Shimadzu DOC-V (updated 3/18/2014)

Standard ranges: DOC: 0.25-10 mg L-1; TDN: 0.05-10 mg L-1

**Quick Start-Up Checklist**

* Fill all water vessels (next to autosampler, next to DOC, vial 0) and ensure tubing hits bottom of vessel
* Empty drain bottle on floor
* Ensure correct gas flow (~400 KPa, > 400 psi, regulator valve completely open)
* Inside DOC-V check:
  + drain vessel
  + halogen scrubber
  + drain catch
* Ensure that all I-Chem vials are level in the ASI-V
* Turn on TOC-V and TN
* Set up run using Sample Table Editor – ensure that all vials are accounted for and placed correctly
* Connect
* Open “background monitor” and ensure that all parameters are stable (as indicated by green checkmarks)
* Start the run
  + Can choose to ‘shutdown’ or ‘keep running’ when run is complete; choose ‘shutdown’ if you have no more runs and won’t be around to manually shut down machine. Choose ‘keep running’ if you have subsequent runs.
* Monitor run periodically, checking the standard curve and QCs before leaving for the day
* When run is done, be sure to turn off air flow, enter information in logbook, remove sample vials, and dispose of any extra standard or QC flasks in the refrigerator

**Record-Keeping**

* The sign-up calendar for the TOC can be found on Google calendar. If you don’t currently have access to the calendar, you will need a Gmail account. Contact Brooke to gain access to the calendar.
* Each run should be recorded in the Access data table located on rivercenter**\**analytical lab\samplelogs.mdb
  + Enter appropriate information on ‘TOC’ form, and then close form to save data. Make sure to enter calibration curve info when run is complete

**Solution Set-Up**

*Reagants*

* The HCl and Phosphoric acid (usually replaced w/ DI) bottles should be at least a quarter full. If HCl is low, replace with 2N HCl located in media bottle in acid cabinet

Containers are located between the TOC-V and ASI-V. If reagents are depleted, please use these recipes:

* + Phosphoric Acid: In a 250ml flask, add SLOWLY 50ml 85% phosphoric acid to ~150 ml of DDI, and then bring up to 250 ml with DDI.
    - **NOTE: this bottle is filled with DDI water unless running the IC method**
  + Hydrochloric Acid: In a 250ml flask, add SLOWLY ~41.25ml 37% (~12M) HCl to 125ml DDI, and then bring up to 250 ml with DDI.

*Rinsing Vessels*

* Fill the 2 DI reservoirs to the top with fresh DDI daily. It is helpful to use another empty bottle to put the lines in while carrying the vessel to the sink. Also fill the flask located near the front of the TOC-V, “vial 0”, with fresh DDIW.

*Standards and QC’s*

* The appropriate standards and QC needed are dependent upon your samples’ estimated C/N content and your desired analysis. The analysis typically run is NPOC-TN 10/10; also have method for NPOC-TN 5/20.
  + NPOC-TN 10/10
    - This analysis typically uses two separate standard solutions:
      * 10 ppm/10 ppm solution of C and N (typically vial 3)
        + 2.5 ml of 1000 ppm C stock solution + 2.5 ml of 1000 ppm N stock solution (either NO3-N or NH4-N) in 250 ml flask, dilute to volume with DDI
      * 1 ppm/1ppm solution of C and N (typically vial 2)
        + 0.25 ml of 1000 ppm C stock solution + 0.25 ml of 1000 ppm N stock solution (either NO3-N or NH4-N) in 250 ml flask, dilute to volume with DDI
    - QC
      * You can use a 4 ppm C/0.93 ppm N QC from a glutamic acid stock solution that contains 1000 mg C/L and 233.218 mg N/L
        + In a 250 ml volumetric flask, add 1 ml of this glutamic acid stock and dilute to volume with DDI
  + NPOC-TN 5/20
    - For this analysis, the 5/20 represents the upper range expected for the samples (and thus for the calibration curve). Therefore, the standard solution should contain:
      * 1.25 ml of 1000 ppm C stock solution + 5 ml of 1000 ppm N stock (either NO3-N or NH4-N) in 250 ml flask, dilute to volume with DDI
  + NPOC-TN high resolution

*Samples*

* The TOC needs at least 10 mL of sample in each vial to run. If using only 10 ml, probably want to run 2 min/3 max injections instead of 3 min/5 max injections per sample
* The maximum detection of the TOC (without dilution) is 1000 ppm C and 200 ppm N. If running high TOC concentrations, make sure there are not also high salt concentrations; this leads to high salt deposits on the combustion catalyst. If analyzing salty samples, be sure to dilute 10x or 20x.
* QCs and standards should be filled to the top of the I-Chem vial.
* Be sure all vials are level on the tray before starting your run.

