UCI KCCAMS Facility

Graphitization protocol
Hydrogen reduction method
(carbonate samples)
December 26, 2011

SUMMARY

Preconditioning the line

1. Remove the heaters from the reactors, record residual pressures, print out the pressure vs time plots.
2. Evacuate the reactors individually, then open them all and let them pump.
3. Put 2 scoops of Fe into 12 reactor tubes.
4. If perchlorate needs to be changed, put 1/4"– 3/8" of.perchlorate into 12 tubes.
5. Flush the line and reactors 3 times with 1 atm of H_2, then fill all the reactors with >1 atm of H_2, valve them off, and evacuate the line.
6. For each reactor: remove, label and cap the graphite tubes, replace the perchlorate tube if required, attach a tube with new Fe, evacuate.
7. Flush the line and reactors 3 times with 1 atm of H_2, then fill all the reactors with 1 atm of H_2, valve off, and evacuate the line.
8. Close the H_2 bottle and needle valve.
9. Place the heaters on the reactors, set the timer to 45 min, temperatures to 400°C, and cycle the temperature controller power to start.
10. Start the monitoring computer
11. Enter the residual pressures in the Ivine6 spreadsheet.

Graphitization: getting started

1. Put dry ice/methanol slush on the water trap, fill LN dewar, initial and date the perchlorate card.
2. Evacuate the line and reactors, toggle all valves, and close the reactors, valve #4, #7, and the bypass.
3. Collect a set of hydrolyzed carbonates, replace the phosphoric acid on the Vacutainer septa with water.
4. Isolate and remove the bellows, regrease the O ring, check the frit.
5. Prepare two needle fittings and dummy Vacutainers and check that they pump down.

Graphitization: adding CO_2

6. Isolate the needle fitting, blow off any water, and remove the Vacutainer.
7. Push a new Vacutainer halfway on to the needle and evacuate. Open to the water trap when P $<10^{-2}$ Torr.
8. When P $<10^{-3}$ Torr, isolate the Vacutainer from the pump, push it fully on to the needle, and leave for at least 1 minute.
9. Put LN on the sample collection tube, wait 10 seconds, open valve #4 to transfer.
10. Record any non-condensibles >1 Torr (MV pressure), then pump away any residual gas.
11. Close valve #4, move LN to the MV.
12. Prepare the next Vacutainer and connect it to the water trap (steps 6-8).
13. Isolate the sample in the MV, thaw, and record the pressure.
14. If the sample is too large, expand to the x4 or x10 volume, isolate a portion in the MV, pump away via the bypass, then close all valves when P $<10^{-3}$ Torr.
15. Cool the desired reactor with LN, wait 10 seconds, open valve #7 and the reactor to transfer, wait 10 seconds, close the reactor, remove the LN.
16. Evacuate any residual gas from the line via the bypass, toggle valves, close valve #7 and the bypass when P ~5 to 6 x10^{-4} Torr.

17. Repeat steps 6-16 until all reactors are filled. Replace the needle fitting every 6 samples (or as required) and reinstall and evacuate the cracker bellows at the end.

Graphitization: adding H2

18. Record all reactor CO_2 pressures
19. Isolate the water trap and remove the slush
20. Flush the line three times with 1 atm of H_2
21. Starting with the smallest sample, adjust the line H_2 pressure to 2x the reactor CO_2 pressure, cool the reactor with LN, wait 10 seconds, add H_2. Close the reactor immediately. Record the MV H_2 pressure.
22. When all reactors are filled, thaw, and record all total pressures. Close the H2 bottle and needle valve.

Graphitization: starting the reaction, cleanup

23. Place the heaters on the reactors, set the timer to 3 hours, temperatures to 550°C, and cycle the temperature controller power to start.
24. Start the monitoring computer.
25. Copy the information on the index cards into the spreadsheet in Irvine6.
26. Evacuate the line, replace the index cards, dispose of needles and Vacutainers.

