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NUCLEAR WASTE MANAGEMENT PROGRAM PROCEDURE

SP 12-2

USE AND MAINTENANCE OF THE UIC, INC. MODEL CM5014 CO₂ COULOMETER, CM5130 ACIDIFICATION MODULE AND CM5120 FURNACE APPARATUS

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(printed name) (signature) date

1.0 Purpose and Scope

Operation guidelines for the UIC, Inc. CM5014 CO₂ Coulometer, the CM5130 Acidification Module and the CM5120 Furnace Apparatus are included in this project specific procedure (SP). This SP will be used to analyze for total carbon (C), carbon dioxide (CO₂), carbonate (CO₃) and surface carbon and will support the activities described in several test plans (TP), including, but not limited to, TP 99-04 "Disturbed Rock Zone Characterization Test Plan"; TP 00-02 "Collection and Analysis of Downhole Cement and Steel Samples During Borehole Plugging and Abandonment"; TP 00-04 "Laboratory Analysis of Samples Collected from the Disturbed Rock Zone"; and TP 00-07 "Experimental Study of WIPP MgO Backfill at Sandia National Laboratories' Carlsbad Facility".

Acronyms and definitions for terms used in this procedure may be found in the Nuclear Waste Management Program (NWMP) Glossary located at the Sandia National Laboratories NWMP On-line Documents web site.

2.0 Implementation Actions

2.1 General Function of the CO₂ Coulometer

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. CM5014 CO₂ Coulometer, the CM5130 Acidification Module or the CM5120 Furnace Apparatus. The user is responsible for reading and understanding the manuals, which are available at the site of use for each apparatus.

The CM5014 CO₂ Coulometer provides for the highly accurate and absolute determination of carbon in any gas stream containing carbon dioxide (CO₂). When coupled with either of the two carbon front

end units, (the CM5130 Acidification Module or the CM5120 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 CO₂, whereas the furnace apparatus administers extreme heat (500°C-1000°C) to complete this process. Both instruments then purge the CO₂ 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 5 g of 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 CO₂ coulometer cell compartment between the light source and the photodetector.

During sample analysis, CO₂ 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 CO₂ moves into the cell, it is absorbed by the cathode solution and reacts with the monoethanolamine to form a tritatable acid. This acid then reacts with the colorimetric pH indicator, causing the solution to fade or clear. As subsequent CO₂ enters the cell, the photodetection 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 CO₂ 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 CO₂ 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 CM5014 CO₂ Coulometer. During sample analysis, the CO₂ 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 (CO₂), carbonate (CO₃) and surface carbon.

Both the Sandia National Laboratory (SNL) and contractor personnel will use this SP. Responsibilities and interfaces affected by this SP are promulgated in TP 99-04, TP 00-04 and TP 00-07.

2.2 CO₂ Coulometer Cell Setup

2.2.1 Cathode Cell Body and Platinum Electrode

1. Start with a clean, dry CO₂ 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 100-125 ml of carbon cathode solution, 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 a fire proof 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.

2.2.2 Anode Cell Side Arm and Silver Electrode

1. Add 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 fire proof 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.

2.3 Operation of the CM5130 Acidification Module

Samples are acidified at room temperature or in the heated reaction vessel to evolve forms of inorganic carbon as CO₂. Internally compressed air, scrubbed free of CO₂, serves as a carrier gas for the evolved CO₂, transporting it from the sample flask of the sample column assembly through a post-scrubbing system and into a cell in the CO₂ coulometer for quantitative measurement.

2.3.1 Pre-Scrubber (Air Scrubber)

1. The pre-scrubber is employed to remove initially accumulated CO₂ from the system and to remove CO₂ 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 45 g of KOH and dilute to 100 ml with deionized water (DI H₂O). Use caution when adding DI H₂O to the KOH, as this is an exothermic reaction.
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 H₂O. 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.

