

## Desktop

**TOC-Control V:** program for TOCV instrument

**ShimadzuTOCV\_ShortManual:** condensed operator manual

**ShimadzuTOCV\_Manual:** full operator manual

**Shortcut to Data:** the folder that contains personnel folders and data

**TOC\_DataRunGuide.pdf:** guide to running samples on the TOCV instrument

**TOC\_Guide.pdf:** this comprehensive guide to running the TOCV instrument

## Methods

**Principle of Method:** Shimadzu TOC-V Total Organic Carbon Analyzer measures the quantity of total organic carbon (TOC) as non-purgeable organic carbon (NPOC) and/or total nitrogen (TN) in water and soil extracts. NPOC is measured by acidifying an aliquot of water or soil extract and then sparging the sample to strip off any purgeable organic and inorganic carbon. The sample is then injected into a combustion tube that contains a catalyst material. A redox reaction occurs that evolves carbon dioxide gas (CO<sub>2</sub>) which is then detected by a non-dispersive infrared (NDIR) detector for carbon. For nitrogen analysis, the sample is combusted to NO and NO<sub>2</sub>, then reacted with ozone to form NO<sub>2</sub> in an excited state. The resultant photon emission is measured by a Chemiluminescence detector. Quantitation is achieved by calibrating the TOC-V instrument with known standard materials.

Local Disk (C) → Program Files → Shimadzu Corporation → TOC3201 → Methods → NPOC\_TN\_2019.10.1.met

Local Disk (C) → Program Files → Shimadzu Corporation → TOC3201 → Cal Curves → NPOC\_2019.10.1.cal and TNacid\_2019.10.1.cal

## Turning on the TOCV

Press the button on the front bottom of the TOCV instrument; the switch on the lower right side of the TN unit should be on; leave instrument on for ~24 hours before calibrating

# Calibration

Desktop → TOC-Control V → Sample Table Editor → User: System, Password: TOC6001 → File → Open → navigate to the “Data” folder, open the template named “Template\_Calibration\_NPOC\_TN” → File → Save As → save in “Data” folder as “CalCurve\_MN\_DY\_YEAR”

Use the standard vials in the refrigerator that are for calibration only

Remove TOCV lid and carousel and place the standards in the carousel as follows:

- 62–64 = MilliQ water (should be filled)
- 65–66 = high standard (OC = 50, TN = 5) (should be filled)

***Do NOT waste calibration standard solutions in the vials; do NOT pour out the standard vials, just refill them using the standard solutions for calibration and store in the refrigerator***

CAREFULLY place the TOCV carousel back in the TOCV instrument, making sure that the metal tabs are securely holding the carousel in place (gently try to rotate the carousel to make sure it is being held in place)

Make sure that all the vials are fully inserted into the carousel (they should all be at the same level/height)

Replace the lid for the carousel for the TOCV instrument

**Open main valve for gas tank (Ultra Zero Air)**

**Check gas pressure and flow rate!**

- Total amount of gas  $\geq 600$  psi (right sensor on regulator)
- **Do NOT run a full run if gas is  $< 600$  psi**
- **Running the TOCV without proper gas pressure will destroy the detector!**
- Flow rate:  $\sim 400$  kPa (left sensor on regulator)

**IMPORTANT! When the calibration run is complete, you must disconnect the instrument and turn the gas flow off as soon as possible!** Otherwise, much expensive gas is wasted and it will damage the instrument if the gas runs out while the instrument is still connected. If you cannot be back within a few hours of the end of the run, don't start it!

### Use sign-in sheet:

- Record the date, your name, amount of gas remaining (psi), and note it is a calibration

### Tasks:

- Ensure that the bottle containing 1 N HCl to the left of the TOCV instrument is at least 1/3 full (**Caution! You must read the Safety Data Sheet (SDS) for HCl**)
- Using MilliQ water, fill the front container of water to the “Hi” level mark
- Using MilliQ water, fill the back container of water (via the open blue tube) to ~1 cm below the black tube that extends from the top right of the container