**Machinery and Physical Set-Up**

1. Turn on gas tank (Zero Grade Air) and make sure the machine is receiving flow. Check regulator at gas tank to make sure there is enough and at correct pressure (check right gauge on regulator: need at least 400 psi per full sample run; check left gauge of regulator: should read 400 kPa)
2. Check that snorkel vent is on (dial should not be at 0)
3. The dilution and rinse tanks should be filled with **fresh** DDI. Also check the large flask, “vial 0” and fill with fresh DDI.
4. Open front panel of DOC-V and check the halogen scrubber (copper colored stuff in tube on far right wall of DOC-V). Replace if there is more than 1 inch of black discoloration.
   * Check the water containers inside DOC on right side. The water level for the front reservoir (humidifier) should be between the min and max lines on the container. The container farther in the back (drain catch) is filled to just below the tubing
5. Open lower right panel of the top of DOC-V and check the SOx scrubber; it should be white and powdery. Replace if it appears to have solidified.
6. Open middle panel on top of DOC-V and inspect injector plate. Remove the thumb screw on the injector, and slide out the plate that holds the injector line. Check the underside of the plate and line for salt accumulation and rinse with DI if there is noticeable salt on either.
   * Check for salt accumulation on the slider valve of the combustion column. Remove the screw on the slider plate and slide out to check for residue (and make sure that the tubing DOES NOT extend beyond the edge of the plate, as it will scratch the other side of the plate).
7. Close door and turn on DOC-V (button in lower right front corner). The TN module should turn on also unless switched off by previous user.

**Software Startup**

1. Turn on computer and open “TOC-V” program- shortcut is on desktop.
2. When window appears, double-click on “Sample Table Editor” and press “ok” after it prompts for a user id (it’s ok to leave this blank).
3. In next window, select “new” and then “sample table.” A blank spreadsheet will open where the sequence will be entered.
4. It is a good idea to start the run with a few washes to check the background noise. To do this, insert a sample using the below method and choose vial 0 for the location. You should place these “wash” samples before the calibration curve.
5. Your QC samples should be placed immediately after the calibration curve and throughout the run (~every 20 samples). The QC sample can be inserted using the sample insertion method below.
6. You can insert samples one at a time or using the “autogenerate” feature. Autogenerate is generally quicker. For the “autogenerate” procedure, see “To insert many samples” below.
7. To insert one sample:

Insert -> sample

* 1. Window that opens will prompt you to choose the method. Do so. If your method does not appear, see “To create a new method” below.
  2. Identify a sample name and ID. Unless you want your sample diluted, keep 1.00. “Determinations” refers to the number of times the sample will be run. This number is typically 1, unless you’d like to run many washes.
  3. Next choose the appropriate calibration curves for your analysis. If an appropriate calibration curve does not appear, see “To insert a calibration curve” below.
  4. Select “Finish” and the “ASI/Port Sampler Vials” window should appear. Enter the location of your sample (i.e., vial #) and that location should appear highlighted on the diagram. Press OK.
  5. Your sample should appear in the sample table.