I. Introduction

This protocol outlines graphite sample preparation procedure used in the KCCAMS prep lab. It is not intended to replace individual training by experienced lab personnel, and it does not cover details of all sample materials. **If you don't understand something, or if something seems wrong, ask a lab assistant.**

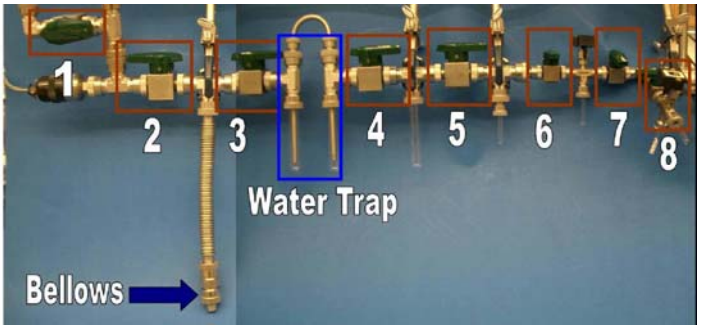
The CO_2 produced from raw materials is cryongenically purified and quantified in a calibrated volume. It is then reduced to graphite via the Bosch reaction, using H_2 over Alfa Aesar -325 mesh iron powder catalyst (Vogel et al, 1984; Lloyd, et al. 1991). The reaction is summarized as:

$$CO_2 + 2H_2 \xrightarrow[\text{Catalyst (Fe)}]{\text{550 - 650°C}} C + 2H_2O$$

but actually takes place as two successive reductions: first to carbon monoxide (CO) and then to graphite, which grows as filaments on the surface of the iron powder catalyst. Depending on sample size, the process takes up to ~ 120 minutes to reach completion. Water is removed by magnesium perchlorate (the white material visible in Fig. 3), that is replaced after three graphitizations to avoid saturation (Santos et al, 2004). A numbered index card follows each sample along the line and is used to record graphitization information.

Figure 1 shows one of the graphitization lines, that are made from glass and stainless steel, and pumped by turbomolecular pumps backed by oil free diaphragm pumps Each line has a main section that allows us to cryogenically separate CO_2 from other gases and water and a calibrated "measure" volume (MV) where CO_2 is measured manometrically (Fig. 2), plus 12 H_2/Fe reactors made from modified 1/4" Utlra Torr tees and 6 x 50 mm Pyrex culture tubes. Each reactor has its own pressure transducer and heater (Fig. 3).

Fig.1: Graphitization line.



II. Preconditioning the Fe catalyst:

Prior to graphitization, the Fe powder catalyst is baked for 45 min at 400 °C under 1 atm of H_2 to remove any contaminating carbon from the surface by converting it to methane. If there is a card on the line that states that the Fe was "Preconditioned" skip this step and proceed to Section III.

1. The reactors on the line will contain graphite from the last set of samples. Remove the heaters and hang them on the bar (ensure the leads all hang the same way to avoid tangles). Record the residual pressures on the sample cards (wait for the tubes to cool down if the heaters were recently on). Print out the pressure monitor plots from the laptop: select line A, B or C (upper left) then hit the print button (upper right).
2. Evacuate the reactors individually (to avoid exposing them to residual gases from another sample), then close the valve when the thermocouple gauge reaches baseline (1-2 x 10^{-3} Torr or high 10^{-4}'s, depending on the state of the perchlorate) and proceed to the next one. Then open all the valves and allow the reactors to pump for several minutes.
3. Take 12 prebaked 6 x 50 mm tubes from the wet cabinet on line A.
4. Take the Fe powder and scoop from the drawer labeled "graphitization tools" (each graphite line has its own tools).
5. Weigh between 5 and 6.5mg of Fe powder (2 scoops) into the tubes and record the weights (white cards in the graphitization logbook under line A). Distribute the iron over 1/8" – 3/16" inside the end of the tubes by rolling them on the bench.
6. If the $MgClO_4$ card above the line is full (used 3x), the perchlorate must be replaced. The perchlorate bottle and a spatula and a metal strainer to sieve unwanted fine powder can be found in the labeled drawer on line B, and a waste container is on bench A. Sieve a suitable amount of perchlorate, fill a set of 12 tubes with between 1/4 and 3/8 inches of material, return unused perchlorate to the bottle (remember to close and retape it) and put up a new perchlorate card (from Bench B, top right drawer).
7. Flush the reactors with 1 atm of H_2. First open the H_2 bottle and open the needle valve on the H_2 line to 6 on the linear micrometer scale (do not adjust the regulator). Then close valve #1 to isolate the system from the pump (Fig. 1), fill the line to ~760 Torr using the plug valve on the H_2 line, then evacuate the entire line by opening valve #1, and wait until the thermocouple gauge reaches baseline. Flush 3 times, then close valve #1, fill the line with just over 1 atm of H_2, close off all the reactors, and evacuate the line again.
8. For each reactor: replace the perchlorate tube (if appropriate), remove the graphite tube and cap it (caps are in the "graphitization tools" drawer) and label it with the UCIG#, carefully insert a tube

containing Fe, and open the reactor to the line (open the valve slowly to avoid disturbing the Fe and $MgClO_4$). Do this one reactor at a time to minimize exposure of the reactor to air. Note a) some people find it easier to label the graphite tubes while they are still on the reactors, others do it on the benchtop; b) the O rings are deliberately kept quite dry – make sure the tubes are pushed fully home.

