

ABSTRACT

Inorganic carbon (IC) in calcareous soils has two components, calcitic carbon (CC) and dolomitic carbon (DC). Even though, there are several procedures for quantifying IC, available literature pertaining determination of CC and DC is very scarce. Our objective was to develop a method to directly quantify calcitic-carbon and dolomitic-carbon in calcareous soils. Total analysis of IC is done gravimetrically with the Carbonate-Meter, and determination of calcite and dolomite is done complexometrically in the acidic solution with Na₂-EDTA. The Carbonate-Meter can be prepared in the laboratory with one 50-ml Erlenmeyer flask, one 6-ml glass vial, one number-1 rubber stopper with one hole assembly with 2-inches of glass tubing 4mm OD flash with the bottom. NIST, dolomitic limestone; Certified Reference Material, magnesite; and Leco, CaCO₃ standards; were analyzed gravimetrically for IC, and volumetrically with Na₂-EDTA for calcite and dolomite. Carbonate-Meter was used to determine IC in 0.200 + 0.020 g of sample with 4.0 ml of 0.8 M HCl. The acidic solution containing Ca or Ca and Mg in the Erlenmeyer flask is separated from the soil residue by filtration, spiked with 1 ml 2% MgCl₂, then brought to 100 ml volume with pure water, homogenized well, and analyzed for Ca and Mg at pH = 10.00 with 0.02N Na₂-EDTA on a 20 ml aliquot, in the presence of Eriochrome-black. Calcium was analyzed at pH > 12.5 after Mg precipitation with 2M NaOH, on a 20 ml aliquot using murexide as indicator. Results showed for dolomitic limestone, magnesite and Leco CaCO₃, IC precisions of 1.03, 1.06 and 1.26 % and recoveries of 99.68, 101.75 and 97.85 %, respectively. Dolomite, magnesite and CaCO₃ precisions were 1.14, 0.45 and 0.57 %, respectively, while recoveries of 98.51, 100.96 and 98.50 % were found for dolomitic limestone, magnesite and Leco CaCO₃ standards, respectively. The procedure is easy to follow in the laboratory, it is economical, and has a good accuracy and precision.

INTRODUCTION

- In calcareous soils, total inorganic carbon (IC) could be equal to calcitic-carbon (CC), or dolomitic-carbon (DC) or the addition of both.
- There are several procedures in the literature for quantifying IC (Goh and Mermut, 2008, Sherrod et al., 2002, Self and Rodriguez, 1999, Leco Corporation, 2007) whereas, available literature pertaining determination of calcite and dolomite in calcareous soils is scarce.

OBJECTIVE

- Determine calcite and dolomite volumetrically with Na₂-EDTA in the acidic solution, after measuring inorganic carbon gravimetrically with the Carbonate-Meter.

MATERIALS AND METHODS

Carbonate-Meter

- The carbonate-meter consists of a 50-ml Erlenmeyer flask, one 6-ml glass vial, one rubber stopper number-1 with one hole, assembly with 2 inches of glass tubing 4 mm OD flash with the bottom.

Gravimetric Procedure: Inorganic Carbon

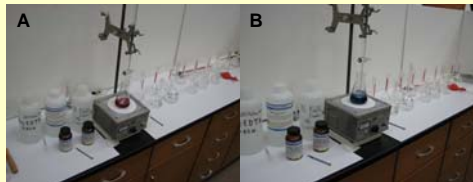
- Weigh 0.2000 g. + 0.0200 of fine soil (<0.15 mm) in an Erlenmeyer flask. Prepare a soil blank by weighing 0.2000 g. + 0.0200 of fine non-calcareous soil in another Erlenmeyer. Run 10 % of soil blanks with each batch.
- Measure 4.0 ml of 0.8 M HCl in a glass vial. With a reverse action forceps, carefully place the vial inside the Erlenmeyer containing the soil sample. Using low pressure, cup the Erlenmeyer with the rubber stopper assembly with the glass tubing flash with the bottom.
- Register the weight of the Carbonate-Meter with four decimals as Initial Weight.
- Allow the decomposition reaction take place by tilting the vial and pouring the acid over the soil; place the flasks on a shaker for 15 min. at 150 O.P.M. Let the reaction continue for 16-20 hrs or overnight, then again register the weight of the Carbonate-Meter with four decimals, as Final Weight.
- The difference between the two weights is registered as Gross CO₂, and after blank correction, the Net CO₂ is obtained and used to calculate total IC in the soil.

Volumetric Procedure: Calcitic-C and Dolomitic-C

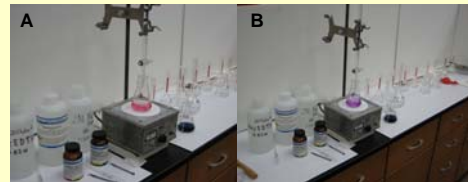
- The acidic solution containing the Ca or the Ca and Mg in the Erlenmeyer flask is separated from the soil residue by filtration with ashless whatman-42, spiked with 1 ml 2% MgCl₂, then brought to 100-ml volume with pure water, and homogenized well.
- Ca and Mg were analyzed at pH = 10.00 with 0.02N EDTA, on a 20 ml aliquot in the presence of Eriochrome-black. Calcium alone was analyzed at pH > 12.5 after Mg precipitation with 2M NaOH, on a 20 ml aliquot using murexide as indicator (Skoog et al., 1990).



