Coulometer User Guide

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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 (CO_2) 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, CO_2 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 CO_2 evolved is calculated from the duration and magnitude of the current required to balance the acid by CO_2 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 CO_2 titrated.

Chemical reactions occurring in the coulometer cell follow:

Absorption of CO_2 by the cathode solution (cathode reaction):

$$\mathbf{CO_2 + HOCH_2CH_2NH_2 \longrightarrow HOCH_2CH_2NHCOOH}$$

Electrochemical generation of OH^- (cathode reaction):

$$2H_2O + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-$$

Neutralization of absorbed CO_2 reaction product by electrochemically generated OH^-:

$$HOCH_2CH_2NHCOOH + OH^- \longrightarrow HOCH_2CH_2NHCOO^- + H_2O$$

Anode reaction:

$$AgO \longrightarrow Ag^+ + e^-$$

Interferences

A variety of carrier gases can be used for coulometry (O_2, N_2, He, and dry air). The JRSO uses N_2 for the measurement. Interferences caused by compounds such as SO_2, SO_3, H_2S, HCl, HBr, HI, and Cl_2 are removed with KOH and $AgNO_3$ 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.

Figure 2. Acidificat

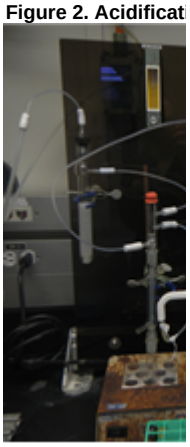


Figure 3. Cahn Electrobalance.

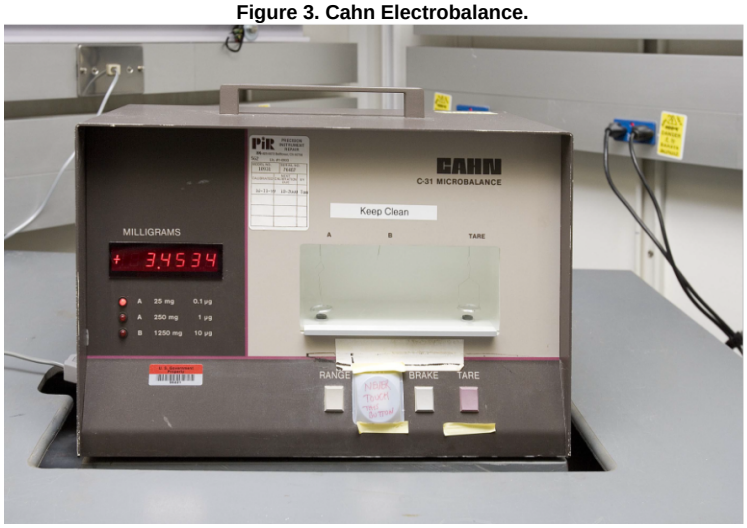
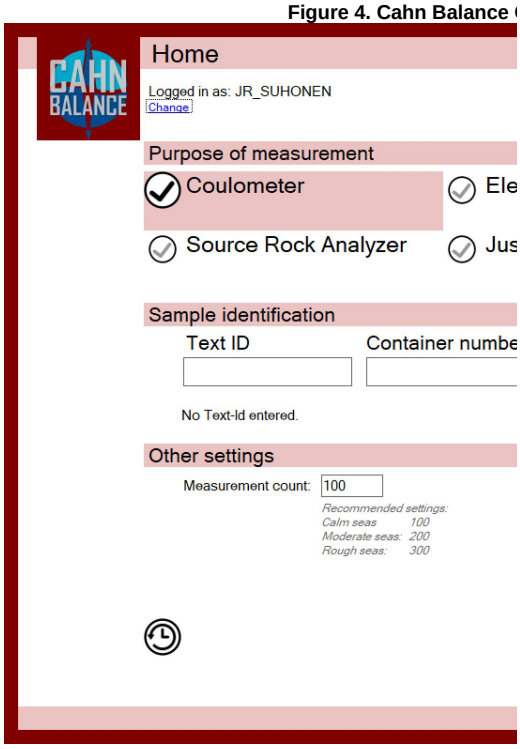


Figure 4. Cahn Balance



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). Sample material must be measured on the Cahn balance (unless the sample is larger than ~1 gram) (***Figure 4***).

