Coulometer User Guide

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User Guide Contents

Introduction

Coulometer analysis determines carbonate concentration in a variety of samples, including pure carbonates, soils, rocks, and liquids. Coulometry quantifies the carbon dioxide evolved from acidified samples and uses this to determine the carbonate content in the original sample. The inorganic carbon value obtained from this method is used in conjunction with TC (total carbon) measurements from the CHNS to arrive at an organic carbon value.

Theory of Method

IODP's UIC Coulometrics CM5011 CM5015 coulometer provides absolute determination of the concentration of carbon dioxide (CO₂) evolved from an acidification process. The coulometer cell is filled with a proprietary solution containing monoethanolamine and a colorimetric pH indicator. A platinum cathode and silver anode are positioned in the cell, and the assembly is located between a light source and a photodetector. When a gas stream passes through the solution, CO₂ is quantitatively absorbed, reacting with the monoethanolamine to form a titratable acid. This acid causes the color indicator to fade. A spectrophotometer monitors the change in the solution's percent transmittance (%T). As %T increases, the titration current is automatically adjusted to generate a base at a rate proportional to the reduction of %T. When the solution returns to its original color (original %T), the current stops. The amount of CO₂ evolved is calculated from the duration and magnitude of the current required to balance the acid by CO₂ evolution.

Based on the principle of Faraday's Law of Electrolysis (the quantity of a substance produced by electrolysis is proportional to the quantity of electricity used), each mole of electrons added to the solution is equivalent to 1 mole of CO₂ titrated.

Chemical reactions occurring in the coulometer cell follow:

Absorption of CO₂ by the cathode solution (cathode reaction):

\[
\text{CO}_2 + \text{HOCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{HOCH}_2\text{CH}_2\text{NHCOOH}
\]

Electrochemical generation of \(\text{OH}^-\) (cathode reaction):

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-
\]

Neutralization of absorbed CO₂ reaction product by electrochemically generated OH⁻:

\[
\text{HOCH}_2\text{CH}_2\text{NHCOOH} + \text{OH}^- \rightarrow \text{HOCH}_2\text{CH}_2\text{NHCOO}^- + \text{H}_2\text{O}
\]

Anode reaction:

\[
\text{AgO} \rightarrow \text{Ag}^+ + \text{e}^-
\]

Interferences

A variety of carrier gases can be used for coulometry (O₂, N₂, He, and dry air). The JRSO uses N₂ for the measurement. Interferences caused by compounds such as SO₂, SO₃, H₂S, HCl, HBr, HI, and Cl₂ are removed with KOH and AgNO₃ scrubbers.
Apparatus, Reagents, & Materials

Hardware

- Coulometer unit (UIC CM5011CM5015) with titration cell (*Figure 1*)
- Acidification module (similar to UIC CM5030) (*Figure 2*)
- Dual balance system, motion-compensated, with control software

![Figure 1. Model CM5011 CM5015 Coulometer.](image)

![Figure 2. Acidification Module.](image)

![Figure 3. Cahn Electrobalance.](image)

![Figure 4. Mettler-Toledo Dual Balance Control Software.](image)

Dual Balance System Hardware

A Cahn balance and 2 Mettler Toledo XS204 analytical balances with motion compensation software are used to measure the mass of samples and chemicals. The Cahn balance (*Figure 3*) measures samples for the Coulometer.

Software

Dual Balance System Software

Motion compensation software developed in house allows the user to weigh the mass of chemicals and samples at sea. Reagents must be measured on the Mettler-Toledo XS204 balance using the Balance Master program (see Balance User Guide)(*Figure 4*). Sample material must be measured on the Cahn balance (unless the sample is larger than ~1 gram) (*Figure 5*).
### Sample Preparation

**Liquid samples** are pipetted directly into the sample tube. Most samples use 2 mL volume. If samples are suspected to contain high sulfur contents, use 0.5 mL to avoid overloading the AgNO₃ trap.

**Solid samples** must be dried, ground, and weighed before introduction into the prepared Coulometer apparatus. The workflow for solid sample preparation is as follows:

1. A scientist or staff member logs wet sample information into *SampleMaster* at the sampling table. The sample is given the name *CARB* to ensure proper routing.
2. Freeze-dry the sample.
3. Homogenize (grind) the sample.
4. Weigh the sample, assign a container and code, and upload the mass data to LIMS.
5. Prepare the coulometer acidification for analysis.

### Freeze-Drying the Sample

1. Cut the sample bags or roll back the top to ensure an open orifice during the freeze-drying process.
2. Place the sample in the freeze-drier in the Chemistry Lab under vacuum for 12 hr. If sample is finely divided and is clumpy, freeze-drying may take >12 hr. Sample should appear dry and powder easily (in mortar and pestle). If the sediment feels cold when removing from the freeze drier then it has not fully dried. Allow additional time for drying.
3. Do not overload the freeze dryer.

