Food and Agriculture Organization of the United Nations

Standard operating procedure for soil calcium carbonate equivalent

Titrimetric method

GLOBAL SOIL PARTNERSHIP

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SOIL CALCIUM CARBONATE EQUIVALENT

Titrimetric Method

VERSION HISTORY

N°	Date	Description of the modification	Type of modification
01	28 October 2019	Review of the draft SOP at the 3rd GLOSOLAN meeting	Finalization of the SOP
02	1 March 2021	Units of measures updated as per the decisions made at the 4th GLOSOLAN meeting	Revision of the units of measure
03			
04			
Etc.			

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Contents

1. Introduction

Calcium carbonate ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], and magnesian calcite [$Ca_{1-y}Mg_yCO_3$] are the most common carbonate minerals. They account for more than 90 percent of natural carbonates (Lal, 2006). Calcite is the dominant form in soil. Aragonite and siderite are also found in some specific soils. Carbonates are common in many soils of the world, especially arid, semi-arid, and subhumid soils (Lal, 2006). Their origin can be primary (inherited from lithogenic) or secondary (pedogenic) (Loeppert and Suarez, 1996).

The amount and distribution of carbonate are two of the most important factors influencing the physical, chemical, and biological properties of soils. For example, carbonates have a significant effect on soil pH, sorption-desorption, precipitation-dissolution, and cementation processes. Due to reactivity and alkaline character, the carbonate minerals act as a pH buffer. The pH of soils that contain carbonate ranges from 7.1 to 8.5 (Lal, 2006; Loeppert and Suarez, 1996). Carbonates precipitation on soil particles and pores may form layers (e.g., a calcic horizon) that prevent water movement within the soil profile. Certain layers may become hard and cemented (e.g., a petrocalcic horizon) and cause water to move laterally (Lal, 2006). The active carbonate surface may adsorb essential plant nutrients and adversely influence their availability for plants. Iron deficiency chlorosis in plants has been attributed to the interaction of Fe and HCO^{3-} in calcareous soils (Inskeep and Bloom, 1987; Lindsay and Thorne, 1954). Sorption and desorption of heavy metals of environmental concern (e.g., Cd^{2+} and Pb^{2+}) on carbonates affect the metals mobility and bioavailability (Lal, 2006).

Carbonates play an important role in the global carbon cycle, although their role in greenhouse emissions has not been well known (Lal *et al.*, 1999). Soils are the largest terrestrial C pool (approximately 1500 billion tones in organic form and 970 billion tones as inorganic carbonates) and are thus the third largest C reservoir in the world, after oceans and fossil fuels (Lal and Kimble, 2000).

Calcium carbonate equiv. is used in soil classification as an index for a mollic epipedon, a calcic horizon, and the rendolls suborder. If free calcium carbonate is present in soil, the amount and depth are criteria for soil series identification. The accumulation and transportation of carbonates in the soil profile are used to identify and interpret soil formation processes (Soil Survey Staff, 2014).

In soils affected by carbonates, the content of calcium carbonate varies from negligible to more than 80 percent (Loeppert and Suarez, 1996). Calcium carbonate equivalents are determined if soil pH is above 7 or if effervescence is observed after treatment with 1M HCl. Carbonates are typically present in neutral to alkaline soils, but solid phase carbonates as nodules are also in some acid environments.

Soil carbonates are typically measured by dissolving carbonates in acid solution (equations 1 and 2) and then determining either H^+ consumption, Ca and Mg production, or CO_2 production.

$$CaCO_3+2H^+ \rightarrow Ca^{2+}+CO_2+H_2O \qquad \text{Equation 1}$$

and

$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \qquad \text{Equation 2}$$

2. Scope and field of application

This method estimates the amount of soil carbonate by digestion with excess acid. It is applicable to all soils; however, it may overestimate calcium carbonate equiv. (CCE) in soils that have a high content of organic matter. In such soils, HCl can react with the organic matter. This method is described by Estefan *et al*. (2013).

3. Principle

This method determines the carbonates as a percentage of the soil using acid neutralization. Hydrochloric acid is added to the soil sample, and carbonates decompose as indicated in equations 1 and 2. CCE is measured using alkaline to back titrate the consumed H^+.