Laboratory Supplies

Apparatus

- KOH pre-scrubber trap
- $AgNO_3$ post-scrubber trap
- Reaction flask/reaction vial
- Bottle-top dispenser, 5 mL
- Agate mortar and pestle

Materials

- Wax paper boats
- Scoop
- Tweezers
- Sample containers

Reagents

- Potassium hydroxide (KOH)
- Silver nitrate ($AgNO_3$)
- Potassium iodide (KI)
- Sulfuric acid (H_2SO_4)

- Hydrochloric acid (HCl)
- Anode solution (UIC proprietary)
- Cathode solution (UIC proprietary)

Gases

- Nitrogen (99.995% or better) is used as carrier gas to minimize the amount of CO_2 the scrubber (KOH) must absorb

Reagent Solutions

- 45% KOH ([%w/v]: add 90 g KOH pellets to water and make up to 200 mL once fully dissolved) (to make 500 mL, add 225 g KOH pellets to water and make up to 500 mL once fully dissolved)

  Warning! This procedure liberates caustic fumes and heat. Perform in a fume hood.

- 3% $AgNO_3$ ([%w/v]: dissolve 3 g silver nitrate in water and make up to 100 mL when fully dissolved) (to make 250 mL, dissolve 7.5 g silver nitrate in water and make up to 250 ml once fully dissolved)
- 2N H_2SO_4: add 55.5 mL concentrated sulfuric acid to water and make up to 1L (to make 100 mL, add 5.55 mL concentrated sulfuric acid to water and make up to 100 mL)
- 2N HCl: add 166 mL concentrated hydrochloric acid to water and make up to 1L

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 $AgNO_3$ 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
5. Prepare the coulometer 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 hrs. If sample is finely divided and is clumpy, freeze-drying may take >12 hrs. 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

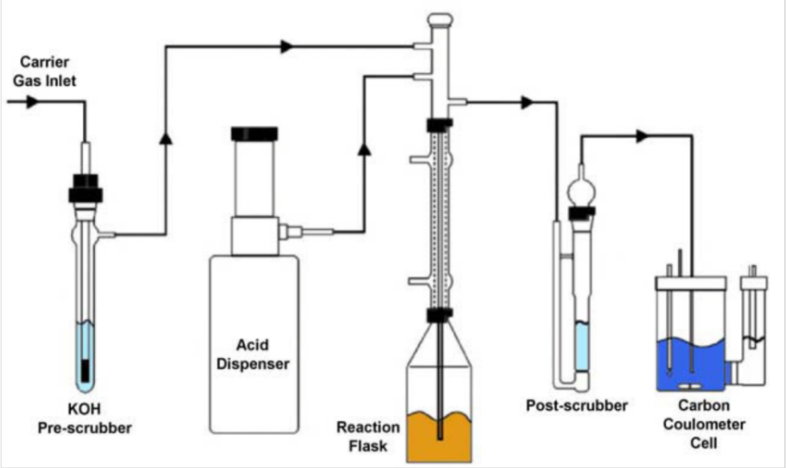
1. Log into **Cahn Balance** software. The log-in is the same as the LIMS database ID.
2. Select **Coulometer**. Set Measurement count to based on sea state. Scan the Text ID of the sample into the **Text ID** field. Enter the number of the vial into the **Container number** field.
3. Fold a small piece of weighing paper (~3 cm x 2 cm) on opposite edges to create a weighing "boat". Place the paper boat on the left weighing pan. Place a similar size paper boat on the tare pan (right). Close the door and click **Tare**.
4. Once the tare is finished, add the sample on the weighing pan (~11–13 mg) using a scoop. Observe the weight on the display on the balance, taking the tare value into account, until the weight is acceptable.
5. Press **Weigh** on the screen.
6. Once the measurement is finished, write the mass in the coulometer notebook and click **Save**.

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 the "100" mark.

3. Fill the small section of the Carbon Coulometer Cell with anode solution to to the "100" mark.
4. Important! 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 $AgNO_3$ post-scrubber trap 1/2 full of 3% $AgNO_3$ solution.
7. Add 3 drops of 2N H_2SO_4 to the $AgNO_3$ trap.
8. Attach the input gas tube (carrier gas inlet) to the KOH trap.
9. Turn on the gas flow and set to 100 cm^3/min.
10. Connect the KOH trap to the reaction flask.
11. Connect the reaction flask to the horizontal fitting on the $AgNO_3$ trap.
12. Connect the top of the $AgNO_3$ trap to the Carbon Coulometer Cell.
13. Connect the anode/cathode to the titration cell ports next to the titration cell.

Figure 5. Acidification Module and Carbon Coulometer Cell.



Sample Analysis

Once the sample is placed in the reaction vial, acid is added to release CO_2 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 **$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%) $CaCO_3$ can be calculated.

