The Comparison of The Results of The Automated Inorganic Carbon (C-CO$_3$) Analyzer (Model Calcis Auto) and The Scheibler Calcimeter

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OUTLINES

• Scheibler Calcimeter, Advantages and Disadvantages
• How Automated Inorganic Carbon (C-CO$_3$) Analyser Works and A New Approach: Static Headspace Method
• Advantages and Disadvantages of Inorganic Carbon (C-CO$_3$) Analyser
• Measurement Results of Samples for Both Methods
• Discussion of Results
Scheibler Calcimeter

The carbonate content of soil is determined by treating the sample with acid in an enclosed reaction cylinder (sample cup). Carbon dioxide (CO$_2$) gas is evolved during the reaction between the acid and carbonate fraction of the soil sample. The resulting pressure or volume of CO$_2$, generated in the closed reactor is proportional to the calcite (calcium carbonate) equivalent of the sample. These pressure and volume are measured with a pressure gauge and volumetrically in U-tube respectively (ASTM 4373 and ISO 10693).
Advantages and Disadvantages

- Low cost of ownership
- Simple
- Low cost of operation
- Poor quality of results
- Operator dependent; prone to personnel errors
- Labor intensive
Working Principle of Automated Inorganic Carbon Analyzer (Calcis Auto)

1. Weigh 0.1-2.0 g sample in to vial

2. Load Vial to Autosampler
3. Acid is injected inside vial through 1st channel of needle
4. Then air is sent through 1st channel of needle
5. Mixing with air
6. The evolved CO$_2$ is collected through 2nd channel of needle and measured by NDIR detector

ALL BELOW STEPS ARE DONE BY ANALYZER
A NEW METHOD: STATIC HEADSPACE
(working principle)
In order to commonize sample-acid reaction, addition of acid is done by operator after weighing sample.

1. Weigh 0.1-2.0 g sample in to vial
2. Add 6 ml of 4 M HCl
3. Wait for 1 hour (common wait time for all samples) to get all CO₂ completely formed
4) Load vials to the autosampler (72 capacity)
Analysis time: 1 sample/minute

Evolved CO$_2$ gas is carried to NDIR detector for the analysis

**FINAL ANALYSIS SPEED**
Sample weighing: 45 sec/analysis, Acid addition: 15 sec/analysis, Reaction competition: 0.5 min/analysis, Analysis time: 1.0 min/analysis, Overall: 2.5 min/analysis
Literature

According to ASTM D 4373-02

*Testing times may be extensive (longer than 1 h) for some carbonate species (such as dolomite) if calcite equivalents within about 1 % are required.*

If soil sample that contains dolomite C-CO$_3$ source, the reaction between acid and sample to get all C-CO$_3$ as CO$_2$ gas will take up to 1 hour, that means analysis speed will be 1 sample/hour.
Advantages and Disadvantages of Automated Inorganic Carbon (C-CO$_3$ Analyzer (Calcis Auto))

- **Automated acid addition**
- **Autosampler: Unattended analysis of samples up to 147 samples**
- **Mixing done by analyzer**
- **Interference free CO$_2$ specific detector (NDIR)**
- **Accuracy and Sensitivity due to instrumentation technology**
- **Full completion of acid-carbonate Reaction**

- High cost of ownership compared to Scheibler
- High cost of operation compared to Scheibler
- Need operator with instrumentation experience
Developed to overcome main disadvantages of
1- Scheibler Calcimeter
2- Pressure Unit
3- Inorganic Carbon Module attached to Elementel Analyzers
Highlights Prior to Results

- Soil samples contains less than 1% C-CO$_3$ are analyzed at LOW range with High Sensitive NDIR Detector.
- Soil samples contains more than 1% C-CO$_3$ are analyzed at HIGH range with Standard NDIR Detector.
- Oven dry at 110 ±5°C for a period of 12 to 24 h. Pulverize the entire sample with a mortar and pestle (or hammer) until all of the particles pass a No. 40 (0.425-mm) or finer sieve. Smaller particles react faster than larger particles when treated with acid.
Measurement results of samples for both methods

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<th>HIGH CONCENTRATION (1-100%CaCO3)</th>
<th>Sample Name</th>
<th>%CaCO3 (Scheibler)</th>
<th>%CaCO3 (Calcis)</th>
<th>%RSD</th>
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<th>LOW CONCENTRATION (1-100%CaCO3)</th>
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<th>%CaCO3 (Calcis)</th>
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Sample Weights: 0.1-2.0 gram depending on concentration
Calibration: 5 point calibration with CaCO₃ powder (Criteria R² >0.995)
Number of Repeats: 3
% RSD of Sample Repeat: (Criteria <5%)
Validation: Every 10 samples (Criteria within ±5% Accuracy), both by CaCO₃ and NaHCO₃
Results and Discussion-1

- Results at High Range are in coherent with Scheibler Calcimeter, higher results are obtained since acid-sample reaction time completed with the static headspace method.
- Results at Low Range differs, some more analysis must be performed with Scheibler Calcimeter.
- Validation and Calibration is performed by CaCO₃ and NaHCO₃, there must be more analysis done also with CRMs.
Results and Discussion-2

- Static Headspace method is very fast (<3 min/analysis including sample preparation steps) compared to Scheibler Calcimeter.
- Static Headspace technique is very complementary to existing Macro Analyzer to achieve %C-CO$_3$ and %TIC.
- Static Headspace technique has the advantage of low cost of ownership and low cost of operation per analysis compared to other instrumentational techniques (combustion based.)
THANK YOU FOR YOUR ATTENTION