

Total Carbon (TC) Coulometry

Purpose

Total Carbon coulometry (TC) measures the amount of carbon contained in lake sediments. The TC content of sediments can be related to a number of factors such as lake productivity, mineral precipitation, or rates of post-burial organic matter decomposition.

Principles

Carbon dioxide gas evolved by combustion of organic matter and carbonates in the sample is swept by an oxygen gas stream into a coulometer cell. The coulometer cell is filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. Carbon dioxide is quantitatively absorbed by the solution and reacts with the ethanolamine to form a strong, titratable acid which causes the indicator color to fade. The titration current automatically turns on and electrically generates base to return the solution to its original color (blue).

The value obtained in terms of carbon detected in the carbon dioxide coulometer is the sum of both inorganic and organic carbon in the sample or Total Carbon (TC). If the sample is free of carbonates the TC value is equivalent to the TOC value. If significant carbonates are present it is necessary to run TIC analyses and then subtract the TIC from the TC to arrive at TOC. Note that the TOC is not the same as total organic matter as determined by LOI (loss-on-ignition). The relationship between the two is approximately ($\text{TOC} \times 2 = \text{OM}$, i.e., half of organic matter is carbon), although this differs with organic matter type, source, and preservation.

Equipment and Procedure

To measure total carbon (TC) contained within sediment from a variety of sources (e.g. carbonate minerals, algae, dead fish, charcoal), we use a UIC model 5020 Total Carbon apparatus with a Model 5022 Ladle introduction component. Samples are combusted in the Total Carbon apparatus oven at 950° C which serves to evolve CO₂ which is swept into the carbon coulometer where it is detected and displayed on a digital screen in terms of micrograms (or any other operator-selectable units) of carbon.

The coulometer cell is typically left set up (a change from the older procedure), so unless you are getting bad numbers, you should rarely have to clean or refill the cell.

Cell Preparation

Turn ON the furnace and set the temperature to 950°C. (This should be done before anything else, to allow the furnace to heat up and purge any water vapor.)

Note: you must wear appropriate gloves when handling coulometry solutions. A pair of butyl rubber gloves hangs in the cabinet with the coulometry solutions. For the rest of this procedure, lab gloves are not recommended, because the only hazard is the hot ladles and ceramic boats - if you touch these when hot, you'd rather not have latex melt to your skin.

1. Fill the main chamber of the coulometer cell with 50-75 mL of cathode solution (large plastic bottle).
2. Place the stir bar (magnet) in the bottom of the cell body and insert the cell top with the coiled platinum electrode into the cell. The electrode should be opposite the fritted arm.
3. Add 0.25 cm (enough to cover the bottom) potassium iodide (KI) to the bottom of the side arm (anode compartment) of the cell.
4. Fill the side arm with 10 or more mL of anode solution so as to cover the filter and submerge at least 0.5 cm of the silver anode in solution; the amount of liquid will vary as the anode is consumed (over a period of months) in the analysis.
5. Place the solid silver electrode into the side arm with the silver submerged into the solution.
6. Make sure the glass of the cell is clean and free of grease, fingerprints, water spots, etc., which affect transparency (and thus %T). Wipe/polish with a paper towel or Kim-Wipe, or wash if necessary.
7. Place the assembled cell into the coulometer cell holder. The side arm should extend out the front and against the right wall of the holder, with the platinum electrode and gas inlet tube toward the back of the holder, *out of the light path*.
8. Change dry scrubber(s): three dry materials are used to scrub air exiting the furnace. In order, they are magnesium perchlorate (white chunks), acid dichromate on silocel (tan coarse powder), and manganese dioxide (black fine powder). The magnesium perchlorate is a desiccant, and protects the latter two scrubbers from contamination with water. The magnesium perchlorate scrubber should be changed daily, or when it appears wet or recrystallized, whichever is sooner. The acid dichromate must be changed when 50% or more of the material takes on a yellow-green color (weekly or monthly, depending on use). Manganese dioxide should be changed whenever acid dichromate is changed. See "Scrubber Changing" at the end of this document for procedure.

