



Chapter S

Carbonate carbon by coulometric titration

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Table

1. Analytical performance summary for carbonate carbon (percent) as CO_2 S-6

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Principle

Carbonate carbon in geologic material is determined as carbon dioxide, CO_2 , by coulometric titration. The sample is treated with hot 2 N perchloric acid and the evolved CO_2 is passed into a cell containing a solution of monoethanolamine. The CO_2 , quantitatively absorbed by the monoethanolamine, is coulometrically titrated using platinum and silver/potassium iodide electrodes (Jackson and others, 1987).

Interferences

Processing samples containing high concentrations of sulfur quickly exhausts the sample prescrubber. The analyst must monitor the build-up of black sulfide precipitate in the prescrubber solution closely.

Scope

The lower reporting limit is 0.04 percent CO_2 and samples containing up to 50 percent CO_2 may be analyzed. Sample size is adjusted from 0.2 g for the range 0.01 to 5 percent CO_2 , 0.1 g for the range 5 to 10 percent CO_2 , and 0.02 g for greater than 10 percent CO_2 . Generally, 20 to 30 samples can be analyzed per day. The analysis of shales often requires 30 to 40 minutes for complete liberation of carbon dioxide.

Apparatus

Carbonate Carbon Acidification Model 5130 with Carbon Dioxide Coulometer Model 5012 (U.I.C. Inc.), and a computer with a Coulometer Interface IBM PC program.

Reagents

- Deionized water (DI)
- Acetone, $\text{C}_3\text{H}_6\text{O}$
- Potassium hydroxide, KOH, 45 percent solution
- Perchloric acid, HClO_4 , (70 percent), Baker "Instr-analyzed" reagent
- Hydrogen peroxide, H_2O_2 , 30 percent solution, Baker reagent grade
- Sulfuric acid, H_2SO_4 , conc
- Potassium iodide, KI
- Silver sulfate, Ag_2SO_4

Perchloric acid, 2 N solution: Dilute 170.3 mL HClO_4 (70 percent) to 1 L; store in a plastic bottle

Coulometer solution: Proprietary solution of monoethanolamine and thymolphthalein indicator, available from Coulometrics, Inc.

Silver sulfate solution: Add 1.5 g Ag_2SO_4 to 100 mL DI water and stir for 2 hours on a magnetic stirrer. Add 2.0 mL conc H_2SO_4 and mix. Store in a glass bottle.

Safety precautions

The instrument should be operated in a fume hood. Lab coat, proper gloves, and safety glasses must be worn. Preparation of reagents and handling of acids and bases shall be done under an operating chemical hood. Use perchloric hood for all analytical procedures involving perchloric acid (HClO_4) and wash it down at end of each day's use. See the *CHP* and *MSDS* for precautions, effects of overexposure, first-aid treatment, and disposal for chemical products used in this method.

Procedure

Additional details of the procedure and internal calibration are in the on-site instruction manuals by Coulometrics Incorporated (1978). Reference materials used for the analysis include USGS standards PCC-1, STM-1, and MAG-1 and reagent grade CaCO_3 . Depending on the amount of carbonate expected in the samples, one or more of these standards are used at the beginning of each day.

1. Place approximately 0.2 g of ground geological material into a dry sample tube and then weigh accurately to four significant figures. Reduce the amount of sample to 0.1 or 0.02 g if the subsequent analysis indicates concentrations of CO_2 in excess of 5 and 10 percent respectively.
2. Place a small magnetic stirring bar in the clean coulometer cell beaker. Add 80 mL coulometer solution.
3. With a small spatula, add 0.1 g KI to the bottom of the anode cell compartment.
4. Insert the silver electrode into the anode compartment, then lift slightly so anode solution may be added by a dropper. The level of the coulometer solution should be the same as the level of the anode solution when the electrode is immersed. The tip of the silver electrode should be slightly above (approximately $\frac{1}{4}$ ") the potassium iodide crystals. As the anode wears away through usage, the holder must be readjusted.
6. Place the electrode cell assembly in the beaker containing the coulometer solution and place on the coulometer apparatus, making sure the electrodes and air jet are to the back of the cell holder and not in the path of the light beam.
7. Connect the Teflon air tubes from the cell assembly to the Teflon air tubes in the back of the compartment.
8. Connect wires from the electrodes to proper color-coded receptacles (red to red, black to black).