In the titration method, two equivalents of acid are assumed to react with one mole of $CaCO_3$. Therefore, one equiv. of acid is assumed to correspond to one-half mole of $CaCO_3$ (Estefan *et al.*, 2013).

4. Equipment

1. Precision balance, accuracy of ± 0.001 g
2. Burette for the titrant solution, 50 mL, accuracy of ± 0.05 mL
3. Volumetric pipettes, 10 mL, 20 mL
4. Erlenmeyer flasks, 250 mL
5. Volumetric flasks, 1000 mL
6. Watch glass
7. Hot plate

5. Reagents and standards

1. Deionized or distilled water, EC < $1.5*10^{-3}$dS m^{-1}
2. Hydrochloric acid (HCl), 1N, standardized. Dilute 98.33 mL concentrated HCl (32%, sp. gr. 1.16) in DI water, mix well, let cool, and bring to 1-L volume. Standardize with 1 N Na_2CO_3 solution. Determine the exact normality of the HCl solution (according to step 7.1).
3. Sodium hydroxide (NaOH), 1 N, standardized. Dissolve 40 g NaOH in DI water, transfer to a 1-L flask, let cool, and bring to volume. Standardize with 1 N HCl solution. Determine the exact normality of the NaOH solution (according to step 7.1).
4. Sodium carbonate solution (Na_2CO_3), 1N, Dissolve 53 g anhydrous Na_2CO_3 in DI water and bring to 1 L volume. Do not keep longer than one week.
5. Phenolphthalein Indicator [$C_6H_4COOC(C_6H_4\text{-}4\text{-}OH)_2$]: Dissolve 0.5 g phenolphthalein indicator in 100 mL ethanol (ethyl alcohol).
6. Methyl-Orange Indicator [$4\text{-}NaOSO_2C_6H_4N{:}NC_6H_4/\text{-}4\text{-}N\ (CH_3)_2$]: Dissolve 0.1 g methyl-orange indicator in 100 mL DI water.

6. Sample preparation

The soil samples should be air dried, ground, passed through a 10-mesh sieve (2 mm nominal pore size), and then to ensure the sample is uniform, the sieved soil should be ground to very fine powder using suitable mortar.

7. Procedure

7.1 Standardization of hydrochloric acid (1 N solution and sodium hydroxide (1 N solution

7.1.1. Pipette 10 mL 1 N Na_2CO_3 solution into a 100-mL Erlenmeyer flask, add 2 drops methyl-orange indicator, add 1 N HCl to the burette, and titrate. The solution color changes from light to dark orange. The HCl normality is:

$$N_{HCl} = \frac{(10 \times N_{Na_2CO_3})}{V_{HCl}} \qquad \text{Equation 3}$$

where:
N_{HCl}= Normality of HCl solution
$N_{Na_2CO_3}$= Normality of Na_2CO_3 solution
V_{HCl} = Volume of HCl solution used (mL)

7.1.2. Pipette 10 mL standardized 1 N HCl solution into a 100-mL Erlenmeyer flask, add 2 drops phenolphthalein indicator, add 1 N NaOH solution to the burette, and titrate. The solution color changes from colorless to pink. The NaOH normality is:

$$N_{NaOH} = \frac{(10 \times N_{HCl})}{V_{NaOH}} \qquad \text{Equation 4}$$

where:
N_{NaOH} = Normality of NaOH solution
N_{HCl}= Normality of HCl solution
V_{NaOH} = Volume of NaOH solution used (mL)

7.2. Determination of the total carbonate in soils

7.2.1. Weigh a soil sample of 1 to 10 g (±0.001 g) into a 250-mL Erlenmeyer flask. Use table 1 to determine the recommended sample weight for analysis.

Table 1. Sample weight estimation

Effervescence and appearance after adding HCl 1M	$CaCO_3$expected (%)	Sample weight(g)
Non, slight, very slight but for a short time	<8	10
Strong, bubbles form low foam	8–16	5
Violent, thick foam forms quickly	>16†	2.5

†Note: If a soil contain 32 percent $CaCO_3$, or more, a 1 g sample should be weighed.

