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ACTIVITY/PROJECT SPECIFIC PROCEDURE

SP 12-2
USE AND MAINTENANCE OF THE UIC, INC. MODEL CM5015 CO_2 COULOMETER, CM5130 ACIDIFICATION MODULE, CM5300 FURNACE APPARATUS AND CM5390 AUTOMATED BOAT INLET
Revision 3

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1.0 Purpose and Scope

Operation guidelines for the UIC, Inc. CM5015 CO_2 Coulometer, the CM5130 Acidification Module, CM5300 Furnace Apparatus and the CM5390 Automated Boat Inlet Apparatus are included in this activity/project specific procedure (SP). This SP will be used to analyze for total carbon (C), carbon dioxide (CO_2) and carbonate (CO_3) and will support the research activities of the Waste Isolation Pilot Plant (WIPP) project.

Acronyms and definitions for terms used in this procedure may be found in the Glossary located at the Sandia National Laboratories (SNL) WIPP Online Documents web site.

2.0 Implementation Actions

2.1 Responsibility

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure is responsible for implementing the requirements of this procedure.

The technical staff is responsible for performing the measurements, following the requirements of this procedure, documenting the results, and assuring that the use of the latest revisions of this document is followed.

2.1.1 Safety and Training

The activities described in this SP shall conform with SNL Environmental Safety and Health programs (ES&H). Of particular concern is the handling of acids, thermal hazards, and disposal of waste. The ES& H Standard Operating Procedure *Activities in the Sandia National Laboratories/Carlsbad Program Group laboratory* details the handling of specific hazards in the Carlsbad Laboratory.

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2.2 CO_2 Coulometer Operation Description

A general operating procedure for the instruments in this SP will be described here; detailed operating and calibration procedures are given in the each of the instrument user manuals, and will be referred to where appropriate. Guidelines for implementing and documenting quality assurance (QA) procedures are also given in this SP. This document is not meant to substitute for the manufacturer's instruction manuals for the UIC, Inc. CM5015 CO_2 Coulometer, the CM5130 Acidification Module, CM5300 Furnace Apparatus or the CM5390 Automated Boat Inlet. The user is responsible for reading and understanding the manuals, which are available at the site of use for each apparatus.

The CM5015 CO_2 Coulometer provides for the highly accurate and absolute determination of carbon in any gas stream containing carbon dioxide (CO_2). When coupled with either of the two carbon front end units, (the CM5130 Acidification Module or the CM5300 Furnace Apparatus), this coulometer should detect carbon mass ranging from 0.01 μg to 100 mg with accuracies of 0.3% or better in less than 20 minutes (manufacturer's claim). The acidification module employs a certain mineral acid to convert carbon to CO_2, whereas the furnace apparatus administers extreme heat (500°C-1000°C) to complete this process. Both instruments then purge the CO_2 into a cell in the coulometer where it is quantitatively measured. The coulometer cell body is filled with a carbon cathode solution containing a colorimetric pH indicator and monoethanolamine. The cell body lid supports a platinum electrode, a gas inlet tube and a gas exit vent line. The cell's smaller sidearm is filled with a carbon anode solution and approximately 5 g of dry potassium iodide (KI) and requires a silver electrode. A glass frit between the cathode cell body and the anode cell sidearm allows for communication between both compartments and for the generation of an electrochemical current within the cell. The cell assembly is positioned in the CO_2 coulometer cell compartment between the light source and the photodetector.

During sample analysis, CO_2 is swept from one of the carbon front end units into the coulometer cell using either an internal air pump or an external carrier gas source. As CO_2 moves into the cell, it is absorbed by the cathode solution and reacts with the monoethanolamine to form a titratable acid. This acid then reacts with the colorimetric pH indicator, causing the solution to fade or clear. As subsequent CO_2 enters the cell, the photo detection sensor monitors the cathode solution's color change as a percent transmittance (%T). At 100 %T, the solution is clear; at 29.5 % T, the solution is blue. As the %T increases, an indication of increased CO_2 flux, a titration current within the cell is systematically activated to electrochemically generate basic solution at a rate proportional to the change in %T (approximately 1.5 mg/min). When the CO_2 flux ceases, the cathode solution returns to its original blue color (29.5 %T), and the titration current stops. Because the current in this system is the titrant, there is no need for the analyst to calibrate the CM5015 CO_2 Coulometer. During sample analysis, the CO_2 coulometer continuously measures and integrates the titration current to operator selected units (weight, volume or some other analyst- determined measurement unit) and displays the sample's concentration on the instrument's screen. The operator has the ability to analyze for total carbon (C), carbon dioxide (CO_2), carbonate (CO_3) and surface carbon.

