**Procedure for Shimadzu GC-17A ver. 3 (ECD and FID detectors and methanizer) Revised 7/6/2009, Jen Morse, Revised 7/21/2011 MBS**

**Revised 4/15/13 (B. Hassett)**

Hardware

Gas chromatograph: Shimadzu GC-17A ver. 3, retrofitted on 6/11/2007 to approximate the GC-2014 Greenhouse Gas Analyzer (with methanizer, ECD, FID and automated Valco valves (10 port, 4 port) See Figure in GC binder

Serial number C11124205576SA

Main tech support number: 1-800-477-1227

Tekmar Headspace Autosampler 7000, configured for 9ml headspace vials

Serial number US04257002, account number 259075

Main tech support number: 1-800-543-4461

Permapure drying tube: MD-070-12-F-2. MD-Series drying tube (Teflon, 12” length, 1/8” fittings).

Requires drying air to flow countercurrent to sample flow, to draw water vapor across Nafion membrane

Periodic Maintenance:

Be sure to keep the water vent tube bottle at 10cm of head. (Check it ~monthly).

The methanizer needs repacking ~annually.

Gases:

For GC: UHP (ultra-high purity) gases:

- N2 (ECD grade)

- H2

- Scientific Air

For drying tube: Compressed air (breathing quality, yellow tank). **This is used up extremely quickly.**

200 psi minimum in cylinder for operation (100 psi for drying air)

Use Teflon tape to reduce chance of leaks around regulators

**Check for leaks** using Snoop (soap+water)

Squirt a few drops on connections around regulators each time you change a cylinder

Flow rates/pressures:

N2 carrier gas: 50 psi on regulator

P5: 40 psi on regulator

Air, H2 pressure: 40 psi on regulators

Drying air: 1-2 psi max

Cold start-up (How to turn on gases, GC and software)

1. Check pressure in gas tanks. Be sure there is enough carrier (N2) for all of your runs. If you have to change the carrier tank midway through, the whole system must be shut down and restarted.
2. Turn on N2 and P5 gas using knob on tank (N2 should be at 50 psi and P5 should be at 40 psi) and wait a few minutes
3. Turn on GC power and wait 5 minutes
4. Press SYSTEM at the top of the front panel on the GC and wait for instrument startup to complete. After the start time is complete, the GC will come to life and start heating
5. **Check for leaks** using Snoop (soap+water): Squirt a few drops on connections, especially around drying tube and around regulators
6. Set Temperatures on instrument – press appropriate button on front panel of GC (col, aux1, etc), key-in temperature, press Enter (e.g., COL →110→ENTER)
   1. For bake-out, to remove impurities; recommended after a series of runs and when the instrument has been off for a while.
      1. Set oven (COL) temperature to 110C to bake for at least 2 hours
      2. Set FID (AUX1) and INJ temps to 95C and ECD (DET) to 340C during bake-out
      3. After bake-out, set COL temperature to 80C, INJ to 380C, AUX1 to 250C
      4. allow baseline to stabilize at least an hour
      5. Note: there is a method to have the GC bake out and return to the GHG parameters
         1. Open GC Solutions software & create a new batch file (see “Starting a Run” step 2).
         2. Use method: C:\GCSolution\Data\Methods for General GC Use\ GHG\_bake \_return\_new.gcm.
         3. This method is helpful if you want to start the GC up before you leave for the day, have it bake out and get the ECD to stabilize overnight. (Don’t run the FID overnight without samples – it is a waste of gases.)
         4. Once program is complete, to set temperature to analysis conditions while in GC Solution, click on ‘System On’ in the left panel.
            1. Lower half of screen will have a box with tabs for each component; put appropriate temperature in box
            2. After all temperatures have been entered, click ‘download’ on right side of screen to send setpoints to GC
   2. For FID & ECD analysis, temperatures:

COL = 80, INJ = 380, DET = 340, AUX1 = 250.

* 1. For ECD only (N2O analysis only) set INJ and AUX1 temps at 80.
     1. Note: set the temps on the GC as well as in the GC solutions method file for run

1. Light FID (if using):
   1. Turn on H2 and Air (not breathing air) gas tanks (should both be at 40 psi)
   2. If using keypad on GC:
      1. Wait 30 seconds and hit the IGNIT, ON, then ENTER buttons on the GC or the FLAME ON button in the software
   3. If using GC Solutions:
      1. Wait 30 seconds and go to System On screen
      2. On right side of screen, click the ‘on’ button next to ‘FLAME’
   4. Check the FID flame to make sure water vapor is forming (flame is lit). You will need to lift the GC top cover and aim your metal reflecting surface at the back of the FID.
   5. Allow FID to warm up at least 30 min before beginning analysis
2. Turn on CBM-102 and autosampler
   1. When GC is Ready (ready light on), close out of GC solutions if open
   2. turn on CBM-102 then turn on autosampler
      1. Autosampler on switch is on back right side
      2. Autosampler will go through a startup sequence that requires you to hit ‘OK’
      3. After the self-tests and warm-up period are finished, the A/S will be on Hold
      4. Check settings on display screen:

**Method=1, Platen Temp=30, Sample Loop Temp= 30, Line Temp= 30**

If method 1 isn’t loaded, touch METH button on main screen, choose 1 and then hit Run

1. Open GC solutions software
   1. Choose Operation tab
   2. Then choose Real Time Analysis
      1. Default login is user: admin, no password
   3. Software will open to screen that was last in use
2. Check System On screen for configuration, temperatures, signal acquisition, etc.
   1. To get to ‘system on’ select ‘top’ arrow in left panel
   2. For ECD+FID run, make sure both channels are acquiring data. Check baselines under Instrument Parameters or System On screen. If only one detector is of interest, make sure that it is checked as Acquiring Data.
      1. Note: sometimes you have to zoom out to see the ECD line. Try looking around 2.5uV(x1000).
      2. a zoom in to 1,000 uV with the y-axis in units of 0.5 is a good zoom level with which to observe stability

Starting a Run

1. If the instrument has been properly warmed up, and the System On screen is showing that it is Ready (i.e., all parameters have reached their set values), and the baseline is stable then the run can be started.
2. Set up batch.
   1. Go to ‘Batch Processing’ on the left side of the screen.
   2. Fill in a new table with vial numbers and sample names (can be cut & pasted from excel)
   3. Choose method file by selecting the down arrow button in the top cell in ‘method file’ column
      1. Can copy and paste full file path name into remaining cells in column
   4. Choose a data filename
      1. In top toolbar, select Batch → Settings and select the ‘Data Filename’ tab.
         1. Check box to ‘create names automatically with:’
         2. Select ‘batch filename’ and ‘sample name’ (or whatever you want) and hit ‘ok’
         3. This will make the Data Filename column yellow
   5. Save batch file (File → Save Batch File As) in your project folder in C:\GCsolution\Data\
3. Set up autosampler
   1. Load samples, seal end up, in carousel in order defined in batch table
      1. **No stickers or tape should be on vials! If so, remove, or A/S will jam!**
   2. Press F2 on autosampler to define the starting and stopping position for the batch
      1. Change the existing settings by pressing ‘Enter’, the number, then ‘Enter’ again. Then exit the menu
      2. If you forget to check & change this, autosampler could either stop too soon, or continue sampling past end of run (autosampler doesn’t communicate with batch file regarding # of samples
   3. Select the ‘Auto’ button on the autosampler
4. Begin run
   1. In GC solution, select green arrow (play button) in left panel next to batch table.
      1. Software will ask if you want to save method (can choose either yes or no)
   2. GC software will wait in Ready (Standby) mode for autosampler to start
   3. On autosampler, press ‘start’ button
      1. Select ‘yes’ to accept default method parameters for run
         1. Check that timing parameter on A/S method matches the data acquisition time on the GC
      2. autosampler should move to and take first vial
   4. Turn on drying air (yellow breathing air tank) and set regulator to 1-2psi.
      1. Does not need to be on while running standards, but must be on when running samples (turning on just before start of run will not impact baseline stability)
5. Ending sample analysis
   1. If another batch will be run in next few days:
      1. Leave GC on with carrier gas flowing through and all temperatures at analytical settings
      2. Close out of Real Time Analysis and GC Solutions software
      3. Turn off CBM using switch in front
      4. Turn off A/S using switch in back
      5. If using FID, turn off flame (IGNITE → OFF → ENTER)
      6. Turn off Scientific Air and H2 cylinders using knobs on top of tanks
      7. Turn off Drying air and P5 cylinders
      8. DO NOT TURN OFF N2!
   2. If GC will be idle for **more than 3 days**, turn off system:
      1. If using FID, turn off flame (IGNITE → OFF → ENTER)
      2. Turn off the Scientific air, H2, P5 and drying air cylinders
      3. Set all temperatures (COL, INJ, DET, AUX1) to 25C and allow system to cool down
      4. Close out of software and turn off CBM
      5. When all temperatures are <40C, turn off switch GC using switch on left side
      6. After GC is turned off, turn off N2 cylinder
   3. \*\*\*If you aren’t going to be in the lab to cool things down when the last run is over, you can use an auto-cool down method from the Methods for General Use folder. GHG\_last\_sample\_cool\_down.gcm. It takes ~2-3 hours for the system to cool down enough to shut things down using this method. Just be sure to an extra sample into the batch sheet and use the method on **only** the last sample. Put an extra junk vial in the autosampler. The autosampler may not return the final vial to the sample rack. You will probably have to abort it to get it to spit out the vial before turning everything off.
6. Checking your standard curve – you can do this during the run, a good check to make sure the instrument is running properly before running your samples.
   1. In main GC solution window (not real time analysis) click on ‘Postrun Analysis’
   2. Click on ‘Data’ tab in lower left side of window
   3. Click on folder icon in upper right of the Data Explorer window, and navigate to folder where the batch file is saved.
      1. There is a file for each samples
      2. Note: this window doesn’t automatically refresh; in order to see sample files as they are coming off the GC, must manually refresh by navigating away from that folder, and then back to that folder
   4. Open a file for a standard
      1. A green table appears in lower right of screen
      2. Click on ‘compound’ tab in that table
         1. Can only look at either the FID or ECD outputs at once
         2. To switch between the detectors, click on the little white box with ‘1’ or ‘2’ at center top of screen
            1. Channel 1 is FID (CO2 and CH4)
            2. Channel 2 is ECD (N2O)
      3. Note that the chromatograms are raw, uncalibrated integrations (thus only a rough estimate of standard curve)
         1. If red baseline is not in correct location for integrating peak, can change integration manually
            1. Right-click on peak and select ‘manual peak integration’
7. Viewing and exporting data
   1. In main GC solution window (not real time analysis), click on ‘Postrun Analysis’
   2. On left panel, select ‘Batch Processing’
   3. Select folder where data is located by clicking on yellow folder icon in data explorer window- ‘batch’ tab and then selecting folder in which you want to save data
   4. Select the ‘data’ tab to see a list of data files
   5. Double-click on a file name to open chromatograms
      1. Switch between FID (Channel 1) and ECD (channel 2) data by selecting box 1 or box 2 from toolbar above chromatograms
   6. To edit peak integration (if necessary; usually for very large peaks), in the upper chromatogram, drag a box around the part you want to change. This will make the zoomed-in selection appear in lower chromatogram box.
      1. Right-click and select ‘Manual Peak Integration’. This will bring up the manual integration toolbar
      2. select a tool to adjust your peak integration
      3. if adjusting baseline horizontally or vertically, move floating line to part of peak you wish to change and click once; then move line to desired location and click again.
         1. Baseline should adjust accordingly; if not correct, click on backwards arrow on manual integration toolbar to undo.
      4. When finished adjusting all peaks on chromatogram, click on another file name in data explorer window
         1. When prompted to save file, select yes.
   7. To export data, click on ‘top’ arrow to get to main left panel screen
      1. Select ‘report generator’
      2. Click on ‘summary compound’ box in toolbar (to left of one that looks like cactus)
      3. Draw a box on the white page on ‘report’ tab
      4. In ‘GC summary compound properties’ box that pops up on screen, click on ‘view’ tab
         1. Uncheck ‘display chromatograms’ box
         2. On ‘table’ tab, select to display ‘title’, ‘sample name’ and ‘area’
      5. On ‘Data’ tab in Data Explorer box, highlight the data files you want to export, then drag and drop them into the box drawn on report screen
         1. Shortcut: to export many files at a time, click first file, hold shift and click last file
      6. Save as pdf
         1. File → Print and select ‘pdf writer’ from the printer dropdown box
      7. Open pdf file and save as text file for import into excel