### Grinding the Sample

1. Remove the freeze-dried sample from the sample bag and place in a mortar. If the sample volume is too large to be ground in the mortar, grind it in separate smaller portions and recombine.
2. Grind the sample with a pestle to a fine, powder-like consistency with no large clumps. If the sample is too hard to grind in a mortar and pestle, use the mixer mill (see the X-ray technician for assistance in operating the mixer mill).
3. Transfer the sample to a new bag or container. Use the Wheaton 16 mL glass vials with plastic snap caps.

### Weighing the Sample

1. Log into the Dual Balance system for the Cahn Balance. Answer *Yes* or *OK* on all prompts that appear during the log-in process. The user’s log-in ID must be same as the LIMS database ID.
2. Click *Test Option*, and enter a number (usually >100 based on sea state; see the technician for guidance). Click *Save/Exit* to return to the main window.
3. Fold a small piece of wax paper (~0.5 cm x 0.5 cm) on opposite edges to create a U-shaped wax paper sample boat. Place the wax paper boat on the left weighing pan. Place a similar size of paper on the tare pan (right). Close the door, click Tare, and then Start on the plot screen.

4. Once the measurement is finished and the value is acceptable, click Get Mass. The tare value will be changed and the display will clear.

5. Put the sample on the weighing pan (~7–13 mg) using the scoop.

6. Press Weigh on the screen and then Start on the plot panel. The Weigh measurement will not begin if you do not press Start.

7. Once the measurement is done and the value is acceptable, click Get Mass. Final mass value (under the weigh button) will be changed and the display will clear.

8. Select COULOMETRE from the Objective from the list, then and enter a part of the text ID or label ID of the sample, then click Search.

9. Select a the appropriate sample from the list, then click Assign to return to the main window.

10. Enter a container number, and click Save to save the mass value into the LIMS. Write down on a piece of paper the mass, container number, and text_id. Keeping a good logbook of your experiments is highly recommended!

Preparing Acidification Module and Coulometer Cell

1. Add granular KI to the empty small section of the Carbon Coulometer Cell (the anode cell) to a depth of 5 mm from the bottom of the cell (Figure 5, far right).

2. Fill the large section of the Carbon Coulometer Cell with cathode solution to a mark 4 cm from the base.

3. Fill the small section of the Carbon Coulometer Cell with anode solution to a mark 4 cm from the base.

4. Important! Do this Add the anode solution quickly (within 1 min) after filling the cathode cell, or else the cathode solution will start filtering through the junction between the cells and contaminate the anode solution.

5. Fill the KOH pre-scrubber trap 1/2 full of 45% KOH solution.

6. Fill the AgNO₃ post-scrubber trap 1/2 full of 3% AgNO₃ solution.

7. Add 3 drops of 2N H₂SO₄ to the AgNO₃ trap.

8. Attach the input gas tube (carrier gas inlet) to the KOH trap.

9. Turn on the gas flow and set to 100 cm³/min.

10. Connect the KOH trap to the reaction flask.

11. Connect the reaction flask to the horizontal fitting on the AgNO₃ trap.

12. Connect the top of the AgNO₃ trap to the Carbon Coulometer Cell.

13. Connect the anode/cathode to the titration cell ports next to the titration cell.

Sample Analysis

Once the sample is placed in the reaction vial, acid is added to release CO₂ gas. This gas is carried through the coulometer cell and into the titration cell, where the sample is titrated by the coulometer automatically and the software plots µg carbon vs. time. The software evaluates the slope of the plot against a drift threshold and then compares the slope against $\text{Threshold\_slope}$ (method-determined value equivalent to 29% transmittance) to determine when the titration is complete. When the threshold is reached, titration halts and the final result is expressed in µg C, from which weight percent (wt%) CaCO₃ can be calculated.
Figure 6: Coulometer software sample list screen. Options to refresh the list, append a new sample, edit an existing sample, or delete a sample or locate on the top right. The bottom left button allows the user to view the measurement history. The Measure button commences a measurement for the currently highlighted sample.

Running Samples

1. Turn on the heating unit and power to the main coulometer unit.
2. Choose emulation mode on the screen.
3. Click **Run Cell Setup** on the screen.

4. On the transmittance screen that appears, check to see that the value is **between 2,700 and 4,000**. If not, swivel the carbon coulometer cell until a value in this range is acquired. Do not move the cell once this position has been found. Click **Next**.

5. Click **Start Analysis**. The **Cell Activity** screen will appear. The %T should be between 99.8-100.1 and the Cell I should be 0.0.

