Standard Operating Procedure

Shimadzu TOC-L$_{\text{CPH/CPN}}$
(NPOC/TC/TN/IC Liquids Analysis)

Introduction

The Shimadzu TOC-L$_{\text{CPH/CPN}}$ (TOC) instrument measures the total amount of carbon (TC), inorganic carbon (IC), the total amount of organic carbon (TOC) and the total amount of non-purgeable organic carbon (NPOC). The TOC works on the principle of oxidative combustion infrared (IR) analysis. The carbon samples are combusted to form $CO_2(g)$ and analyzed in a non-destructive infrared analyzer (NDIR). The TOC can measure total nitrogen (TN) in water samples using a chemiluminescence analysis of $N_2(g)$. The limit of quantification (LOQ) for TOC for the TRACES Centre system is set from 1000 ppm down to around 250 ppb. The limit of quantification (LOQ) for TN for the TRACES Centre system is set from 1000 ppm down to around 500 ppb.

Purpose

The purpose of this document is to introduce the user to the routine operation of the Shimadzu TOC-TN. This document also outlines the special safety concerns introduced when using the instrument.

Scope

This protocol applies to established procedures of analysis using the standard configuration (NPOC/TN) for the TOC. Individuals must complete a hands-on one-on-one training session with a TRACES staff member. Other fields are measure are covered in the hands-on training if requested.

Referenced Documents

- Shimadzu TOC-L$_{\text{CPH/CPN}}$ User's Manual Lab Solutions (p/n 638-94834)
- Shimadzu TOC-L$_{\text{CPH/CPN}}$ TOC System User's Guide (p/n 638-94829)
- Shimadzu TOC-L$_{\text{CSH/CSN}}$ User's Manual (p/n 638-94599J)
- Shimadzu TOC-V$_{\text{CPH/CPN}}$ & TOC- Control V Software (p/n 638-94241A)
- Shimadzu TOC Application Handbook (p/n G3430-90015)
- TOV Virtual Advisor: https://tocvva.ssi.shimadzu.com/home
- Shimadzu Model TOC-5000 Instruction Manual
- USP 643: Total Organic Carbon Determination

Responsibilities

1. **TRACES Users**
    1.1. All Users must obtain training with TRACES Staff prior to system operation. It is the responsibility of the User to ensure they have a good understanding of the instrument and all operation protocols. All standards and their preparation are the responsibility of the user.
    1.2. If additional training sessions are needed it is the responsibility of the User to schedule these with TRACES Staff.
    1.3. User must ensure that the compressed air cylinder required for impending analysis is available in TRACES*.

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1.4. Instrument time must be booked by the User via the online booking system prior to system operation.

1.5. **It is the user's responsibility to ensure that they purchase the correct vials for TOC analysis. The vials can be purchased through Restek (p/n: 21796) or VWR (p/n: 10803-256).**

    1.5.1. Other vials must be vetted by TRACES Staff BEFORE using the TOC.

2. **TRACES Staff**

2.1. It is the responsibility of TRACES Staff to provide introductory and, if required, subsequent training to all users.

Equipment

- Shimadzu TOC-L (referred to as TOC)
- Shimadzu TN-L (referred to as TN)
- Shimadzu ASI-L (referred to as ASI)
- Shimadzu SSM-5000A (for solid sample analysis ONLY)

Safety

> **IMPORTANT:**
> - The TOC uses very high temperatures.
> - The compressed air cylinder uses high pressure gas.
>   - Take the appropriate precautions
> - Seek assistance from TRACES Staff if you have any concerns

Initial Setup

1. Ensure the compressed air AND compressed oxygen contains MORE than 500 psi in the cylinder. If you expect a long run time, contact a TRACES personnel
   a. Turn the regulators to 'OPEN'
   b. The regulator on the compressed air should read between 45-60 psi (delivery)
   c. The regulator on the compressed oxygen should read between 45-60 psi (delivery)
   d. SSM-5000A pressure must be read 0.25L/min (*)

2. Fill the Cooler Drain Container (Fig.1) with deionized water by removing the rubber cap
   a. Located Using deionized water fill the container till it is visibly draining into the waste container
   b. Recap the drain