Setup and preparation of carbonate-meters.



Initial (red wine; A) and end (blue; B) points for the Ca + Mg titration with Na₂-EDTA and Eriochrome Black T indicator.



Initial (pink; A) and end (lavender; B) points for the Ca titration with Na₂-EDTA and Murexide indicator.

RESULTS AND DISCUSSION

Results of precision and recovery for Inorganic-C, Dolomitic-C and Carbonate-C for three standards: NIST-Dolomitic Limestone, CGL-Magnesite and Leco-CaCO₃, are presented in Table 1. Dolomitic Limestone precision for IC, and Dolomite was 1.03 %, and 1.14 %, respectively. CGL-Magnesite precision for IC and Magnesite was 1.06% and 0.45 %, respectively. Leco-CaCO₃ precision for IC and CaCO₃ was 1.26% and 0.57 %, respectively. Recovery of Dolomitic Limestone for IC was 99.68 % and 98.51 % for Dolomite; the IC and Magnesite recoveries for the CGL-Magnesite were 101.75%, and 100.96 %, respectively. Leco-CaCO₃ recoveries for IC and CaCO₃ were 97.85 % and 98.50 %, respectively.

Table 1. Inorganic-C, Dolomitic-C, Magnesite-C, and Carbonate-C precision and recovery. Reported values were measured with procedure presented here (Meas.) and reported by manufacturer of each source.

Sample Size	NIST-Dolomitic Limestone		CGL-Magnesite		Leco CaCO ₃	
	IC	Dolomite	IC	Magnesite	IC	CaCO ₃
	Meas. NIST	Meas. NIST	Meas. CGL	Meas. CGL	Meas. LECO	Meas. LECO
0.1094	12.66	12.65	13.50	13.38	11.85	98.62
0.1224	12.63	12.65	13.59	13.38	11.59	98.25
0.1059	12.57	12.65	13.70	13.38	11.82	98.31
0.0979	12.70	12.65	13.35	13.38	11.83	97.22
0.1053	12.69	12.65	13.69	13.38	11.69	98.74
0.1235	12.70	12.65	13.81	13.38	11.47	97.92
0.1220	12.70	12.65	13.77	13.38	11.95	98.87
0.0985	12.54	12.65	13.53	13.38	11.66	99.02
0.1022	12.30	12.65	13.59	13.38	11.73	98.73

Parameters	NIST-Dolomitic Limestone		CGL- Magnesite		Leco-CaCO ₃	
	IC	Dolomite	IC	Magnesite	IC	CaCO ₃
n	9	9	9	9	9	9
Mean %	12.61	95.99	13.61	94.80	11.73	98.41
Std deviation	0.13	1.10	0.14	0.43	0.15	0.56
Precision %	1.03	1.14	1.06	0.45	1.26	0.57
Recovery %	99.68	98.51	101.75	100.96	97.85	98.50

Gravimetric results for inorganic carbon, found in twelve USDA calcareous soils with the Carbonate-Meter, and volumetric results for calcite and dolomite with Na₂-EDTA are presented in Table 2. Gravimetric inorganic carbon ranges from 0.17 % to 8.44 %. Volumetric results for calcite and dolomite ranges were 0.87 % - 68.10 % and 2.06 % - 46.64 %, respectively. Precision range for the gravimetric procedure was 0.20 % - 7.20 %. The volumetric technique precision range for calcite was between 0.24 % to 3.61 % while the one for dolomite was between 0.72 % and 11.01 %.

Table 2. Results of inorganic carbon, calcite and dolomite found in twelve calcareous soils with the Carbonate-Meter and Na₂-EDTA.

Soil ID	Number of Analysis n	Gravimetric Carbonate-Meter		Volumetric Na ₂ -EDTA			
		% IC	Precision	% Calcite	Precision	% Dolomite	Precision
Arkansas	9	0.17	5.93	0.00	0.00	2.19	11.01
Montana	9	0.25	4.61	0.87	2.86	3.04	8.39
Nevada-1	9	0.33	3.47	1.26	3.61	3.02	5.39
Washington	9	0.30	7.20	0.00	0.00	5.03	9.25
California	9	0.59	2.49	6.71	3.54	2.06	8.03
Utah	9	1.09	5.30	7.19	0.24	2.90	10.03
Oklahoma	9	1.82	4.10	14.79	1.52	0.00	0.00
South Dakota	9	2.73	1.49	9.01	2.13	11.82	5.42
Indiana	9	3.29	1.40	9.83	3.43	14.95	3.99
Nevada-2	9	5.51	0.20	30.23	0.38	19.62	9.69
Wyoming	9	6.87	0.73	5.49	1.63	46.64	0.72
West Virginia	9	8.44	0.40	68.10	0.51	0.00	0.00

CONCLUSION

These findings indicated that the gravimetric technique with the Carbonate-Meter and the volumetric technique with Na₂-EDTA, have a good accuracy and precision, are simply, economical, and easy to follow in the laboratory for analyzing total inorganic carbon, calcite and dolomite in calcareous soils.

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