7.2.2. Using a volumetric pipette, add 20 mL of standardized 1N HCl to the flask.
7.2.3. Cover the Erlenmeyer flask with a watch glass and boil the soil-acid mixture for 5 minutes.
7.2.4. Add 50–100 mL deionized water using a graduated cylinder. Allow it to cool.
7.2.5. Add 2 or 3 drops phenolphthalein indicator.
7.2.6. Titrate with 1N NaOH solution while swirling the flask. Take the reading when a faint pink color develops.
7.2.7. For quality control, use a certified reference material (CRM) or quality control sample and follow previous steps.

7.3. Technical remarks

This estimate of carbonate is typically somewhat high because other constituents react to some degree with the acid.

Foaming can be minimized by adding alcohol to those soil samples that have a high content of calcium carbonate.

Typically, 20 mL 1 N HCl dissolves up to 1 g $CaCO_3$. Therefore, 20 mL of acid solution can be expected to dissolve all of the carbonate in 1 g of soil.

When a soil is reacted with acid to dissolve carbonates, other soil components may also consume acid. Most of the latter reactions are assumed to be reversible; that is, if the suspension is back-titrated, the acid is released again. For this reason, it is not recommended to filter the suspension and titrate the clear filtrate. The endpoint is easier to determine in a clear solution, but the titration may overestimate the actual content of $CaCO_3$ in the soil (Estefan *et al.*, 2013).

Not all reactions involving acid and soil components are completely reversible; therefore, the acid titration of the soil suspension may also slightly overestimate the actual content of carbonates in the soil. The acid titration method can be calibrated against the calcimeter method.

Consumption of H^+ is not specific to the carbonate dissolution reaction (e.g., the cation exchange complex can be a sink for H^+). The methods of H^+ consumption that involve reaction with a strong acid are typically not suitable. An example is HCl addition and back titration of the unreacted acid. Such methods have problems due to consumption of H^+ by other soil components, acid-generating hydrolysis during mineral decomposition, high partial pressure of CO_2, and volatilization of acid. Methods that have been successful include the reaction of a weak acid, such as acetic acid (Loeppert and Suarez, 1996), for determining total soil carbonate and the reaction of pH 4.0 sodium acetate (Bloom *et al.*, 1985) for determining carbonates in the clay-size fraction.

Carbonate minerals are rarely distributed uniformly in the soil; therefore, the samples used for carbonate analysis should be well ground to minimize errors.

8. Calculations

$$\mathrm{CaCO_3\ equiv.,\%} = \left(\frac{\mathrm{V_{HCl}N_{HCl}} - \mathrm{V_{NaOH}N_{NaOH}}}{\text{grams of soil}}\right) \times 0.05 \times 100 \quad \text{Equation 5}$$

Where $\mathrm{V_{HCl}N_{HCl}}$ and $\mathrm{V_{NaOH}N_{NaOH}}$ are the volume and normality of HCl and NaOH respectively.

9. Health and safety

Hydrochloric acid is corrosive. Causes severe skin burns and serious eye damage. Precautions should be taken. Keep away from open flames and heat sources. Measure the concentration of HCl in the air regularly. Carry out operations in a fume hood with exhaust ventilation. Never dilute by adding water to acid; always add the acid to the water.

All titrations and handling of chemicals, especially the heating of acidified samples, should be performed in a fume hood.

10. Quality assurance and quality control

10.1. Accuracy test

10.1.1. Recovery test

Analyze the certified reference material (CRM) in accordance with the standard operating procedure (SOP) of the particular parameter. Analyze the CRM sample in the same manner as the sample. Calculate the percent recovery based on equation 6. Compare result with the target recovery for the analyte concentration as indicated in Table 2: expected recovery as a function of analyte concentration (AOAC, 1998). If recovery test fails acceptance criteria, identify the root cause(s), develop corrective and preventive actions, and address the problem.

$$\text{Recovery}, \% = \frac{\text{mean of observed value}}{\text{true value}} \times 100 \qquad \text{Equation 6}$$

Table 2. Expected recovery as a function of analyte concentration

Analyte, %	Analyte ratio	Unit	Mean recovery, %
100	1	100%	98–102
10	10^{-1}	10%	98–102
1	10^{-2}	1%	97–103
0.01	10^{-3}	0.1%	95–105
0.001	10^{-4}	100 ppm	90–107
0.0001	10^{-5}	10 ppm	80–110
0.00001	10^{-6}	1 ppm	80–110
0.000001	10^{-7}	100 ppb	80–110
0.0000001	10^{-8}	10 ppb	60–115
0.00000001	10^{-9}	1 ppb	40–120

10.1.2. Interlaboratory test

Participate in an interlaboratory proficiency test at least once a year. The PT z-score should be less than 2. If not, identify root cause(s), develop corrective and preventive actions, and address the problem.