9. Wait until the vacuum reaches baseline and toggle the reactor valves to release any trapped gases.
10. Flush the reactors 3 times with H_2, then fill the line with just over 1 atm of H_2 and close the reactor valves, evacuate the line and turn off the H_2 bottle and the needle valve (use one finger only on this – it's delicate).
11. Slip the heaters onto the reaction tubes and set the timer to 45 minutes and the temperature controls to 400°C (make sure all the individual controllers are switched on, press the "sel" button and use the up and down buttons to change the set point temperature. For line C, you must be pressing up or down before you hit "sel").
12. Start pressure monitoring on the laptop: select line A, B, or C (upper left) and hit the start button (upper right). Then start the heaters by turning the main temperature controller power off and on.
13. Take the index-cards to the Irvine6 computer and record the residual pressures in the Sample Master List spreadsheet**.**
14. Place the graphite samples in a box with the client's name on it, attach the index cards, and put the box in the wet cabinet by the pressing station

III. Preparation for graphitization:

1. Prepare a slush of dry ice + methanol for the water trap. Make it quite sloppy, to ensure efficient heat transfer from the glass water trap. Fill a small dewar with liquid nitrogen (LN) for transferring CO_2. Initial and date the perchlorate use card above the line.
2. Check the H_2 pressure in each reactor (rotary switch on the pressure readout box). If the reactors were not leaking, the pressures should be within a few Torr of each other.
3. Evacuate the H_2 from the reactors, wait until pressure reaches baseline (1-2 x 10^{-3} Torr or high 10^{-4}'s depending on the state of the perchlorate), and toggle the reactor valves to remove any trapped gases. Check the pressure readouts for the reactors and the measure volume, and zero them if necessary (the "z" adjustments on the front panel; small screwdrivers are kept in drawers below each line).
4. Gather the set of hydrolyzed samples in Vacutainers, and their index cards. Wipe the phosphoric acid off each Vacutainer septum with a damp Kimwipe and replace it with a drop of MQ water to help prevent air leaks.

5. Take apart two 1/4" Utra Torr fittings from the graphitization tools drawer, grease the O rings with vacuum grease from the drawer under the line, and put hypodermic needles into the fittings. The needle goes in first, then the O-ring, then the Ultra Torr ferrule. Lightly grease the needles and push old (dummy) Vacutainers halfway on to them.
6. Isolate and remove the cracker bellows, remove the frit from the Ultra Torr tee and check if it's clean, regrease the O-ring, and replace the frit in the tee.
7. Check that both needle fittings pump down: insert one in the tee, close the valve at the left hand (LH) end of the bypass, open valve #2 to evacuate, and open the valve to the water trap (valve # 3) when the pressure drops below 10^{-2} Torr. When the pressure reaches baseline, isolate the fitting, remove it, and repeat for the other one. If either leaks, try tightening the 1/4" Ultra Torr, or you may have to replace the needle. When the gauge reaches baseline on the 2nd fitting, open the LH bypass valve.

IV. Graphitization: filling the reactors

1. Once the line is pumped down to baseline (mid 10^{-4} range when the reactors are closed), toggle valves #2-7 to release trapped gas, then close valve #4, and #7 plus both bypass valves.
2. Check that the Vacutainer # matches the sample card, and fill in the date, operator initials and destination reactor # on the card.
3. Close valves #2 and #3 to isolate the Vacutainer and needle fitting, and blow off any water with Dustoff aerosol. Remove the Vacutainer from the fitting and lightly regrease the needle.
4. Push the next Vacutainer **halfway** on to the needle (**NOT all the way, or you will loose the sample**), Evacuate the headspace by opening valve # 2, and clip the index card on to the bar above the fitting.
5. Monitor the vacuum, and open the valve to water trap (valve # 3) when the pressure drops below 10^{-2} Torr. Toggle valve #2 slightly (not completely closed) to remove trapped gas.
6. Once the gauge reaches baseline (~10^{-3} Torr), **close valve #2 to the pump**, and push the Vacutainer all the way on to the needle.
7. Leave the released gases open to the water trap for at least 1 minute.
8. While you are waiting, submerge the bottom inch of the 13 x 100 mm tube between valves # 4 and 5 (Fig. 2) in LN.
9. Freeze down the CO_2 by opening valve # 4 to the collection tube and waiting for at least ten seconds. More time will required if sample contains lots of non-condensable gases (check the readout for the Measure Volume. (MV) pressure transducer): if these are present, raise the LN level using the lab jack, wait another ten seconds and repeat as necessary. Move the index card to follow the sample.
10. Record any finite (> 1 Torr) non-condensable gas pressures on the index-card.