6. Switch the cell to **On**, on the main coulometer unit.
7. Allow the cell to **equilibrate for 30-45 minutes** before continuing. The %T should be 29.6 and steady.
8. Login to the Coulometer software using a LIMS login.
9. Calibrate the instrument (see **Calibration**) or verify calibration (**Calibration Verification**), as applicable.
10. Highlight a sample to be measured. Replicates of a sample (same TEXTID) are stored within the same line of the sample list. A dropdown option appears over the sample name allowing the user to select the desired replicate.
11. Connect the sample vial to jacketed condenser component of the sample introduction system (Figure 6). Ensure the connection is airtight.
12. Then slowly add 5 mL of 2N HCl using the connected repeater dispense. If the measurement is delayed the results may underestimate the calcium carbonate percentage. A measurement screen will appear displaying real time data acquisition, the options to abort or stop the measurement, and to save/not save the results. The slope threshold is a measurement of the µg carbon with respect to time, and may be adjusted to specify the stopping point of the titration. Setting the slope threshold too low increases measurement times with the possibility of including circuit noise in the results, whereas setting the threshold too high will cause the measurement to prematurely terminate. The default slope threshold is 0.1.
13. The cell solution will fade upon dissolution of carbon dioxide and will return to a blue color (i.e., the start point) during titration.
14. After the measurement is complete, press **Save** or **Don't Save** to keep or disregard the data. A few reasons to not save data:
   a. Sample powder coated the sides of the vial and was not dissolved by the acid.
   b. The amount of calcium carbonate was so low its signal is greatly influenced by instrument noise.
   c. The slope threshold was set incorrectly.
   d. There may be constituent siderite in the sample that confounds the results. Siderite tends to react with the acid less quickly than calcium carbonate
15. After saving the data the measurement screen will revert to the sample list screen.
Shutting Down the Coulometer

Shut down the instrument after each run.

1. Turn off cell power, unit power, and heater power.
2. Unplug the electrodes and remove the titration cell.
3. Place the appropriate jumper between the red and black cell output fittings.
4. If the instrument is not to be run in next few days, remove all traps and dispose of solutions appropriately.
5. Rinse/dry all glassware.

Cleaning the Glassware

- **Sample tubes:** rinse sample tubes with DI water and place into the oven to dry. They do not need to be acid washed.
- **Cell:** clean the cathode/anode cell in a fume hood by adding acetone to the anode cell. The acetone will leach through the bridge between the cells and clean it. Follow the acetone rinse by placing DI water in the anode cell and letting that leach through.
- **Platinum electrodes:** Electrodes can acquire surface coatings from the solutions. Remove this coating by placing the electrode in a solution of 1:1 concentrated nitric acid: water for 20 seconds. Rinse with DI water immediately.

Data Handling

Weight percent calcium carbonate is calculated from µg carbon measured during the titration as follows:

\[
\% \text{CaCO}_3 = \frac{\mu g \text{ C}}{\text{sample mass}} \times 8.333
\]

Sample mass is stored in LIMS associated with the container ID that the coulometer analysis is associated with.
Quality Assurance/Quality Control

QA/QC for Coulometer analysis consists of instrument calibration and continuing calibration verification using check standards, along with blanks and replicate samples.

Range and Rate

The working range of the CO₂ coulometer is <1 to 10,000 µg C per sample (optimum range = 1000–3000 µg C). The coulometer cell solution can absorb >100 mg of C. Titrating at maximum current (200 mA), the coulometer can titrate 1500 µg of carbon (or 5500 µg CO₂(−)) per min.

Analytical Batch

An analytical batch is a method-defined number of samples with which QC samples including calibration verification, blank check, and replicate samples are run. Because samples are grouped into QC batches, if problems arise, affected samples can be identified and reanalyzed. Analytical batches for the coulometer are typically 10 samples.

Control Limits

Each QA/QC sample has one the following results:

- In Control
- In Control (exceeds warning limit)
- Out of Control (exceeds control limit)

For a system to be considered in control, all QA/QC samples (blanks, calibration verification [CV] standards, and replicate samples) must be in control.

In Control

A QA/QC sample is in control when the sample analysis result is within a certain tolerance of acceptable limits (usually 1σ). Calibration verification standards should be within acceptable limits of the actual value of carbonate, blanks should be within acceptable limits of background levels of carbonate, and replicate samples should be within acceptable limits of precision. When the system is in control, as indicated by acceptable results on QA/QC samples, analytical results for unknown samples are considered to be reliable.

In Control (Warning Limit Exceeded)

When QA/QC samples exceed the warning limits (generally 2σ but 1σ to 3σ, the system is considered to be in danger of becoming out of control (but is not yet out of control). Typically, the warning situation indicates that the operator must decide whether to take action. The operator can continue the analysis if he or she does not think that the control limit will be exceeded.

Out of Control

If the control limits are exceeded (generally 3σ), the instrument system is considered out of control and all samples in the current analytical batch are invalid and should be reanalyzed once corrective action has been taken to put the system back in control.

Blanks

A blank is run every N (defined by method) samples. The blank result is evaluated against $CL, the method-defined percent threshold that the measured blank value can deviate from standard value and still be considered in control, and $WL, the method-defined percent threshold that the measured blank value can deviate from the standard value before setting a warning flag.

- If the blank result is <$WL and <$CL, the system is in control and analysis can continue.
- If the blank result is >$WL and <$CL, the system is flagged with warning limits, although analyses can proceed.
- If the blank result is >$CL, the system is out of control and samples in the analytical batch (between the previous blank and the current blank) are invalid and must be rerun.