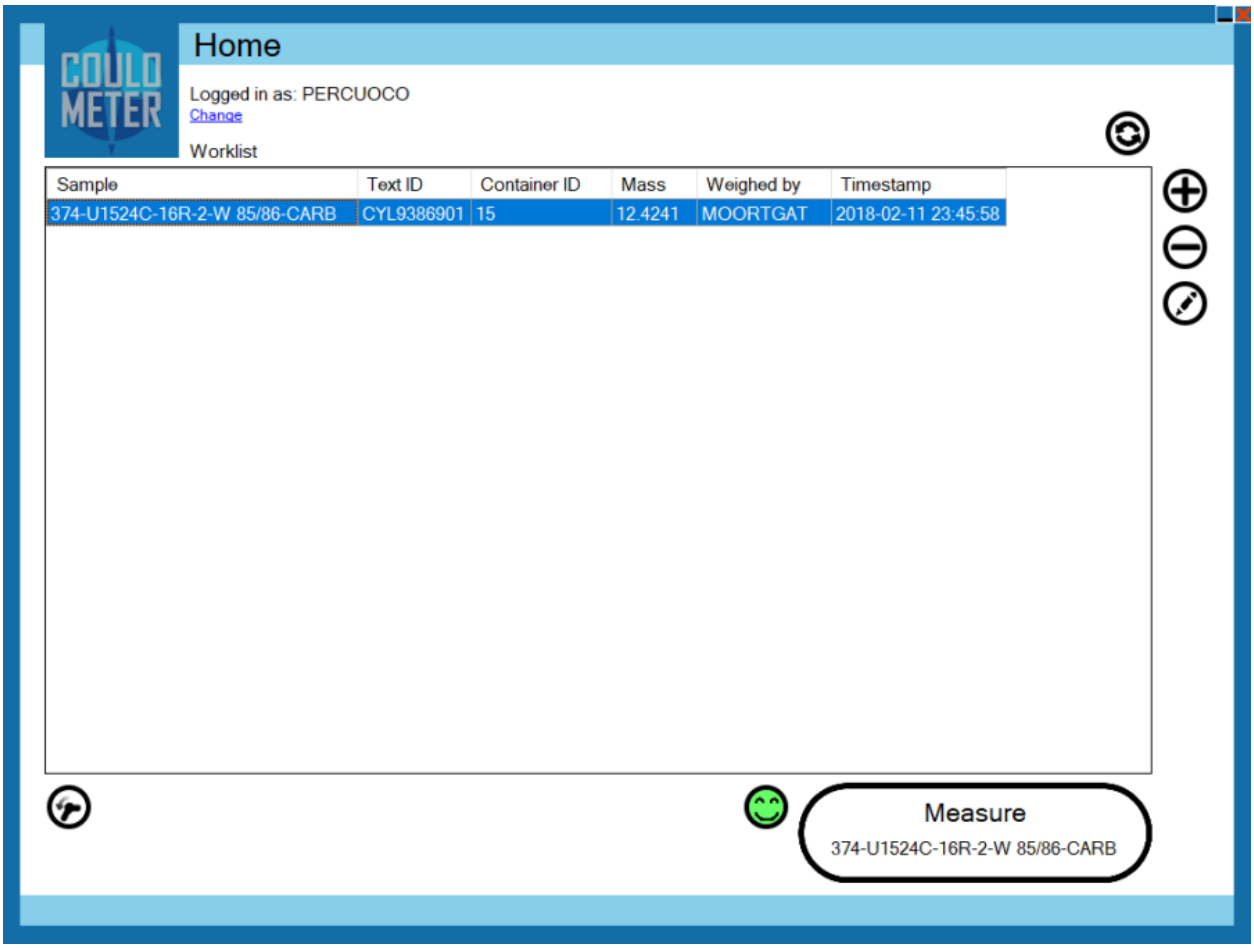
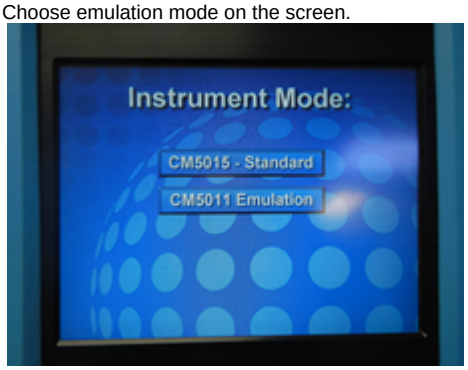


Figure 6: Coulometer software sample list screen. Options to refresh the list, append a new sample, edit an existing sample, or delete a sample on the top right. The bottom left button allows the user to view the measurement history. The Measure button commences a measurement for the currently highlighted sample.

