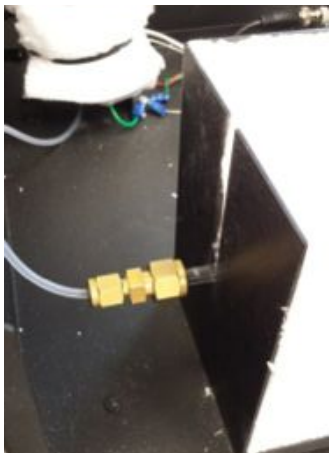
12b

Section 12 Organic Carbon/Elemental Carbon Analyzer Protocol

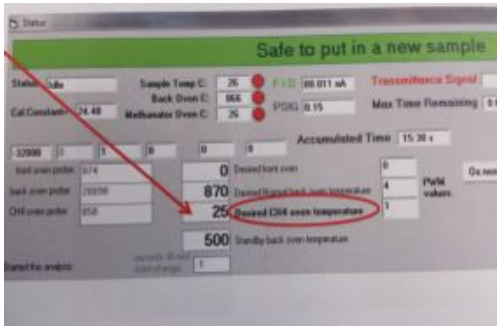
Jacqueline Yakobi, April 2015

START UP:



The following outlines the startup procedure for the organic carbon/elemental carbon (OC/EC) analyzer assuming the instrument was previously shutdown:

1) Open all five gas cylinders (Hydrogen, Helium, Air, Methane/Helium mix & Oxygen/Helium mix) and ensure gas cylinders have sufficient levels of gas and the gas output pressure is set to the correct value (see mark on regulators). You shouldn't need to adjust the regulator pressure, as it has been already adjusted out output pressure (ie. 20psi).
2) Remove the cover from the FID box (small red button on front) and using a ½" and 9/16" wrenches, carefully remove the Swagelok fitting on the end of the methanator quartz oven (see pick on right and pg 95 in manual). This will allow the condensing water vapour to drip out of the oven while undergoing the re-heating temperature steps.



3) Turn on the main OC/EC analyzer power switch located at the back of the main large black box (do not turn on the methanator oven power yet).
4) Open the OC/EC program and make sure the instrument is in "standby mode" (carbon analysis pane, "standby" box should be checked). Next enlarge the "Status" pane (top right of pane). Set the "Desired CH4 oven temp" to 25°C as the oven is pre-set to 500°C (you can never have just zeros in the cell box, so you may need to play around to get it to accept 25, see pic on right).
5) Once the CH4 oven temp is set to 25°C, flip the power switch that powers the methanator oven, located on the back of the FID box.
6) Open the "Gas flows pane". On the box below the FID, adjust the H2 and He3 knobs on the box below the FID to the left until the Hydrogen and He3 values on the Gas flows pane equal between 40 and 50 cc/min. Let the gases purge for about 5 minutes.
7) After 5 minutes, adjust the methanator oven temp up to 100°C. Leave the methanator at 100°C for 30 mintues. Then increase the methanator to 200°C and leave for another 30 minutes. Repeat this process every 30 mins until the oven is at 500C. You will likely see water vapor condensing on the exit port of the methanator and dripping down which is

normal. Once at 500C, wait about 10 mins and ensure there is no more moisture on the oven exit port tube. If there is, you can use a cotton swap or kimwipe to remove the moisture.

8) Carefully re-attach the Swagelok fitting to the methanator exit tube and then replace the FID box cover. Set the He3 and H2 flows back to trickle flow (turn knobs all the way to the right, but not too hard or you will damage needle valves). Let the instrument equilibrate for another 30 minutes.

