

Total Inorganic Carbon (TIC, Carbonate) Coulometry

Total Inorganic Carbon coulometry (TIC) measures the amount of inorganic carbon contained in lake sediments or water samples. The TIC content of sediments can be related to a number of factors such as rates precipitation of carbonate minerals or introduction of detrital carbonates into the system. The LRC CO₂ Coulometer can be used to rapidly determine TIC from either water or sediment samples.

Principles

Carbon dioxide gas evolved by dissolution in acid from carbonates in the sample is swept by a 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).

Equipment and Procedure

To measure TIC, carbon contained within carbonate minerals such as calcite, dolomite, siderite, etc., we use a UIC model 5030 Carbonate Carbon apparatus. Five mL of acid (we prefer HCl) serves to evolve CO₂ from the sample 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.

Cell Preparation

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.

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, you must wear regular lab gloves to protect your hands from the acid. Cell filling and cleaning must be done in a fume hood.

1. Fill the main chamber of the coulometer cell with 50-75 mL of cathode solution (large plastic bottle).
2. Place the magnetic stir bar 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 in 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*.

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

8. 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.
9. Rotate the TIME SET thumb wheel until the desired analysis time is displayed (generally 4-7 minutes for TIC).
10. Set the RUN/LATCH switch to the RUN position for continuous analysis. LATCH freezes the display at the time set.
11. Set the COUNTS/TIME switch to COUNTS position so that you can watch the counts of carbon on the display.

Operation

12. Make sure coulometer cell current is OFF.
13. Turn ON the main power switch.
14. Set air flow for internal and adjust to 75-100 cc/min.
15. Connect the cell to the cell to the Carbonate Carbon Apparatus using a one-way (check) valve. Only inset the gas tube in the cell when air is flowing, to avoid coulometer cell solution being siphoned back into the KI scrubber.
16. Attach the electrodes to the cell outlet terminals - red to red, black to black.

17. Turn ON coulometer cell current.
18. Allow cell current to titrate the cell solution to its endpoint (solution color becomes blue with %T at 29. If it is lower than 29%, check that the light path is unobstructed and adjust the arrangement of the tube and electrode to correct).
19. (Heater control is broken - do not use.)

You are now ready to begin the analysis.

Analysis Procedure

1. Run a blank sample using an empty sample container. The blank is normally less than 10 $\mu\text{g C}$ in five minutes.
2. 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.
3. Weigh a sample or standard into a clean, dry, tared test tube and attach to apparatus. 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. Record sample weight in spreadsheet.
4. Pump 5 mL of acid into the reaction tube. RESET the coulometer.
5. When all of the CO_2 is evolved and titrated, (recognized by a stable coulometer display and a %T of 29), record the value in the spreadsheet.
6. Remove the sample tube, pour residue into a waste container, begin next analysis. Wash tubes and rinse in DI water; let dry completely (can use 100 C oven) before reusing.
7. Neutralize the waste acid with soda ash as you go.
8. Run one standard and one duplicate analysis every ten samples (or more if desired).

Calculations

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

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

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

For pure calcium carbonate the value should be 12.00%. (We accept values from 11.75%-12.25%.) Other carbonates will have varying carbon percentages according to the table below.

Mineral	Cation(s)	C	O ₃	mw	%C
CaCO ₃	40.08	12.01	48.00	100.09	12.00%
MgCO ₃	24.31	12.01	48.00	84.32	14.24%
(Ca,Mg)CO ₃	64.39	12.01	48.00	184.41	13.03%
FeCO ₃	55.85	12.01	48.00	115.86	10.37%
ZnCO ₃	65.38	12.01	48.00	125.39	9.58%
MnCO ₃	54.94	12.01	48.00	114.95	10.45%

Shut-down (Carbonate Carbon Apparatus)

The Carbonate Carbon Apparatus should be shut down during periods of non-use.

Remove the tube from the cell.
Turn off main power switch.

Note: To prevent residual acid from marring the exterior of the apparatus, keep a sample tube connected to the apparatus when the system is not in use.

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.

Overnight or longer

Turn OFF the cell current and main power supply.

Cell Changing and Clean-up

Note: Solutions should also be replaced when over 100 mg of carbon have been titrated (for 100 mL of cathode solution).

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

Air Scrubber (40% KOH)

The KOH solution 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 the reaction is 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.

Sample Scrubber (50% KI, pH=3)

Preparation

Weight out 50g of KI and dilute to 100 mL with DI water.
Use H₂SO₄ to acidify to approximately pH = 3.
Fill the fritted sample scrubber with 10-15 mL of the scrubbing solution.
Acid Solution

One can use a variety of acids to react with the carbonates. Originally we used a 2N HClO₄ solution but have since switched to using 2N HCl. The procedure for mixing these solutions is given below.

2N HClO₄ Dilute 109 mL of 9.2 N HClO₄ in 391 mL of DI water.
2N HCl Dilute 172 mL of 37% HCl in 328 mL of DI water

Note: Always add the acid to the water, not the water to the acid.