Application Note
Total carbonates analysis in sand mixtures using the FOGII Digital Soil Calcimeter™

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Introduction

Inorganic carbon forms are present in soils and sediments typically as carbonates. In soils and sediments, the most common carbonate minerals found are calcite ($CaCO_3$), magnesite ($MgCO_3$) and a mixture of them that is called dolomite [$CaMg(CO_3)_2$]. Depending on soil genesis and formation conditions or where the sediment source was located, other forms of carbonate minerals may be present, e.g., siderite ($FeCO_3$). All these minerals are called as 'calcium carbonate' for ease. The total carbonate content of the soil is an important indication of the fertility of the soil. The quantification of inorganic carbon (IC) in soils and sediments is an important tool for understanding biogeochemical processes or liming practices. Potential applications are the calculation of carbon fluxes and budgets in terrestrial systems on a regional and global scale, rates of precipitation of carbonate minerals, introduction of detrital carbonates into the system and the investigation of the carbon storage potential of soils.

Materials and methods

Principles

The calcium carbonate content of the mixture was determined by treating a 1.000 g (+/- 0.001 g) dried silica sand-calcium carbonate mixture specimens with 6N hydrochloric acid (HCL) reagent grade, in an enclosed reaction cartridge (reactor vessel). Carbon dioxide gas is evolved during the reaction between the acid and carbonate fraction of the specimen. The reaction is described as follows:

$$\mathbf{(CaCO_3 + MgCO_3\ etc) + 2\ HCl \rightarrow (CaCl_2 + MgCl_2\ etc) + H_2O + CO_2\uparrow}$$

The resulting pressure generated in the reaction cartridge under constant conditions of temperature and volume is proportional to the carbonate content of the specimen. The instrument uses a multi-sensor philosophy, which combines simultaneous measurement of pressure and temperature.

This technology is innovative and published under the World Intellectual Property Organization number WO2014060782A1. FOGII Digital Soil Calcimeter™ is patented from the Hellenic Industrial Property Organisation (OBI) – Patent No. 1008089.

The digital soil calcimeter complies with EN ISO 10693:2013, ASTM D4373-02(2007) and Soil Science Society of America standard test methods for calcium carbonate content in soils and sediments.
The total carbonates analysis is based on a pressure method that utilizes the FOGII Digital Soil CalcimeterTM, which is a portable apparatus. The test method is quickly and accurately performed for soils and mixtures containing calcium carbonate and mixtures of sand and calcium carbonate.

FOGII Digital Soil Calcimeter™

The materials needed for the analysis procedure were the FOGII Digital Soil Calcimeter™, a data book, safety glasses, disposable plastic cuvettes with a 4ml volume and 6N hydrochloric acid solution prepared with a dilution of 500 ml concentrated HCl with distilled water up to 1000 ml, lab-grade silica sand and calcium carbonate reagent grade.

Sample preparation and measuring procedure

Samples ideally would be dried and finely ground (< 0.5-mm diameter) to facilitate reaction with acid. Sand/$CaCO_3$ mixtures (0, 1, 5, 10, 50 and 80 % $CaCO_3$ by dry weight) were used for the testing designation. The procedure incorporated three experiments in a completely randomized experiment with 5 replicates. Control was 0 % $CaCO_3$ by dry weight. The calibration curve was created using a standard of pure reagent grade $CaCO_3$. Approximately 1.000 g (+/- 0.001 g) of prepared dry samples were weighed and transferred into the reactor vessel, recording the exact weight. The use of safety glasses from this step onward was mandatory. Afterward, the cuvette was filled till ¾ of its height with HCl 6N solution and placed into the reactor vessel. 300 μL of distilled water was added to moisten the sample for standard uniformity. The vial was sealed with the cup of the vessel and shaken orbital. The end of the reaction was determined automatically, as the calcimeter measures the gas pressure 100 times per second and records the mean value and the variance. When the variance was tending to zero and was steady for 10 seconds at least, then the measurement stopped and the total carbonate content was calculated. The procedure was validated by preparing Sand/Soil mixtures (0, 1, 5, 10, 50, and 77.5 % $CaCO_3$ by dry weight) from a BIPEA (International Bureau for Analytical Studies) proficiency testing program with soils of different origins.