### Running the calibration:

- Click the yellow lightning bolt icon (“connect”) to connect the software and instrument
- Ensure the flow rate for the TNM unit is at ~0.5 L/min
- Open door of TOCV instrument:
  - Ensure that the pressure is at ~200 kPa
  - Ensure that the carrier gas flow is at ~130 mL/min
- Click the adjacent left icon (“background monitor”) to check the status of the instrument; navigate through the three tabs and once all the signals are green, the instrument is ready to run (this could take several minutes)
- Click the green light icon (“start”) → click Standby → click OK → click Start
- To abort analyzing a sample or to stop a run, use the stop sign icons
- When the analysis is done, click the yellow lightning bolt icon (“connect”) to disconnect the software and instrument; in the popup window, check the box that says “disconnect” and click OK
- **Once the instrument is disconnected, close main valve for gas tank (Ultra Zero Air)**

New calibration curves will save in the “Cal Curves” folder

Local Disk (C) → Program Files → Shimadzu Corporation → TOC3201 → Cal Curves → sort by date and find the new NPOC and TN calibration files; open each and determine the success of the calibration curve by checking the results in the graph

Local Disk (C) → Program Files → Shimadzu Corporation → TOC3201 → Cal Curves → find files named “NPOC\_2019.10.2019\_10\_01\_20\_17\_51.cal” and “TNacid\_2019.10.2019\_10\_01\_22\_37\_16.cal” and rename them as “SAMENAME.n.cal” where “n” is the largest number previously used +1

Rename the new NPOC and TN calibration curves respectively as “NPOC\_2019.10.2019\_10\_01\_20\_17\_51.cal” and “TNacid\_2019.10.2019\_10\_01\_22\_37\_16.cal”

*Note: renaming the new calibration curves aligns these curves with the parameters of the sample run template; otherwise, a new sample run template would need to be created for each new calibration*

## **Sample Set Up**

- You can run up to 60 samples per run
- Use the 40 mL glass vials with blue/white lids with septas
- Use 4 mL of your filtrate + 16 mL of MilliQ water for typical cold-water soil extractions
- Do NOT label vials or lids!
- Your samples should be ordered from 1–60 (keep track of the order of your vials)
- Once you are done with the vials and lids with septas, take care to clean them well, dry them, and return them to the cardboard containers; they are reused by all lab members

## Data Analysis

Open main valve for gas tank (Ultra Zero Air)

Check gas pressure and flow rate!

- Total amount of gas  $\geq 600$  psi (right sensor on regulator)
- **Do NOT run a full run if gas is  $< 600$  psi (each run of 60 samples uses  $\sim 400$  psi)**
- **Running the TOCV without proper gas pressure will destroy the detector!**
- Flow rate:  $\sim 400$  kPa (left sensor on regulator)

**IMPORTANT! When your sample run is complete, you must disconnect the instrument and turn the gas flow off as soon as possible!** Otherwise, much expensive gas is wasted and it will damage the instrument if the gas runs out while the instrument is still connected. If you cannot be back within a few hours of the end of the run, don't start it! (each sample takes  $\sim 25$  minutes, so running 60 samples takes  $\sim 28$  hours and  $\sim 400$  psi)

Use sign-in sheet:

- Record the date, your name, method, # of samples, and amount of gas remaining (psi)

Tasks:

- Ensure that the bottle containing 1 N HCl to the left of the TOCV instrument is at least 1/3 full (**Caution! You must read the Safety Data Sheet (SDS) for HCl**)
- Using MilliQ water, fill the front container of water to the "Hi" level mark
- Using MilliQ water, fill the back container of water (via the open blue tube) to  $\sim 1$  cm below the black tube that extends from the top right of the container

Samples:

- Remove TOCV lid and carousel and place your samples in the carousel slots from 1–60
- Slots 61–68 are water, standards (in refrigerator on door), and blanks as follows (fill vials to at least 20 mL):
  - 61 = blank (your extraction solution; if using salt solution, please use low concentration, i.e.,  $\leq 0.1$  M)
  - 62–64 = MilliQ water
  - 65–66 = high standard (OC = 50, TN = 5)
  - 67 = medium standard (OC = 25, TN = 5)

- 68 = low standard (OC = 5, TN = 1)
- ***Do NOT waste standard solutions in the vials; do NOT pour out the standard vials, just refill them (when between runs, store the 61–68 vials in the plastic rack for the TOCV standards and put it in the refrigerator)***
- CAREFULLY place the TOCV carousel back in the TOCV instrument, making sure that the metal tabs are securely holding the carousel in place (gently try to rotate the carousel to make sure it is being held in place)
- Make sure that all the vials are fully inserted into the carousel (they should all be at the same level/height)
- Replace the lid for the carousel for the TOCV instrument