2.3 Quality Control

Calibration is not required; however, instrument check standards bracketing the expected range shall be analyzed before analyzing any samples, and at a minimum after every 10 samples and at the end of analysis sequence. Two instrument check standards should be chosen that will bracket the expected sample carbon range. If analyzing a solid sample, the selected instrument check standards shall be freshly dried (used within two weeks after drying at 100C for 2hr) and kept in a desiccator. If analyzing a liquid sample the selected instrument check standards shall be mixed to the appropriate concentrations, and used within two weeks. (Some recommended standards are Sucrose, Sodium Carbonate and Sodium Bicarbonate) The value of the instrument check standard should be within 20% the expected value, for both liquid and solid samples.

Sample shall be analyzed in duplicates and the difference between two readings should be lower than 30% of their average. If the samples being analyzed were originally set up in duplicate form (i.e. PbCO3 1.0 CO3-1, PbCO3 1.0 CO3-2) a duplicate analysis is not necessary. If the percent difference between the sample and or sample duplicate is greater than 30% then each sample should be analyzed in duplicate again (i.e. two runs for PbCO3 1.0 CO3-1 and two runs for PbCO3 1.0 CO3-2). To determine the percent difference between the duplicates, the following equation will be used:

$$\% \text{ Diff} = \left| \frac{x_1 - x_2}{(x_1 + x_2)/2} \right| \times 100$$

If the instrument standard checks are not within the specified acceptance limits, reanalyze the standard (or sample). If the reanalyzed result is still not within the control, the operator should determine the root cause and correct before analyzing more samples.

A blank must be analyzed before sample analysis. For liquid samples a blank of <100ug must be obtained and for solid samples a blank of <10ug must be obtained before the user can begin the sample analysis.

2.4 CO_2 Coulometer Cell Setup

Cathode Cell Body and Platinum Electrode

1. Start with a clean, dry CO_2 coulometer cell. Place a Teflon™ coated magnetic stir bar (of suitable size) in the bottom of the cell body (the larger of the two compartments). This is the cathode compartment.
2. Fill the body of the cell with carbon cathode solution to the 100mL mark on the cell, ensuring that the coiled platinum electrode is submerged in the fluid. The cathode solution is a product of UIC, Inc. (Part No. CM300-001) and is stored in flammables cabinet. Take care not to splash the solution during filling.
3. Cover the cell body with the cell top containing the coiled platinum electrode, the gas inlet tube and the gas exit vent line. Position the top in such a way that the electrode and the sample gas inlet tube will not block the path between the emitting light source and the light detector.
4. Adjust the cell inlet tube so that the pointed tip is directed toward the back wall of the cell, away from the light path. If this is not done, air bubbles may interfere with the cell set-up.

Anode Cell Side Arm and Silver Electrode

1. Add approximately 5 g of potassium iodide (KI) to the bottom of the coulometer cell side arm (smaller compartment). This is the anode compartment.
2. Fill the anode compartment with 15-25 ml of carbon anode solution, covering the KI. This solution is a product of UIC, Inc. (Part No. CM300-002) and is stored in a flammables cabinet. Take care not to splash the solution during filling.
3. Make sure that the level of the anode solution is just below the level of the cathode solution.
4. Place the silver electrode in the side arm, making sure the electrode is in the solution and not in the solid KI. Press the side arm top into place.

2.5 Setting Parameters

1. Turn '**ON**' the CM5015 CO_2 Coulometer (wait 30 minutes before conducting cell set-up).
2. **Screen**

3. **Main Menu** **START ANALYSIS**
RUN CELL SETUP
SYSTEM PARAMETERS
Select SYSTEM PARAMETERS

4. **Screen** **CHANGE SETTINGS**
PRINT SETTINGS
SET DATE & TIME

5. The first time the machine is set up, select SET DATE & TIME

6. **Select** '**CHANGE SETTINGS**'.

7. **Screen** **ANALYSIS TYPE:**
CARBON
CO_2
CO_3
SURFACE CARBON
Select the type of the analysis desired.

8. **Screen** **CALCULATIONS BASED ON:**
WEIGHT
VOLUME
UNITS ONLY
Select the desired units.

9. **Screen** **UNIT OF WEIGHT:**
MICROGRAMS (ug)
MILLIGRAMS (mg)
GRAMS (g)
Select the weight units desired.

10. **Screen** **% DIFFERENCE CRITERIA:**
This screen requires that the analyst enter a value to determine the coulometer timing mode endpoint of each analysis. The analysis will continue until the difference between successive readings is less than the input value. When analyzing solid samples, a difference of 0.1%-0.5% is desired. For liquid or fluid samples, change the setting to a 0.5%-1.0% difference. Higher Difference % values terminate the analysis more quickly than lower values, but may result in erroneously low carbon concentrations if CO_2 is evolving very slowly from the sample. The default value for this setting is 0.5%. If using a **FIXED NUMBER OF READINGS** then the % Difference Criteria is inconsequential.
Type in the desired value and press '**NEXT**'.