9. In exact sequence:
- a. Turn on the coulometer power switch and adjust the transmission control so that it reads 100 percent T. Once the transmission control is set initially for the day, it should not be changed. If it cannot be set to 100 percent T, check to see if something is obstructing the light beam.
 - b. Turn on the power on the acidification apparatus. Turn the heating element up to 4 on the dial.
 - c. Open the air valve and set air flow to read 100 cc/min on the gauge. Check for leaks.
 - e. Put on a blank tube and add 4 ml of 2 N HClO₄ from a Repipet bottle.
 - f. On the coulometer apparatus, turn the Cell switch on to begin the titration. The color of the liquid in the cell will eventually turn blue.
11. Turn on the computer and load the program. After a 20 minute warmup period, run a blank.
12. Enter "Blk" into the computer, put on a new blank tube, add 4ml of 2N HClO₄, move the tube assembly to the heater position, switch the "Lift" to lower the tube into the heater. Press "R" and then "enter" on the computer to start titration. After 5 minutes, the microgram count should read less than 5 µg. When the microgram count is greater than 5, suspect something is wrong and proceed to troubleshooting the system.
13. Remove the tube and save. Wipe the Teflon intake tubing and the inner portion of the condenser dry. If there is acid left on the tubing or condenser, it may release CO₂ prematurely when the next sample tube is connected.
14. Enter the next sample number and weight into the computer. Connect the sample tube to the condenser and make sure of an air-tight seal.
15. Press "R" and "enter" on the computer to start titration. Slowly add a few milliliters of acid to the sample tube from the Repipet and then add the remainder of the 4 mL acid.
16. Place the tube assembly into the heater position and allow the reaction to proceed. Maintain incipient boiling and flow rate of 100 cc/min during the evolution of CO₂. Adjust heat as needed to prevent bumping and possible ejection of sample into the condenser tube.
17. Completion of CO₂ release and titration, is indicated by the stability of readings, (less than 10 µg difference in 2 min). Normal samples usually require 5 to 10 min. As an example, if the count is 20 µg at 6 min, 24 µg at 7 min, and 28 µg at 8 min, it can be assumed equilibrium has been reached. Often there will be duplicate counts on successive minute intervals at equilibrium and usually before 10 min.
18. Remove the sample tube and if there are more samples to run, repeat the procedure from step 13.

19. For shutdown:

- a. Turn off power switch on the coulometer apparatus and reset the Cell switch to the middle position.
- b. On the acidification apparatus, close the air valve and turn off power switch.
- c. Turn off computer.

This sequence must be followed to avoid damage to the electrical system.

20. Remove the last sample tube, clean the inlet tube with a small wire and flush out the residue into a plastic beaker using a small amount of acid from the dispenser. Rinse the inside of the condenser with distilled water from a small squeeze bottle. This cleaning procedure should be performed between samples if a large amount of residue builds up in the inlet tube and/or if bumping ejects sample into the condenser neck.
22. Disconnect the air tubes and electrode leads from cell assembly and remove the beaker promptly from the apparatus. Brush off any yellow deposit that forms on the anode, rinse off and dry. Deterioration of the electrode can result if it is left in the used solution for long periods of time.
23. At the end of the day, pour the coulometer solution and the anode solution into a waste container properly labeled and rinse with water. Brush gently to dislodge the potassium iodide from the frit and rinse with water. Rinse the stopper with water, dry and put away.
24. Pour the spent sample wastes into a waste container labeled "2N Perchloric Waste". Clean out all the used sample tubes by rinsing with water and using a brush to remove all sample residue. Rinse with distilled water and store in a rack upside down.

Trouble Shooting

The system should be continually monitored to see if any conditions requiring troubleshooting are necessary.