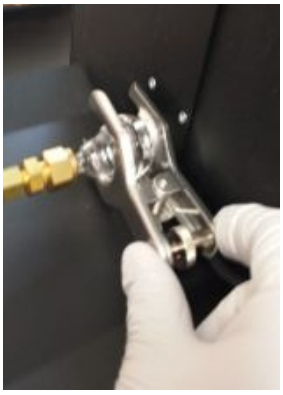
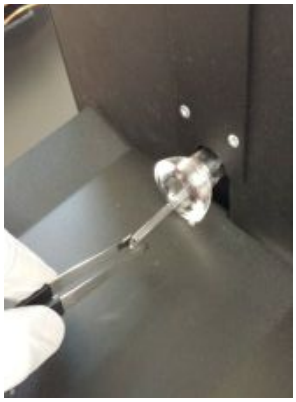
PREPARING WORKSTATION:

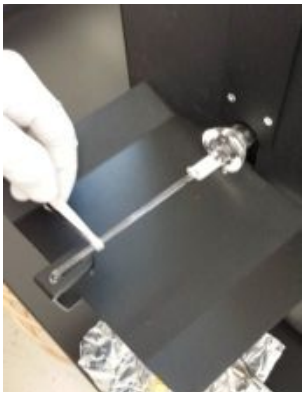
1) Lay down a new piece of aluminum foil to work on in front of the OC/EC instrument and tape down the edges. Put on gloves.
2) Bring out tools (two forceps, poke, filter holder and punch) and place on aluminum foil. Clean edge of punch, metal forceps, poke, filter holder needles and aluminum foil work area using discarded blank quartz filter. Place filter holder on top of FID cover (over methanator oven). The warmth of the methanator helps dry the sucrose standard on the filter.

PREPARING TO CONDUCT AN ANALYSIS USING OC/EC ANALYZER

Placing a sample in the analyzer oven:

1) Set the OC/EC analyzer flows to the settings recommended on the "Gas Flows" pane.
2) To light the FID, turn the H2 flow up to 60-70 cc/min, leave for about 10 seconds and press the red ignition button on the FID box. You should hear a little pop and then check using the forceps to make sure the FID is lit (hold edge of forceps to top of FID exhaust tube and look for steam). Once lit, turn the H2 gas flow down to 50-54 cc/min.

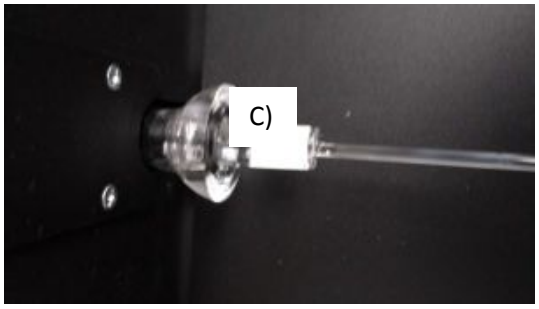


3) Now the quartz sample spoon needs to be taken out of the oven. To do this, use the following steps:
    a. Loosen the metal clamp holding the helium gas line with quartz fitting and the front of the quartz front oven together and clamp to release (make sure the helium gas line with the quartz fitting doesn't drop, see pic A). Place the quartz piece under the catch tray on a piece of aluminum foil.
    b. Using the Teflon coated forceps reach about an inch into the front oven and grip the end of the quartz sample spoon. Gently pull out the spoon until there is about 2

inches of the spoon back end showing (see pic B). Lower the spoon end and release the grip with the Teflon coated forceps.

c. Using the metal forceps, grip the spoon handle about 2 inches from the end and gently pull out the spoon (see pic C). Set the tip of the spoon end into the farthest back hold on the spoon handle catch (see pic D). Using the metal forceps, remove any old quartz filter that is resting on the square part of the spoon.

4) Retrieve a blank 47mm quartz filter and punch out a piece on the aluminum foil. To help remove the filter from the punch, stick the metal poke through the small hole on the side of the punch to help prod the filter out far enough so it can be gripped using the metal forceps. Transfer the quartz punch to the square part of the spoon and align so no parts are overhanging and it sits between the vertical glass piece and the two small knobs on the spoon (see pic below).

