ANALYSIS OF TOTAL NITROGEN (TN), DISSOLVED NITROGEN (DN), TOTAL ORGANIC CARBON (TOC), AND DISSOLVED ORGANIC CARBON (DOC) USING THE SHIMADZU TOC-L2 INSTRUMENT EQUIPPED WITH A TOTAL NITROGEN MODULE (TNM-L)

TABLE OF CONTENTS:

Page

1. SCOPE AND APPLICATION 2
2. SUMMARY OF THE METHOD 2
3. EQUIPMENT AND SUPPLIES 3
4. CHEMICALS, REAGENTS, AND STANDARDS 3
5. SAMPLE HANDLING AND PRESERVATION 8
6. SAMPLE PREPARATION AND ANALYSIS 9
7. DATA ARCHIVAL 12
8. MAINTENANCE/TROUBLESHOOTING 13
9. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES 15
10. SAFETY/WASTE MANAGEMENT/POLLUTION PREVENTION 16
11. REFERENCES 16

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1. SCOPE AND APPLICATION

1.1. This SOP details the analysis of Total Nitrogen (TN), Dissolved Nitrogen (DN), Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) in surface waters, ground waters, effluents and influents. The tests covered by this SOP are: W-TN, W-DN, W-TOC, and W-DOC.

1.2. Results for TN and DN are reported without qualification in the range from the practical quantitation limit (PQL) 0.50 mg N/L up to 5.0 mg N/L. Samples with higher concentrations are reported after dilution into the range or qualified appropriately. Samples with TN concentrations below the PQL will be re-analyzed following SOP NU-105.

1.3. Results for TOC and DOC are reported without qualification in the range from the practical quantitation limit (PQL) 1.0 mg C/L up to 100 mg C/L. Samples with higher concentrations are reported after dilution into the range or qualified appropriately. The method detection limit (MDL) is 0.50 mg C/L.

2. SUMMARY OF THE METHOD

2.1. The described procedure is based on ASTM D8083-16 for TN/DN analysis and Standard Methods 5310 B-2011 for DOC/TOC analysis.

2.2. The acidified samples are purged with ultra-high purity (UHP) air using an external sparge kit prior to injection in order to remove the inorganic carbon fraction. Samples (50 ul) are introduced by the sample injector into a combustion tube.

2.3. The organic carbon and nitrogen components of the sample are combusted at 720 ºC in the presence of a platinum catalyst to form carbon dioxide and nitrogen oxide (NO), respectively. Carbon dioxide is detected by infrared analysis. Nitrogen oxide reacts with ozone to form excited state NO_2. As the NO_2 returns to the ground state the emitted radiation is detected using a chemiluminescence detector.

2.4. The method measures nonpurgeable organic carbon (NPOC). In many surface and ground waters, the purgeable organic carbon contribution to TOC is negligible. Therefore, in practice, the nonpurgeable organic carbon determination is substituted for TOC. Elemental carbon may not be oxidized at the furnace temperature, but it is not expected to be a constituent of the water samples analyzed. In addition, the method does not measure N_2 as gas.

2.5. This procedure is applicable only to nitrogenous and organic matter in the sample that can be injected into the apparatus reproducibly by means of a microliter type

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syringe or pipette. An external sparge kit is used as a mixing mechanism to suspend small particles that may otherwise settle over time. The openings of the autosampler needle and injection syringe limit the maximum size of particles included in the analysis.

2.6. Interferences: Acid preservation of samples minimizes interferences that can cause results to be low. Gases of halide components may interfere with the detection system. They are eliminated by passing the reaction gas through a halogen scrubber. Samples with a high particulate loading may need to be homogenized prior to analysis. Samples containing high total suspended solids (TSS) may cause TN analysis to be biased low. Dissolved inorganics in the sample that are not volatized may result in devitrification or solidify in the catalyst tube resulting in decreased flow rates. Total organic carbon (TOC) up to 300 mg/L does not interfere with the TN analysis.