3. Fill the Humidifier Container (Fig.2) with deionized water by removing the rubber stopper
   a. Fill above the 'Hi' level
   b. Re-stopper the container
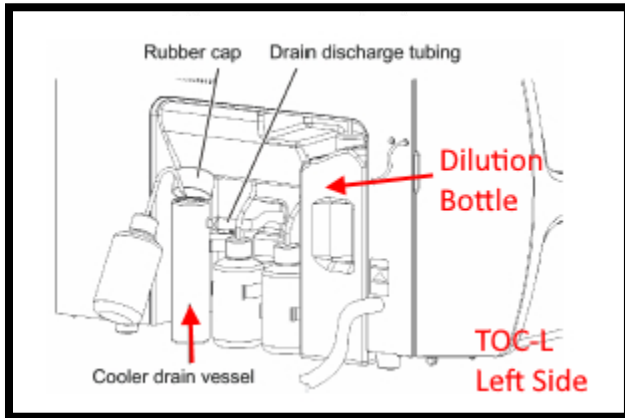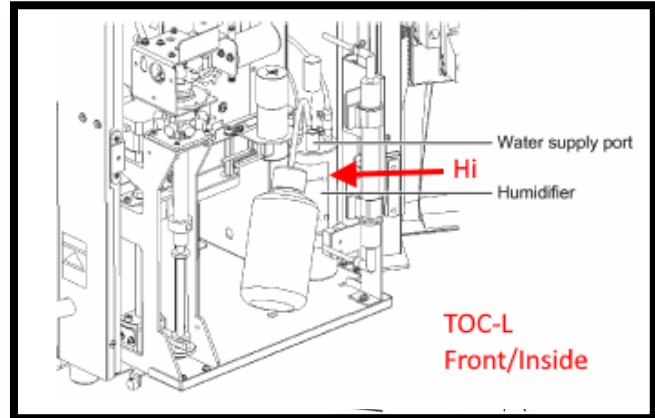
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Figure 1

Figure 2

4. Ensure that RINSE (behind the autosampler) and DILUTION Bottles (Fig.1) are topped up to the 2L mark with deionized water.
5. Check the ACID BOTTLE located between ASI and TOC. Ensure the acid tubing is near the bottom of the acid bottle and that the bottle is topped with 1M HCl.

TOC Initial Setup Section

1. Press the Power button located on the left-hand corner of the TOC unit
2. Log on to computer using the Username and Password provided
3. Select the 'LabSolutions Manager icon on the desktop
   a. Enter the User ID and Password provided
      i. Select the 'Instruments' tab
      ii. Click on 'Select Project'
         1. Select the appropriate 'Project' (based on research group)
         2. Ensure 'Current Project' reflects the 'Selected Project'
   b. Double Click on the 'TOC_L' icon
   c. 'TOC Sample Table Editor' window should open
      i. If NOT select the 'Sample Table' tab at the bottom
4. Create a new 'Sample Table' by selecting 'New'
   a. Select 'Liquid' & 'Normal' in the H/W Settings pop up and then OK
   b. Label the sample table accordingly and press 'Save" and then OK
      i. Enter a filename with a date representation (i.e., **20220914LakeOnt**)
      ii. Save the Sample Table
      iii. A new blank table will now be displayed
5. Connect to the instrument: Click the 'Connect' button at the top right corner
      i. The remaining icons will become active
      ii. If commencing from a cold start- the 'Not Ready' will be illuminated
6. Select 'Monitor' to check the instruments temperature and gas settings
   a. Check the TOC Gas Settings
      i. TOC Carrier Gas Flow: 150mL/min
      ii. TOC Supply Gas Pressure: 200 KPa
         ==ALLOW 40 MINUTES OF WARM-UP TIME==

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Instrument Settings

1. BEFORE commencing the analysis, the instrument settings must be reviewed
   a. The settings are set for NPOC/TC/TN/POC/IC analysis only
   b. Ensure the instrument indicator 'Ready' is visible
2. Select 'Monitor' to check the instruments temperature and gas settings appear as below:
   a. TOC
      i. NDIR
         1. Baseline Pos: OK
         2. Baseline Fluc: OK
         3. Baseline Noise: OK
      ii. Gas Settings
         1. TOC Carrier Gas Flow: 150mL/min
         2. TOC Supply Gas Pressure: 200 KPa
         3. Sparging Gas Flow: 80mL/min
      iii. Temperature
         1. Furnace: OK 720°C (+/- 0.3 °C)
         2. Dehumidifier: OK ($\leq$ 1.2 °C)
         3. NDIR: OK 65.0 °C (+/- 0.2 °C)