Calibration
The Coulometer instrument electronics are calibrated by the manufacturer. Each time the reagents are changed a calibration curve is constructed by running the following standards:

- Blank: 0% CaCO$_3$
- STD 1: standard level to bracket the lower end of expected sample value range
- STD 2: standard level to bracket upper end of expected sample value range
- CaCO$_3$: 100% CaCO$_3$

The calibration curve is calculated using linear fit, least-squares method as measured CaCO$_3$ vs. STD CaCO$_3$:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y = STD_CaCO3$</td>
<td>$(mass_C_std \times mass_std) \times (100.087/12) \times 100% = 834% \times mass_C_std \times mass_std$</td>
</tr>
<tr>
<td>$m = slope$</td>
<td>$(STD_CaCO3 \times Sample_CaCO3)$</td>
</tr>
<tr>
<td>$b = intercept$</td>
<td>STD_CaCO3</td>
</tr>
<tr>
<td>$x = meas_CaCO3$</td>
<td>$(mass_C_sample \times mass_sample) \times (100.087/12) \times 100% = 834% \times mass_C_sample \times mass_sample$</td>
</tr>
<tr>
<td>$y = mx + b$</td>
<td>$(834% \times mass_C_std \times mass_std) = m \times (834% \times mass_C_sample \times mass_sample) + b$</td>
</tr>
</tbody>
</table>

A transfer function relates measured µg carbon from the instrument to normalized %CaCO$_3$. This transfer function is applied to all measurements in the range for which the calibration is valid.

**Calibration Verification**

A check standard is run every 6 hr of Coulometer instrument operation or every 10 samples (whichever comes first). Check standards consist of a 100% CaCO$_3$ standard (reagent grade calcium carbonate).

The check standard result is evaluated against the threshold for %variance limits for calibration verification standard ($X$) against true value as follows:

$\left(\frac{834\% \times mass\_C\_normal}{mass\_normal}\right) = m \times \left(\frac{834\% \times mass\_C\_check}{mass\_check}\right) + b$

- If the check standard $X > 1\%$, then rerun the standard.
- If the check standard $X > 1\%$ on the rerun, then change the reagent solution, recalibrate the instrument, and rerun all samples in the corresponding analytical batch.
- If the verification check standard run falls within actual value ±1%, then run the check standard again to determine one of the following:
  - If the verification check standard is considered successful and analysis can continue.
  - If the verification check standard $X > 1\%$, then change the reagent solutions, recalibrate the instrument, and rerun all samples in the corresponding analytical batch.

**Precision**

Every N (defined by method) samples, a single sample is analyzed in replicate. The deviation between the two sample results is evaluated against $CL$, the method-defined maximum percent deviation allowable for the precision to be considered in control, and $WL$, the method-defined percent deviation allowable for the precision before setting a warning flag.

- If precision is <$WL$ and <$CL$, the system is in control and analysis can continue.
- If precision is >=$WL$ and <$CL$, the system is flagged with warning limits, although analyses can proceed.
- If precision is >$CL$, the system is out of control and samples in the analytical batch are invalid and must be rerun.

**Accuracy**

Typical accuracy using the UIC Coulometer is as follows:

- Carbonate carbon in calcium carbonate: 12.00%/12.00% ± 0.05%
- Titration accuracy is ±0.15% in samples with >1000 µg C.
- If sample volume limits CO$_2$ evolution to small amounts, accuracy is better than ~1 µg C.
LIMS Integration

Sample Characteristics

- Analysis is typically performed on a homogenized powdered subsample
- Sample type can be homogenized powder or aqueous
- Analysis is destructive

Analysis Characteristics

Weight Analysis

Data have the following dependencies on weight analysis:

- Mass of carbonate sample (measured)
- Container ID (directly input)

Coulometer Analysis

The following analysis components are uploaded from the coulometer into the LIMS with each sample result:

- Sample ID
- Instrument serial number
- Analysis timestamp
- µg carbon measured (measured)
- Slope threshold
- Analysis duration
- Method reference
- Calibration information
- Slope ($m$)
- Intercept ($b$)
- $R^2$
- Timestamp

LIMS Analysis Components

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Component</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>COUL</td>
<td>calcium_carbonate_percent</td>
<td>Concentration of CaCO$_3$ in sample</td>
<td>wt%</td>
</tr>
<tr>
<td></td>
<td>carbon_mass</td>
<td>Mass of carbon in sample</td>
<td>µg</td>
</tr>
<tr>
<td></td>
<td>carbon_percent</td>
<td>Concentration of carbon in sample</td>
<td>wt%</td>
</tr>
<tr>
<td></td>
<td>container_number</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mass</td>
<td>Mass of sample</td>
<td>mg</td>
</tr>
<tr>
<td>COUL_QAQC</td>
<td>calcium_carbonate_expected_percent</td>
<td>Concentration of CaCO$_3$ expected in standard</td>
<td>wt%</td>
</tr>
<tr>
<td></td>
<td>calcium_carbonate_percent</td>
<td>Concentration of CaCO$_3$ in sample</td>
<td>wt%</td>
</tr>
<tr>
<td></td>
<td>carbon_expected_mass</td>
<td>Mass of carbon expected in a standard</td>
<td>µg</td>
</tr>
<tr>
<td></td>
<td>carbon_expected_percent</td>
<td>Concentration of carbon expected in standard</td>
<td>wt%</td>
</tr>
<tr>
<td></td>
<td>carbon_mass</td>
<td>Mass of carbon found in standard</td>
<td>µg</td>
</tr>
<tr>
<td></td>
<td>carbon_percent</td>
<td>Percent carbon found in standard</td>
<td>wt%</td>
</tr>
<tr>
<td></td>
<td>container_number</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>corr2</td>
<td>Correlation coefficient $R^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>intercept</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mass</td>
<td>Mass of sample</td>
<td>mg</td>
</tr>
<tr>
<td></td>
<td>slope</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>standard_percent</td>
<td>Percent of carbon expected in standard as determined from standard</td>
<td>wt%</td>
</tr>
</tbody>
</table>
Health, Safety, & Environment