2.3.2 Acid Solutions

1. Mineral acids are employed by the module for the evolution of CO₂. The investigator or 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 H₂SO₄): sulfate precipitation may occlude portions of the sample's inorganic carbon.
 - c. Perchloric acid (2N HClO₄): 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 (SnCl₂) or iron sulfate (FeSO₄) may be used.
5. For special applications, other acids and or different concentrations may be employed.
6. When using sulfuric acid (2N H₂SO₄) to evolve CO₂ 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 CO₂ from the sample, the recommended post-scrubber solution is silver nitrate (3% AgNO₃) acidified to pH 3.

2.3.3 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. Saturated silver sulfate (3-6% Ag₂SO₄) acidified to pH 3.
 - b. Silver nitrate (3% AgNO₃) acidified to pH 3. Use with hydrochloric acid (2N HCl).
 - c. Potassium iodide (50% KI) acidified to pH 3. Use with sulfuric acid (2N H₂SO₄).
3. Preparation of the post-scrubber solution.
 - a. Weigh out the appropriate amount of chemical to prepare 100 ml of scrubbing solution:
 1. Ag₂SO₄ (3-6 g).
 2. AgNO₃ (3 g).
 3. KI (50 g).
 - b. Dissolve the chemical in 100 ml of DI H₂O.
 - 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 (H₂O₂) 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 10 of section '2.5.3 Run Analysis' in this SP).

2.3.4 Sample Analysis

2.3.4.1 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 '2.5.3 Run 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 H₂O to flush sample to the bottom of the flask.
3. The sample flask should be $\leq 30^{\circ}\text{C}$. 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. Turn 'ON' the acidification module's main power switch.
6. Select the carrier gas setting; either 'INT' when using the internal air pump or 'EXT' when using an externally connected gas source. **Note.** An external carrier gas supply is not required when using the UIC, Inc. Model CM5014 CO₂ Coulometer. This coulometer is

equipped with an internal air pump. If an external carrier gas source is required, make sure the incoming gas is regulated to 5-7 psig.

7. Carrier gas is allowed to flow through the sample column assembly and the sample flask in order to purge atmospheric CO₂ for 1-2 minutes.
8. Open the valve on the flow meter and set to 100 ml/min.
9. Make sure the Teflon™ tubing exiting the post-scrubber is attached to the intake valve in the back of the CO₂ coulometer (blue fitting).
10. 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.
11. When the screen on the CO₂ coulometer reads:

Screen **SAMPLE ENTRY SCR-3**
READY TO RUN
'ENTER' TO BEGIN

and the system has been purged of atmospheric CO₂ (1-2 min), press '**ENTER**'. Analysis will begin.

12. After 10 seconds, slowly and evenly dispense an aliquot (2-4 ml) of mineral acid (refer to section '2.3.2.7 Acid Solutions' in this SP) into the sample column assembly. The acid will react with the sample and form CO₂. The CO₂ will then be swept into the CO₂ coulometer cell where it can be quantitatively measured.
13. When all the CO₂ has been evolved and the CO₂ coulometer has finished titrating, the coulometer will briefly display the final results of the analysis and generate a printout of these results. This printout should be saved in a project-specific binder or entered into the project's scientific notebook (SN).
14. The CO₂ coulometer prompts for another sample.

15. **Screen** **SAMPLE ENTRY SCR-4**
RUN ANOTHER SAMPLE?
Y for YES N for NO

Answering '**Y**' prompts the **SAMPLE ENTRY SCR-2** screen to appear. Repeat steps 13 through 17 of section '2.5.3 Run Analysis' in this SP, until all samples have been analyzed.

Answering '**N**' to the prompt terminates the analytical mode and the '**SUMMARY REPORT**' is printed. This printout should be saved in a project-specific binder or entered into the project's SN.

2.3.4.2 Liquid Samples

1. Fluid liquids are directly injected through the septum of the sample column adapter using a syringe and are analyzed using the same method as for solids (refer to section '2.3.4.1 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 '2.3.4.1 Solid Samples' in this SP).

2.3.5 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.