Results

Table 1. $CaCO_3$/Sand mixtures using a standard of pure reagent grade $CaCO_3$ > 99 % dry basis

$CaCO_3$/Sand mixtures	**Recovery $CaCO_3$ %**					
$CaCO_3$ %	REPL1	REPL2	REPL3	REPL4	REPL5	Avg
0	0	0	0	0	0	0
1	1.0	0.8	0.9	1.0	0.8	1.0
5	5.2	4.9	5.1	4.7	5.0	5.2
10	10.0	9.9	9.7	9.8	9.7	10.0
50	49.4	49.3	49.6	49.5	49.4	49.4
80	79.5	79.7	79.0	79.6	79.6	79.5

Table 2. Soil/Sand mixtures from BIPEA (International Bureau for Analytical Studies) proficiency testing program with soils of different origins. Assigned value for proficiency testing 77.50 ± 3.5 std % $CaCO_3$

$CaCO_3$/Sand mixtures	**Recovery $CaCO_3$ %**					
$CaCO_3$ %	REPL1	REPL2	REPL3	REPL4	REPL5	Avg
77.5 ± 3.5	80.1	81.4	78.5	80.7	81.1	80.4
38.75 ± 1.75	40.6	40.1	39.3	39.6	40.2	39.9
25.83 ± 1.17	26.0	26.2	26.8	26.5	26.7	26.4
19.38 ± 0.88	19.3	20.4	19.6	19.7	20.1	19.8
15.50 ± 0.70	15.4	16.3	15.9	16.2	15.6	15.9

Conclusions

The instrument uses a multi-sensor philosophy, which combines simultaneous measurement of pressure and temperature. In addition to the measurement of temperature, the instrument has a built-in module for automatic temperature compensation, so that performs single-run total carbonate measurements with higher accuracy. The excellent entire performance tests showed that FOG II Digital Soil Calcimeter™ can replace easily other analog devices for soil total carbonates testing. The device is portable and easily can be carried for fieldwork.

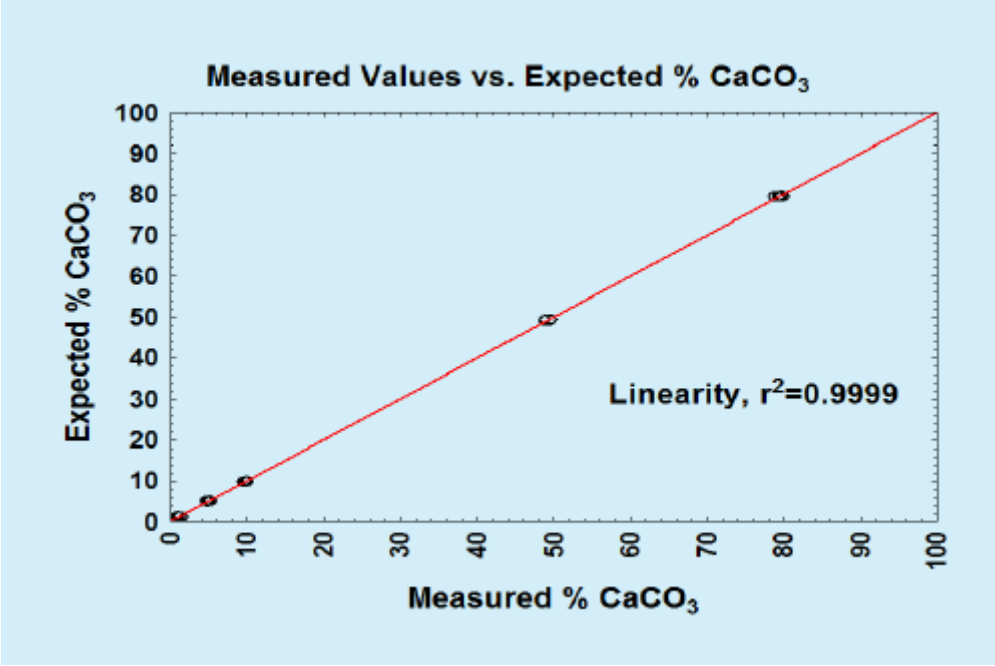

Figure 1. Measured vs Expected % $CaCO_3$ for Sand/$CaCO_3$ standard of pure reagent grade.

References

1. ASTM D4373-02. 2007. Standard Test Method for Rapid Determination of Carbonate Content of Soils.
2. Barouchas Pantelis. inventor; Barouchas Pantelis. assignee. 2014a. Automatic portable and digital soil calcimeter. WIPO Patent Priority Number WO2014060782 A1. Apr 24. 2014.
3. Barouchas Pantelis. E. 2014b. FOG II - A new innovative portable instrument for the total calcium carbonate soil testing. 20th World Congress of Soil Science. June 8-13. 2014 - Jeju. KOREA. Friday. 13 June 2014. P4-106. AF2494.
4. EN ISO 10693:2013. Soil quality - Determination of carbonate content - Volumetric method (ISO 10693:1995).
5. Evangelou et al. 1984. An automated manometric method for quantitative determination of calcite and dolomite. SSAJ 48: 1236-1239.
6. Loeppert. R.H. and D.L. Suarez. 1996. Carbonate and gypsum. pp. 437-475 in: Sparks. D.L. [ed.]. Methods of Soil Analysis. Part 3. Chemical Methods—SSSA Book Series no. 5.. 677 S. Segoe Rd.. Madison. WI 53711. USA.