1. The presence of large amounts of sulfide precipitate indicates that the scrubbing capacity of the solution is becoming depleted, which if not corrected means future sample runs may be in error. The precipitate may also clog the scrubber frit.
2. When sulfide precipitate (black) is detected in the prescrubber at the back of the apparatus or in the Teflon tubing, separate the prescrubber from the system, along with the Teflon tubing. Flush out with conc HCl and then thoroughly with water. Rinse with DI water. Add silver sulfate solution (saturated) to the mark (4 mL) and add nine drops 30 percent H_2O_2 . Reconnect the system. NOTE: Traces of HCl, a result of insufficient rinsing with water, will react with silver sulfate to form a white precipitate of silver chloride.
3. Periodically check the platinum electrode wire for dirt or film. Wipe clean with tissue or clean with dilute HNO_3 and rinse with DI water.

4. If there is excessive frothing in the 45 percent KOH scrubber, if it becomes cloudy, or when the air-flow rate through the sintered glass plug cannot be corrected by the addition of a little DI water, remove the tube from the system. Clean the sintered glass plug by passing DI water through it. Add 12 mL 45 percent KOH to the cleaned scrubber tube and re-assemble in the apparatus. Addition of a little DI water to the scrubber will usually correct the condition. After this has been done ten times or so, it will be necessary to replace the KOH.
5. To clean the sintered glass frit in the silver sulfate sample scrubber, drain sample scrubber and rinse with DI water. Fill the scrubber with ammonium hydroxide and warm in a water bath to clean the frit. Rinse thoroughly with DI water. When the frit is clean and dry, the tube may be refilled with silver sulfate solution.
6. Clean a dirty and clogged frit in the anode cell compartment with saturated potassium iodide solution. Use an aspirator to draw the solution through the frit and then flush with DI water.
7. If a run is interrupted for 1 hour or more, continue operating the system with a blank tube.
8. Replace the cell solution if over 300 mg CO₂ is exceeded in a day.

Calculation

If a programmed computer is hooked up to the titration instrumentation (coulometer), a printout for mg values for CO₂ can be generated. By entering the sample weights and corresponding mg CO₂ values, the percent CO₂, or carbonate, results are calculated automatically. If calculations are made by hand use the following formulas:

- a. To determine percent CO₂

$$\% \text{ CO}_2 = \frac{\text{CO}_2(\mu\text{g})}{\text{sample } (\mu\text{g})} \times 100$$

- b. To determine percent carbonate carbon

$$\% \text{ carbonate carbon} = \frac{C(\mu\text{g})}{\text{sample } (\mu\text{g})} \times 100$$

Assignment of uncertainty

Table 1 shows the carbonate carbon (quoted as CO₂) results for reference materials, duplicate samples, and method blanks by coulometric titration.

Table 1.—Analytical performance summary for carbonate carbon (percent) as CO₂

[Proposed values from Potts and others, 1992]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

<i>Reference</i>	<i>Description</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>pv</i>	<i>% RSD</i>	<i>% R</i>
STM-1	syenite	10	0.019	0.002	0.026 ?	11	73
BHVO-1	basalt	14	0.013	0.002	0.036 15	36	
G-2	granite	16	0.073	0.001	0.08	1	91
GXR-2	soil	114	0.020	0.007	0.09	35	22
SDC-1	schist	10	0.093	0.001	0.099	1	94
GSP-1	granodiorite	30	0.104	0.006	0.11	10	95
PCC-1	peridotite	78	0.171	0.007	0.15	4	114
GSD-12	stream sediment	68	0.04	0.01	0.18 ?	25	22
MAG-1	marine mud	20	0.459	0.005	0.47 ?	1	98
GSD-6	stream sediment	10	1.96	0.01	2.01 ?	0.5	97
SRM 88b	dolomite limestone	10	47.0	0.3	46.37 cv	1	101

Table 1.--Continued--Duplicate samples results

<i>Duplicate samples</i>	<i>k</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>% RSD</i>	<i>Concentration range</i>	<i>No. of < (total)</i>	<i>No. of < (pairs)</i>
	91	2	5.59	0.07	1	0.01 to 46	36	17

Table 1.—Continued—Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

<i>Method blank</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>3s</i>	<i>5s</i>
	29	0.002	0.001	0.003	0.004

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