2.4 Operation of the CM5120 Furnace Apparatus

Samples are combusted with oxygen to convert organic and inorganic forms of carbon to carbon dioxide (CO₂). The combustion temperature is operator selected (up to 1000 °C) to completely oxidize either all carbon forms or to selectively oxidize organic carbon. Samples are introduced to the system using either a quartz glass ladle or a syringe. 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 CO₂. Non-carbon combustion products that can interfere with CO₂ measurement, (ie., SO₂, SO₃, HX, NO_x) are removed from the gas flux using a series of chemical post-scrubbers. The remaining CO₂ subsequently enters the coulometer cell and is quantitatively measured by the instrument.

2.4.1 Pre-Scrubber (Air Scrubber)

1. The furnace apparatus is equipped with a pre-scrubber that is identical to that on the acidification module. Refer to section '2.3.1 Pre-Scrubber (Air Scrubber)' in this SP for use and maintenance of the pre-scrubber.

2.4.2 Magnesium Perchlorate Post-Scrubber

1. The magnesium perchlorate (Mg(ClO₄)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(ClO₄)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(ClO₄)₂ post-scrubber.
 - a. Mg(ClO₄)₂ can form a solid mass as it becomes hydrated, blocking the gas flow through the system.
 - b. The Mg(ClO₄)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.

2.4.3 NO_x Post-Scrubber

1. This scrubber is filled with acid dichromate on silocel and a specially prepared manganese dioxide.
The dichromate and MnNO₂ 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 MnNO₂ 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 MnNO₂ is exhausted, therefore it should be changed when the acid dichromate is replaced.

2.4.4 Initial Preparation

1. Connect the appropriate pre-scrubber, post-scrubbers and combustion tubes as described in the instrument's user manual.
2. Regulate the pressure of the oxygen supply at the tank to 5-10 psig.
3. Set the O₂ 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 Lindberg 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 CO₂ coulometer. If the system is leak-free, the pressure caused by the blocked line will stop the bubbling in the KOH pre-scrubber.
9. When a new or repacked combustion tube is first used, overnight conditioning is recommended before running any samples. The combustion tube is conditioned by running the empty furnace at 650°C for 2 hours.

2.4.5 Sample Analysis

2.4.5.1 Total Carbon Analysis (TC)

1. TC analysis requires no chemical pretreatment of the sample. Combustion temperatures are typically set to 900°C-1000°C.

2.4.5.2 Total Organic Carbon Analysis (TOC)

1. Method I: 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 650°C). Samples are not chemically pretreated, although bicarbonates must be abrogated prior to analysis by heating the sample to 130°C.

2.4.5.3 Solid Samples

1. Finely ground and homogenous, solid samples are introduced into the furnace's combustion tube by means of a quartz glass ladle.
2. Weigh the sample into either a platinum or porcelain boat. The sample size should be selected so that the sample contains **1-3 mg C (organic and inorganic carbon)**. **Note**. A 'blank' must be run before any of the weighed samples can be analyzed (refer to step 9 of section '2.5.3 Run 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. Place the filled platinum or porcelain boat into a dry, cool ladle.
5. Unscrew the solid brass cap on the breach block and carefully insert the ladle into the combustion tube. Make sure the sample does not enter the furnace.

6. Hand tighten the solid brass cap on the breach block and allow 1-3 minutes for any atmospheric CO₂ that has entered the system to be purged by the O₂ and the pre-scrubber.
7. At this time, the screen on the CO₂ Coulometer should read:
Screen SAMPLE ENTRY SCR-3
READY TO RUN
'ENTER' TO BEGIN
Press '**ENTER**'. Analysis will begin.
8. After 10 seconds, carefully move the ladle into the furnace using a magnet, making sure not to spill the contents of the ladle in the combustion tube.
9. When all the CO₂ has been evolved and the CO₂ coulometer has finished titrating, the coulometer will briefly display the final results of the analysis and generate a printout of these results. This printout should be saved in a project specific-binder or entered into the project's scientific notebook (SN).
10. Using the magnet, remove the ladle from the furnace and allow the ladle to cool in the combustion tube before opening the breach block, removing the ladle and beginning the next analysis. **Note**. Take care when introducing and removing the ladle, for it is extremely delicate.
11. The CO₂ coulometer prompts for another sample.
12. **Screen SAMPLE ENTRY SCR-4**
RUN ANOTHER SAMPLE?
Y for YES N for NO