Safety

Carbon Cathode Solution (CM300-001)

–Hazardous components: Dimethyl sulfoxide, Monoethanolamine, Tetraethylammonium bromide (TEAB)
–Hazards:
  • Inhalation: irritant; TEAB toxic
  • Absorption: irritant; TEAB toxic/potential mutagen
  • Ingestion: TEAB toxic
–Handling: absorbs CO₂; keep tightly closed.
–Storage: keep away from oxidizers, heat, and ignition sources
–PPE: gloves, safety glasses
–Reactivity: stable; incompatible with oxidizers, acids, alkali metals, CO₂

Carbon Anode Solution (CM300-0002)

–Hazardous components: Dimethyl sulfoxide, potassium iodide
–Hazards:
  • Inhalation: irritant
  • Absorption: irritant
–Storage: keep away from heat/ignition sources and oxidizing agents
–PPE: gloves, safety glasses
–Reactivity: stable; incompatible with oxidizers, acids, alkali metals, CO

Potassium Iodide (CM300-003)

–Hazards:
  • Inhalation: irritant
  • Absorption: irritant
  • Ingestion: irritant

–Incompatible materials: alkaloid salts, chloral hydrate, potassium chlorate, metallic salts, tartaric and other acids, bromine trifluoride, fluorine perchlorate

Waste Management

Waste of cathode and anode solutions should be collected in a bottle until it can be removed during the next port call. The potassium hydroxide and silver nitrate solutions may be disposed of in the sink.

Maintenance/Troubleshooting

Common Problems

Poor Results

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Problem Description</td>
<td>Solution</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Non-coulometer malfunction</td>
<td>Inspect other components of the system for leaks, clogs, expended solutions or scrubber chemicals</td>
</tr>
<tr>
<td>Clogged frit in cell</td>
<td>See Thorough Cleaning, below</td>
</tr>
<tr>
<td>Silver electrode not in cell</td>
<td>Lower electrode into solution</td>
</tr>
<tr>
<td>Excessive deposits on silver electrode</td>
<td>Clean electrode with saturated KI solution, rinse with water</td>
</tr>
<tr>
<td>No excess KI in anode compartment</td>
<td>Add KI to anode compartment</td>
</tr>
<tr>
<td>Excessive deposits on platinum electrode</td>
<td>Clean platinum electrode with 1:1 concentrated nitric acid to water solution, then rinse thoroughly with water</td>
</tr>
<tr>
<td>Exhausted coulometer solutions</td>
<td>Replace coulometer solutions</td>
</tr>
<tr>
<td>Improper cell alignment</td>
<td>Align cell and run new Cell Setup</td>
</tr>
<tr>
<td>Faulty coulometer calibration</td>
<td>Perform Electronic Calibration Check (and contact UIC if it fails)</td>
</tr>
<tr>
<td>No stir bar in cell</td>
<td>Place stir bar in cell</td>
</tr>
</tbody>
</table>

### Instrument Not Operating Properly

<table>
<thead>
<tr>
<th>Check</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age of titration solution</td>
<td>If &gt;50 samples have been analyzed using current titration solution, make new</td>
</tr>
<tr>
<td>Age of reagents in the traps</td>
<td>If &gt;50 samples have been analyzed using reagent in traps, replace solutions</td>
</tr>
<tr>
<td>Are the traps assembled correctly?</td>
<td>Verify that the traps are assembled correctly and in the proper order</td>
</tr>
</tbody>
</table>

### Endpoint Never Reached

If the endpoint never seems to occur (the instrument continues to register small amounts of carbon long after the expended endpoint is reached), check the following:

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
</table>
| Sample takes a long time to break down | Some samples take longer to break down than others  
Sample was not homogenized to a fine enough powder  
Use a slightly stronger acid for CO$_2$ evolution  
Make sure heater element on the block is working. |
| Titration solution is old    | Change titration solution and recalibrate the instrument                                           |
| KOH scrubber is exhausted    | Change out all reagents in scrubber                                                               |
| Fittings are leaking         | Any leaks in fittings allows atmospheric air into the system                                        |

### Readings Are Too Low

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inadequate sample pickup</td>
<td>Check that inner plastic tubing in the sample is within 5 mm of bottom of glass sample tube</td>
</tr>
</tbody>
</table>
| Leaks                 | Check tubing connections for leaks  
Make sure plastic screws that connect the adapters are not cracked  
Check sulfuric acid O-ring |

### Silver Nitrate Tube Clogged

This tube is prone to clogging. To clean, use compressed air, then rinse with DI water. Note: Blow air through the tube over the sink to silver nitrate isn't blown all over the lab.