11. **Screen** **FACTOR:**
This is a user defined sample dilution value used in the final calculations of each sample. For example, if the analyst has diluted a sample to ½ of its original concentration, a Factor of 2 could then be selected to compensate for this. The default value for this setting is 1 and should be changed if required.
Press '**NEXT**'.

12. **Screen** **NUMBER OF READINGS:**
The value entered in this screen is the minimum number of readings taken before the coulometer applies the endpoint Difference % criteria entered in step 10 of section '2.5 Setting Parameters' in this SP. The default value is 5.
Press '**NEXT**'.

13. **Screen** **INTERVAL (minutes):**
This screen prompts for the time taken between sample readings. Only whole numbers are used. The measured value is then printed for that selected time. The default value is 1 minute.
Press '**NEXT**'.

14. **Screen** **TIMING METHOD:**
AUTO ENDPOINT
FIXED NUMBER OF READINGS
The analyst chooses whether to have the coulometer determine the endpoint after the Difference % criteria has been met or to simply have a fixed number of readings terminate the analysis. If choosing **FIXED NUMBER OF READINGS**, 16 is a good place to start.

15. **Screen** **SAMPLING METHOD:**
AUTOSAMPLER
MANUAL
Select '**1. AUTOSAMPLER'**.
***NOTE**: If acid unit is being used, **MANUAL** should be selected.

16. **Screen** **AUTOSAMPLER TYPE:**
CM5200
CM5240
AUTO BOAT INLET
Select 'AUTO BOAT INLET'

17. **Screen** **PRINT OUT FORMAT**
STANDARD
CAL. TEST FORMAT
Select **STANDARD**

18. **Screen** **INSTRUMENT AND ANALYST ID**
The instrument ID will be displayed in the box it will not change; 1595015177, press **ENTER**. The user will then type their initials in the box labeled Analyst ID, and press **ENTER**.
This will prompt the **SYSTEM PARAMETERS** screen.

19. **Screen** **SYSTEM PARAMETERS**:
Press BACK to go to the Main Menu. From Main Menu select, **RUN CELL SET-UP**

2.6 Run Cell Setup

1. Insert the CO_2 coulometer cell that has been prepared as specified in section '2.4 CO_2 Coulometer Cell Setup' in this SP.

2. Connect the gas inlet tube (blue fitting) and the gas exit vent line (red fitting) from the cell cathode compartment to the inside of the cell chamber.

3. Plug in the 'banana plug' platinum cathode (black).

4. Plug in the silver anode (red).

5. Position the cathode cell top so that the platinum electrode is opposite the side arm and does not block the light path in the coulometer cell compartment. The cathode cell body is positioned to the left of the anode sidearm.

6. **Screen** **CELL SET UP**
   The value shown above should be between 2700 and 4000 and stable within 10 digits. Press NEXT to continue.

   A value below 2700 may indicate a failing lamp, clouded optical filter, failing photo-detector or interference in the light path through the cell.

   A value above 4000 may indicate an over-voltage condition in the lamp. Contact UIC for procedures to correct this condition.

   If the value is not stable within 10 digits (from lowest displayed value to the highest) this may indicate that the carrier gas bubbles entering the cell are crossing the light path or there is contamination in the cell that is interfering with the light path. Adjust the position of the cell to obtain a stable value.

   IMPORTANT: Once the cell set up has been completed DO NOT change the position of the cell. If the cell is moved you will need to perform a new cell set-up with clear cathode solution. Close cell door.

7. '**RUN CELL SETUP**' is now complete. Go back to Main Menu.

2.7 Sample Analysis

1. Select START ANALYSIS from the main menu screen.

2. **Screen** **99.8-100.1** **0.0**
   %T **CELL I**

3. Turn on the Cell Current switch.

   The CO_2 coulometer will titrate to the end point **(29.5-29.6%T**) and (**0.0-0.1 Cell I**). The titration should be finished within 10 minutes. Select '**NEXT**' when titration is finished.

4. **Screen** **HOW MANY SAMPLES?**
   Enter the number of samples you want to process. In most cases the user will choose 1. Select '**NEXT**' to continue.

5. **Screen** **SAMPLE DATA ENTRY**
   SAMPLE #1 of 1

SAMPLE NAME: BLANK_____.
SAMPLE SIZE: _____ µg/mg/g.

6. **IMPORTANT**. Before analyzing every new suite of samples, a 'blank' must be run. The CM5015 CO_2 coulometer will correct each analysis run for the initially determined 'blank' value. Press enter after typing in '**BLANK**'.

7. Running the 'blank':

   CM5130 Acidification Module: attach an empty sample flask to the condenser of the sample column assembly as described in '2.9 Sample Analysis' in this SP. Wait 1-2 minutes before proceeding. This is to expunge any atmospheric CO_2 that may be in the system. The word 'blank' must be keyed into the screen shown in step 5 above.