Answering '**Y**' prompts the **SAMPLE ENTRY SCR-2** screen to appear. Repeat steps 13 through 17 of section '2.5.3 Run Analysis' in this SP, until all samples have been analyzed.

Answering '**N**' to the prompt terminates the analytical mode and the '**SUMMARY REPORT**' is printed. This printout should be saved in a project specific binder or entered into the project's SN.

2.4.6 Overnight Apparatus Shut Down

1. Lower the temperature on the furnace to 200°C. Do not lift the lid to the furnace while the furnace is '**ON**'.
2. Set the O₂ flow on the furnace apparatus to 10-20 cc/min.
3. **NEVER** shut off the O₂ while the furnace is '**ON**'.

2.4.7 Long Term Apparatus Shut Down

1. Remove the cell from the CO₂ Coulometer.
2. Set the O₂ flow on the furnace apparatus to 10 cc/min.
3. Lower the temperature on the furnace to 25°C. Do not lift the lid to the furnace.
4. When the furnace has cooled to room temperature (25°C), the unit may be turned '**OFF**'. This not only prevents an explosion from occurring, but will help prolong the life of the heating elements and protect the combustion tube from thermal shock.
5. **NEVER** shut off the O₂ while the furnace is '**ON**'.
6. Turn '**OFF**' the furnace apparatus main power switch.
7. Turn '**OFF**' the O₂ at the furnace and then shut '**OFF**' the O₂ at the tank.
8. Keep the lid to the furnace closed to help protect the combustion tube.

2.5 Operation of the CM5014 CO₂ Coulometer

2.5.1 Setting Parameters

1. Turn 'ON' the CM5014 CO₂ Coulometer (wait 30 seconds).
2. **Screen** **UIC, Inc. with blinking 'READY'**
Press any arrow (←↑→↓).
3. **Main Menu** **RUN ANALYSIS**
CELL SETUP
RUN DIAGNOSTICS
Arrow down and highlight 'RUN DIAGNOSTICS'.
Press 'ENTER'.
4. **Screen** **DIAGNOSTICS SCR-1**
 1. **CHANGE SETTINGS**
 2. **PRINT SETTINGS**
 3. **SET DATE AND TIME**
 4. **EXIT DIAGNOSTICS**
5. At this point, make sure the Epson LQ-570+ printer is connected properly and turned 'ON'.
Note. The printer requires continuous feed computer paper (tractor pull paper) for the coulometer to work properly.
6. **Note.** Select '3. SET DATE AND TIME' the very first time the machine is activated. After the initial date and time settings are input, they do not need to be changed again.
7. Select '1. CHANGE SETTINGS'.
8. **Screen** **ANALYSIS TYPE**
 1. **CARBON**
 2. **CO₂**
 3. **CO₃**
 4. **OXYGEN**
 5. **SURFACE CARBON**Select the type of the analysis desired.
9. **Screen** **SELECT UNITS**
W for WEIGHT
V for VOLUME
N for UNITS
Select the desired units.
10. **Screen** **WEIGHT UNITS**
 1. **for GRAMS**
 2. **for MILLIGRAMS**
 3. **for MICROGRAMS**Select the weight units desired.

11. **Screen**

DEFAULT SETTINGS
DIFFERENCE %

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 CO₂ is evolving very slowly from the sample. The default value for this setting is 0.1%.

Press 'ENTER'.

12. **Screen**

DEFAULT SETTINGS
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 it's 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 'ENTER'.

13. **Screen**

DEFAULT SETTINGS
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 13 of section '2.3.1 Setting Parameters' in this SP. The default value is 5.