TOC Calibration Table Setup

1. The TOC LabSolutions software is able to use various calibration curves and apply them to your sample. It would be advantages at this point to setup several high concentration and low concentration calibration curves to obtain a more accurate results for your unknowns
2. Click on the Calibration Curve tab Click 'New'
3. Calibration Curve Wizard will commence
   a. System: Liquid (->next)
   b. Normal (->next)
      i. Normal if using an external calibration
      ii. Check 'Use dilution from standard solution' for stock dilution option
         1. The instrument can dilute to a maximum of 50X.
   c. Analysis: Select NPOC/TC/TN/POC/IC (->next)
      i. Analysis: NPOC
      ii. Default Sample Name:
      iii. Default Sample ID:
      iv. Calculation Method: Linear Regression
      v. Check box for Zero Shift: Leave blank
      vi. Check box for Multiple Injections: select
      vii. Calibration File Name: i.e., **20220914cal** (->next)
   d. Select appropriate Calibration Parameters. Below is default for NPOC analysis:
      i. Units' mg/L
      ii. Number of injections: Min=2 Max=3
      iii. Number of washes 2
      iv. SD Max 0.1000
      v. CV Max 2.0%
      vi. 5:00min for sparing time & 1.5% Acid Addition (->next)
         1. **NOT REQUIRED FOR TC or TN & IC uses phosphoric acid**

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    e. Calibration Points List must start with lowest calibrant. Follow step below:
- i. Add calibrants starting with low<u>est</u> concentration
- ii. Enter Standard Solution concentrations
- iii. Select 'Auto Dilution Factor'
- iv. Number of injections: Min=2 Max=3
- v. SD Max 0.1000
- vi. CV Max 2.0%
- vii. Click 'OK'

    f. Peak Time Parameters –change as appropriate
    g. Do NOT enable 'History Log'
    h. Click 'Finish'

4. Inserting Calibration Standard
   a. Highlight/cursor position on first line of the Sample Table
   b. Open 'Insert Menu' and select the 'Calibration Curve'
   c. Select the Calibration file (from above)
   d. Click the 'View Vial Settings'
      - i. Ensure that the vial numbers and concentrations match
      - ii. Select Start
      - iii. OK
5. Calibration analysis will commence at this point
6. Once the calibration has been 'COMPLETED'
   a. Select the 'Measurement Parameters' icon
   b. Select 'Graph'
      - i. Minimum correlation coefficient is 0.995 for TOC and 0.99 for TN

Note: The greater the accuracy of the standard concentration the greater the accuracy of your measurement. I advise all users to calculate concentrations using weight (analytical balance (4 decimal places)).

TOC Method Setup

1. Click on the Method tab and select 'New'
2. Method Wizard will commence
   a. Select NPOC, IC, NPOC/TN. Below is default for NPOC analysis:
      - i. Analysis: NPOC
      - ii. Default Sample Name& ID:
      - iii. Default Values: Determinations
      - iv. Default Values: Dilution
      - v. Method Name: (->next)
   b. Select appropriate calibration curve (max. of three)
   c. Select appropriate Sample Injection Parameters. Below is default for NPOC analysis:
      - i. Units: mg/L
      - ii. Number of injections: Min=2 Max=3
      - iii. Number of washes: 2
      - iv. Autodilutions: 1

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    v.   SD Max: 0.1000
    vi. CV Max: 2.0%
    vii. 5:00 min for sparing time & 0.5% Acid Addition (->next)
        1. **NOT REQUIRED FOR TC or TN & IC uses phosphoric acid**
    viii. Shimadzu recommends not enabling any of the remaining parameters (-> next)

TOC Sample Analysis Setup

1. Select 'Multiple Samples' from Insert Menu
2. Select the appropriate Method (->next)
3. Enter the number of samples to be run, vial locations and ID the samples (->next)
4. Select the appropriate calibration curve (several can be chosen) (->next)
   a. In most cases the previously run calibration method is chosen
5. Controls can be designated in the Calibration Curve Check section (->next)
6. Shimadzu recommends not changing or enabling any of the remaining parameters unless there is a mitigating reason for it (-> next)
7. Measurement Start (review all locations and values).
   a. At this point you can select;
      i. Keep running (if you wish to run a further sample set)
      ii. Shutdown (after sample analysis is completed)

TOC Data Evaluation

1. TOC data will appear on 'Sample Table' once the analysis is completed
2. If data manipulation is required, it is STRONGLY urged to save the existing data with a different filename-to avoid the loss of the original data set
3. All 'Print' functions will provide a PDF copy of the desired results
   a. No physical printers are available
   b. Data can be transferred via email or ftp servers
4. Print the 'Table'
   a. Printing of the sample name and concentration values of the sample
5. Print the 'Sample Report'
   a. Printing of the sample data, area, mV response of each injection analysis for all the samples and calibration data located in the 'Sample Table'
6. 'Ascii Export'
   a. 'Export Sample Table and Each Injection' using common CSV data output
   b. 'Export by Analysis Type' segregates each analysis (TOC, NPOC, TN..) separately using Common CSV data output

*The TRACES Manager will provide further details during hands-on training.