   CM5300 Furnace Apparatus: A volume/weight for the 'blank' is not required when using the furnace apparatus. When analyzing liquids, use 100-200uL of DI water as the blank (depending on your sample size). When analyzing solids, press '**ENTER**' and proceed with an empty boat. The word 'blank' must be keyed into the screen shown in step 5 above

   A 'blank' value of less than 10 µg is required when analyzing solids. (Blanks are calculated as follows when using Fixed # of Readings: (ug of CO2/minute)(# of readings-1), when using Fixed # of readings and 200uL of DI water as a blank, an acceptable blank value is less than 100ug. The first few blanks in a run may be high; higher blanks may be a function of the increased flow rate when the DI water goes into the furnace. As the water vaporizes, it increases the pressure in the system. The additional flow going into the cell may interfere with the light path through the cell (the air bubbles can momentarily increase the %T through the cell and cause an artificially high result).
8. If a normal blank value is not obtained or blank results are not improving after approximately 3 attempts you may try the following. High 'blanks' are those values greater than 10 µg for solids and 100ug for liquids and indicate excessive quantities of CO_2 in the system. High 'blanks' can occur for several non-exclusive reasons (listed below) and must be rerun after troubleshooting and remediating the problem:
   a. The external carrier supply or oxygen supply is contaminated (**replace the gas supply**).
   b. The KOH solution in the pre-scrubber is exhausted (**replace the KOH solution**) (Only applicable if using the acid module).
   c. Post-scrubber solutions or compounds are exhausted (**replace**).
   d. The combustion tube of the furnace apparatus has not been 'conditioned' (**condition the tube; refer to step 9 in section '2.8.2 Initial Preparation' in this SP**).
   e. The barium chromate in the pre-combustion tube is exhausted (**replace the $BaCrO_4$** tube).
   f. Residual carbon in the boat or ladle from a previous sample (**condition ladle and boat in furnace to burn off residual carbon)**
   g. Leaks in the system (**check the lines and connectors and seal the leak**).

For more Trouble shooting ideas, consult the CM5300 Furnace Apparatus Manual (pg. 24) and the CO2 CM5015 manual (pgs 35-36).

9. After running a 'blank', begin analysis.

Screen **SAMPLE ENTRY:**
SAMPLE NAME: (enter sample name)
SAMPLE SIZE: (enter sample weight/volume)
Select 'ENTER' after enter sample information.
IMPORTANT: Load sample into ceramic boat **BEFORE** pressing **'ENTER'**

10. Manually load a measured sample into one of the front end devices; either the CM5130 Acidification Module or the CM5390 Automated Boat Inlet, Sample Entry. Select '**Enter**' and '**BEGIN ANALYSIS**' after loading sample into boat. It may also be necessary to press the '**ANALYZE'** button on the CM5390 Automated Boat Inlet apparatus.

11. The CO_2 coulometer quantitatively analyzes the sample and will stop automatically when two sequential readings fail to vary by more than the '**DIFFERENCE %**' value entered during step 10 of section '2.5 Setting Parameters' in this SP, or the analysis will stop when the desired number of readings has been reached. A purge time of 292 seconds is recommended.

12. When sample is finished, press 'NEXT' and repeat steps 11 and 12 for following samples.

13. Remove and clean the cell (refer to section '2.11 Daily Maintenance of the CO_2 Coulometer Cell' in this SP).

2.8 CM5300 Furnace Apparatus Operation

Samples are combusted with oxygen to convert organic and inorganic forms of carbon to carbon dioxide (CO_2). The combustion temperature is operator selected (up to 1100 °C, usually furnace temperature is set between 500-900 °C) to completely oxidize either all carbon forms or to selectively oxidize organic carbon. Samples are introduced to the system using a ceramic boat. Evolved gases generated from the extreme heat are swept through a barium chromate combustion catalyst and then into a combustion tube to ensure the complete oxidation of carbon to CO_2. Non-carbon combustion products that can interfere with CO_2 measurement, (i.e., SO_2, SO_3, HCl, HBr, HI, NO_x) are removed from the gas flux using a series of chemical post-scrubbers. The remaining CO_2 subsequently enters the coulometer cell and is quantitatively measured by the instrument.

2.8.1 Description of Scrubbers

Pre-Scrubber (Air Scrubber)

1. The furnace apparatus is equipped with a Carbon Dioxide Adsorption tube (CM210-022) which serves as a pre-scrubber for the system. Refer to the CM5300 Furnace Apparatus Operation Manual for maintenance.