Press 'ENTER'.

14. **Screen**

DEFAULT SETTINGS
TIMING INTERVAL

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 'ENTER'.

15. **Screen**

SELECT IF TIMING METHOD IS
1. COULOMETER ENDPOINT DETERMINATION
2. 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.

Select '1. COULOMETER ENDPOINT DETERMINATION'.

16. **Screen**

SELECT SAMPLING METHOD
1. MANUAL
2. AUTOSAMPLER

The lab does not employ an autosampler.

Select '1. MANUAL'.

17. **Screen** **SELECT PRINTOUT METHOD**
 1. **CAL TEST**
 2. **NORMAL**

CAL TEST is used for factory testing. **NORMAL** allows for the standard printing of all analyzed data.
Select '**2. NORMAL**'.

18. **Screen** **SELECT WRITE TO DISK**

Y – YES
N – NO

Select '**Y**' if data archiving is desired and insert a correctly formatted disk. The data is stored in '.TXT' format. Otherwise select '**N**'. The '**SUMMARY REPORT**' that is printed at the end of analysis is adequate documentation for QA purposes.

19. **Screen** **DIAGNOSTICS SCR-1**
 1. **CHANGE SETTINGS**
 2. **PRINT SETTINGS**
 3. **SET DATE AND TIME**
 4. **EXIT DIAGNOSTICS**

Select '**2. PRINT SETTINGS**' to obtain a printout of the current instrument settings.
Select '**4. EXIT DIAGNOSTICS**' to return to the main menu.

20. END OF DIAGNOSTICS SCR-1.

21. **Main Menu Screen** appears.

2.5.2 Run Cell Setup

1. Arrow up and highlight '**RUN CELL SETUP**'.
2. Press '**ENTER**'.
3. **Screen** **INSERT CELL AND ADJUST FOR MAXIMUM RESPONSE, PRESS F2**
CELL #### (blinking)
4. Insert the CO₂ coulometer cell that has been prepared as specified in section '2.2 CO₂ Coulometer Cell Setup' in this SP.
5. 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.
6. Plug in the 'banana plug' platinum cathode (black).
7. Plug in the silver anode (red).
8. 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.
9. The screen displays an 'unprocessed' response value having a range between 0 and 4095. At 4095, the system's electronics are at their maximum and the 'true' 100%

transmissivity (100%T) and the 29%T 'end point' will be calculated erroneously. To correct for this, physically reposition the CO₂ Coulometer cell by carefully rotating the cell to either the left or right, making sure that the response level recorded on the screen is between 3900 and 3949. **This value is not to exceed 3950.** Ensure that the detector light path is not blocked by the cell silk screening, the platinum cathode or the sample gas inlet tube.

10. When a maximum value of 3900-3949 has stabilized, press '**F2**'. This value represents the cell's maximum transmissivity (100%T) and will be retained in the system memory until the CO₂ coulometer is either shut down or the settings are changed.
11. **Turn the cell current switch 'ON' before proceeding.**
12. **RUN CELL SETUP'** is now complete.
13. Close the cell compartment door to assure that the cell is not inadvertently repositioned.
14. **Main Menu Screen** appears.

2.5.3 Run Analysis

1. Arrow up and highlight '**RUN ANALYSIS**'.
2. Press '**ENTER**'.
3.

<u>Screen</u>	100.00	0.0
	%T	CELL I
4. The CO₂ coulometer will titrate to the end point (29.5%T) to remove CO₂ initially present in the cathode solution. **Allow the CO₂ coulometer to titrate for a minimum of 30 minutes.** Press '**F2**'.
5. If the (%T) requires manual adjustment between analysis runs, the cell must be allowed to reach a new endpoint before beginning any subsequent analysis. This is accomplished by disconnecting the gas inlet flow line from the check valve in the back of the CO₂ coulometer (blue fitting) and carefully blowing into the valve until the cell solution in the cathode compartment is clear. Turn the cell current switch '**ON**' and allow the cell to titrate to its endpoint. After 30 minutes of titration, press '**F2**'. The next screen to appear is **SAMPLE ENTRY SCR-1**.
6.