A) B)  D)

5) To place the quartz spoon back in the oven, use the metal forceps to pick up the quartz spoon end about 2 inches from the end, gently lift up and transfer into the oven until the forceps hit the quartz piece on the front oven. Grab the Teflon coated forceps, grip the very end of the quartz spoon and gently direct the remaining distance into the oven until it hits the back of the oven. Replace the helium line with the quartz fitting, but ensure the rubber o-ring is still on in and in place. Tighten using the metal clamp.

<u>Conducting Daily and weekly QC Checks:</u>

Daily QC Check:

1) The daily QC check involves baking a blank filter (first run of day), running an instrument blank and running a sugar sample for calibration.
2) Place a blank quartz filter punch on the sample spoon and insert into the oven. The blank sample needs to be baked to remove any trace carbon levels before conducting the instrument blank (and ultimately the weekly standard check). Open the "Carbon Analysis" pane and under "Sample ID#" type "FirstofDay(date)" (ex. FirstofDay10-12-13). Ensure the "niosh870.par" file is selected in the "Parameter file" cell and for the "Output Raw Data file" click on the small browse button and create a new folder with the current date and select that folder. Next, replace the .txt section with the project name and current date (ex. c:\ocec831\rawdata\10-12-2013\HERC-10-12-13.txt). Type your initials into the "Analyst" cell, select 1.00sq cm punch area and hit "Start Analysis". The run should take approximately 15 mins.

3) Once the run has completed (you may notice the FID detected a little carbon, this is normal), run another sample with the same settings only use "Instrument blank(date)" as the Sample ID. You do not need to rename the Raw Data file ID as the data will be added to the first file you created. Start this analysis.
4) You should not see any FID signal during the sample run (except for the cal-gas peak at the end of the run). To ensure that the filter is "carbon free", open the Calc317 program (pinned to task bar) and open the file you just created (ex. HERC-10-12-13). Hit the "Calculate first sample" button on the left of the pane. Whenever you hit the calculate button, the instrument saves an excel.csv file that you can view with excel. The first result will be your "firstrunofday", so hit "Calculate next sample" to see the instrument blank. In the results section, located in the middle of the pane, you should see "Total C". This total carbon value should be at or close to zero. If this is the case, the instrument ready to use for the sucrose standard QC check.

5) Remove the quartz blank sample from the oven and poke the corner of the filter onto one of the two needles on the filter holder so it is stable.
6) Retrieve the sucrose standard and shake for 20 seconds (always do this before using the standard). Pipette a small amount (ie. 5 ul) into a small beaker twice to purge the pipette and then pipette about 5 ul onto the middle of the blank filter, making sure the pipette actually touches the filter, which will ensure all of the material has been deposited. Set the filter holder back on top of the methanator oven so it will dry faster (see pic on right). If you plan to conduct multiple QC checks, you should punch out another blank quartz filter, insert into the oven and do another run (can call it filter clean). Once that run has been completed, the new blank filter will be ready to be loaded with another sucrose standard. Also it usually takes around 15 minutes for the sucrose to dry on the filter, which means the first filter should be ready for analysis by the end of the cleaning run.
7) Once the sucrose has dried on the filter (can no longer see "wet" spot), it can be inserted back into the oven on the sample spoon. This time, name the sample ID and Raw data file "Sucrose(conc)-(date)" (ex. Sucrose6.964µg -10-12-13). Once again make sure 1.00 sqcm is selected for the punch area and start the analysis run.
8) After the sucrose run has finished, you can open the Calc317 program again and open the file you just created. Calculate the sample and check to make sure the organic carbon is within 5% of the actual concentration. Once the standard has been run and verified, you are ready to conduct sample analyses. If a standard varies by more than 5% of the recorded value (re-run a few times to make sure), you may need to adjust the Cal Constant (see under Routine Instrument Checks section).Note: currently there is no official standard for EC. Also, you can re-use a sucrose std punch a few times before it needs to be discarded.

