   stop tag number to the desired sample and select OK. Reanalyze the
   calibration solutions, check the daily factor, and proceed with the analysis

14.5 Post Sample Analysis Shut Down
a. The Sleep/Wake-Up function of the software is formatted to bring the
   instrument to shut down conditions after all samples in the carousel have
   been analyzed or after a specific sample.

b. Remove all sample vials from the carousel and clean up any spills on the
   carousel. Return all analysis materials to appropriate locations of the
   shelf and remove personal items from the station. Flush remaining water
   samples down the sink with tap water to dilute to a neutral pH. Rinse the
   vials with tap water and transfer the vials to the 2% HCl acid tub. The
   vials should remain in the acid bath for a minimum of 2 hours and be
   promptly removed afterward. Dry the vials upside down on a paper towel
   and transfer them to a large sealed bag for storage.
c. Check the waste bottle for free board volume and dispose of waste properly if the bottle is already ¾ full.

14.6 Export and Save Data

a. When the analysis is complete export the liquiTOC II document as an Excel file by selecting File on the toolbar and then clicking Export on the submenu. The Select Document Name box will appear, if the name is correct, click OK. The default location is the Shared Documents file. If the Shared Documents file is not in the window, navigate to the correct file by clicking to navigate to My Computer and the Shared Documents file. Click on the All Analyses file, change the file type to an MS Excel Files (.xls) within “Save As Type” field, and click save. A box will appear that reminds the user that no graphical data will be saved with the Excel file, click yes to acknowledge. Back up data to a removable drive by clicking Export, navigating to the removable drive, and saving the file.

b. When the data is viewed in any other software program the column titles change and all available columns are included during the export. No figures are exported to Excel. The “Stored” column contains information as to when the data was exported. “SDateTime” includes the date when the sample was analyzed. The “Name” column includes sample ID information. “Fact” is the daily factor that was the Dil. Factor on the temp late and is the daily calibration factor.

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<th>Version</th>
<th>Stored</th>
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Figure 2. Excel File Column Titles.
“Conc1” is the concentration of TIC in the sample reported in mg/l.
“Conc2” is the concentration of NPOC in the sample reported in mg/l.
“Conc3” is the concentration of TC in the sample reported in mg/l. Conc 4 and 5 are related to modes of analysis that OEWRI is not using. There will be zeros in column that are not related to the mode of analysis.
“Conc6” is the concentration of TOC in the sample reported in mg/l.
“Area1”, “Area 2”, and “Area 3” are the areas under the peaks for TIC, NPOC, and TC respectively. Area 4, 5, and 6 columns should be filled with zeros. “ConcRang” is related to the viewing window or the expected range of carbon forms in the sample. The “ConcRang” column should be filled with 20ppm for surface water analyses. NumOfScans indicates the number of times the NDIR detector scanned the CO₂ gas. It is normal for columns titled Info, Memo, and Tagged to not include any information in them or be full of zeros.

15 Data acquisition, calculations, and reporting
15.1 The data from each batch will be saved to the TIC/TOC computer and the same data will be exported as an Excel file for project management use.

15.2 The liquiTOCII does not perform absolute measurements but determines the value by calculations. Standards of known element content are used to make a series of standards that vary in concentration and are used for both instrument and factor calibration. Calibration employs the equation below to represent the relationship between the detector signal and its concentration. The liquiTOCII software automatically computes the calibration function and illustrates the calibration plot as well as the calibration coefficients.

\[ c = \frac{a + bI_k}{IV} \]

where:  
- \( a \) = represents the offsets
- \( b \) = slope of the line
- \( IV \) = injection volume
- \( I_k \) = peak areas corrected by the blank value of the flushing volume.

The calibration coefficients are included in the data file and are printed with a standard report.

15.3 There are no water sample dilutions associated with this method.

15.4 Results should be reported to 0.01mg/l.

15.5 The evaluation of MDL and precision require calculation of standard deviation. Standard deviations should be calculated as indicated below, where \( n \) = number of samples, \( x \) = concentration in each sample. Note: This is the sample standard deviation calculated by the STDEV function in Microsoft Excel.
The Method Detection Limit (MDL) is the lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero and is $3.14$ (standard deviation) = $3.14(s)$.