3. EQUIPMENT AND SUPPLIES

3.1. TOC-L2-$_{CPH}$: Shimadzu Total Organic Carbon Analyzer equipped with an autosampler, external sparge kit, and Total Nitrogen Module (TNM-L).

3.2. Assorted volumetric flasks (Class A)

3.3. Eppendorf and Oxford pipettes

3.4. Fisher 24 mL Screw Thread Vials with PTFE/Silicone Septa (03-339-30H) or equivalent

Note: *Only the **TOC-L2-CPH** instrument is equipped with the external sparge kit for mixing. Thus, only the TOC-L2-CPH can be used for running W-TN and W-TOC analysis simultaneously.*

4. CHEMICALS, REAGENTS, AND STANDARDS (SEE DEP SOPs NU-041 and NU-042)

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

Note: All reagent and standard preparations must be documented in the Reagent and Standard Logsheet for W-TN/W-TOC analysis. This excel sheet (NU-RGTSTD) is located in the REAGENT_PREP folder on the Nutrients drive located in the subfolder \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\TOC\TN_TOC\TOC_TN. It needs to be updated whenever a reagent or standard is newly prepared. For every analysis file print the Reagent and Standard Logsheet and place it

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into the analysis folder.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard and reagent are generated in the module and documented in the reagent and standard sheet submitted with each analysis folder. If available, a Certificate of Analysis for each purchased reagent and standard is maintained in the REAGENT_PREP folder on the Nutrients drive located in the subfolder \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\TOC\TN_TOC\Certificates of Analysis. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: Prior to using the chemicals in this analysis, please read their MSDS and the safety notes found in Section 11 of this SOP.

4.1. Deionized (DI) water

4.2. UHP Grade Compressed Air

4.3. Concentrated sulfuric acid (H_2SO_4) (A.C.S. Grade) and hydrochloric acid (HCl) (A.C.S. Grade)

4.4. Potassium Nitrate (KNO_3)(Certified) and Ammonium Sulfate ($(NH_4)_2SO_4$) (A.C.S. Grade)

Mixed Stock Standard Solution (1000 mg N/L) - This solution is used for the preparation of the calibration standards. Holding time for the Stock standard is 180 days.

4.4.1. Dry 8g of Potassium Nitrate and 5g of Ammonium Sulfate at 120 ^oC for 2 hours. Cool in a desiccator.

4.4.2. Add approx. 800 mL of DI water to a clean 1 L flask. Add 2 mL of concentrated H_2SO_4 and mix.

4.4.3. Weigh out 3.609 g of the dried KNO_3 into a weighing boat.

4.4.4. Weigh out 2.360 g of the dried $(NH_4)_2SO_4$ into a separate weighing boat.

4.4.5. Rinse the contents of the weighing boats into the flask using DI water. Dilute to the mark and mix thoroughly. Label this flask 'TN STOCK 1000 PPM'.

Note: This solution is also used for low-level TN analysis. See SOP NU-105.

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4.5. KNO_3 Stock (1000 mg N/L)- This solution is used for the preparation of the Initial Calibration Verification/Continuing Calibration Verification (ICV/CCV) standard. Holding time, 180 days.

4.5.1. Dry 4g of Potassium Nitrate at 120 ^oC for two hours. Cool in a desiccator.

4.5.2. Add approximately 100 mL of DI water to a clean 250 mL flask. Add 0.5 mL of concentrated H_2SO_4 and mix.

4.5.3. Weigh out 1.803 g of the dried KNO_3 into a weighing boat.

4.5.4. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Label this bottle '1000 PPM KNO3'

4.6. Potassium hydrogen phthalate (KHP); Certified A.C.S. Grade

Stock Standard Solution (1000 mg C/L) - This solution is used for the low spike (V1) for W-TOC, laboratory fortified blank (LFB_V1) for W-TOC, and the continuing calibration verification (ICV/CCV) standard. Holding time for the Stock standard is 180 days.