1. To insert many samples:
   1. Select “Insert” then “Autogenerate.” Choose the method. Insert the number of vials (i.e. samples) you would like to autogenerate. The start vial refers to the numbered location of your vial on the ASI tray.
   2. Choose a sample name and check “Index Start.” This generates a series of samples that will start as “SampleName1” through “SampleNamen” in which n is the number of samples you are running and SampleName is your sample name.
2. Insert a calibration curve:
   1. If the calibration curve you need already exists (say, a 10/10 curve):
      1. Select “Insert” 🡪 “Calibration Curve” 🡪 your C curve (say, “NPOC\_10ppm.cal”)
      2. Select “Insert” 🡪 “Calibration Curve” 🡪 your N curve (say, “TN\_10ppm.cal”)
      3. Insert the correct vial numbers for the curve (say, 1, 2, 2, 3, 3, 3)
   2. If you need to create a new calibration curve:
      1. Select “File”, “New” and “calibration curve” (leave system as TOC/TN unless you are doing gas sampling)
      2. In the second window select “edit calibration points manually) and “dilution from a standard solution”
      3. In the third window select the appropriate analysis from the drop down list. You will also want to make sure there is a check in the “multiple injection” box. Give the curve a file name that contains the analysis and the concentration (i.e. NPOC\_15ppm).
      4. Next select the appropriate parameters for injection. Usually 2/3 injections will work (the machine will run 2 reps, and a third if the deviation is too high), but standard procedure is to run 3/5 injections. Acid addition for NPOC should be around 1.5% and the sparge time around a minute and a half unless you have very alkaline samples.
      5. On the next screen you will be adding points to the curve. Hit “add,” enter the concentration of the stock you intend to use, then a dilution factor to get the desired end concentration of the point. Enter as many points as needed, and skip the last few screens.
      6. *Note:* If you are doing combination analyses, you will be able to make the standards in the same vial. You will still have to run the curves separately, but you will be able to have the DOC sample from the same vial for the different curves.
3. If you need to create a new method:
   1. If you are running combinations of analyses a method is necessary, but it is also useful for single analyses.
   2. Select “File”, “New”, then “method”. Skip the first screen.
   3. Select the appropriate analysis from the drop down menu, and give the method a file name that indicates the analyses and the concentrations.
   4. The next screens will allow you to set the calibration curve for each analysis, as well as the parameters such as injections for those analyses. You can use either calibration curves that already exist (namely, you won’t have to run the curves again before your samples) or use newly created curves.
4. Once your washes, calibration curves, QCs, and samples are inserted, be sure that all your vials are accounted for. Select “View” 🡪 “ASI Port Sample Vials.”
5. Select the “Connect” button (yellow lightning bolt). Select “Use Settings on PC.”
6. Once the connection is complete, hit the button next to the connect button that says “background monitor.” Wait until all green check marks appear on all parameters.
7. Close background monitor. Run through the “Quick Start-Up Checklist” one more time before starting the run.
8. Hit the “Run” button (a green stoplight). Select “shut down” and hit “standby.” Leave external acid addition checked. Select OK - This starts the run!

**During and After the Run**

* Check your washes to monitor background noise. If washes are showing peaks greater than 0.5, more washes may need to be run or troubleshooting may be in order.
* It’s a good idea to stick around to see your QCs before you take off for the day.
* Each sample takes about 15 minutes. Calibration curves take longer.
* After your run, be sure to turn off the regulator valve (the leftmost black knob) on the gas tank. Enter your run into the logbook and remove your vials. Be sure to note any maintenance or troubleshooting in the blue log book.
* Your run should automatically save under the given file name. It’s a good idea to save your run on the lab drive as well as the computer. To export the data to a text excel file, select “File”, “ASCII Export,” and save as your desired filename on the lab drive. **Do this now, because you will not be able to open your run while another run is in progress!**

**Basic Maintenance**

* Catalyst regeneration
* Residue removal
* Catalyst replacement

**Troubleshooting**

* **General things to consider:**
  + Be sure that humidifier water level lies between the “hi” and “lo” marks.
  + Be sure that the drain container (see pg 12 of manual for diagram) water level is just below the attached tubing
* **Baseline Position Error**
  + This is likely a flow problem. Check the gas tank knobs.
* **Baseline Fluctuation Error**
  + The combustion column may have been displaced. Carefully place column back into the O-ring.
* **High washes**
  + Check the values from the last run. If they were very high, more washes may be needed to clear the system.
  + Change the Vial 0 flask and refill it with fresh DDIW.
* **Inconsistent Peaks (for a given sample, no peaks followed by high peaks)**

**To Change the Combustion Tube:**

* Wait until the combustion tube has cooled!!
* The sliding sample injector must be removed. Remove the tubing labeled “TC” from the block and set aside. Also remove the tubing that connects the side of the sliding sample injector to the humidifier. Unscrew the two screws, located above and on the left of the sample injector. Loosen the screw that connects the sample injector to the grooved moving mechanism. Detach the drain tubing exiting the slide injector to the Y-fitting of the system drain line. The sample injector can now be removed.
* Disconnect the bottom of the combustion tube from the tubing. Remove the tube.
* For directions on how to clean the catalyst and combustion tube materials, see pg. 239. For directions on how to assemble the catalyst materials, see pg. 39.
* To re-connect the tube,
  + See pg. 40
  + To re-install the sliding sample injector (before step 3 on pg. 40):
    - Fasten the two thumbscrews on the upper left. Unscrew the other thumbscrew (connected to the grooved moving mechanism) and remove the upper sliding block. To reconnect the TC tubing, screw the tubing in *just below* the edge of the block. Re-attach the upper sliding block. Screw the single thumbscrew until finger-tight. Attach the tubing that connects the side of the sliding sample injector to the humidifier, screw in only finger-tight.