### Display Not Lit
<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power not on</td>
<td>Turn on power</td>
</tr>
<tr>
<td>Blown fuse</td>
<td>Replace fuse</td>
</tr>
<tr>
<td>Defective display</td>
<td>Contact UIC for repair</td>
</tr>
</tbody>
</table>

### Coulometer Lamp Not Lit

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defective lamp</td>
<td>Replace lamp or contact UIC for repair</td>
</tr>
</tbody>
</table>

### No Cell Current

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell current switch in OFF position</td>
<td>Switch cell current switch to ON position</td>
</tr>
<tr>
<td>Loose electrical connection</td>
<td>Check both red and black electrode connections; check electrode continuity</td>
</tr>
<tr>
<td>Defective power supply</td>
<td>Contact UIC for repair</td>
</tr>
<tr>
<td>Defective current source</td>
<td>Contact UIC for repair</td>
</tr>
</tbody>
</table>

### Low %T

A solution color change from the light blue at 29% transmittance to a royal dark blue at 0% indicates high silica in the sample, typical of a diatom mat. Ask the scientists to refrain from taking CARB samples from diatom layers.

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamp brightness has deteriorated with age</td>
<td>Replace lamp (CM140-005)</td>
</tr>
<tr>
<td>Path to detector is blockedLight path blocked</td>
<td>Check for physical blocking of the light path; you will need to run a new Cell Setup once the cell is moved</td>
</tr>
<tr>
<td>Lamp voltage is incorrect</td>
<td>Measure lamp voltage (see Measure Lamp Voltage)</td>
</tr>
<tr>
<td>Detector and/or filter are cloudedDefective photodiode</td>
<td>Replace filter (CM140-001) or photodiode (CM140-002). It is best to replace entire photodiode subassembly (CM101-178). Contact UIC for repair</td>
</tr>
<tr>
<td>Detector is defectiveDefective amplifier circuit</td>
<td>See Evaluate Electronics Contact UIC for repair</td>
</tr>
<tr>
<td>Loose connection on front end board</td>
<td>Locate the front end board (CM110-020). Ensure all connectors to the board are plugged in securely; reset connectors by pushing on them.</td>
</tr>
<tr>
<td>Electronic problem on circuit board</td>
<td>Run electronics checks (see Evaluate Electronics) If CM110-020 board is replaced electronic calibration is necessary. It is best to replace with a set of calibrated boards (CM01-138) or complete calibration kit: filter, lamp, detector, and calibrated boards (CM101-177).</td>
</tr>
</tbody>
</table>

### Cell Current Won’t Shut Off

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defective main board</td>
<td>Contact UIC for repair</td>
</tr>
<tr>
<td>Bubbles flowing through light path</td>
<td>Reposition cell and run new Cell Setup</td>
</tr>
<tr>
<td>Cathode solution is expended</td>
<td>Clean and refill cell</td>
</tr>
</tbody>
</table>
Low Maximum Current (less than 200 mA when %T is greater than 62)

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clogged frit in cell</td>
<td>See Thorough Cleaning below</td>
</tr>
<tr>
<td>Excessive deposits in silver electrode</td>
<td>Clean electrode with saturated KI solution, rinse with water</td>
</tr>
</tbody>
</table>

Solution Rising in Anode Compartment

<table>
<thead>
<tr>
<th>Potential explanation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blocked vent cell tube</td>
<td>Clear or replace vent cell tube</td>
</tr>
</tbody>
</table>

Measure Lamp Voltage

1. Remove cell from coulometer, turn off power, and remove left side panel.
2. Locate the carbon front end board (CM110-020).
3. Attach a volt meter to TP7 (red) and TP8 (black) on the CM110-020 board.
4. Turn volt meter on in DC mode and record lamp voltage.
5. Adjust %T knob full clockwise and measure lamp voltage.
6. If lamp voltage is lower than the recommended range (<2.0–2.3 V), adjust the potentiometer marked RV4 to increase voltage. Do not increase voltage >2.5 V.

Evaluate Electronics

Maximum/Minimum %T Test

1. Remove cell from coulometer.
2. Turn %T knob fully clockwise and record %T (should be ≥100%; factory setting = 110%).
3. Rotate %T knob fully counterclockwise and record minimum %T (factory setting = 12%).

Electronic Calibration Check

An electronic calibration check is performed to verify the proper operation of the internal components of the CM5015. This check does not verify the integrity of the analytical cell, the front-end system, or analytical standards.