4.6.1. Dry 5g of primary grade potassium hydrogen phthalate at 120 ^oC for 12 hrs. Cool in a desiccator.

4.6.2. Add approx. 800 mL of DI water to a clean 1 L flask. Add 2 mL of concentrated H_2SO_4 and mix.

4.6.3. Weigh out 2.1254 g of the dried potassium hydrogen phthalate into a weighing boat.

4.6.4. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Pour this solution into the reagent bottle labeled 'TOC STOCK: 1000 PPM'.

Note: This solution is also used for W-TOC analysis on TOC-V and TOC-L instruments. See SOP NU-062.

4.7. Primary Grade Dextrose; A.C.S. Grade

Stock Standard Solution (10000 mg C/L) - This solution is used for the calibration standards and the practical quantitation limit (PQCK4). Holding time for the Stock standard is 180 days.

4.7.1. Dry 5 g of primary grade dextrose at 120 ^oC for 12 hrs. Cool in a

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desiccator.

4.7.2. Add approx. 20 mL of DI water to a clean 100 mL flask. Add 0.2 mL of concentrated H_2SO_4 and mix.

4.7.3. Weigh out 2.505 g of the dried dextrose into a weighing boat.

4.7.4. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Pour this solution into the reagent bottle labeled 'STOCK DEX 10000'.

Note: This solution is also used for W-TOC analysis on TOC-V and TOC-L instruments. See SOP NU-062.

4.8. Preparation of QC and calibration Standards- Holding time, 30 days

4.8.1. Blank Standard/Diluent (0 mg C/L, 0 mg N/L) - To a 2 L volumetric flask containing approx. 1.5 L of DI water, carefully add 4.0 mL of concentrated H_2SO_4. Dilute to the mark and mix thoroughly. Used for the method blank (MBLK) and continuing calibration blank (CCB).

Note: This solution is also used for W-TN and W-TOC analysis following SOP NU-105 (low level TN) NU-062, respectively.

4.8.2. PQL Check for W-TOC initial QC (PQCK4, 1.0 mg C/L) - To a 1 L volumetric flask containing approx. 900 mL of diluent (4.8.1.), add 0.1 mL of the 10000 mg C/L stock standard (4.7.), fill up to the mark with diluent and mix thoroughly.

Note: This solution is also used for W-TOC analysis. See SOP NU-062.

4.8.3. ICV/CCV (20 mg C/L, 2 mg N/L) - To a 2 L volumetric flask containing approx. 1 L of diluent (4.8.1.), add 40 mL of the 1000 mg C/L stock standard (4.6.), add 4 mL of the 1000 mg N/L KNO_3 Stock (4.5.), and fill up to the mark with diluent and mix thoroughly.

4.8.4. Mixed TOC TN calibration standards: Add about 250 mL diluent (4.8.1) to each 500 mL volumetric flask. Add volumes of the stock solutions as described in the table below and make the volume up to the mark with diluent.

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TABLE 1. Mixed Calibration Standards

Standard Name	Volume of 'STOCK DEX 100000' (mL) (4.7.)	Volume of 'TN Stock 1000 PPM' (mL) (4.4.)	Final Volume (mL)	TN conc mg N/L	TOC conc mg C/L
MDLSPK	0.04	0.25	500	0.50	0.80
CAL STD 1	0.05	0.40	500	0.80	1.0
CAL STD 5	0.25	2.5	500	5.0	5.0
CAL STD 20	1.0	0.625	500	1.25	20
CAL STD 100	5.0	1.0	500	2	100

4.9. Acid Rinse (ACID RINSE) for Catalyst Regeneration - To a 1 L volumetric flask containing approx. 800 mL of DI water, carefully add 164 mL of concentrated HCL. Dilute to the mark and mix thoroughly. Holding time, 90 days.