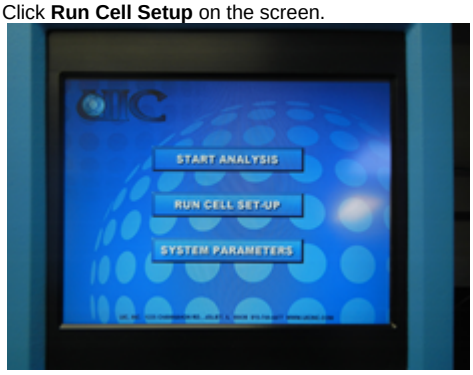
Running Samples

Prepare the coulometer cell, place it in the coulometer and connect the leads before turning on power.

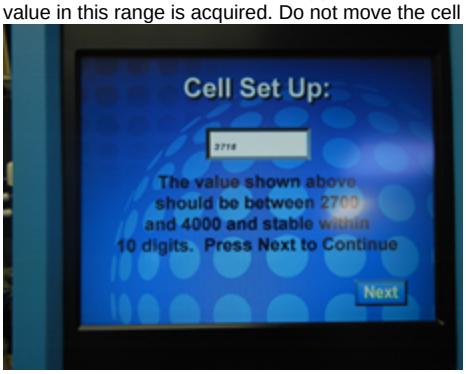
1. Turn on the heating unit and power to the main coulometer unit.
2. Choose emulation mode on the screen.



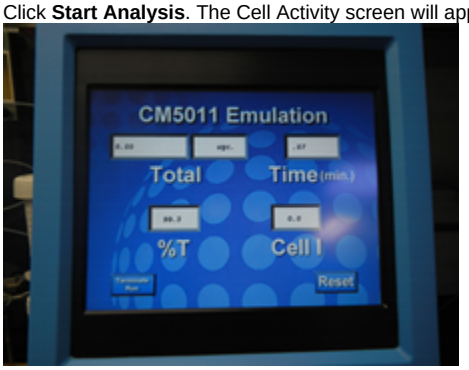
3. Click **Run Cell Setup** on the screen.



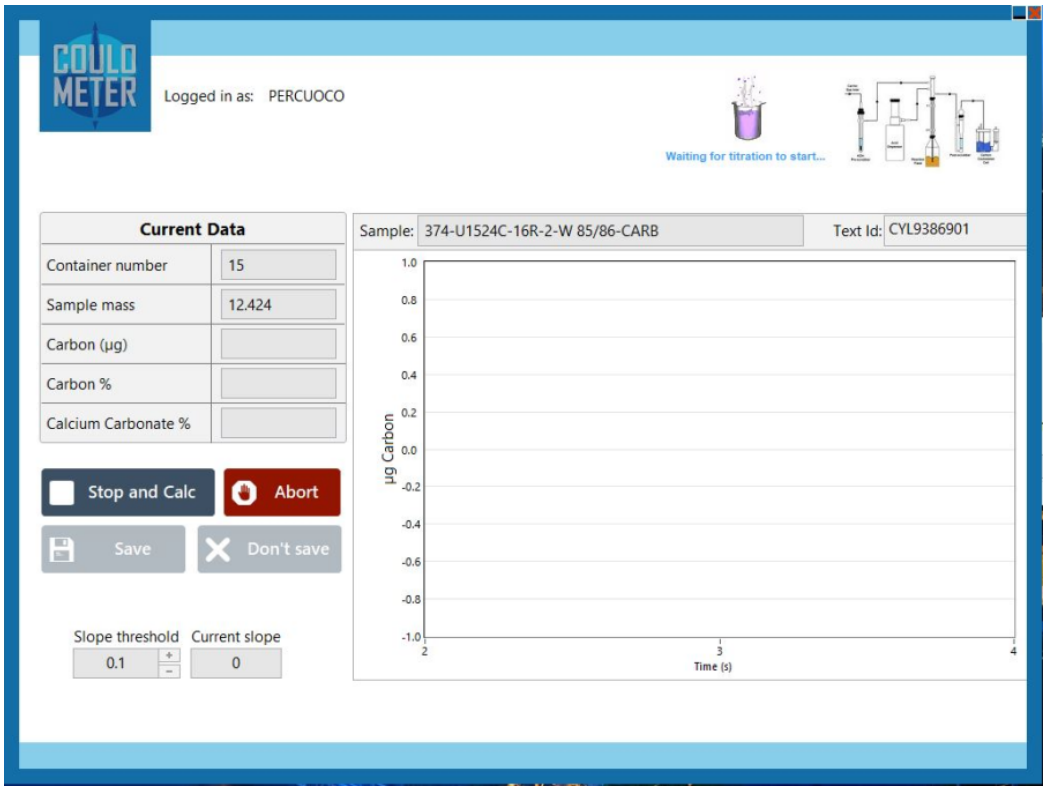
4. On the transmittance screen that appears, check to see that the value is **between 2,700 and 4,000**. If not, swivel the coulometer cell until a value in this range is acquired. Do not move the cell once this position has been found. Click **Next**.



