UCI KCCAMS Facility

Leaching/hydrolysis protocol
(carbonate samples)
December 26, 2011

Summary

Leaching

1. Label a Vacutainer and tare on the balance
2. Crush a carbonate sample to coarse powder and weigh in the Vacutainer.
3. Determine the acid strength and volume for the desired leach.
4. Add acid and place the Vacutainer on a 70°C heat block until bubbling stops (20-30 minutres).
5. Remove, pipette off the acid, rinse with MQ water, pipette off the water, and dry on the heat block.
6. Cap the Vacutainers as soon as the sample are dry.

Hydrolyzing

1. Put needle fittings on the carbonate line, grease the needles, put old Vacutainers on the needles and check that they pump down.
2. Put a drop of water on each sample Vacutainer septum.
3. Fill the syringe with phosphoric acid.
4. Evacuate each Vacutainer, pull it halfway off the needle, blow off the water, close the valve, remove from the needle, put a drop of phosphoric on the septum.
5. Put the next Vacutainer on the needle and evacuate.
6. Grease the syringe needle and inject 0.8 mL of phosphoric though the septum.
7. Repeat steps 4-6 for the next port on the line, until all samples are hydrolyzed.
8. Place the Vacutainers on a 70°C heat block until bubbling stops (~1 hour).

Leaching carbonate samples

Carbonate samples should be leached to remove any secondary carbonate. The percentage to be removed depends on the sample cleanliness and/or amount of material available (ideally the remaining amount of material should produce a target of >0.7 mgC graphite). We typically leach forams 10-20% and shells 30-50%. In extreme cases of very chalky shells, they are first Dremeled to remove gross secondary deposits. Leaching is conducted in the same 3 ml Vacutainer vials used for hydrolysis, using HCl:

$$\mathbf{CaCO_3 + 2HCl \rightarrow Ca^{+} + 2Cl^{-} + H_2O + CO_2}$$

1. Label a Vacutainer with the sample UCIG#, remove the septum, and tare on the balance. If there are static problems you may have to wrap the vial in Al foil before taring.
2. (If necessary) crush the carbonate to a coarse powder by e.g. wrapping with Al foil and hammering.
3. Decide much carbonate you want to leach off and how much you need to start with. If samples are small, the starting weight and the amount to be leached are obvious – a 10% leach on 5 mg will take off 0.5mg. If there's enough sample, ~8mg of carbonate will give 0.8 mg of carbon: **if samples are large, add enough extra carbonate to have 8mg after the leach**. For example: if a 30% removal is desired and you need a final wt of 8mg, ~12mg of calcium carbonate would be required initially. For a 50% leach, you'd have to start with 16mg.
4. Place an appropriate amount of carbonate in the Vacutainer and reweigh. Record the sample wt on the index card.
5. Check the strength of the acid to be used (use the blue pH paper).
6. Add the appropriate amount of HCl based on how much carbonate you want to remove. You can calculate it (2 moles of H are required to remove 1 mole of CaCO3), or use the table below. Always check the sample ID, check the table, and check that you picked up the right acid bottle. **If you mess up, you could loose the entire sample.** You can use a graduated pipette or an autopipettor to determine the amount precisely, but using a squeeze bottle and estimating by comparing to a marked Vacutainer (holds 3.5 mL to the base of the septum) is easier and is usually sufficient.
7. Place the vial on the heat block at ~70°C (do not replace the septum). Cover the vials with an Al foil tent and wait at least 25 minutes, until no bubbles are visible.
8. Pipette off the acid with an ultra-fine disposable pipette, rinse the samples with MQ water, then pipette off the water and dry on the heating block under an Al foil tent. Try to pipette off as much liquid as possible each time. Be careful with fine powder samples: allow them to settle before pipetting or you'll loose sample.
9. When the samples are dry, remove the vials from the heat block and replace the septa **tightly.**