4.10. ALTQC - A certified quality control standard is purchased. For the expiration date of the purchased stock refer to the manufacturer's certificate. The stock ALTQC standard may be diluted appropriately so that the concentration falls within the calibration range. Two ALTQC standards are needed. Holding time of the diluted standards, 30 days.
TN: Currently there are no certified reference standards available for TN. The ERA 'Simple Nutrients' (or equivalent) standard is analyzed adding the certified values for ammonia and nitrate/nitrite to reflect TN. The acceptance limit for the sum was taken from the more stringent limit of the individual components.
TOC: The Inorganic Ventures 'Demand' standard or equivalent.

4.11. Glycine ($C_2H_5NO_2$); Purity 99+%

Organic Nitrogen Stock Solution (1000 mg N/L)-This is used for the preparation of the Total Organic Nitrogen Check solution.

4.11.1. Dry about 3 g of glycine at 120 ^oC for 2 hours. Cool in a desiccator.

4.11.2. Add approx. 150 mL of DI water and 0.50 mL H_2SO_4 to a clean 250 mL flask.

4.11.3. Weigh out 1.3392 g of the dried glycine into a weighing boat. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Label this flask 'ORGANIC NITROGEN STOCK 1000 PPM'. Holding time, 180 days.

Note: This solution is also used for low-level TN analysis. See SOP NU-105.

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4.12. Total Organic Nitrogen Check (TONCHCK, 2 mg N/L)-To a 250 mL volumetric flask containing approx. 100 mL of diluent (4.8.1), add 0.5 mL of the 1000 mg N/L glycine stock solution (4.11.). Dilute to mark with diluent and mix thoroughly. Label this flask 'TONCHCK 2 PPM N'. Holding time, 30 days.

4.13. Sodium Carbonate; Certified A.C.S., Anhydrous (Na_2CO_3)

Inorganic Spiking Solution (1000 mg C/L)

4.13.1. Dry about 5 g of sodium carbonate at 120 ^oC for 12 hrs. Cool in a desiccator.

4.13.2. Add approx. 150 mL of DI water to a clean 250 mL flask.

4.13.3. Weigh out 2.2125 g of the dried sodium carbonate into a weighing boat. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Pour this standard into a reagent bottle labeled 'IC SPK 1000 PPM'. **Do not acidify this standard**. Holding time, 180 days.

Note: This solution is also used for W-TOC analysis. See SOP NU-062.

4.14. Mixed Spiking Solution (500 mg N/L, 10000 mg C/L): Used for W-TOC high spike (H1). Laboratory fortified blank for W-TN (LFB_N1) and the W-TN spike (N1)

4.14.1. Dry about 6 g of dextrose and 1 g of potassium nitrate at 120 ^oC for 2 hours. Cool in a desiccator.

4.14.2. Add approx. 50 mL of DI water and 200 uL H_2SO_4 to a clean 100 mL flask.

4.14.3. Weigh out 0.3609 g of the dried KNO_3 into a weighing boat.

4.14.4. Weigh out 2.505 g of the dried dextrose into a weighing boat.

4.14.5. Rinse the contents of the weighing boats into the flask using DI water. Dilute to mark and mix thoroughly. Label this flask 'MIXED SPK'. Holding time, 180 days.

5. SAMPLE HANDLING AND PRESERVATION

5.1. Samples are preserved with sulfuric acid at collection and stored on ice or at ≤ 6 °C (not frozen). Samples submitted to the laboratory for DN/DOC analysis must be filtered in the field prior to acidification All samples must be analyzed within

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28 days of collection date for results to be reported unqualified.

5.2. Samples are stored in the Nutrient refrigerators in the receiving room of the FDEP laboratory. Allow samples to come to room temperature before processing.

6. SAMPLE PREPARATION AND ANALYSIS (SEE DEP SOP NU-033)

6.1. Open program TOC-CONTROL-L.

6.2. Choose Sample Table Editor icon →hit ok.

6.3. To start a new file and run: Click on the *New* button in the top left corner. Select the H/W settings on the drop-down menu → TOC-L2-CPH-SPARGE. To save the file, click *Save* and name the file YYMMDDLN# (where # is a number 1, 2, etc., that indicates the 1st, 2nd, etc., run of the day. Ex.: 120211N1). → *Save*.