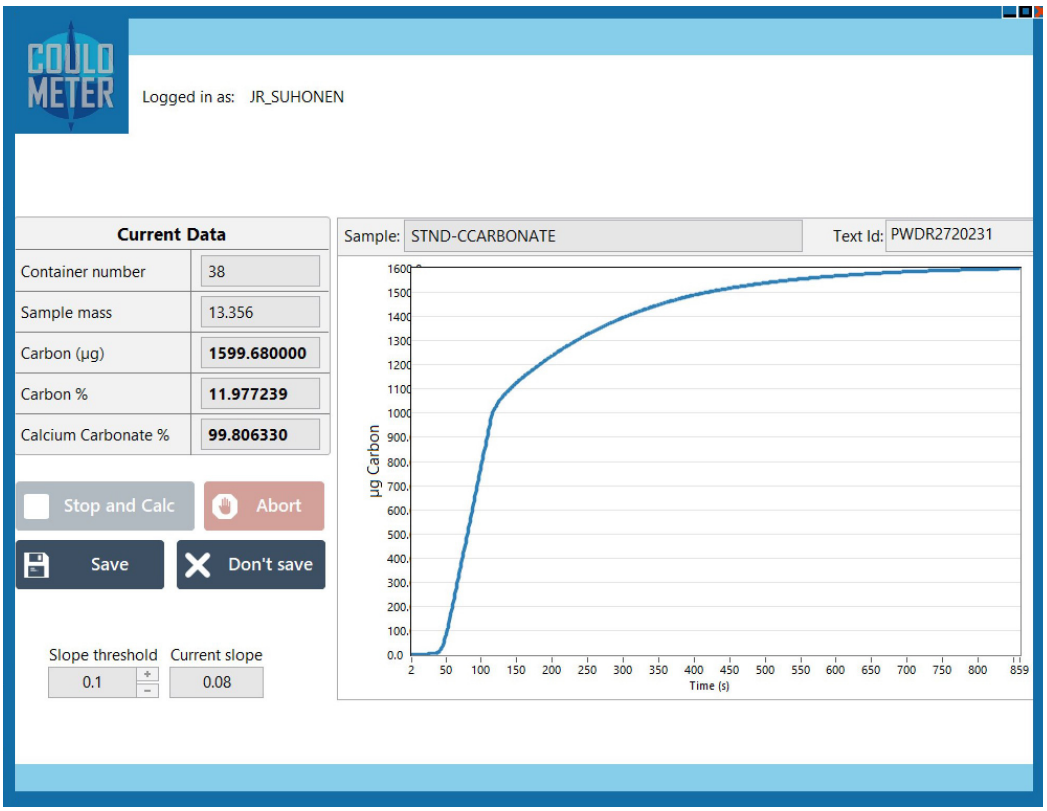
5. Click **Start Analysis**. The Cell Activity screen will appear. The %T should be between 99.8-100.1 and the Cell I should be 0.0.



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. Ensure the connection is airtight. Then slowly add 5 mL of 2N HCl using the connected bottle-top dispenser.
12. Quickly press **Measure** in the sample list page of the coulometer software. 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.



The sample measurement screen



A completed check standard measurement

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** (The electrode that goes in the larger cell compartment)**:** 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.
- **Silver electrodes** (The electrode that goes in the smaller cell compartment)**:** Can rinse with ethanol and DI water along with light scrubbing with a sponge.

Data Handling

Weight percent calcium carbonate is calculated from µg carbon measured during the titration as follows:
$\%CaCO^3$ = µg C x 8.333/sample mass
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 CO_2 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 $_{1500\ \mu g\ of\ carbon\ (or\ 5500\ \mu g\ CO^2\{\sim\})}$ 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 1¿). 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 2¿ but ¿ to 3¿¿, 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 3¿), 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
- CaCO3: 100% $CaCO_3$

The calibration curve is calculated using linear fit, least-squares method as measured $CaCO_3$ vs. STD $CaCO_3$:

Variable	**Calculation**
y = STD_CaCO3	(*mass_C_std*/*mass_std*) x (100.087/12) x 100% = 834% x *mass_C_std*/*mass_std*
m = slope	(*STD_CaCO3*/*Sample_CaCO3*)
b = intercept	STD_CaCO3
x = meas_CaCO3	(*mass_C_sample*/*mass_sample*) x (100.087/12) x 100% = 834% x *mass_C_sample*/*mass_sample*
y = mx + b	(834% x *mass_C_std*/*mass_std*) = *m* x (834% x *mass_C_sample*/*mass_sample*) + *b*

