TOC-V w/TN

Operating Procedures for Normal Sensitivity **TC**, **VOC**, **NPOC, IC,** and **TN** Analysis

(Rev. I; 4Feb20)

Background & Nomenclature

Total Carbon/Nitrogen: consists of several components. The TOC-V is capable of measuring only the soluble (non-particulate) components. Categorized as follows:

TC: Total (dissolved) Carbon: includes VOC, NPOC, & IC. Samples collected in a sealed vial with no headspace and injected directly onto the combustion tube without exposure to air. Carbon in the sample is converted to CO2 and measured via NDIR detection. Samples are NOT acidified.

VOC: Volatile Organic Carbon: portion of carbon that can be purged from the sample by exposure to air and/or bubbling carrier gas through the non-acidified sample. VOC can be measured using IC mode without acid addition. Samples are collected as for TC.

NPOC: Non-Purgable Organic Carbon: portion of carbon remaining in solution AFTER the sample is acidified with 2 N HCl to pH $\leq$2 and purged sufficiently (3-5 minutes typically) to remove IC and VOC. Acid is added to sample vials and standards. Samples are purged in the sampling syringe and are then injected onto the combustion tube. The resultant CO2 measured via NDIR detection.

IC: Inorganic Carbon (carbonate & bicarbonate). Samples are collected as for TC and are NOT acidified externally. Samples are acidified with 2N HCl to 5% acid within a sealed syringe and are then purged with carrier gas. The resultant CO2 is transferred via the instrument plumbing to the NDIR detector for measurement.

TN: Comprised of organic and inorganic nitrogen. Samples (acidified or not) are injected onto the combustion tube. If analyzing in conjunction with DOC the samples must be acidified. The resultant NOx is reacted with ozone and measured via Chemiluminescence detection. The inorganic species (NO2, NO3, NH4) must be measured separately and subtracted from the TN value to achieve organic TN concentrations.

*All glassware must be acid washed and/or heat treated. See 'Glassware Washing Procedures' in SOP manual.
*All reagents and standards are prepared using Nanopure or equivalent water that has been purified through an organic free cartridge.
* All samples must be filtered thru at least a 0.45-micron filter prior to analysis.

Stock Standards

TC/NPOC Calibration Stock (1000 ppm C): 0.5313g Potassium Biphthalate dried 2 h @ 120°C in 250mL. Refrigerate stock solution in amber glass bottle. Good for one year.

IC Calibration Stock (2000ppm C): 1.75g Sodium Bicarbonate + 2.205g dried Sodium Carbonate in 250mL. Refrigerate. Good for one year.

TN Calibration Stock & QC (100ppm N): 0.3034g Sodium Nitrate in 500mL. Refrigerate. Good for one year.

TN Digestion Check (100 ppm N): 0.4397 g Nicotinic Acid (Niacin in 500 ml). Good for one year.

TOC/TC QC: Solution purchased from Fluka or ERA TOC std 1000 mg/L. Stored in fridge.

IC QC Check (1000 ppm C): Solution purchased from ERA Custom Standard 1000 ppm stored in fridge.

Working Standards and Sample Prep

Working Standards are prepared from dilutions of the above stock solutions. Use the designated glassware on the benchtop and the stock solutions from the mini fridge in GWC 637. TC & IC standards should be made fresh every run. NPOC/TN or NPOC standards, when acidified, can hold up to two weeks. Each method is set up to make auto dilutions in the ranges shown below. Be sure to check the method's calibration measurement settings to ensure proper dilutions.

Current method standard concentrations:

NPOC & TN –

NPOC: 5 – 200 mg/L TN: 0.5 – 10 mg/L

TC:

12.5 – 500 mg/L (can go up to 1000 mg/L if needed)

IC:

2 – 100 mg/L

Prepare enough Standard/QC to fill the required number of vials according to your sample table:

- 40 mL vials filled completely can be sampled 4 x's

***NPOC samples and standards** must be acidified to pH ≤ 2. This can usually be achieved by adding 2N HCl to the sample in a 1:100 ratio (acid: sample): for example, 0.2 mL acid per 20 mL sample/standard. Acidification w/ 2 drops conc. HCl per vial is also acceptable. Confirm sample pH by placing a drop on pH paper.

2N HCl preparation: 30 mL conc. HCL + 150 mL water (Stock container located in acid cabinet in GWC 637 below hood.)

General Instrument Conditions

Carrier gas (Ultra Zero Air) cylinder pressure: ≥300 psi
Breathing air cylinder pressure (used for TN only): ≥ 500 psi
Carrier gas tank regulator pressure: 80-100 psi
Instrument carrier gas flow: 100 mL/min
Instrument carrier gas pressure: 4-5 kg/cm^2
Furnace temp: 720°C for NPOC/TN, 680°C for TC, NPOC & IC alone
Dehumidifier temp: 1°C
TN Detector Temp: 50°C

Analysis Procedures

1. Turn on carrier gas for DOC (Ultra Zero air) and for TN (Breathing air) if analyzing at tank and check pressures (see above).

2. Turn on power to instrument. Button lower right hand side of instrument.

3. Open door and check liquid levels in drain vessel, and dehumidifier trap. Rinse container (behind computer) and dilution container (next to instrument), and 2N HCl if running IC. Adjust levels with Nanopure water as necessary.

4. Open "TOC-Control V" program from Windows desktop.

5. Open the template sample table you wish to use or build a new table.

6. **IMMEDIATELY click "File→ Save As" then save with time-stamped file name**.

7. On top menu bar, click "Connect" and then "Background Monitor". TC Furnace should be at 720deg. C if running DOC/TN and 680 deg. C if running DOC only.

8. TN Detector at 50 deg. C. Dehumidifier temp. at 1 deg. C.

9. Instrument will need to stabilize for at least 30 min before analysis. Confirm baseline conditions are OK before proceeding. View background monitor from pull down menu.

   NOTE: If running IC, ensure the acid line going to the 8-port valve is primed. Seek assistance from METAL staff if it is not.

10. Modify sample table according to your sample set. If using existing sample table be sure to delete all data. (Be sure to Save as). Delete or add rows as necessary but make sure samples remain bracketed by blank and QC every 10 samples.

NOTE: If SALT (KCL, K2SO4, etc) matrix samples are being analyzed be sure to add a Nanopure water sample using "cleaning" method to end of run. The ceramic wool atop the catalyst bed should be change after approx. every 60 salt samples.

11. Place samples, calibration standard(s), and QC samples in auto-sampler rack. Click on auto-sampler icon in second tier of menu bar to add the placement for the vials in the instrument run. Samples for the cleaning and blank samples are from the rinse container as vial zero (0). All other standards and samples will need vial assignment.

12. Check background monitor one last time for all green checkmarks and baseline.

13. On top menu bar, click "Start". Select Standby options on the pop-up screen according to instrument use schedule then click "Standby".

14. If only running one set of samples, select the "Shutdown" option on the pop-up screen.

15. Verify vial positions then click "OK".

16. To monitor progress, right-click sample name in left window then select "Sample Window". If hidden, click "Window→ Sample Window" from menu bar.

Shutdown

1. If the" Shutdown" option was selected, and the instrument is off, shut off gas cylinders at valves.

2. Data can be exported to an excel file. Please be sure to log and bill your analysis in iLab.

3. Clean all glassware; waste placed into appropriate containers. Acidified samples can be added to waste for HCl acid bath in GWC 639.