Magnesium Perchlorate Post-Scrubber

1. The magnesium perchlorate ($Mg(ClO_4)_2$) post-scrubber is a dessicant employed to protect the NO_x-scrubber from excessive moisture.
2. Filling the magnesium perchlorate post-scrubber
   a. Remove the silicone rubber tube fittings from the glass scrubber tube.
   b. Place a small plug of quartz wool into one end of the tube.
   c. Fill the tube with loosely packed $Mg(ClO_4)_2$.
   d. Secure the perchlorate in the tube with another small plug of quartz wool.

   e. Replace the silicone rubber scrubber tube fittings and attach the tube to the scrubber module.
3. Maintaining the $Mg(ClO_4)_2$ post-scrubber.
   a. $Mg(ClO_4)_2$ can form a solid mass as it becomes hydrated, blocking the gas flow through the system.
   b. The $Mg(ClO_4)_2$ should be changed daily when the instrument is in use or when the gas flow through the tube becomes restricted through hardening of the magnesium perchlorate.
   c. When finished with the material, dispose of as Hazardous Waste.

NO_x Post-Scrubber

1. This scrubber is filled with acid dichromate on silocel and a specially prepared manganese dioxide.
   The dichromate and MnO_2 oxidizes and removes NO_x combustion products from the evolved gas stream.
2. Filling the NO_x post-scrubber.
   a. Remove the silicone scrubber tube fittings from the scrubber tube.
   b. Place a small plug of quartz wool in one end of the tube.
   c. Fill 2/3 of the tube with acid dichromate and secure it in place with a quartz wool plug.
   d. Fill the remaining 1/3 of the scrubber tube with MnO_2 and secure it in place with a quartz wool plug.
   e. Replace the silicone scrubber tube fittings and attach the filled tube to the scrubber module.
3. Maintaining the NO_x post-scrubber.
   a. The NO_x post-scrubber should be changed if it becomes wet or when 75% of the acid dichromate has turned green. There is no way to determine if the MnO_2 is exhausted, therefore it should be changed when the acid dichromate is replaced.
   b. Dispose of the scrubber as Hazardous Waste.
   NOTE: Chromate is a hazardous substance and can cause Cancer and birth defects, a pregnant woman should not handle substances containing Chromate. Extreme caution shall be employed when handling Acid Dichromate.

2.8.2 Sample Analysis Using the Furnace Apparatus

Initial Preparation

1. Connect the appropriate pre-scrubber, post-scrubbers and combustion tubes as described in the instrument's user manual. If scrubbers look "wet" they will need to be replaced before coulometer operation.
2. Regulate the pressure of the oxygen supply at the tank to 5-10 psig.
3. Set the O_2 gas flow meter on the furnace apparatus to 75-125 cc/min.
4. If any questions arise concerning the operation of this furnace, address the Furnace Manual for more specific details.
5. Turn the furnace apparatus '**ON**'.
6. Set the furnace temperature to the desired value.
7. To prolong the life of the heating elements, the combustion tube and pre-combustion tubes, avoid overheating the furnace.
8. Check the system for leaks. Insert a closed piece of tubing into the union connecting the one-way check valve to the CO_2 coulometer. If the system is leak-free, the pressure caused by the blocked line will stop the bubbling in the KOH pre-scrubber (Acid module) or the O2 flow meter on the CM5300 Furnace Appratus will drop markedly.
9. When a new or repacked combustion tube is first used, overnight conditioning is recommended before running any samples.

Carbon Analysis Methods

Total Carbon Analysis (TC)

1. TC analysis requires no chemical pretreatment of the sample. Combustion temperatures are typically set to 900°C-1000°C. 935°C is a good place to start.

Total Organic Carbon Analysis (TOC)

There are several methods of determining total organic carbon in a sample.

1. Method I: By difference- TOC = TC – Total Inorganic Carbon (TIC). TC and TIC are determined using separate analytical procedures.
2. Method II: Samples can be pretreated with acid and sparged to remove all inorganic carbon and then analyzed by the same procedure as for TC to determine TOC.
3. Method III: Low temperature oxidation of the sample. If the sample has a relatively high inorganic carbon content and a low organic carbon content, this method is recommended. Combustion temperatures are lowered to oxidize only the organic compounds (500-700°C; recommended 500-900°C). Samples are not chemically pretreated, although bicarbonates must be abrogated prior to analysis by heating the sample to 130°C.

Solid Samples

1. Finely ground and homogenous, solid samples are introduced into the furnace's combustion tube by means of a ceramic boat.
2. Tare a small ceramic boat (a size that can be easily placed into the larger ceramic boat in the Sample Entry Box of CM5390) and record the sample weight. The user should attempt to select a sample size so that the sample contains 1-3 mg of Total Carbon (this is the most accurate range of measurement for the instrument). **Note**. A 'blank' must be run before any of the weighed samples can be analyzed (refer to step 7 of section '2.7 Sample Analysis' in this SP).
3. **DO NOT** use quantities of sample that contain more than 10 mg of carbon as violent or **EXPLOSIVE** reactions may result.
4. Open the secured Sample Entry Box located on the CM5390 Automated Boat Inlet and place the filled platinum or porcelain boat into the large ladle (Use tweezers to handle boat). Secure the Sample Entry Box lid securely.
5. Input the sample information and begin analysis. (refer to Section 9-10 of 2.7). When sample is finished select 'NEXT' and continue to next sample.
6. Most sample analyses will be complete in five to seven minutes. Longer analysis times will result if the sample contains more than 3 mg of C or if it contains compounds which are not readily oxidized (such as stable carbonates).
7. Calculations for Solid samples:

$$\%\text{Total Carbon} = \frac{(\text{display value in ug C}) - (\text{blank value in ug C})\ X100}{\text{Sample weight in ug C}}$$