11. Evacuate any non-condensable gases by opening valve #2 to the pump. Wait until the vacuum reaches the low 10^{-3}'s and the rate of pressure drop slows right down. At this point all that remains is residual water, and further pumping will only allow more water to freeze into your CO_2.
12. Isolate the frozen CO_2 and the MV by closing valve #4. Remove the LN dewar from the 13 mm tube with frozen CO_2 and place it on the MV tube (between valves # 6 and 7).
13. When the 13 mm collection tube has warmed up and the CO_2 has transferred to the MV, close valve #6 to isolate the MV

Note: To save time while step 13 is proceeding, prepare the next sample by repeating steps 2-7. **FROM THIS POINT ON, THERE WILL BE TWO SAMPLES IN DIFFERENT PARTS OF THE LINE. USE THE INDEX CARDS TO KEEP TRACK OF WHICH SAMPLE IS WHERE.**

14. Remove the LN from the MV to allow the CO_2 to thaw.
15. Record the amount of CO_2 recovered (MV pressure reading) on the index card. If the pressure goes offscale (>1650 Torr), close valve #5 and open #6 to expand the gas into a x4 volume to allow a proper reading, and record the pressure on the card as "x 4".
16. If the sample produced <450 Torr of CO_2 (for a 1 aliquot sample), proceed to step 18.
17. If the sample produced >450 Torr of CO_2, reduce the sample size by evacuating some of the CO_2 using the bypass section of the line. **Be careful – you can lose your sample if the wrong valve is left open.**
    a. To evacuate 1/10 of the total CO_2, open valves #5 and #6 to expand the gas into the x10 volume between valves # 4 and 7. Wait 10 seconds, **close valve #6**, and pump away the CO_2 trapped between valves # 6 and 7 by opening valve #7 and both bypass valves.
    b. To evacuate 1/4 of the total CO_2, close valve #5 and open valve #6 to expand the gas into the x4 volume between valves # 5 and 7. Wait 10 seconds, **close valve #6**, and pump away the CO_2 trapped between valves # 6 and 7 by opening valve #7 and both bypass valves.
    c. When the pressure drops below 10^{-3} Torr, **close valve #7 and both bypass valves.**
    d. Repeat as necessary to get to 400-450 Torr (~0.8 mgC). Note that this is equivalent to 100-110 Torr in the x4 volume, 40-45 Torr in x10.
18. Before transferring the CO_2 to the selected reactor, check that the reactor pressure is still zero.
19. Submerge the selected reactor tube in LN to the level of the magnesium perchlorate. When the hissing sound stops, the reactor is cold: wait for another 10 seconds.
20. Check that the bypass valves are closed, and then transfer the CO_2 from the MV to the selected reactor by opening valve #7 and the reactor valve. Transfer the index card.

21. Wait 10 seconds, **close the reactor valve**, and remove the LN to allow the CO_2 to thaw.
22. Evacuate the line to remove any residual gas by opening valves # 5-7 and both bypass valves. When the pressure reaches 10^{-3} Torr, toggle valves #5-#7 to release any trapped gasses. When the pressure drops to 5-6 $x10^{-4}$ Torr, **close valve #7 and both bypass valves**.
23. Repeat steps 1-22 for each sample. Replace the needle fitting every 6 samples (or earlier if it becomes difficult to insert or remove Vacutainers). When the last sample has been transferred to the MV, isolate and remove the needle fitting, and reinstall and evacuate the bellows.
24. After the CO_2 is fully thawed within each reactor, record the CO_2 pressure for each sample.

V. Graphitization: hydrogen addition:

To reduce CO_2 to graphite, an amount of hydrogen nominally equal to twice the CO_2 pressure must be added to each reactor. The line is filled with H_2 until the pressure is 1-2% above the required value for each reactor (or 1-2 Torr over for very small samples), the CO_2 in the reactor is frozen down, and then the reactor valve is opened momentarily and immediately closed again.