Weekly and Long-term QC Check:

1) Every week or two, or after a prolonged instrument shutdown, three sucrose standard concentrations should be checked. Run 1ul, 5ul & 10ul (ex 6.964µg, 34.82µg & 69.64µg) sucrose injections and ensure the instrument is recording within 10% of the actual value.
2) If there is a desire to conduct an inter-laboratory comparison to verify the accuracy of the analyzer's results, a Sunset Laboratory OC, EC and TC (total carbon) ambient standard can be run through the instrument. This filter standard has known quantities of OC and EC on the filter (tested at sunset laboratories) and can be used to compare to our analyzers results. This standard can only be purchased through Sunset Laboratories.

RUNNING SAMPLES AND ANALYZING DATA:

1) After the OC/EC instrument prep runs have been completed (first of day, instrument blank & sucrose std), you are ready to run your first sample. Retrieve the quartz filter sample (stored in refrigerator) and using your metal forceps, pick up the filter and lay sample side up on the aluminum foil. Use the punch to punch out a piece of the filter, making sure you are only taking sampled area (not too close to edge) but are also leaving room to take multiple punches if necessary (see pic on right). Poke out the filter so it is easy to grab and transfer to the sample spoon. Insert the spoon into the oven. **Note: You must clean punch and forceps between each sample (use baked filter from previous sample to clean equipment)**
2) Setup a sample run similar to your sucrose std, but type in the actual sample ID listed on the sample's filter cassette. Once again choose the niosh870.par method. **However, you must choose a punch area of 1.50 sq cm for the actual sample runs**. This is important because the calculation program needs to correct punch size when it reports OC and EC in µg per sq cm.
3) A duplicate sample should be run every 10 samples!
4) Once the sample has finished, open the Calc317 program and calculate the OC-EC content on the filter. Once again, these values are in µg per sq cm. You will now need to calculate the total OC and EC that was deposited on the entire filter. To do this you need to calculate the total area of the sample filter (Area=πr^2). For example, if the quartz filter was 47mm (diameter) in size use the flowing equation: Area = 3.14*(4.7cm/2)^2, Area = 3.14*5.52, Area = 17.34 cmsq
5) Once you have the total area of your sample filter, simply multiply the area by the calculated OC, EC or Total OC/EC µg/sq cm. This will give you the total carbon values in ug for your entire filter.
6) To calculate the concentration of OC/EC per volume of air (ie. µg/m^3), you need to use the following equation:
   OC/EC Mass in µg/((Sampling time in minutes*avg flow rate in L/min)/1000)

For example:

Start time	Stop time	Total minutes sampled	Average flow rate	Total liters of air sampled	Total volume of air sampled	Total filter OC/EC Mass
08:00	12:00	240	10 L/min	2400 L	2.4 m^3	110µg

OC/EC concentration = 110/((240*10)/1000), OC/EC concentration = 110/2.4,
OC/EC concentration = 45.83 µg/m^3

Possible Instrument Data Irregularities:

1) If you see the FID detector picking up a signal near the end of the sampling run (not including the cal peak), you may need to re-run the sample at a higher temperature. If this is the case, you will need to add the OC, EC and TC levels of both runs together to get the actual total carbon amount.
2) If you see a large peak during the large temperature step in the middle of the run, you may actually be analyzing carbonate carbon. If this is the case, you can add a few drops of HCl to a duplicate sample punch and re-analyze. If the peak is gone, you know if as carbonate and not organic carbon.
3) If you can't open a specific file using the Calculation program because it gives you an error, try coping and pasting the data text file into another folder and re-open with the program. This should allow you to create new csv files.
4) If the cal peak at the end of a run does not reach the minimum FID max, try increasing the cal-gas flow a little and re-run a sucrose std.