6.4. In some cases, it may be helpful to perform an optional rinse before the calibration. To add the rinse sequence to the beginning of the run (the rinse blank result will be calculated from a previous calibration), highlight line 1, right click, and select *Insert→ Multiple Samples*. This opens the Sample Group Wizard.

6.4.1. Page 1 Sample Source: Select *Method* option and browse button. Then select 'NPOC_TN_EXSPARGE. met' → *Open* → *Next*.

6.4.2. Page 2 Sample Parameters. Set options as follows:
Number of Samples = 1
Start Vial = 0
Sample Name = Enter file name (Ex.200101N1)
Sample ID = RINSE→ Finish

6.5. To setup a calibration sequence, highlight line two, right-click, and select *Insert-Calibration Curve* → Select 'NPOC CAL CURVE_EXSPARGE' → *Open*.

6.6. After inserting the calibration, select the autosampler image in top right corner. Assign vial numbers as follows:
0 mg C/L standard = 1 (diluent, 4.8.1.)
0.8 mg C/L standard = 2 (MDLSPK, TABLE 1)
1.0 mg C/L standard = 3 (CAL STD 1, TABLE 1)
5.0 mg C/L standard = 4 (CAL STD 5, TABLE 1)
20.0 mg C/L standard = 5 (CAL STD 20, TABLE 1)
100.0 mg C/L standard = 6 (CAL STD 100, TABLE 1)
Select *OK* to complete. The vial column numbers should read 1,2,3,4,5,6

6.7. To setup the next calibration sequence, highlight line 3, right-click, and select

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Insert- Calibration Curve → Select 'TN CAL CURVE_EXSPARGE' → *Open*.

6.8. After inserting the calibration, select the autosampler image in top right corner. Assign vial numbers as follows:

0 mg N/L standard = 1 (diluent, 4.8.1.)
0.5 mg N/L standard = 2 (MDLSPK, TABLE 1)
0.8 mg N/L standard = 3 (CAL STD 1, TABLE 1)
1.250 mg N/L standard = 5 (CAL STD 20, TABLE 1)
2.0 mg N/L standard = 6 (CAL STD 100, TABLE 1)
5.0 mg N/L standard = 4 (CAL STD 5, TABLE 1)

Select *OK* to complete. The vial column numbers should read 1,2,3,5,6,4

6.9. To setup a sample sequence, highlight line four, select *Insert -Multiple Samples*. This will open the Sample Group Wizard.

6.9.1. Page 1 Sample Source; Select Method option and browse button. Then select method 'NPOC_TN_EXSPARGE'→ Next. This method has both calibration curves that were just created (6.5, 6.7).

6.9.2. Page 2 Sample Parameters; Set options as follows:
Number of Samples = 87
Start Vial = 7
Sample Name = Enter file name. (Ex.200101N1)
Sample ID = Leave blank
→ Finish → OK.

6.10. For sample and QC that only need to be analyzed for W-TN or W-TOC, highlight the row where you want to insert the sample, select *Insert-Calibration Curve* and select the corresponding file (6.5 or 6.7) and add a single sample as before.

6.11. A template has been created so that a new run sequence does not need to be performed for every analysis. Select *open* in the top left of the software. Select 'TEMPLATE_HIGH LEVEL TN'. Insert the sample IDs and save the file name. Then go to File→*print*. This will be the bench sheet.

6.12. Pour samples and QC-standards into labeled 24 mL vials with septa according to the run sequence. Place them in the autosampler rack and return rack to turntable for realignment. Make sure that all vials are correctly seated.

6.12.1. For each batch (20 samples or less) : Select a quality control sample prepared in duplicate to assess precision for W-TN and W-TOC. Prepare a 2 mg N/L and 40 mg C/L matrix spike (spike code M1) by adding 80 µL of the MIXED SPK (4.14.) to one 20 mL portion of the selected sample. Prepare a laboratory fortified blank (LFB) following the same procedure as the 2 mg N/L/40 mg C/L matrix spike by substituting blank standard

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(4.8.1.) for the sample. Effluent samples are batched separately.