Minimum Quantification Interval is the lowest level that can be quantitated accurately and is generally defined as four times the method detection limit = $4(MDL)$.

All OEWRI project data will be transferred into an OEWRI Project Results template and additional QA/QC data will be added from the original data set.

**Computer hardware and software**

16.1 Microsoft Word: this document is prepared using Word.

16.2 The Word document file name for this SOP is: TICTOC-R01.doc

16.3 The liquiTOCII software controls all aspects of the instrument and sample analysis calculations.

**Method performance**

17.1 The desired performance criteria for this measurement are:

a. Detection limit: carbon = 1mg/l for all forms of carbon.

b. Precision: ± 20%

c. Accuracy: ± 20%

d. Minimum Quantification Interval: 0.01mg/l

17.2 The operating range for this instrument is 0 to 100,000 mg/l. The sample volume range is 0.05 ml to 4 ml.

17.3 The instrument will be recalibrated when the daily factors for any form of carbon is outside the range of 0.9 to 1.1. The “Fact” is the daily factor in the final exported data sheet. This factor should be recorded with each data sheet to illustrate the quality of the data.

**Pollution prevention**

All wastes from these procedures shall be collected and disposed of according to existing waste policies within the MSU College of Natural and Applied Sciences. Volumes of reagents made should mirror the number of samples being analyzed. These adjustments should be made to reduce waste.
19 Data assessment and acceptable criteria for quality control measures

19.1 The analyst should review all data for correctness (e.g., calculations).

19.2 Precision values are calculated for pairs of duplicate analyses and are recorded as a percent. The desired precision is ± 20%.

19.3 The desired detection limit is 1mg/l for all forms of carbon.

19.4 All data is reviewed by the analyst’s supervisor or the OEWRI QA coordinator.

20 Corrective actions for out-of-control or unacceptable data

20.1 The results for precision and blank data are compared to the acceptable values for this analysis; ± 20% and 0 for all forms, respectively.

20.2 If a precision value exceeds ± 20% then the analyst should note that the data are associated with an out-of-control duplicate analysis in the data report given to the QA/QC manager. The upper control limit (UCL) = 20%.

20.3 If a LRB value exceeds the MDL then the analyst should note that the data are associated with a LRB value that exceeds the detection limits in the data report given to the QA/QC manager.

20.4 If data are unacceptable for any reason, the analyst should review their analytical technique prior to conducting this analysis again.

20.5 If there is sufficient volume of sample remaining for all samples, the batch may be re-analyzed. Quality control data from both batches is recorded.

20.6 The instrument may require trouble shooting techniques if the data are unacceptable:
   a. Perform a leak test if MFC flow and FM flow are not correct by selecting options on the menu bar, choosing diagnostics from the submenu, and selecting leak check. Report results to the laboratory supervisor.
   b. The message “Invalid System Pressure or Flow” is the most common error message and is displayed when the pressures are too high or low. The analyses will stop when this error message is displayed. To correct the pressure flows:
      1. Adjust the pressure manually using regulator on the ZAG.
      2. Click to start a continuous run.
   c. Check drying tubes for discoloration.
   d. Check halogen absorber for discoloration.
   e. Check all seals and tubes for cracks or wear.
f. Contact the laboratory supervisor to request manufacturer service for the instrument.

21 Waste management
21.1 The wastes generated in this method are hazardous because of a low final pH. The samples may be neutralized by the addition of water in accumulation container (e.g., a large beaker or flask). Add sufficient amounts of water to adjust the pH to between 2 and 12.5. When the pH is > 5 (for acidic wastes) the solution can be discarded in the laboratory drain followed by an equal volume of water.

21.2 Outdated chemicals are discarded following the procedures of the MSU Environmental Management Department

22 References
22.1 High Temperature TOC/TNb Analyzer liquiTOCII Operating Instructions for instruments starting with serial No. 35 06 1001. February 2006. Elementar Analysensysteme GmbH, Hanau-Germany.


23 Tables, diagrams and flowcharts
All tables, diagrams, or flowcharts for this method are in the body of this SOP.