Liquid Samples

1. Carefully aspirate 100-200uL of sample into a syringe and enter the sample information into the Coulometer 'SAMPLE ENTRY' screen. (normal sample size for liquid samples is 200uL, however if the sample contain high C, the volume can be reduced to 100uL)
2. The volume used for the samples should be the same volume used for the standard checks for proper standardization of procedure
3. Do not use samples containing more than 10mg of total Carbon (violent explosive reaction can occur), Do not use combustible or flammable materials in the furnace.
4. Allow porcelain ladle to cool between samples for 2-5 minutes, before opening Sample Entry Box.

5. Carefully open the Sample Entry Box located on the CM5390 Automated Boat Inlet and dispense measured sample directly into cooled ceramic boat, making sure not to splash the liquid out of the boat.
6. Close the Sample Entry Box lid securely and begin analysis.
7. Calculations for Liquid Samples (if display reads mg C/L):

$$\text{mg C/L} = \frac{\text{(display value as ug C)} - \text{(blank value as ug C)}}{\text{volume of sample in mL}}$$

2.8.3 Furnace Apparatus Shut Down

1. Close the valve on the gas flow meter.
2. Remove and properly dispose of the used sample.
3. Clean and thoroughly dry the sample cell. (unless using the next day, using the same cell without cleaning more than 2 days in a row is not recommended)
4. Disconnect the oxygen one-way check valve.
5. Turn OFF the CM5300 Furnace Apparatus
6. Turn OFF the CM5390 Automated Boat Inlet
7. Turn OFF the CM 5015 CO2 Coulometer power button and the cell switch.

2.9 CM5130 Acidification Apparatus Operation

Samples are acidified at room temperature or in the heated reaction vessel to evolve forms of inorganic carbon as CO_2. Internally compressed air, scrubbed free of CO_2, serves as a carrier gas for the evolved CO_2, transporting it from the sample flask of the sample column assembly through a post-scrubbing system and into a cell in the CO_2 coulometer for quantitative measurement.

2.9.1 Description and Preparation of Starting Materials

Pre-Scrubber (Air Scrubber)

1. The pre-scrubber is employed to remove accumulated CO_2 from the system and to remove CO_2 from compressed air generated by an internal air pump or from an external carrier gas.
2. Preparation of the pre-scrubber solution.
   a. A solution of ~45% (wt/vol) potassium hydroxide (KOH) is used as the pre-scrubbing solution.
   b. Weigh out about 45 g of KOH and dilute to 100 ml with deionized water (DI H_2O). Use caution when adding DI H_2O to the KOH, as this is an exothermic reaction. Record the preparation in scientific notebook.
3. Filling the pre-scrubber.
   a. Remove the dispersion tube, bushing and o-ring from the pre-scrubber assembly. This assembly is housed on the front, left side of the acidification module. Place 15-20 ml of the 45% KOH solution in the body of the scrubber and save the remaining KOH solution.
   b. Replace the dispersion tube, the o-ring and the bushing. Make sure that the fritted end is on the bottom of the scrubber. Hand tighten the bushing/o-ring seal and place the filled scrubber in its clamp.
4. Maintenance of the pre-scrubber.
   a. The KOH solution should be changed weekly during regular use or when the solution becomes thick and foamy.
   b. Rinse the pre-scrubber with DI H_2O**.** **DO NOT** rinse the pre-scrubber with acetone or any other organic solvents. Vapors left from such solvents can be sparged into the heated reaction chamber and react **EXPLOSIVELY**.

Acid Solutions

1. Mineral acids are employed by the module for the evolution of CO_2. The analyst will decide which mineral acid to use depending upon the sample composition.
2. UIC, Inc. recommended mineral acids include:
   a. Hydrochloric acid (2N HCl): HCl may overload the post-scrubber. If HCl is used, an auxiliary sample scrubber is recommended by the manufacturer.
   b. Sulfuric acid (2N H_2SO_4): sulfate precipitation may occlude portions of the sample's inorganic carbon.
   c. Perchloric acid (2N $HClO_4$): this acid is non-oxidizing in dilute solution. Most perchlorate salts are soluble. Care should be taken to avoid concentrating this acid.
3. Dispense 2-4 ml of acid into the sample column assembly for each analysis.
4. When there is concern about the oxidation of organic materials, particularly in a soil sample, antioxidants such as tin chloride ($SnCl_2$) or iron sulfate ($FeSO_4$) may be used.
5. For special applications, other acids and or different concentrations may be employed.
6. When using sulfuric acid (2N H_2SO_4) to evolve CO_2 from the sample, the recommended post-scrubber solution is potassium iodide (50% KI) acidified to pH 3.
7. When using hydrochloric acid (2N HCl) to evolve CO_2 from the sample, the recommended post-scrubber solution is silver nitrate (3% $AgNO_3$) acidified to pH 3.
8. When using Perchloric acid (2N $HClO_4$) to evolve CO_2 from the sample, the recommended post-scrubber solution is silver sulfate (3-6%) Ag_2SO_4 acidified to pH 3.