6.12.2 Inorganic spike (spike code IS): For each analytical run, prepare one inorganic sample spike. Add 400 µL of the 1000 mg C/L inorganic spiking solution (4.13.) to one 20 mL portion of a selected sample.

6.12.3. Each run begins with the following sequence:

Rinse (6.4) (optional)
Calibration (6.5, 6.7)
MDLSPK (TABLE 1)
TONCHCK (4.12)
PQCK4 (PQL, 4.8.2.)
ALT#_TOC (ALTQC, 4.10.)
ALT#_TN (ALTQC, 4.10.)
ICV/CCV (CCV, 4.8.3.) and **CCB** (Blank Standard, 4.8.1.) – these continuing calibration checks are scheduled to bracket every 10th analysis on the run.
Batched samples including **MBLKs** (4.8.1.), **LFBs** (6.12.1.), duplicate samples and spiked samples (6.12.1. and 6.12.2)
Final **CCV** and **CCB**

Note: The first CCV after a new calibration is called the Initial Calibration Verification standard (ICV). The first CCV is labeled as the ICV on each new run and all subsequent CCVs are labeled as CCV.

6.13. Connect Instrument: Click *Connect.* Wait for connection and ready indicator, then press *Start*→ Check Shut down instrument box → press Run to start the run.

Note: Print the run file that was just created by going to *file* → *print*→ *sample table.*

6.14. Post-run Procedure: Results are exported as an ASCII file and converted into a raw file in the QC manager for performing calculations and uploading to LIMS.

6.14.1. *File* → *ASCII Export Setting* → *Detail* → *Data.* Check the following export options; Sample ID, Dilution, Date/Time, Mean Conc., Result, and Vial. Also make sure the export data box is checked. Under the "Misc" tab that asks for the separator settings, choose "tabulator," and check the box for "Export strings in quotation marks…".

6.14.2. To export file: *File* → *ASCII Export* → *Detail* (Include Injection Data) → *Filename* → *Save.*

6.14.3. Export to C:\TOC-L2_TN\Data for TOC-L2 in the current years' subfolder. This is the local drive for the instrument workstation.

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6.14.4. Open C:\TOC-L2 in Windows Explorer. Locate the text file you just created, as well as the peak (*.pkt), calibration (*.cal) and sample table (*.t32 or *.tlx) files associated with the analysis and copy all four files from the local drive to the appropriate instrument folder (TOC-L2) in the current year's subfolder located at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Tocv\TOC-L2_TN.
Note: the exact location of the data files within instrument folder structure is determined by the software settings (Tools > Organize Files; please see User manuals for details).

6.4.5. Print a copy of the final report and data table containing injection peaks by selecting: *File* → *Print* → *Sample Report –All*, then *File* → *Print* → *Sample Table.*

6.15. Quantitation/Calculations:

6.15.1. The instrument will give the values for NPOC in mg C/L and Total Nitrogen in mg N/L. The value given by the instrument is the average of three injections for a given sample that have a percent relative standard deviation of less than 5 %. The calibration consists of five standards plus a blank. The regression model applied is linear.

6.15.2. The QC Manager will calculate spike and standard recoveries and RPDs. For general calculations including RPDs and spike recoveries, see the FDEP Quality Manual Section 5.9.

6.15.3. The calibrants are all prepared manually (see section 4.8. and 6.5.). The correlation coefficient for the calibration is calculated by the instrument software. Use the current NU-TOC_TN form located at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Tocv\ to calculate the recoveries of the calibrants. Open the form, enter the header information and the slope, intercept, and mean area results to calculate the recovery of calibrants. Acceptance limits for the recoveries of the calibration standards above the PQL are 90 – 110 % and 70 – 130 % for the PQL-level standard. For TOC, the 0.8 mg C/L standard (MDLSPK) acceptance limits are 62.5-150%.