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:
(834% x mass_C_normal/*mass_normal*) = m x (834% x *mass_C_check*/*mass_check*) + *b*
(834% x *mass_C_normal*/*mass_normal*) = *normalized*%CaCO3_

- 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 check standard rerun falls within actual value ±1%, then run the check standard again to determine one of the following:
- If the verification check standard run falls within actual value ±1% then the 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

Analysis	Component	Definition	Unit
COUL	calcium_carbonate_percent	Concentration of $CaCO_3$ in sample	wt%
	carbon_mass	Mass of carbon in sample	µg
	carbon_percent	Concentration of carbon in sample	wt%
	container_number		
	mass	Mass of sample	mg
COUL_QAQC	calcium_carbonate_expected_percent	Concentration of $CaCO_3$ expected in standard	wt%
	calcium_carbonate_percent	Concentration of $CaCO_3$ in sample	wt%
	carbon_expected_mass	Mass of carbon expected in a standard	µg

	carbon_expected_percent	Concentration of carbon expected in standard	wt%
	carbon_mass	Mass of carbon found in standard	µg
	carbon_percent	Percent carbon found in standard	wt%
	container_number		
	corr2	Correlation coefficient R^2	
	intercept		
	mass	Mass of sample	mg
	slope		
	standard_percent	Percent of carbon expected in standard as determined from standard	wt#

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 CO_2; keep tightly closed.
–Storage: keep away from oxidizers, heat, and ignition sources
–PPE: gloves, safety glasses
–Reactivity: stable; incompatible with oxidizers, acids, alkali metals, CO_2

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

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

Instrument Not Operating Properly

Check	Specifications
Age of titration solution	If >50 samples have been analyzed using current titration solution, make new
Age of reagents in the traps	If >50 samples have been analyzed using reagent in traps, replace solutions
Are the traps assembled correctly?	Verify that the traps are assembled correctly and in the proper order

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:

Potential explanation	Solution
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

Potential explanation	Solution
Inadequate sample pickup	Check that inner plastic tubing in the sample is within 5 mm of bottom of glass sample tube
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

Potential explanation	Solution
Power not on	Turn on power
Blown fuse	Replace fuse
Defective display	Contact UIC for repair

Coulometer Lamp Not Lit

Potential explanation	Solution
Defective lamp	Replace lamp or contact UIC for repair

No Cell Current

Potential explanation	Solution
Cell current switch in OFF position	Switch cell current switch to ON position
Loose electrical connection	Check both red and black electrode connections; check electrode continuity
Defective power supply	Contact UIC for repair
Defective current source	Contact UIC for repair

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.

Potential explanation	Solution
Lamp brightness has deteriorated with age	Replace lamp (CM140-005)
Path to detector is blockedLight path blocked	Check for physical blocking of the light path; you will need to run a new Cell Setup once the cell is moved
Lamp voltage is incorrect	Measure lamp voltage (see ***Measure Lamp Voltage***)
Detector and/or filter are cloudedDefective photodiode	Replace filter (CM140-001) or photodiode (CM140-002). It is best to replace entire photodiode subassembly (CM101-178).Contact UIC for repair
Detector is defectiveDefective amplifier circuit	See ***Evaluate Electronics*** Contact UIC for repair

Loose connection on front end board	Locate the front end board (CM110-020). Ensure all connectors to the board are plugged in securely; reset connectors by pushing on them.
Electronic problem on circuit board	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 (CM01-139) or complete calibration kit: filter, lamp, detector, and calibrated boards (CM101-177).

Cell Current Won't Shut Off

Potential explanation	Solution
Defective main board	Contact UIC for repair
Bubbles flowing through light path	Reposition cell and run new Cell Setup
Cathode solution is expended	Clean and refill cell

Low Maximum Current (less than 200 mA when %T is greater than 62)

Potential explanation	Solution
Clogged frit in cell	See Thorough Cleaning below
Excessive deposits in silver electrode	Clean electrode with saturated KI solution, rinse with water

Solution Rising in Anode Compartment

Potential explanation	Solution
Blocked vent cell tube	Clear or replace vent cell tube

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 voltmeter 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 (CO_2 and CO_3 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

1. 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.
6. On the How Many Samples? screen enter 2 and touch Next.
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.
14. Touch Begin Analysis.
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 JRSO 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 CO_2 and CO_3, successively as the Analysis Type.
20. Use the data that was collected from the three analyses to make the following calculations:

Analysis Type	Theoretical Value	Actual Result	Time	Normalized Result	% Difference
Carbon	1493.8				
CO_2	5473.5				
CO_3	7463.1				

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 CO_2) = 5473.5
- Mode 5 (µg CO_3) = 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.

