DETERMINATION OF CARBONATE CARBON AND DISSOLVED CO_2 IN SOLID AND LIQUID SAMPLES WITH AN AUTOSAMPLER

Figure 1: CM245 Total Inorganic Carbon (TIC) Analyzer with Autosampler

PRINCIPLES OF OPERATION

Automated front-end acid digestion unit (CM5700B TIC Autosampler) is used to convert inorganic carbon species into CO_2. The generated CO_2 is transported in an inert (nitrogen) carrier gas stream to a CM5017 Coulometer. In the coulometer, the CO_2 is absorbed in a titration cell containing monoethanolamine and a colorimetric pH indicator. The CO_2 reacts with the monoethanolamine to form a strong, titratable acid. The acid decolorizes the pH indicator. A photo detector monitors the indicator color change, and titration current is automatically activated in direct proportion to the fading of the indicator to electrochemically generate base to return the solution to its original color. Since the current is, in effect, the titrant, there is no need for user calibration of the coulometer.

PROCEDURE

1. Assemble and prepare the components for operation as described in the Instruction Manuals.
2. Charge the glass sample flasks (further in text referred to as flasks) with a known weight of sample and place them into the carousel. Up to 15 (with 80 ml flasks) or 30 samples (with 20 ml flasks) can be analyzed in a single run. Sample size ideally should be selected to contain 1 – 3 mg carbon. Use provided plastic caps and septa to seal each flask.

NOTE: Samples can be either weighed into re-useable Teflon™ cups that are thereafter placed into flasks or weighed directly into the flasks. It is important to record precise weights. Water and liquid samples that are handled with a syringe can be directly injected into flasks through the septa, in which case precise volume should be recorded.

3. If temperatures higher than 45 C are used, connect the condenser to a water source/sink or a cooling bath.
4. Perform the leak check. Refer to the CM5700B Manual for leak check procedure. If there are no leaks proceed to step four. If there are leaks, resolve them before continuing.
5. Place an empty flask for Blank measurement in position 1 (it is recommended to measure two Blanks, in positions 1 and 2).
6. Place flasks with samples in other positions (after blanks, one or more positions can be used for flasks with standards).
7. Select parameters on the CM5700B TIC Autosampler and on the CM5017 Coulometer.
8. Press Begin Analysis on the CM5017 Coulometer and it will activate the CM5700B. The system will measure all the flasks positioned in the carousel.
9. When all CO_2 is evolved and titrated, the CM5017 automatically detects the endpoint, ends the analysis, and prints the result to a USB Flash Drive and/or printer*. After the analysis is terminated by the Coulometer, the CM5700B goes through a cleaning cycle.

(*) – *Endpoint determination and result calculations are performed automatically based on user selectable settings entered into the CM5017 Carbon Coulometer.*

RESULTS

When samples contain over 1000 µg C, the titration accuracy is better than +/-0.15% relative. Overall accuracy is typically +/-0.3% relative. When sample availability or volume limits the amount of CO_2 evolved to lesser amounts, the accuracy is generally better than 1 µg C. For waters, dissolved CO_2 accuracy is better than +/-0.5 ppm C when 5 ml samples are used (Larger sample sizes are possible, but sample stability normally limits the accuracy and any benefits from using larger samples).

Analysis times are typically 6 to 8 minutes. For some samples, such as dolomitic limestones, the reaction time with acid is very slow, thus extending the analysis time. Heating and stirring capabilities are included with the CM5700B TIC Autosampler to assist in the evolution of carbon dioxide.

A major advantage of the Carbon Coulometer is that the analysis completion can be seen, avoiding low results due to incomplete analysis times or wasted time due to overly long analysis times. Other advantages include the easy addition or modification of scrubbers, the ability to use different acids and the ease of using wetting/emulsifying agents and indicators in the acid.

ADDITIONAL INFORMATION

Additional details about this method are included in the ASTM D-513 Method G, "Carbon Dioxide CO_2 Evolution, Coulometric Titration Method". The method is under jurisdiction of ASTM Committee D19.05 and is available from ASTM.

For information about the instrument's capabilities for specific types of samples, contact UIC Europe.