Post-Scrubber (Sample Scrubber)

1. The post-scrubber is employed to remove product gases generated from the acidification of sample materials.
2. Manufacturer's recommended scrubbing solutions:
   a. Silver sulfate (3-6% Ag_2SO_4) acidified to pH 3. Use with sulfuric acid (2N H_2SO_4).
   b. Silver nitrate (3% $AgNO_3$) acidified to pH 3. Use with hydrochloric acid (2N HCl).
   c. Potassium iodide (50% KI) acidified to pH 3. Use with sulfuric acid (2N H_2SO_4).
3. Preparation of the post-scrubber solution.
   a. Weigh out the appropriate amount of chemical to prepare 100 ml of scrubbing solution:
      1. Ag_2SO_4 (3-6 g).
      2. $AgNO_3$ (3 g).
      3. KI (50 g).
   b. Dissolve the chemical in 100 ml of DI H_2O.
   c. Fill the fritted sample post-scrubber with 10-15 ml of the scrubbing solution (save the remaining post-scrubber solution).
   d. If using one of the silver solutions, add 1 ml of 30% hydrogen peroxide (H_2O_2) to the solution in the scrubber daily.
4. Maintenance of the post-scrubber.
   a. The post-scrubber solution should be changed on a weekly basis. Change earlier if the frit becomes clogged or if the analysis 'blanks' register high (refer to step 8 of section '2.7 Sample Analysis' in this SP.

2.9.2 Sample Analysis using the Acidification Apparatus

1. Assemble the apparatus according to the operation manual for acidification module.
2. If the procedure requires heating of the sample (some samples require heating to aid digestion), move the sample column assembly into position so that the sample flask is in the heater (consult the operator's manual). Heating requires the flux of water through the condensing column to prevent sample loss due to evaporation. The sample is typically heated to 100°C-150°C.
3. Make sure the Teflon™ tubing exiting the post-scrubber is attached to the intake valve in the back of the CO_2 coulometer (blue fitting).

4. Turn '**ON**' the acidification module's main power switch.
5. Select the carrier gas setting; either '**INT**' when using the internal air pump or '**EXT**' when using an externally connected gas source. The incoming gas should be regulated to 5-7 psig.
6. Open the valve on the flow meter and set to 100 ml/min.
7. Set heater on 5-6 if heating is needed. This can be increased or decreased as desired for specific analysis.

Solid Samples

1. Deliver a known weight of sample into a sample flask. The sample size should be selected so that the sample contains **1-3 mg C (inorganic carbon)**. **Note**. A 'blank' must be run before any of the weighed samples can be analyzed (refer to step 9 of section '2.7 Sample Analysis' in this SP).
2. The sample can be weighed into a porcelain boat or other inert vessel and transferred into the sample flask or weighed directly in the sample flask. Take care when weighing finely powdered samples for static electricity can cause this particle flour to stick to the walls of the sample flask. The mineral acid will not react with sample particles that are not properly washed to the bottom of the flask before analysis. Use DI H_2O to flush sample to the bottom of the flask.
3. The sample flask need not be dry, but **MUST** be acid free.
4. Attach the sample flask to the condenser of the sample column assembly using a threaded joint connector. This connector is rust colored.
5. Carrier gas is allowed to flow through the sample column assembly and the sample flask in order to purge atmospheric CO_2 for 1-2 minutes.
6. After 10 seconds, slowly and evenly dispense an aliquot (2-4 ml) of mineral acid (refer to section '2.9.1 Acid Solutions' in this SP) into the sample column assembly. The acid will react with the sample and form CO_2. The CO_2 will then be swept into the CO_2 coulometer cell where it can be quantitatively measured. To begin analysis set-up refer to section 2.7 of this SP.
7. When all the CO_2 has been evolved and the CO_2 coulometer has finished titrating, the coulometer will briefly display the final results of the analysis. Select '**NEXT**' to analyze the next sample.

Liquid Samples

1. Fluid liquids are directly injected through the septum of the sample column adapter using a syringe or directly into the sample column and are analyzed using the same method as for solids (refer to section above 'Solid Samples' in this SP).
2. Viscous liquids should be introduced to the system in the same manner as a solid sample and analyzed using the same method (refer to section '2.7.5.1 Solid Samples' in this SP).