Run time: For a full tray of samples for GHG analysis, run time is about 8 hours; 9.6 minutes per sample.

**Troubleshooting**

1. If you started a run, had to stop in the middle, and want to restart the same batch:

* Change the autosampler to start and stop at the appropriate numbers.
* In batch processing, highlight the samples you want to run.
* Click on Batch, Partial batch run… It should already be queued to start and end at the highlighted numbers. Once the autosampler and baseline are ready, click run.
* If you turn off the Autosampler and CDM before exiting GC Solutions but leave the GC running for another day, you may get an error that says the wrong GC type is specified in the setup. This was fixed by cooling down the GC, powering it down, then powering it up following the above protocols for a cold startup.

**Current Method parameters for CH4, CO2, and N2O analysis (as of 9/9/07)**

General tab of Advanced method parameters

Time Event

(3.35 CH4 peak)

4.20 Valve 92 closes (flow to Methanizer)…. Relay 92, value = 1

4.80 Valve 91 closes (flow to ECD)…. Relay 91, value = 1

(5.40 CO2 peak)

(5.80 N2O peak)

8.00 Valve 92 switches back…. Relay 92, value = 0

8.00 Valve 91 switches back … Relay 91, value = 0

**Modifications:**

CH4 only: Delete all the events, and change the Column Temperature Program hold time to about 5 min.

CO2 only: Delete the Valve 91 events, and change the Valve 92 event to maybe 3 mins. You should let the sample go for at least 8 min. With really high CO2 concentrations, you may need to let the analysis go for 10-15 minutes, so that baseline can be attained before the next sample

N2O only: Delete the Valve 92 events, and change the Valve 91 event to maybe 3 mins. The new sample analysis duration may be 6 or 7 min. You also need to change the analysis time to 6 minutes in the Column tab, there is a table with the columns: rate, temperature, hold time. Change hold time to 6 minutes. These changes cannot be made once the run has started. Save these changes to your method file.

Remember to change the GC sample run time in the A/S method to reflect the sample hold time in the GC software. Press F1 Meth, select a method to edit (not 1), Edit, page down to GC Sample Time, change to 6 min (or whatever you changed the sample analysis time to).