

TROUBLESHOOTING BAD COULOMETRY STANDARDS

Policies and preaching:

For both TC and TIC, your standards should be close to 12.00% carbon – in general, anything between 11.75% C and 12.25% C is acceptable, but different researchers may have more or less precise demands.

Getting standards close to 12.00% C means that the system (and the technician!) are functioning properly. If your standards are outside the acceptable range, you must locate and fix the problem before you run any samples. The standards are our only check on the integrity of the system, and there is no way to correct *sample* analytical values after the fact – we have to trust that they are good because the *standards* are good.

You should always run two standards at the beginning of the day (after the blank and before any samples), plus at least one standard for every ten samples, and one standard at the end of the day. This may seem like a waste of time, but seeing a bunch of great standards in the spreadsheet will make the researcher feel much more confident about his or her data. While we're on the subject, you should also run at least one duplicate analysis (i.e., re-run a sample you've already run) for every ten you analyze.

If you have a bad standard in your spreadsheet, don't be ashamed . . . and don't erase it. Try to figure out why it was bad, and put a note in that line of the spreadsheet (to the right of all the data, or in the cell to the left of "sample number") explaining it. Seeing this will also make the researcher feel good. If you really can't figure it out, say so. Sometimes there are just weird flukes.

Troubleshooting:

Some problems are specific to either the TC oven or TIC acidification parts of the coulometer, and some are common to both analyses. Most problems cause the standards to come out too low (<11.75%); there are only a couple reasons a standard would come out too high. I'll try to break down the different issues accordingly below. There's also a short discussion of why bad duplicate values might occur, and what to do about it.

Problems common to both TIC and TC:

Standards too high:

- 1) Error in the spreadsheet. It's very easy to put the decimal in the wrong place, especially in the blank value. *Solution:* Make sure there are enough zeros – e.g., if the blank value, read off the coulometer, is 11.2 µg C, enter 0.0112 mg in the spreadsheet.
- 2) KOH solution worn out. The KOH (potassium hydroxide) is the colorless liquid scrubber that the carrier-gas bubbles through before it goes into the place where the sample reacts. Its purpose is to scrub out any CO₂ in the carrier gas so it doesn't get

into the reaction. In the case of TC, the oxygen passes through a KOH scrubber before it goes into the oven; in TIC, the room air passes through KOH before it goes into the acidification test tube. *Solution:* Change the KOH solution in the tube. See coulometer instructions (“changing scrubbers” at end of each procedure) for details. There is usually some KOH already mixed in the right concentration, stored along with the coulometry chemicals.

- 3) The balance is inaccurate or unstable. The balance shouldn't lose calibration, but you can check by weighing a standard mass (small brass weights in a wooden case in a drawer beneath the balance). The balance does sometimes become unstable, that is, it continues to count up or down instead of settling on one weight. This is especially a problem in the winter, when the air is dry and static charge can build up in the room and on the balance. *Solution:* There's a sheet on balance troubleshooting (from the internet) near the balance; read it. It covers most of the problems. Definitely make sure the clear glass cover on the balance is completely closed when weighing. If the balance is counting up, the sample is probably just absorbing water from the atmosphere. In that case, the first stable reading (before it starts to count up) should be pretty accurate. If the balance is counting down, it's a static problem. You need to try to raise the humidity by (1) filling the tiny beaker halfway with water (the strip of paper towel will help the water get into the air) and placing it inside the balance, and/or (2) running the humidifier in the room. Sometimes the static problems are totally insurmountable. I haven't found a magic bullet yet.
- 4) (See also problems specific to TC or TIC, below.)

Standards too low:

- 1) You're not waiting long enough for the sample to finish running (i.e., taking a reading when the coulometer beeps, even though the value is still counting up). *Solution:* Always wait for the readout to slow down to the point where it's changing by only 0.1 μg every few seconds. The cathode solution should be blue, the %T should be 29%, and the Cell Current will be at 0 or fluctuating right around there.
- 2) The standard has moisture in it. *Solution:* Always use CaCO_3 (calcite) standard stored in the desiccator. It should be in a blue Poly-Cons container labeled “dry CaCO_3 .” If you see that this batch is getting low, refill it with about 200 mg of calcite from the large plastic bottle stored in the cabinet above the balance and give it at least overnight to dry out in the desiccator before using it.
- 3) Something in the cathode cell is obstructing the beam of light passing through the cell. To understand how this affects things, a short lesson on the operation of the coulometer is useful. CO_2 coming into the cathode solution generates acid and turns the solution colorless. The amount of light passing through the cell (percent transmittance, or %T) increases because less light is being absorbed by the blue color of the solution. The coulometer generates a base to titrate away the acid. The amount of current used to generate this base is measured and converted to the $\mu\text{g C}$ reading. As the %T comes back down to 29% (its baseline value), the current slows and stops and the reading stabilizes. If the beam of light is blocked, the %T will decrease to