1. Before adding H_2, close valves # 3 and 4 to isolate the water trap, remove the slush and let the water thaw. Open valves #1 and #2, #5-7, and the bypass **(not the reactors)**, and check that the pressure reaches baseline. Open the H_2 bottle and open the needle valve on the H_2 line to 6 on the linear micrometer scale (do not adjust the regulator).
2. Flush the line 3 times with 1 atm of H_2: close valve #1 to isolate the system from the pump, fill the line to ~760 Torr using the plug valve on the H_2 line, then open valve #1 to evacuate the line, and wait until the thermocouple gauge reaches 1-2 x 10^{-3} Torr. Repeat 3 times.
3. Calculate the amount of H_2 needed for each reactor. If you can't multiply by two in your head, write this value on the index card. Add H_2 to the reactors as per steps 4-6, starting with smallest sample and working up.
4. Freeze down the CO_2: move the dewar to the appropriate reactor and raise the lab jack until the tip of the perchlorate is in the LN: **Do not submerge the entire tube**. It is best to have the dewar completely full. Watch the reactor pressure and wait for it to reach zero and the hissing sound to stop (CO2 is frozen), then wait another 10 seconds.
5. Set the H_2 pressure in the line: toggle the plug valve in the H_2 line to add hydrogen, and monitor the amount added using the MV pressure reading. If you add too much, close the LH bypass valve and quickly toggle valve #1 to pump away some of the gas between valves #1 and #3, then open the bypass valve again. For finer control, close valve #2 before toggling valve #1.

6. Add H_2: when the reactor has been cold for 10 seconds, **QUICKLY** open and close the reactor valve. Record the MV pressure on the index card **after** H_2 has been transferred. Remove the LN.
7. Move the readout switch to the next reactor and repeat steps 4-6 until all reactors have H_2.
8. After all the reactors received H_2, allow the gases to thaw. Record the total pressure in each reactor on the index card (CO_2+H_2 Total).

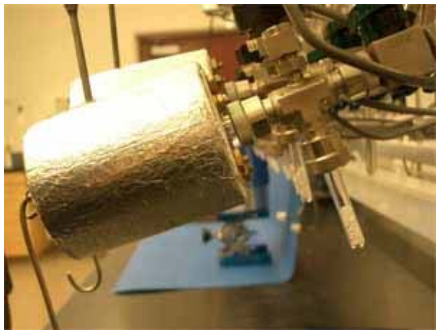


Fig. 4 Showing proper distance of the heater from the Ultra Torr fitting.

9. Slip the heaters onto the reaction tubes. Check that the heaters do not come too close to the Ultra-Torr fitting: there should be 1/8 inch – 1/4 inch clearance (Fig. 4).
10. Set the timer to 3 hours and the temperature controls to 550°C (make sure all the individual controllers are switched on, press the "sel" button and use the up and down buttons to change the set point temperature. For line C, you must be pressing up or down before you hit “sel”).
11. Start the heaters by turning the main temperature controller power off, then on.
12. Start pressure monitoring on the laptop: select line A,B, or C (upper left) and hit the start button (upper right). The pressure in all reactors should increase for a couple of minutes as the gases warm up, and then drop steadily until graphitization reaches completion (flat line). If some samples reach a flat line with others still far from completion, you can turn individual heaters off.
13. Fill the line with 1 atm of H_2 (it may already have that much in it), and briefly open valve #3 or #4 to fill the water trap with H_2, to help it warm up quicker. Close the H_2 bottle and gently close the needle valve (one finger only – it’s delicate).
14. Copy the graphitization information from the cards into the Sample Master list spreadsheet in Irvine6, then place the cards back on the line.
15. Evacuate the line: with the LH bypass valve closed, open valves #3 and #4 to the water trap, then open valve #1 to the pump. This will flush hydrogen from the entire line through the water trap, which will help carry away water vapor efficiently. Open the LH bypass valve when the pressure drops below 10^{-1} Torr.
16. Put caps on the LN and slush dewars and store them in the large cooler. Remove, cap and dispose of all needles (waste container on Bench A) and dispose of the sample Vacutainers (phosphoric acid waste bucket under Bench B).

VI. When all samples are graphitized (all pressure plots are flat-lined), remove the samples from the line and precondition it (see Section II)

References

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