<u>Screen</u>	<u>SAMPLE ENTRY SCR-1</u>
	PLEASE ENTER NUMBER of SAMPLES 50 MAX
	ENTER, BACK to REDO
	<u>01</u> '<i>blinking</i>'

Enter the number of samples to be analyzed. If the **MANUAL** sampling method has been selected, keep the default value of 01.
Press '**ENTER**'.
7.

<u>Screen</u>	<u>SAMPLE ENTRY SCR-2</u>
	SAMPLE #1 of 1
	NAME _____.

WEIGHT _____ $\mu\text{g}/\text{mg}/\text{g}$.

8. **IMPORTANT**. Before analyzing every new suite of samples, a 'blank' must be run. The CM5014 CO₂ coulometer will correct each analysis run for the initially determined 'blank' value.
9. Running the 'blank': if the analysis is being performed on the CM5130 Acidification Module, attach an empty sample flask to the condenser of the sample column assembly as described in '2.3.5 Sample Analysis' in this SP. Wait 1-2 minutes before proceeding. This is to expunge any atmospheric CO₂ that may be in the system. If the CM5120 Furnace Apparatus is being used, make sure the combustion tube is empty and that the breech block assembly has been hand tightened. Wait 1-2 minutes before proceeding to expunge any atmospheric CO₂ that may be in the combustion tube. The word 'blank' must be keyed into the first SAMPLE ENTRY SCR-2. No weight for the 'blank' is required. Press '**ENTER**'. When the CO₂ coulometer has finished analyzing the 'blank', weighed samples may be analyzed. A 'blank' value of less than 1.00 is desired.
10. High 'blanks' are those values greater than 1.00 and indicate excessive quantities of CO₂ 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**).
 - c. Post-scrubber solutions or compounds are exhausted (**replace the solutions**).
 - d. The combustion tube of the furnace apparatus has not been 'conditioned' (**condition the tube; refer to step 9 in section '2.4.4 Initial Preparation' in this SP**).
 - e. The barium chromate of the pre-combustion tube is exhausted (**replace the BaCrO₄**).
 - f. Leaks in the system (**check the lines and connectors and seal the leak**).
 - g. The furnace temperature is too high (**lower the furnace temperature**).
 - h. Coulometer trouble (**call UIC, Inc. @ 1-800-342-5842**).

11. **Screen** **SAMPLE ENTRY SCR-3**
READY TO RUN
'ENTER' TO BEGIN

Press '**ENTER**'. Analysis begins.

12. After the 'blank' has been run ('blank' < 1.00), proceed with the weighed sample analysis.
13. Manually load a weighed sample into one of the front end devices; either the CM5130 Acidification Module (refer to section '2.3.4 Sample Analysis' in this SP) or the CM5120 Furnace Apparatus (refer to section '2.4.5 Sample Analysis' in this SP).

14. **Screen** **SAMPLE ENTRY SCR-2**
SAMPLE #1 of 1
NAME _____.
WEIGHT _____ $\mu\text{g}/\text{mg}/\text{g}$.

Key in the name of the sample (8 digits maximum).
Press '**ENTER**'.

Key in the weight of the sample.
Press **ENTER**.

15. When the sample has been successfully loaded and the CO₂ from the sample flask and column assembly has been purged through the post-scrubbing system (1-2 minutes), press **ENTER**.
16. The CO₂ 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 13 of section '2.5.1 Setting Parameters' in this SP.

17. **Screen** **SAMPLE ENTRY SCR-4**
 RUN ANOTHER SAMPLE?
 Y for YES N for NO

Answering **'Y'** prompts the **SAMPLE ENTRY SCR-2** screen to appear. Repeat steps 13 through 17 of this section until all samples have been analyzed.

Answering **'N'** to the prompt terminates the analytical mode and the **'SUMMARY REPORT'** is printed. This printout should be saved in a project specific binder or entered into the project's SN.