To perform the electronic calibration check:

1. Switch the cell current switch to the OFF (center) position.
2. Disconnect and remove the cell from the cell compartment.
3. Turn on the main power supply and allow the instrument to warm up for a minimum of thirty (30) minutes.
4. From the Main Menu screen, touch System Parameters.
5. From the System Parameters screen, touch Change Settings.
6. Select the following parameters:
   - Analysis type = Carbon (CO₂ and CO₃ will be chosen in subsequent tests)
   - Calculation based on = Units Only
   - % Difference criteria = 0.1 (This value does not matter. It will not be used in any calculations.)
   - Factor = 1.0
   - Number of Readings = 2
   - Interval = 1.0
   - Timing Method = Fixed # of Readings
   - Sampling Method = Manual
   - Print Out Format = Cal. Test Format
   - Instrument ID = Default Value
   - Analyst ID = Default Value
From the Main Menu screen touch Run Cell Set-Up.

2. From the Cell Setup screen, make sure the value is stable. Touch Next to continue.

3. Note: the value will be less than 2700. Expect the value to be between 1200 and 1700.

4. From the Main Menu screen touch Run Analysis.

5. The Cell Activity screen will be presented. Touch Next to continue.


7. On the Sample Entry screen enter BLANK for the first Sample Name and touch Enter (no Sample Size is required).

8. On the Sample Entry screen enter QC for the second Sample Name and touch Enter (no Sample Size is required).

9. The Begin Analysis/Monitor Cell Activity screen will be presented. Keep the Cell Current switch in the OFF (middle) position.

10. Touch Begin Analysis.

11. The Analyzing Sample screen will be presented. The %T should show 99.7—100.2 and the Cell I (cell current) should be 0.0—0.1.

12. After 1 minute the analysis will end and the Sample Complete screen will be presented momentarily as the data are written to the SD card.

13. The Begin Analysis/Monitor Cell Activity screen will be presented. Switch the Cell Current switch to the TEST (lower) position.


15. The Analyzing Sample screen will be presented. The %T should show 99.7—100.2 and the Cell I (cell current) should be 199.8—200.1.

16. After 1 minute the analysis will end and the Sample Complete screen will be presented.

17. Record the Result and Time values from the screen. These values will also be printed to the optional printer [the JR SO does not have one], saved to the SD card, and transmitted through the serial and/or Ethernet ports for recovery later.

18. From the Sample Complete screen touch Done.

19. Repeat steps 4 through 22, selecting CO₂ and CO₃, successively as the Analysis Type.

20. Use the data that was collected from the three analyses to make the following calculations:

<table>
<thead>
<tr>
<th>Analysis Type</th>
<th>Theoretical Value</th>
<th>Actual Result</th>
<th>Time</th>
<th>Normalized Result</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>1493.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>5473.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₃</td>
<td>7463.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Actual Result = data collected from Step 22

Time = data collected from Step 22

Normalized Result = Actual Result / Time

% Difference = ((Normalized Result—Theoretical Value)/Theoretical Value)x100%

The calculated % Difference for any of the Analysis Types should be below ± 0.15%. If any of the values are > 0.15%, contact UIC for a bench calibration of the instrument.

Thorough Cleaning

At times, component parts may require a more thorough cleaning. To clean the frit, fill the cell with enough 1:1 concentrated nitric acid to water solution to cover the frit and allow the acid to clean the frit overnight. Dispose of the acid and rinse the cell and frit completely with water before re-use. If the potassium iodide solution turns brown after refilling the anode compartment, the frit has not been sufficiently rinsed.

1. With no cell in coulometer, install a shorting strap and turn on current.

2. Set coulometer as follows:

   - Mode = 15 (CALIB)
   - Run/Latch switch = latch
   - Count/time switch = count
   - Timeset switch = 10.0 (sec)

1. Press Reset and let electronics stabilize for 10 min.

2. Rotate %T fully clockwise until 200 mA current displays.

3. Every 10 s an audible alarm will sound and display should freeze at 100,000 ± 500 counts. Record the results of 10 readings.

Calibration Check for Modes 1–6

1. With no cell in coulometer, install a shorting strap and turn on current.

2. Adjust %T knob so cell current is at 200 mA.

3. Set coulometer as follows:
• Run/Latch switch = latch
• Count/time switch = count
• Timeset switch = 1.0 (min)

1. Set Mode, press Reset, and record reading. Repeat for modes of interest. Expected mode readings:

• Mode 1 (up to 0.1 µg/C) = 1493.8
• Mode 2 (up to 0.01 µg/C) = 1493.8
• Mode 3 (mg C/L) = 7469.0
• Mode 4 (µg CO₂) = 5473.5
• Mode 5 (µg CO₂) = 7463.1
• Mode 6 (µg O) = 1989.8

Evaluate Settings Performance

1. With no cell in coulometer, install a shorting strap and turn on current.
2. Open left side panel of coulometer and locate the main board (top board on left side).
3. Locate toggle switch mounted on main circuit board (normal position is center: RUN). Change to LO (toward left/back of coulometer). This is low current setting.
4. Record cell current (should be 2 mA on LO setting).
5. Toggle switch to HI (toward right/front of coulometer).
6. Record cell current (should be 200 mA on HI setting).
7. Move switch back to RUN position.