- 29% or lower before the reaction is really finished. *Solution:* shift the rubber stopper and/or the cell so that both the inlet tube and cathode rod are out of the beam of light.
- 4) The glass of the coulometer cell wall is dirty. If there is dirt, fingerprints, grease, dust, or other slime on the glass of the cell, the %T will decrease to 29% before the reaction is complete (see point 3 above for a lengthy explanation of why this matters).
Solution: Always keep the cell walls clean. Before servicing the cell, always turn off the cell current. Wipe the outside with a Kim-Wipe or other soft, lint-free tissue before you start analyses, and check during analyses to make sure that there's nothing blocking the light.
 - 5) There's a problem with the electrical connections in the coulometer. This machine is getting old, and its surroundings (acids, CO₂, solvents, dust, crap) have encouraged corrosion. Also, the wires on the electrodes (the silver anode rod and platinum-and-glass cathode rod) can be broken if the connections, which are coated with transparent flexible plastic, are bent too much. *Solution:* Gently wiggle the connections where the red and black wires plug into the coulometer. Watch the Cell Current reading. If it's affected, the connections may need to be cleaned or the instrument may need servicing. Let Amy know. Look at the wires through the clear plastic coating. If you can see a break, replace the anode or cathode with one of the spares in the drawers below the instrument. Let Amy know this, too.
 - 6) There is a leak in the system allowing CO₂ to escape before it is analyzed. This is rare. If the bubbles coming into the cell are frequent and pretty good-sized, there's probably not a leak – but connections can get detached. *Solution:* check all the light blue foam connections on the air lines and make sure nothing has come apart. You can also put your thumb over the end of the air tube that goes into the cell: if the ball-bearing in the airflow gauge sinks near the bottom, there's not a leak.
 - 7) Also see “The balance is inaccurate or unstable,” point 3 above.
 - 8) (See also problems specific to TC or TIC, below.)

Problems specific to TC:

Standards too high:

- 1) There is residual standard or sample left on the boat or in the ladle. *Solution:* Make sure to burn all the boats at the beginning of the day, before you begin analysis. If you spill a sample before you analyze it, that boat must be burned too, because (even if it looks empty), it still has trace amounts of un-burned stuff on it. Keep your work area clean so you don't set a boat down on a dusty surface, and make sure to wipe off instruments between samples.

Standards too low:

- 2) Material is beginning to combust before you put it into the oven. *Solution:* Always place a sample into a cool ladle, never into the one you just took out of the oven.

- 3) Material is being lost between weighing and the oven. *Solution:* Bring the ladle over to the balance, and put the boat directly in, rather than carrying the boat across the room where breezes can lift out some of the material.
- 4) White solid scrubber is wet and/or recrystallizing and blocking airflow. The magnesium perchlorate's job is to absorb water (a product of combustion) and keep it from going into the downstream scrubbers and into the cell. It needs to be changed every day before you start analyses, but it can also get wet over the course of the day, and should be partially or completely changed then too. *Solution:* Replace the wet white scrubber with fresh new material. This can be done without powering off the oven. Instructions are at the end of the TC procedure.
- 5) Other solid scrubbers are exhausted. In addition to changing the white (magnesium perchlorate) scrubber *every day*, the brown (acid dichromate) and gray-black (manganese dioxide) scrubbers need to be changed periodically. The manual says to change both when half of the brown scrubber has turned greenish; we've found that you can't really wait that long. If you have checked all other possibilities, and your values are still low (or otherwise screwy), change both the brown and gray-black scrubber. Instructions are at the end of the TC procedure.

Problems specific to TIC:

Standards too high:

- 1) Excess material is somehow getting into the sample tube. This is unlikely, but is the only explanation I can think of for TIC-specific high standard values.

Standards too low:

- 2) Material is sticking to the inside of the test tube, above the level to which the acid reaches, and is not being dissolved. This happens a lot, especially in winter when it's dry in the lab and there's lots of static electricity around. *Solution:* Rinse down the inside of the tube with high-purity DI water right before putting it on the machine.

Bad duplicate values:

Duplicates (also called replicates) should be close to within the error of the instrument – which is $\pm 0.1\%$ C. So if you have two values for the same sample that are 3.24% and 3.36%, that's pretty good. However, any differences larger than that (say, a difference of 0.2% or greater) will require some repeat analysis and/or a change in sample treatment:

- 1) Be sure that the sample is sufficiently homogenized. Lake sediments are by nature patchy – they may have layers or pockets or different compositions, which all end up in the same small sample. If you can see color differences between large particles in the sample, there are almost certainly chemical differences as well. In general, samples should be crushed or ground – in a mortar (there's a small one in the drawer under the balance) or even with a small spatula, right in the sample container, and you

should always try to get a representative subsample – i.e., the same proportions of different material, if there are particles such as sand grains that are difficult to break down.

- 2) Run the sample a third time. Report all results, and include an explanation of the variability if you have one.