18. When analysis is complete and the **'SUMMARY REPORT'** has been printed, turn the cell current switch and the CO₂ coulometer's main power switch **'OFF'**.
19. Turn the printer **'OFF'**.
20. Remove and clean the cell (refer to section '2.6.1 Daily Maintenance of the CO₂ Coulometer Cell' in this SP).

2.6 Maintenance of the CM5014 CO₂ Coulometer

2.6.1 Daily Maintenance of the CO₂ Coulometer Cell

The CO₂ coulometer cell's cathode and anode solutions need to be emptied after each day's use. The CO₂ coulometer cell should be thoroughly cleaned immediately after emptying the cell of these fluids and then dried. Refill both the cathode and anode compartments just prior to next usage.

1. Turn **'OFF'** the cell current switch and the CO₂ coulometer main power switch.
2. Unplug the electrodes, loosen the gas inlet tube (blue fitting) and the gas exit vent line (red fitting) from the back of the cell compartment and remove the cell from the cell holder.
3. Dispose of the cell solutions and KI as hazardous waste.
4. Rinse the cell body, the cell side arm, both of the tops and the electrodes thoroughly with DI H₂O.
5. Clean the glass frit between the cathode body and the anode side arm compartments of the cell by vacuum pulling methanol (methyl alcohol) and then DI H₂O through the frit from the cell body into the cell side arm.
6. The vacuum tubing is connected to a stopper fitting the anode compartment. Methanol is placed in the cathode body compartment; the vacuum is then turned on, pulling the methanol through the frit and into the anode side arm compartment.
7. Repeat this process using DI H₂O. Pull the DI H₂O from the cathode compartment into the anode compartment.

8. Rinse the CO₂ coulometer cell with DI H₂O and dry in a laboratory oven (84°C).
9. Store the clean cell compartment in the cell holder of the CO₂ coulometer to prevent breakage.

2.6.2 Lifetime Maintenance

1. Over time, component parts will require a more thorough cleaning. To thoroughly clean the frit between the cathode cell body and the anode side arm compartment, fill both compartments with enough 1:1 (nitric acid:DI H₂O) to completely cover the frit.
2. Soak overnight.
3. Dispose of the acid solution in accordance with the SOP when finished. Clean and rinse the cell completely as described in steps 4 through 9 of section '2.6.1 Daily Maintenance of the CO₂ Coulometer Cell' of this SP.
4. If the KI turns brown after refilling the anode side arm compartment, empty and clean with methanol and then DI H₂O as described in section '2.6.1 Daily Maintenance of the CO₂ Coulometer Cell' of this SP.
5. If the platinum electrode appears tarnished, soak the electrode in 1:1 (nitric acid:DI H₂O) for several hours.
6. Always dispose of chemicals properly, as described in the laboratory Standard Operating Procedure (SOP).

2.7 Safety and Training

Safety and training requirements for use of this equipment are dependent upon the nature of the samples being analyzed, and are described in the ES&H Standard Operating Procedure (ES&H SOP), SP-C001, Issue A and in the Preliminary Hazard Screening (PHS) and Hazard Analysis (HA), number SNLA00249-001, for the site at which the work is being performed. These requirements shall be adhered to while doing any work with this equipment. Material Safety Data Sheets (MSDS) will be reviewed prior to the use of all chemicals. All chemicals will be disposed of properly, as described in the laboratory Standard Operating Procedure (SOP).

3.0 Records

Analysis printouts and summary reports will be recorded in laboratory notebooks or in project-specific binders. 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) requirements:

<u>QA Record</u>	<u>Preparer</u>	<u>Records Submitter</u>
• Analysis Printout	Principal Investigator/Technician	Principal Investigator/Technician
• Summary Report	Principal Investigator/Technician	Principal Investigator/Technician
• Scientific Notebook	Principal Investigator/Technician	Principal Investigator/Technician

4.0 Appendices

No appendices are applicable to this SP.

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