2.9.3 Acidification Apparatus Shut Down

1. Close the valve on the gas flow meter.
2. If the heating unit was used, rotate the temperature dial to '0'.
3. Turn '**OFF**' the acidification module's main power switch.
4. Remove and properly dispose of the used sample.
5. Clean and thoroughly dry the sample flask.
6. To prevent residual acid from marring the exterior of the apparatus, keep a sample flask connected to the condenser on the column assembly when the system is not in use.

2.10 Data Collection Methods

2.10.1 Data Storage

All analytical data and instrument parameters are saved to the SD (Secure Digital) Card during operation of the instrument. The SD Card must be installed for proper operation of the CM5015. Install the SD card into the slot on the left side of the instrument. The card is installed with the cold contacts facing the front of the instrument.

2.10.2 External Data Connections

The CM5015 is provided with serial and Ethernet ports for connection of the coulometer to a remote computer for data collection, and is also equipped with a USB2.0 All-in-1 Card Reader.

Serial Data Connection

1. Attach one end of the supplied serial cable (CM161-144) to the serial port on the left side of the CM5015.
2. Connect the other end of the serial cable to an available COM port on the remote computer. Please note that many new computers are supplied without COM ports. In these instances it will be necessary to use a Serial-to-USB converter and utilize an available USB connection.
3. Prepare the remote computer to accept the following serial port configuration settings:
   Baud Rate = 9600
   Data Bits = 8
   Parity = none
   Stop Bits = 1
   Flow Control = Hardware

Ethernet Data Connection

1. Attach one end of the supplied Ethernet cable (CM161-145) to the Ethernet port on the left side of the CM5015.
2. Connect the other end of the Ethernet cable to an available Ethernet port on the remote computer.
3. Prepare the remote computer to accept the following Ethernet port settings:
   Host Address = 192.168.11.2
   Port Number = 5000
   Connect Using = TCP/IP (Winsock)
   *A proper Ethernet connection will not be established until the CM5015 power is turned on.

USB Converter Connection

1. Turn off the CM5015 or make sure that the program is showing the Main Menu Screen (this is to make sure that the SD Card is not running).
2. Carefully remove the SD Card from the left side of the CM5015.
3. Insert the SD Card into the provided USB 2.0 All-in-1 Card Reader device. Make sure that the gold contacts of the SD Card are facing the gold prongs in the USB 2.0 All-in 1- Card Reader slot.
4. Connect the small end of the provided USB adapter cable to the USB 2.0 All-in-1 Card Reader.
5. Transport the device and cable to a computer and connect the USB end (larger end) of the cable to the USB port of a computer.
6. Download the data and save it to the computer, detach the device. Carefully remove the SD Card from the USB 2.0 All-in-1 Card Reader and insert it into the CM5015 (refer to 2.8.1 Data Storage of this SP).

2.11 Clean-Up Procedures and Maintenance

Daily Maintenance of the CO_2 Coulometer Cell

The CO_2 coulometer cell should be cleaned as needed. It is recommended that the user clean the cell approximately every 2-3 days (if samples are very high Carbon, it may need to be cleaned more frequently). The steps for cleaning are as follows:

1. Empty cathode, anode and potassium iodide waste into separate appropriate containers (anode waste and potassium iodide can be combined).
2. Rinse the entire cell thoroughly with DI water.
3. Fill the cathode side with a 1:1 ratio of HNO3 and DI water and allow this to sit over night (at least 8 hours).
4. Dispose of the 1:1 solution of HNO3 in the Acid Waste container.
5. Rinse thoroughly with DI water.
6. Fill the Cathode side of the cell with DI water until it is above the frit opening on the Cathode side.
7. Connect a vacuum pump to the anode arm and pull DI water through the frit until the level is above the frit on the Anode side.
8. Pour out water and Repeat steps 6 and 7 three times.

For more cleaning advice, review the CO_2 Coulometer manual.

2.12 References

1. UIC Inc. *Operation manual for the CM5015 CO_2 Coulometer*. Version 1.1.
2. UIC Inc. *Operation manual for CM5130 Acidification Module* .
3. UIC Inc. *Operation manual for CM5300 Furnace Apparatus*. Version 1.0. CM440-026
4. ASTM. 2005. *Standard Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometeric Detection*. D4129-05. West Conshohocken, PA: ASTM International Standard test methods for total and dissolved carbon dioxide in water.
5. ASTM. 2002. *Standard Practice for Total and Dissolved Carbon Dioxide in Water*. D513-02.West Conshohocken, PA: ASTM International.

3.0 Records

Analysis summary reports will be recorded in laboratory notebooks or in project-specific binders. Readings for the instrument check standards will be documented in the coulometer log book. All records will be prepared and submitted to the WIPP Records Center in accordance with NP 17-1 (Records). The following table summarizes the Quality Assurance (QA) records:

QA Record

- Scientific Notebook
- Summary Report

4.0 Appendices

No appendices are applicable to this SP.

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