Set Analysis Parameters. Check these parameters but most should be already set.

9. Rotate the MODE selection thumb wheel to the 1 position which gives the display of units of micrograms (μg) of carbon to 0.1 units.

10. Rotate the TIME SET thumb wheel until the desired analysis time is displayed (generally 6-7 minutes for TC).
11. Set the RUN/LATCH switch to the RUN position for continuous analysis. LATCH freezes the display at the time set.
12. Set the COUNTS/TIME switch to COUNTS position so that you can watch the counts of carbon on the display.

Operation

13. Ensure that the appropriate scrubber and combustion tubes are in place.
14. Open the oxygen tank by turning the handle on top of the tank and then the brass knob near the regulator. Check gauge to see that pressure is set to 4 psi. If not, turn regulator by increments until gauge reads 4 psi.
15. Set the oxygen flow to 75-125 mL/min on the flow meter.
16. Connect the cell to the cell to the Total Carbon Apparatus using a one-way (check) valve.
17. Only insert the air tube when there is air flow through it - this prevents coulometer solution being siphoned back into the dry scrubbers, which can cause an explosion
18. Attach the electrodes to the cell outlet terminals - red to red, black to black.
19. Turn ON coulometer cell current.
20. Allow cell current to titrate the cell solution to its endpoint (solution color becomes blue with %T approximately 29).
21. Ceramic boats should be clean and free of carbon-bearing material from previous analyses; however, this is not always the case and to be certain, you should pre-burn all the boats. Insert two to four boats into a ladle. Open the cap on the combustion tube, insert the ladle, close the cap, and move the ladle into the furnace using the horseshoe magnet. Watch the "counts" display until it becomes stable, indicating that all residual carbon has been burned off.
22. You are now ready to begin the analysis.

Analysis Procedure

23. Always use tweezers when handling ceramic boats to avoid getting oils from your hands on the boats. Oils contain carbon and thus can skew the analysis.
24. Run a blank sample using an empty sample boat. The blank is normally less than 10 μg C in five minutes.
25. Follow the blank by one or more standards (standard CaCO_3 is found in a desiccator near the balance). For best precision, material for each analysis should contain 1-3 mg of C. For our standard calcite, this means that you should use about 10-20 mg of standard.
26. Weigh a sample or standard into a tared ceramic boat. Record sample weight in spreadsheet. Using tweezers, place the boat in the COOL ladle. (Alternate between two ladles so you're always using a cool one.) Sample should contain 1-3 mg of C; adjust the quantity as you begin to see how much carbon tends to be in your samples.
27. Place the ladle in the unheated portion of the combustion tube and seal the system. Be careful to insert the ladle very straight - it's easy to snap the glass rod.
28. Move the ladle into the combustion tube using the magnet.
29. RESET the system
30. When all of the CO_2 is evolved and titrated (recognized by a stable coulometer display and a %T of 29%), record the coulometer reading. Note: Most analyses will be complete in five to seven minutes. Longer analysis time will result if the sample contains more than 3 mg C, or it contains compounds which are not readily oxidized, e.g., carbonates).
31. Remove the ladle from the furnace and dump the ceramic boat out of it into a glass petrie dish or other heatproof container. Let cool before reusing.
32. Run one standard and one duplicate analysis every ten samples.
33. If you lose a boat in the furnace (i.e., the ladle comes out empty), make a note and retrieve it (them) using the long metal probe when the furnace is cool. (I'm not sure that the probe the metal is made of is good to 950°C.)

Calculations

There is a spreadsheet to calculate %TC and %TOC (ccoul.xls on the desktop). The calculation is as follows:

$$\%TC = \{(\mu\text{g C}[\text{display value}] - \text{per minute } \mu\text{g C}[\text{blank value}]) / \mu\text{g sample weight}\} \times 100$$

$$\%TOC = \%TC - \%TIC$$

Note: the formula subtracts the per minute blank value (blank value/minutes of counting).

For pure calcium carbonate the value should be 12.00%. Other carbonates will have varying carbon percentages.

Shut-down (Furnace)

Short Periods (during the day)

Reduce oxygen flow to a low level, 10-20 cc/min. Reduce the furnace temperature to 500°C.