7. DATA ARCHIVAL

7.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labeled with the test (W-TOC/W-TN), filename/s (YYMMDDN#), and initials of the analyst.

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7.2. Each report folder should contain the following items - run report including raw data and calibration curve, calibration standard recovery sheet, results report method parameters, bench sheet, Reagent and Standard Logsheet, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.3. The report folders are on file with the nutrients supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

7.4. Instrument raw data files, including peak (*.pkt), calibration (*.cal) and sample table (*.t32 or *.tlx) files, are backed up from instrument PCs and stored on the Nutrients drive under \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Tocv\TOC-L2_TN.

7.5. TOC/TN instrument data text transfer files for upload to QC manager are stored in electronic format in appropriate instrument folder (TOC-L2) in the current year's subfolder located at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Tocv\

7.6 Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in \\fldep1\dear\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations.

8. MAINTENANCE/TROUBLESHOOTING

Note: Make sure all maintenance performed is documented in the instrument's maintenance log.

8.1. Maintenance:

8.1.1. Before beginning sample analysis, conduct a general inspection of the instrument to ensure that everything is in order, and that there is enough UHP Air to complete the run.

8.1.2. The humidifier and dehumidifier vessels should be filled with DI water to the fill line on the vessel. Once a month, the humidifier vessel should be drained and refilled with fresh DI water. This prevents contamination.

8.1.3. Keep the rinse water bottle filled with DI water. If running samples overnight, fill the bottle with DI water before starting the run.

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8.1.4. The diluent bottle should be changed with fresh Blank Standard/Diluent (4.8.1.) at least once per month.

8.1.5. Make sure the HCL Intake is changed with fresh 2N HCL (4.9.) at least once every three months.

8.1.6. Inspect the slider and O-rings before analysis and clean with DI water if needed.

8.1.7. Check the waste line daily to ensure proper flow. Waste backup will damage the autosampler. Dump waste down the drain as needed.

8.1.8. Regeneration of TC catalyst should be performed on a case by case basis TC catalyst regeneration has little effect on TN analysis. See instrument manual for regeneration procedure. Regeneration should be followed with a run of at least 20 CCBs and a few CCVs.

8.1.9. Other maintenance may be required periodically, such as replacing catalyst, replacing halogen-scrubber, maintaining syringe and 8-port valve. Please see User's manuals for details.

8.2. Troubleshooting Notes:

8.2.1. To stop the run at any point and delete the calibration,
Click *Stop* button → *Stop* (stop all processes immediately).

8.2.2. To interrupt the run at any point and save the calibration,
Click *Stop* button → *Stop* (after current sample is completed).

8.2.3. In order to restart a run in progress (for example, if there is a QC failure at the beginning of a run) and keep the sample table set up for a new run, previous data gathered or attempted must be deleted prior to restart. Highlight the lines to delete, go to *Edit* → *Clear Measured Data* → *Highlighted* → *Yes*, then click *View Vial Settings* → Assign the vial numbers for rerun samples.

8.2.4. Treat samples suspected to contain humic acids as follows:
a. Split a well-mixed sample into two portions.
b. Keep one portion at pH ≤ 2 and adjust the other to pH 5-7 with 10 N Sodium Hydroxide to increase the solubility of humic acid.
c. Cap and allow both portions to sit at room temperature for ½ hour.
d. Analyze both splits and report the highest result.

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9. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE NU-038 AND NU-043)

9.1. A new calibration must be performed at the beginning of the analysis and the linear calibration range (LCR) must be verified (see 9.2.). Consecutive runs on one day may use the same calibration. The linear calibration consists of five standards (CAL STD 100, CAL STD 20, CAL STD 5, CAL STD 1, MDLSPK) and a blank. It is followed by a sequence of initial quality control standards as described in section 6.12.

9.2. LCR: See the FDEP Quality Manual Appendix B, Section 7.0, 'Protocol for Determining the Test Method Range of Applicability'. The correlation coefficient of the linear regression (r^2) must be equal to or larger than 0.995. Acceptance limits for the recoveries of the calibration standards above the PQL are 90 – 110 % and 70 – 130 % for the PQL-level standard. The acceptance limit for the **TOC** MDLSPK standard (below the PQL) is 62.5 – 150 % recovery.