10.1.3. Analyze check reference

Perform replicate analyses of CRM with this reference method. Compare results from your laboratory with results from other laboratories as provided in the performance analysis report or CRM certificate. Your laboratory result is considered accurate when it is within the reported 95 percent confidence interval of the target value.

10.2. Precision test

Perform replicate analysis of 10 percent of samples in a test batch. Calculate the Percent Relative Standard Deviation (%RSD) to determine if the precision of replicate analyses is within specification. Compare result with the target precision for the analyte concentration as indicated in table 3, expected precision (repeatability) as a function of analyte concentration.

$$RSD, \% = \frac{S}{\bar{x}} \times 100 \qquad \text{Equation 7}$$

Where:
S = Standard deviation of the replicate result
x̄= Mean value

Table 3. Expected precision (repeatability) as a function of analyte concentration

Analyte, %	Analyte ratio	Unit	RSD, %
100	1	100%	1.3
10	10^{-1}	10%	1.9
1	10^{-2}	1%	2.7
0.01	10^{-3}	0.1%	3.7
0.001	10^{-4}	100 ppm (mg/kg)	5.3
0.0001	10^{-5}	10 ppm (mg/kg)	7.3
0.00001	10^{-6}	1 ppm (mg/kg)	11
0.000001	10^{-7}	100 ppb (µg/kg)	15
0.0000001	10^{-8}	10 ppb (µg/kg)	21
0.00000001	10^{-9}	1 ppb (µg/kg)	30

10.3. Control chart

Analyze at least one duplicate of the check sample or internal reference material in every batch analysis. Plot the result in the control chart. Monitor for results that are outside of the specified limits. If a result is observed out of the specified limit, identify the root cause(s), develop corrective and preventive actions, and address the problem.

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12. Appendix I.— Acknowledgements

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13. Appendix II.—List of authors

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- Mr. Richard Ferguson, Kellogg Soil Survey Laboratory**, United States of America**
- Ms. Nopmanee Suvannang, GLOSOLAN Chair, **Thailand**

14. Appendix III.—Contributing laboratories

GLOSOLAN thanks the following laboratories for completing the GLOSOLAN form on the method and providing information on their standard operating procedure for the calcium carbonate equivalent volumetric calcimeter method. This information was used as a baseline for the global harmonization.

From the Asian region:

- ICAR-Indian Institute of Soil Science, Bhopal, **India**
- Department of Soil and Environmental Sciences, The University of Agriculture, Peshawar, **Pakistan**
- Land Resources Research Institute, NARC, Islamabad, **Pakistan**
- Land Development Department, LDD, **Thailand**

From the Pacific region:

- None

From the Near East and North African (NENA) region:

- Soil & Fertilizers Laboratory, Soil and Fertilizers Department, Plant Wealth Directorate, **Bahrain**
- Soil and Water Research Institute laboratory, **Islamic Republic of Iran**
- Soil Chemical Analysis Laboratory, Ministry of Science and Technology, Directorate of Agricultural Research, Soil and Water Resources Center , **Republic of Iraq**

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- Soil, Water and Plant Laboratory, Agricultural Research & extension Authority, Renewable Natural Resources Research Center, **Yemen**

From the African region:

- University of Eldoret Biotech Center, **Kenya**

The majority of laboratories in Africa stated not to use this method.

From the European region:

- None. Laboratories in Europe stated not to use this method.

From the Eurasian region:

- None. Laboratories in Eurasia stated not to use this method.

From Latin America:

- None. Laboratories in Latin America stated not to use this method.

From North America:

- None. Laboratories in North America stated not to use this method.

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GLOSOLAN
GLOBAL SOIL LABORATORY NETWORK

GLOSOLAN is a Global Soil Laboratory Network which aims to harmonize soil analysis methods and data so that soil information is comparable and interpretable across laboratories, countries and regions. Established in 2017, it facilitates networking and capacity development through cooperation and information sharing between soil laboratories with different levels of experience. Joining GLOSOLAN is a unique opportunity to invest in quality soil laboratory data for a sustainable and food secure world.

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