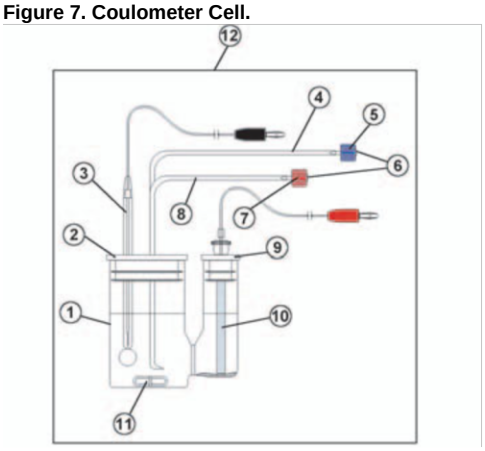
Evaluate Current Reduction System

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.



Part	Name	UIC Part Number
1	Cell with side arm	CM200-051
2	Cathode top	CM192-005
3	Platinum electrode, cathode	CM101-034
4	Cell inlet tube	CM190-002
9	Anode top	CM192-006
10	Silver electrode, anode	CM101-033
11	Stir bar, 1.5 in.	CM121-006
12	Complete cell assembly	CM210-008015

Chemicals

Name	UIC Part Number
Carbon cathode solution, 1 gallon	CM300-001
Carbon anode solution, 16 oz	CM300-002
Potassium iodide, 50 g	CM300-003
Calcium carbonate standard, 100 g	CM301-002
Carbon cell reagent kit CM300-001 CM300-002 CM300-003	CM310-001

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.

UIC Part Number	Name	Estimated usage
CM300-001	Carbon cathode solution	250 mL/wk
CM300-002	Carbon anode solution	32 mL/wk
CM300-003	Potassium iodide	3.2 g/wk
CM101-033	Silver electrode (anode)	400 analyses

CM101-034	Platinum electrode (cathode)	Replace only when broken
CM129-071	Cell inlet tube fitting	1/6 months
CM140-005	Lamp	1/12 months
	45% solution	15–25 mL/month
	2N HCl solution	10 mL/sample
CM210-022	Pre-scrubber	1/year
CM192-003	Check valve, pk/6	10 weeks per valve

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

Vendor Contact Information

UIC Inc. 1225 Channahon Road Joliet, IL 60436 800-342-5842 uicsales@uicinc.com www.uicinc.com

Installation Guide

Site Preparation

Coulometer Site Requirements

- Clean compressed air (oil-free; zero grade preferred) ¿ 40 psi
- Two 110 V outlets; 8 A peak
- Vent for reaction effluent (preferred as effluent smells bad, releasing amine derivatives)
- Counter area ¿ 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