INSTRUMENT STANDBY AND LONGTERM SHUTDOWN:

Instrument Standby:

1) If you are finished using the OC-EC analyzer for the day, and still plan to use the Analyzer again in the next day or two, put the instrument in standby mode. Using this mode will save gases from depleting and reduces the back oven temp to preserve heating coil life. To do this, click the "standby" button on the Carbon Analysis pane. Then turn all of the gases down to their trickle flows (turn adjusting knobs all the way to the right, **but do not over turn as it can damage the needle valves!**). This mode keeps the back oven and methanator ovens on so you do not need to do the methanator oven temperature step as outlined in the "Startup" section of this protocol.
2) To return the OC/EC analyzer to "ready mode", simply unclick the "standby" button, set the gas flows to their recommended settings and re-light the FID (remember to increase

the H2 to 70 cc/min for 1 min prior to lighting the FID, then readjust back to normal level!). The instrument is now ready to use and you can begin your "first of day run".

Prolonged Instrument Shutdown:

1) If the instrument is not going to be used for more than a few days, you should complete a full instrument shutdown. To do this you first need to turn all of the gases down to their trickle flow settings (all the way to the right).
2) Then you will need to turn down the back oven and methanator oven temps. Expand the "Status" pane and set the both oven temps for 25C in the "Desired oven temp" cells (make sure instrument is not in "standby mode" or back oven temp will not decrease). Wait until the ovens cool down below 100C and at least 20 mins before turning the gas flows completely off.
3) Once the ovens have been cooled down, shutdown the OC-EC program and turn off the computer. Next shut the valves on all of the gas cylinders**, but do not touch the regulator valves** (This way when you re-open the gas cylinders, the regulators will already be set at the appropriate pressure).
4) When you want to re-initialize the OC/EC instrument, you will have to follow the complete Startup procedure outlined in the beginning of this protocol (must do the methanator oven step procedure!).

ROUNTINE INSTRUMENT CHECKS/MAINTENANCE:

1) Check the volume of each gas weekly. If any of the gas cylinders are getting low, order new cylinders from Praxair. **However, remember the methane/helium (5% CH_4 in He balance) and oxygen/helium (10% O_2 in He balance) mixes take approximately 3 months to be delivered, so pre-order these cylinders far in advance**.
2) Check temperature readouts on the back oven and methanator and ensure they remain at or close to their controlled temperatures (870°C and 500°C respectively). However, in standby the back oven temp should read around 500°C. Also check that the front oven temperature follows the program during the run.
3) Check the FID signal, and make sure the instrument is giving a high peak height for the calibration peak (at end of every run) in the range of 22,000 – 30,000. If FID1Max says "Offscale", either lower He1 or increase H2.
4) Conduct a Temperature calibration whenever a new main oven or heating coil is installed, or if the insulation is adjusted. See page 96 of the manual for completing this calibration procedure.
5) If you notice the pressure is building to fairly high levels, the back oven may need to be replaced.
6) If the oven temperatures cannot reach their programed settings, the heating coils may need to be replaced (see pg 48 in manual)
7) If you need to change the sample spoon, insert the spoon into the oven backwards and press "clean oven" under "Action" on the Carbon Analysis window. This will bake any carbon off the back of the sample spoon. Then re-insert the spoon in the proper orientation and do another clean oven.

Adjusting the Cal Constant:

1) To adjust the cal constant, you need to open the "Cal constant template" located at C:\OCEC831 and fill in the missing data (gray boxes). You will need to run 5 standards at varying concentrations (ie. 13.93ug, 34.82ug, 69.64ug, 104.46ug & 139.28ug) and record the values in row 6 in the appropriate locations.
2) Next you need to find the value of the current Cal constant which can be found at C:\OCEC831\OCECPAR in the text file "instrument parameters". The cal constant number is the value 5 lines up from the bottom of the text document. This value needs to be pasted into the far left grayed in box in row 14 (other gray boxes will automatically update).
3) Once these values have been recorded in the cal constant template, the average cal constant for all the standard concentrations will automatically be generated in the cell G19. This is your new cal constant. Hit "Save As" on the Excel document and save in a different location so the template does not get over written.
4) This new cal constant now needs to be inserted back into the "instrument parameters" text document. Replace the old cal constant value with the new one, but be careful not to change any other text on the document. The instrument analysis program will now use this new cal constant. Re-run your three weekly standards and re-adjust the cal constant when required.