Always check the acid strength first!	Strength and volume of acid (mL) to be used	
Amount of CaCO3 to be removed (mg)	0.1 N HCl	0.01N HCl
10	2	
9	1.8	
8	1.6	
7	1.4	
6	1.2	
5	1	
4	0.8	
3	0.6	
2	0.4	
1	0.2	2
0.9	0.18	1.8
0.8	0.16	1.6
0.7	0.14	1.4
0.6	0.12	1.2
0.5	0.1	1
0.45		0.9
0.4		0.8
0.35		0.7
0.3		0.6
0.25		0.5
0.2		0.4
0.15		0.3
0.1		0.2

Acidifying carbonate samples (hydrolysis):

Samples are hydrolyzed with 85% phosphoric acid under vacuum, by injecting acid through the septum of an evacuated Vacutainer. Organics are generally resistant to phosphoric, but since the long-term effect of the acid on the rubber septum is unknown, samples should not be hydrolyzed until the day of graphitization. Note that this procedure involves using phosphoric acid in a syringe. Wear eye protection, just in case…

1. Find the carbonate tools – syringe, needles, small beaker and 1/4” Ultra Torr fittings – in the drawer to the left of the carbonate line. Put down Al foil to protect the bench, and have a damp Kimwipe or two around for wiping up phosphoric acid.

2. Dismantle four 1/4” Ultra Torr fittings, 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.
3. Close the valves on the four ports on the line and replace the Ultra Torrs with the needle fittings. Lightly grease the needles with high vacuum grease, push old (dummy) Vacutainers halfway on to each needle and check that all four ports pump down. If any leak, try tightening the Ultra Torr, or you may have to replace the needle.
4. Take the set of Vacutainers with samples, and place a drop of MQ water on each septum to help seal them against air leaks.
5. Fill a small beaker with enough phosphoric acid (from the corrosives cupboard) to cover the number of samples to be acidified. You will need ~0.8mL per sample. Attach a needle to the syringe, remove the plunger and fill the syringe to 5mL with phosphoric acid. Replace the plunger, hold the syringe with the needle up, and expel any large air bubbles.
6. Put the first four Vacutainers on the line and evacuate them as per steps 7 and 8.
7. To evacuate each sample vial, close the valve, lightly grease the needle, and slowly press the Vacutainer halfway on to the needle, then open the valve to the pump.
8. Monitor the vacuum: once the pressure drops below 100 microns (no leaks!), push the vial all the way on to the needle. The pressure will go to about 350 microns and then drop, reaching baseline after a minute or two (very fine powders may take longer).
9. To avoid sucking the water into the vacuum pump, slowly pull the vial half way down the needle, then blow off the water with air duster aerosol. **Close the valve**, completely remove the sample vial, and immediately put a drop of phosphoric from the syringe on to the septum to help seal it against air leaks.
10. Put the next sample on the line, i.e., repeat steps 7 and 8.
11. Lightly grease the syringe needle, stand your sample vial upright on the bench and puncture the septum. Inject 0.8mL of acid and carefully remove the needle from the septum
12. Go to the next port on the line and repeat steps 7-11 until all samples have been processed

Notes:

The needles rapidly become blunt and it will get increasingly harder to insert and remove them, and that’s when you can end up sticking yourself. Very occasionally they can clog with rubber or with excess grease. When you have used a needle 4-6 times, or if at any time it becomes difficult to insert or remove, replace it immediately and cap the old needle.

If you accidentally get water into the line (the pressure will not drop) close the valve immediately, and remove the needle fitting. Blow it out with air duster aerosol and also blow out the 1/2” Ultra Torr above the needle fitting. Replace the 1/4” fitting, regrease the needle, and put a dummy Vacutainer halfway on to it. Open the valve and wait for the line to pump down.

13. Place the vials on the heating block at ~70°C for at least 20 minutes, until the liquid is clear and not bubbling. Larger chunks of solid carbonates, such as pieces of calcite, may take an hour or more.
14. Valve off the four ports; replace the needle fittings with the original Ultra Torr’s; and remove, cap, and dispose of all used needles (including the syringe needle) in the waste container on Bench A.
15. Return any unused acid to the phosphoric acid bottle, rinse the beaker and syringe well with hot water, then rinse them with MQ water several times before drying gently with the heat gun. Return them to the carbonate tool box.