Long Periods

Turn off oxygen flow (after removing air tube from cell!) and close the oxygen tank.
Turn off the furnace.

Shut-down (Coulometer)

Short Periods (during the day)

Before turning off air flow, disconnect inlet gas flow line into the coulometer cell. This prevents coulometer solution from being siphoned out of the cell.

Long Periods (Overnight or longer)

Turn OFF the cell current and the main power supply. Remove and clean the coulometer cell as described below.

Cell Changing and Clean-up

Before turning off air flow, disconnect inlet gas flow line into the coulometer cell. This prevents coulometer solution from being siphoned out of the cell.

Turn OFF cell current and main power supply.

Unplug electrodes and remove cell from holder. Replace jumper strap between cell current terminals to protect them.

Dispose of the main chamber solution (cathode solution) into the cathode waste solution bottle. Be sure to remove the stir bar first or be prepared to retrieve it from the waste bottle with a magnetic stir bar retriever. Start a new waste bottle (and label correctly) if necessary.

Dispose of the side arm solution (anode solution) and residual KI into the anode waste solution bottle. Start a new waste bottle (and label correctly) if necessary.

Rinse both cell body and the electrodes thoroughly with DI water.

Clean the glass frit in the anode compartment by pulling acetone through the frit with a vacuum.

Rinse and dry all components.

Store cleaned cell in cell holder and return other components to the drawer.

Periodic Maintenance and Scrubber Changing

Changing Scrubbers

All scrubber solutions are considered hazardous waste and must be disposed of in appropriate containers in haz waste cabinet. Glass wool that has been in contact with the scrubbers should be put into the bottles as well.

Water Scrubber (Magnesium perchlorate - $Mg(ClO_4)_2$)

Magnesium perchlorate can form a solid mass as it becomes hydrated. This mass can block the gas flow through the system and should be changed at least daily, or when the gas flow through the tube becomes restricted or blocked. If material appears wet, it should be discarded. This material is far less expensive and hazardous than the other two scrubbers, and changing it frequently means that the others don't get used up as quickly.

Remove the scrubber tube from the scrubber module and remove silicone scrubber tube fittings from the glass scrubber tube.

Remove one glass wool plug and discard in haz waste container. Pour magnesium perchlorate from tube into haz waste bottle (use a wooden stir stick to break up or push through recrystallized material if necessary). Discard second glass wool plug.

Replace the silicone rubber scrubber tube fittings and attach the tube to the scrubber module.

NO_x Scrubber (Acid Dichromate on silocel and MnO₂ [manganese dioxide])

Filling

Remove the scrubber assembly from the clamp, and remove the silicone scrubber tube fittings from the glass scrubber tube.

Discard glass wool and scrubber materials in appropriate haz waste containers.

Place a small plug of quartz wool into one end of the tube.

Fill 2/3 of the tube with acid dichromate, and secure it in place with a quartz wool plug.

Fill the remaining 1/3 of the scrubber tube with MnO₂ and secure it in place with a quartz wool plug.

Replace the scrubber assembly in its clip, with the acid dichromate end up. Air flows from the magnesium perchlorate scrubber into the acid dichromate and then manganese dioxide. Reattach silicone plugs and fittings in the appropriate order.

Air Scrubber (40% KOH)

The KOH solution (in place between the oxygen tank and furnace) removes CO₂ from the carrier gas and should be changed once every week during regular use or when the solution becomes thick and foamy. If a fresh KOH solution is foamy, it should be diluted with DI water.

Preparation

Weigh out 40-45 g of KOH and dilute to 100 mL with DI water. Note: Use caution when adding water to KOH as it is very exothermic.

Filling

Remove the dispersion tube, bushing and O-ring from the air scrubber assembly.

Place 15-20 mL of KOH solution in the body of the air scrubber.

Replace the dispersion tube, O-ring and bushing. Slide the dispersion tube through the bushing and O-ring so the fritted end is near the bottom of the scrubber.

Hand-tighten the bushing/O-ring seal and place the filled scrubber in its clamp.