9.3. Each analytical run may contain a number of sample batches, with no more than 20 samples per batch. Each batch is required to have an MBLK, LFB, a matrix spike, and a duplicate sample. The spikes are prepared according to section 6.12.1. Acceptance limits for the LFB and matrix spike recoveries are 85-115 %.

9.4. TN: On every analytical run, one organic nitrogen check (TONCHCK) is run at the beginning of the run (4.10.). The result must be between 85-115 % recovery. If the recovery is outside the control limit the samples must be reanalyzed or reported qualified. The instrument should be checked to ensure that it is operating correctly.

9.5. The AltQC standard (ALT#, 4.10.) is a second source standard with acceptance limits supplied by the manufacturer. One AltQC standard for TN and one AltQC for TOC is analyzed with every analytical run. Acceptance limits are supplied by the manufacturer. See also 4.10.

9.6. One MDLSPK (MDLSPK, TABLE 1) is analyzed for every analytical run. MBLK and MDLSPK results are used for ongoing MDL and PQL verification. The acceptance limit for the MDLSPK standard for TOC (below the PQL) is 62.5 – 150 % recovery, for TN 70 – 130 % recovery.

9.7. One PQL (PQCK, 4.8.2.) level standard for TOC is analyzed for every analytical run. For analytical runs that are longer than 24 hours, at least one PQL standard is analyzed every 24 hrs. Acceptance limits for the PQCK recovery are 70-130 %.

9.8. A CCV/ICV (CCV, 4.8.3.) and a blank (CCB, 4.8.1.) standard are run at the beginning of every run, after every 10^{th} analysis, and at the end of the run.

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Acceptance limits for the recoveries of the check standard are 90-110 %.

9.9. The sample duplicate results should be less than 20 % RPD for results over the practical quantitation limit (PQL).

9.10. Acceptance limits for the blanks (MBLKs and CCBs) are < 0.10 and > -0.10 mg N/L for TN and < 0.50 and > -0.50 mg C/L for TOC.

9.11. For general method performance and acceptance criteria for QC measures and corrective action for out-of-control data and contingencies for handling out-of-control or unacceptable data, refer to DEP SOPs NU-038 and SOP NU-043. If there are any anomalous results (e.g., differing results for multiple analyses of same sample) or any unusual events (spilled sample, cannot locate sample, etc.), see supervisor for further instruction.

10. SAFETY/WASTE MANAGEMENT/POLLUTION PREVENTION

10.1. Refer to the MSDS notebook for information on safe handling of samples and reagents used with instrument.

10.2. Flush sample waste (as long as no other known hazards are present) down the sink with plenty of water.

10.3. Review the laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents).

10.4. Safety glasses, gloves and lab coats should be worn at all times whilst handling samples and reagents.

11. REFERENCES

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

11.1. ASTM D8083-16 and Standard Methods Online, 5310 B-2011.

11.2 Shimadzu TOC-L/TOC-L2 Manual.

11.3. Quality Manual, Bureau of Laboratories, FDEP.

11.4. DEP SOP NU-062, Determination of Total Organic Carbon (TOC) and dissolved Organic Carbon (DOC) Using the Shimadzu TOC Analyzer

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11.5. DEP SOP NU-033, Summary of Analysis Procedures for the General Chemistry and Nutrients Workgroups.

11.6. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

11.7. DEP SOP NU-041, Reagent Preparation Procedure.

11.8. DEP SOP NU-042, Standard Preparation Procedure.

11.9. DEP SOP NU-043, General Chemistry Quality Assurance and Data Authorization Guidelines.

11.10. Laboratory Health and Safety Plan.

11.11. DEP SOP LB-006, Standard operating procedure for records maintenance and storage.

APPENDIX OF SIGNIFICANT CHANGES

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