Evaluate Current Reduction System

1. With no cell in coulometer, install a shorting strap and turn on current.
2. Set %T at maximum (200 mA) using clockwise rotation then rotate slowly counterclockwise until current drops to 199 mA (should correspond to 63% ± 1%T).
3. Continue rotating knob slowly counterclockwise and record cell current at 50%T (should be 130 ± 5 mA), 40%T (69 ± 5 mA), and 35% (39 ± 5 mA).
4. Continue to slowly rotate knob counterclockwise and record the point at which cell current drops to 0 (should be ~29% ± 1%T). Cell current should be 2 mA just above %T cutoff point.

Parts and Consumables

Coulometer Cell Parts

Figure 7. Coulometer Cell.
<table>
<thead>
<tr>
<th></th>
<th>Item Description</th>
<th>UIC Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cell with side arm</td>
<td>CM200-051</td>
</tr>
<tr>
<td>2</td>
<td>Cathode top</td>
<td>CM192-005</td>
</tr>
<tr>
<td>3</td>
<td>Platinum electrode, cathode</td>
<td>CM101-034</td>
</tr>
<tr>
<td>4</td>
<td>Cell inlet tube</td>
<td>CM190-002</td>
</tr>
<tr>
<td>9</td>
<td>Anode top</td>
<td>CM192-006</td>
</tr>
<tr>
<td>10</td>
<td>Silver electrode, anode</td>
<td>CM101-033</td>
</tr>
<tr>
<td>11</td>
<td>Stir bar, 1.5 in.</td>
<td>CM121-006</td>
</tr>
<tr>
<td>12</td>
<td>Complete cell assembly</td>
<td>CM210-008015</td>
</tr>
</tbody>
</table>

### Chemicals

<table>
<thead>
<tr>
<th>Name</th>
<th>UIC Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon cathode solution, 1 gallon</td>
<td>CM300-001</td>
</tr>
<tr>
<td>Carbon anode solution, 16 oz</td>
<td>CM300-002</td>
</tr>
<tr>
<td>Potassium iodide, 50 g</td>
<td>CM300-003</td>
</tr>
<tr>
<td>Calcium carbonate standard, 100 g</td>
<td>CM301-002</td>
</tr>
<tr>
<td>Carbon cell reagent kit</td>
<td>CM300-001, CM300-002, CM300-003</td>
</tr>
</tbody>
</table>

### Expected Consumable Usage

Expected usage levels of consumables are as follows. Actual usage levels will vary depending on sample load, type, matrix, carbon levels, and interfering substance levels.

<table>
<thead>
<tr>
<th>UIC Part Number</th>
<th>Name</th>
<th>Estimated usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM300-001</td>
<td>Carbon cathode solution</td>
<td>250 mL/wk</td>
</tr>
<tr>
<td>CM300-002</td>
<td>Carbon anode solution</td>
<td>32 mL/wk</td>
</tr>
<tr>
<td>CM300-003</td>
<td>Potassium iodide</td>
<td>3.2 g/wk</td>
</tr>
<tr>
<td>CM101-033</td>
<td>Silver electrode (anode)</td>
<td>400 analyses</td>
</tr>
<tr>
<td></td>
<td>Platinum electrode (cathode)</td>
<td>Replace only when broken</td>
</tr>
<tr>
<td>CM129-071</td>
<td>Cell inlet tube fitting</td>
<td>1/6 months</td>
</tr>
<tr>
<td>CM140-005</td>
<td>Lamp</td>
<td>1/12 months</td>
</tr>
<tr>
<td></td>
<td>45% solution</td>
<td>15–25 mL/month</td>
</tr>
<tr>
<td></td>
<td>2N HCl solution</td>
<td>10 mL/sample</td>
</tr>
<tr>
<td>CM210-022</td>
<td>Pre-scrubber</td>
<td>1/year</td>
</tr>
<tr>
<td>CM192-003</td>
<td>Check valve, pk/6</td>
<td>10 weeks per valve</td>
</tr>
</tbody>
</table>

### Additional Consumables

- Silver Nitrate: 4 g per 200 samples
- KOH: 500 g/3000 samples
- Anode solution: 25 mL per 200 samples
- Cathode solution: 150 mL per 200 samples
- KI: 5 g per 200 samples
Installation Guide

Site Preparation

Coulometer Site Requirements

- Clean compressed air (oil-free; zero grade preferred) $\geq$ 40 psi
- Two 110 V outlets; 8 A peak
- Vent for reaction effluent (preferred as effluent smells bad, releasing amine derivatives)
- Counter area $\geq$ 2 ft x 2 ft
- Cooling capacity = 800 btu

Hardware Setup

Be certain that the CM5015 is running in CM5011 emulation mode for proper interface with the JRSO software. Also note that the "latch" commands used with the CM5011 are not applicable to the CM5015.

Coulometer Serial Port Jumper Configuration

1. Turn unit power off.
2. Remove top cover to expose circuit board.
3. Set jumpers 1 and 4 to ON.
4. Set jumpers 2 and 3 to OFF.

Coulometer Serial Port Settings

- Baud rate = 9600 bps
- Data bits = 8
- Stop bits = 1
- Parity = none