### **Running your samples:**

- Desktop → TOC-Control V → Sample Table Editor → User: System, Password: TOC6001 → File → Open → navigate to the “Data” folder, create a folder using your name and open the template named “Template\_NPOC\_TN\_2019\_10\_1” → File → Save As → navigate to your folder and rename the file to identify your samples in the run
- Click the yellow lightning bolt icon (“connect”) to connect the software and instrument
- Ensure the flow rate for the TNM unit is at ~0.5 L/min
- Open door of TOCV instrument:
  - Ensure that the pressure is at ~200 kPa
  - Ensure that the carrier gas flow is at ~130 mL/min
- Click the adjacent left icon (“background monitor”) to check the status of the instrument; navigate through the three tabs and once all the signals are green, the instrument is ready to run (this could take several minutes)
- Click the green light icon (“start”) → click Standby → click OK → click Start
- To abort analyzing a sample or to stop a run, use the stop sign icons
- When the analysis is done, click the yellow lightning bolt icon (“connect”) to disconnect the software and instrument; in the popup window, check the box that says “disconnect” and click OK
- **Once the instrument is disconnected, close main valve for gas tank (Ultra Zero Air)**

## Issues

Sometimes the communication between the software and the instrument “times out” or loses connection. When this happens, turn off the TOCV instrument using the on/off button. Wait 30 seconds and turn it back on. Reconnect the instrument using the yellow lightning bolt icon.

Sometimes the autosampling unit does not connect when the carousel lid is replaced. When this happens, go to Instrument → Maintenance → Mechanical Check → ASI → Move Tray → Reset

## Exporting your data

- Desktop → TOC-Control V → Administration → User: System, Password: TOC6001 → Database Manager → Database → navigate to your folder and name the file the same as the Sample Table you will export → click Open → choose columns → click Create
  - Recommended columns:
    - Sample\_Name
    - Cal\_Curve
    - Analysis
    - Sparge\_time
    - Acid\_Addition
    - Area
    - Conc
    - Result
    - Excluded
    - Inj\_Vol
- Return to your Sample Table (where your result are) → File → Database Export (Access)... → Database → navigate to the database you just created in the previous step (you should have named it the same name as your current Sample Table) → click Open → click Export now
- Excel → open new sheet → Data → Import External Data → Import Data → Desktop → Shortcut to Data → navigate to your folder and open your database with the exported data from the previous step → click OK → save Excel file using the same name as your Sample Table and Database for the data

## **Standards**

To prepare new standard TC and TN 1000 ppm stocks, see page 60 (TC) and 61 (TN) of the TOCV manual

The standard solutions are prepared by adding the indicated amount of TC or TN stock solution (1000 ppm) in mL (e.g. 50 mL and 5 mL, respectively) to a 1 L volumetric flask and filling the flask to the 1 L mark with MilliQ water

Store the standard solutions in glass vials/containers in the refrigerator

## **Maintenance**

The TOC/TN catalyst needs to be washed every several thousand samples. See page 239 of the TOCV manual. Eventually, the catalyst will need to be replaced. See page 240 of the TOCV manual. Page 39 of the TOCV manual describes how to refill the combustion tube (note: pay close attention when removing the combustion tube; note the placement of tubes and lines, etc.; see pages 280-281 of the TOCV manual regarding sample injection spray and slider assembly). After washing/replacing catalyst, run the regeneration of the catalyst 5 times (see page 238 and 262 of TOCV manual). After regeneration, run water samples until the NPOC/TN values stabilize. Then run a new calibration.

The syringe should be checked every ten thousand or so samples and changed if the seal is loose or the plastic stopper is deteriorating. See page 268 of the TOCV manual.

## **Turning off the TOCV**

Press the button on the front bottom of the TOCV instrument; the switch on the lower right side of the TN unit can be left on



# Update Record

**Prepared By:** Cole Gross

**Date:** November 2019

**Update By:** Cole Gross

**Date:** May 2021

**Changes:** Updated multiple directions and added issues, methods, calibration, standards, and maintenance sections

**Update By:**

**Date:**

**Changes:**