LIMS Component Table

ANALYSIS	TABLE	NAME	ABOUT TEXT
COUL	SAMPLE	Exp	Exp: expedition number
COUL	SAMPLE	Site	Site: site number
COUL	SAMPLE	Hole	Hole: hole number
COUL	SAMPLE	Core	Core: core number
COUL	SAMPLE	Type	Type: type indicates the coring tool used to recover the core (typical types are F, H, R, X).
COUL	SAMPLE	Sect	Sect: section number
COUL	SAMPLE	A/W	A/W: archive (A) or working (W) section half.
COUL	SAMPLE	text_id	Text_ID: automatically generated database identifier for a sample, also carried on the printed labels. This identifier is guaranteed to be unique across all samples.
COUL	SAMPLE	sample_number	Sample Number: automatically generated database identifier for a sample. This is the primary key of the SAMPLE table.
COUL	SAMPLE	label_id	Label identifier: automatically generated, human readable name for a sample that is printed on labels. This name is not guaranteed unique across all samples.
COUL	SAMPLE	sample_name	Sample name: short name that may be specified for a sample. You can use an advanced filter to narrow your search by this parameter.
COUL	SAMPLE	x_sample_state	Sample state: Single-character identifier always set to "W" for samples; standards can vary.
COUL	SAMPLE	x_project	Project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises
COUL	SAMPLE	x_capt_loc	Captured location: "captured location," this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2
COUL	SAMPLE	location	Location: location that sample was taken; this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2
COUL	SAMPLE	x_sampling_tool	Sampling tool: sampling tool used to take the sample (e.g., syringe, spatula)
COUL	SAMPLE	changed_by	Changed by: username of account used to make a change to a sample record
COUL	SAMPLE	changed_on	Changed on: date/time stamp for change made to a sample record
COUL	SAMPLE	sample_type	Sample type: type of sample from a predefined list (e.g., HOLE, CORE, LIQ)
COUL	SAMPLE	x_offset	Offset (m): top offset of sample from top of parent sample, expressed in meters.
COUL	SAMPLE	x_offset_cm	Offset (cm): top offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset, converted to cm)
COUL	SAMPLE	x_bottom_offset_cm	Bottom offset (cm): bottom offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset + length, converted to cm)
COUL	SAMPLE	x_diameter	Diameter (cm): diameter of sample, usually applied only to CORE, SECT, SHLF, and WRND samples; however this field is null on both Exp. 390 and 393, so it is no longer populated by Sample Master
COUL	SAMPLE	x_orig_len	Original length (m): field for the original length of a sample; not always (or reliably) populated
COUL	SAMPLE	x_length	Length (m): field for the length of a sample [as entered upon creation]
COUL	SAMPLE	x_length_cm	Length (cm): field for the length of a sample. This is a calculated field (length, converted to cm).
COUL	SAMPLE	status	Status: single-character code for the current status of a sample (e.g., active, canceled)
COUL	SAMPLE	old_status	Old status: single-character code for the previous status of a sample; used by the LIME program to restore a canceled sample
COUL	SAMPLE	original_sample	Original sample: field tying a sample below the CORE level to its parent HOLE sample
COUL	SAMPLE	parent_sample	Parent sample: the sample from which this sample was taken (e.g., for PWDR samples, this might be a SHLF or possibly another PWDR)
COUL	SAMPLE	standard	Standard: T/F field to differentiate between samples (standard=F) and QAQC standards (standard=T)
COUL	SAMPLE	login_by	Login by: username of account used to create the sample (can be the LIMS itself [e.g., SHLFs created when a SECT is created])
COUL	SAMPLE	login_date	Login date: creation date of the sample
COUL	SAMPLE	legacy	Legacy flag: T/F indicator for when a sample is from a previous expedition and is locked/uneditable on this expedition
COUL	TEST	test changed_on	TEST changed on: date/time stamp for a change to a test record.
COUL	TEST	test status	TEST status: single-character code for the current status of a test (e.g., active, in process, canceled)
COUL	TEST	test old_status	TEST old status: single-character code for the previous status of a test; used by the LIME program to restore a canceled test

COUL	TEST	test test_number	TEST test number: automatically generated database identifier for a test record. This is the primary key of the TEST table.
COUL	TEST	test date_received	TEST date received: date/time stamp for the creation of the test record.
COUL	TEST	test instrument	TEST instrument [instrument group]: field that describes the instrument group (most often this applies to loggers with multiple sensors); often obscure (e.g., user_input)
COUL	TEST	test analysis	TEST analysis: analysis code associated with this test (foreign key to the ANALYSIS table)
COUL	TEST	test x_project	TEST project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises
COUL	TEST	test sample_number	TEST sample number: the sample_number of the sample to which this test record is attached; a foreign key to the SAMPLE table
COUL	CALCULATED	Top depth CSF-A (m)	Top depth CSF-A (m): position of observation expressed relative to the top of the hole.
COUL	CALCULATED	Bottom depth CSF-A (m)	Bottom depth CSF-A (m): position of observation expressed relative to the top of the hole.
COUL	CALCULATED	Top depth CSF-B (m)	Top depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
COUL	CALCULATED	Bottom depth CSF-B (m)	Bottom depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
COUL	RESULT	calcium_carbonate_percent (wt%)	RESULT calcium carbonate (wt%): calcium carbonate concentration in sample expressed as weight percent; this is a calculated field.
COUL	RESULT	carbon_mass (µg)	RESULT carbon mass (ug): mass of inorganic carbon in sample expressed as total micrograms of carbon (not a concentration)
COUL	RESULT	carbon_percent (wt%)	RESULT inorganic carbon (wt%): concentration of carbon in sample expressed as weight percent; this is a calculated field.
COUL	RESULT	container_number	RESULT container number: container number of the coulometer sample (used to keep samples straight)
COUL	RESULT	mass (mg)	RESULT sample mass (mg): mass of sample weighed into the container for analysis expressed in mg
COUL	SAMPLE	sample description	SAMPLE comment: contents of the SAMPLE.description field, usually shown on reports as "Sample comments"
COUL	TEST	test test_comment	TEST comment: contents of the TEST.comment field, usually shown on reports as "Test comments"
COUL	RESULT	result comments	RESULT comment: contents of a result parameter with name = "comment," usually shown on reports as "Result comments"

Archive Versions

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