



METHOD FOR ESTIMATION OF CALCIUM CARBONATE IN SOILS FROM IRAQ

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Abstract

Attempts have been made to evaluate four methods of quantitative determination of soil carbonates. Calcium carbonates equivalent were determined by the acid neutralization, calcimeter and acetic acid methods. Also, it obtains by the fourth methods when the acid neutralization method is corrected against proton adsorption. The acid neutralization method gave significantly higher estimates of total carbonates and different from each of the others. The calcimeter method gave the lower estimates of CaCO_3 equivalent. The results showed that the corrected values of CaCO_3 equivalent did not differ significantly from other three methods but the overall mean tended to be higher than the acetic acid and calcimeter methods. It may be concluded that the acetic acid method is simple, can reasonably estimate the carbonate content and requires only a pH meter. It can be used for routine determination of soil carbonate.

Keywords: Calcium carbonate equivalent, calcimeter, acid neutralization, Acetic acid

Introduction

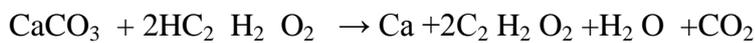
Carbonate is a natural constituent of many soils occurring as sparingly soluble, alkaline earth carbonate, chiefly as calcite and dolomite. Most carbonate minerals found in local soils are calcite and account 90% of total soil carbonates (Al-Kasyi,1989).

Soil properties play a major role in planning land use activities such as agriculture, erosion control, environmental protection and nature conservation. The determination of total carbonate such as CaCO_3 in soil is of great interest on account of high usefulness for diagnosing soil status in terms of structure, texture, biological activity or nutrient content. In calcareous soils carbonates exert a major influence on the chemical properties. Also carbonate content is used as a differentiating criterion for some classes at the family level of Soil Taxonomy (Soil Survey Staff, 2006). Few attempts have been made to evaluate methods of quantitative determination of carbonates in arid and semiarid soils. So, numerous methods

have been used for quantitative determination of soil carbonates (U.S. Salinity Laboratory Staff, 1954; Derimains, 1962; Hassan and Al- Tawil, 1973; Bullok, 1975; Loeppert *et al.*, 1974; Nelson, 1982, El Mahi *et al.*,1987, Moore *et al.*,1987 and Ashworth, 1977). The most commonly used procedures involve dissolution of the solid phase carbonates by reaction with acid. Quantitation is commonly achieved by measurement of evolved CO₂ volumetrically, gravimetrically, manometrically, titrimetrically. Also, it may be achieved quantitatively by measurement of acid consumed during the neutralization reaction. A Fourier transform infrared spectrometer, is employed to determine automatically the total inorganic carbonate in solid and waters based on active photoacoustic absorption of infrared light by carbon dioxide (Wenxin *et al.*, 1999). On the other hand, Zougagh *et al.*, (2005) used two methods for determination of total carbonate soils by continuous flow piezoelectric detection.

Several of the specific procedures are outlined below .The acid neutralization procedure, is probably the most commonly used, due to its simplicity which involves addition of excess acid and back titration with standard base (U.S. Salinity Laboratory Staff ,1954).Another widely used method is quantitative volumetric procedure, in which volume of CO₂ is determined following addition of excess HCl (Derimains,1962 and Bullock,1974).The pressure-calculator in which increase in pressure is measured at constant temperature and volume following addition of excess acid (Martin and Reeve, 1955; Hassan and Al-Tawil,1973 and Presley,1975) provides an alternative procedure for determination of soil carbonate. It is applicable in straight forward manner to soils in low organic matter and containing no dolomite and no appreciable quantity of MnO The calcimeter method is widely used locally to determine soil carbonates.

Another proposed procedure was used to determine soil carbonate which is based on the following reaction:



The neutralization of acetic acid expressed in the reaction



It was based on that a known quantity of acetic acid was added to a known quantity of soils. Then the pH of reaction mixture was determined following complete dissolution of CaCO₃ and equilibrium (Loeppert *et al.*, 1974). Also, El Mahi *et al.*, (1987) reported that the values of carbonate equivalent estimated by acid neutralization were corrected as:

$$\text{CaCO}_3 \text{ equivalent} = \text{acid neutralization \% CaCO}_3 - 0.05 \text{ CEC.}$$

The objective of this investigation is to evaluate and compare the common available procedure for quantitative determination of local soil carbonate with the objective of finding a rapid method that is reasonably accurate and simple.

Materials and methods

The studied soil samples were collected from different profile horizon of different parts of Iraq. Soils were air – dried, ground by hand and sieved through a 2 mm sieve. The lime content (CaCO_3 equivalent) was determined by dissolution of carbonate with 0.5 M HCl and titration of excess acid with 0.2 M NaOH as described by Allison and Moodie (1965). In addition to the calcimeter method described by Bullock (1975) the carbonate was determined by procedure proposed by Loeppert et al., (1974). It was based on adding a known quantity of 0.4 M acetic acid to a known quantity of soil samples (<2 mm fraction). Then the pH of the mixtures was experimentally determined. 2.000 g samples were weight into 50 mL polypropylene centrifuge tubes and 25 mL aliquot of 0.400 M acetic acid was added to each tube. Tubes were shaken for 8 h and the samples were allowed to sit overnight with cap loosed to allow escape of CO_2 produce during the dissolution of CaCO_3 . Tubes were centrifuged and then pH of the supernatant was accurately determined \pm 0.01 pH units with a combination pH electrode which was allowed to equilibrate for exactly 5 min before recording the value. Also, some tubes were allowed to sit over a period of 7 days.

Kaolinite and bentonite (smectite group) deposit from Al – Anbar Province was initially fractionated to obtain the > 2 mm particle size separated and was Ca- saturated by titration to pH 8.0 with $\text{Ca}(\text{OH})_2$. Calcium carbonate (0.25, 0.50, 1.0 and 1.50 g of Ca-saturated kaolinite and / or smectite. The pH of the solution was determined and experimental CaCO_3 contents calculated as previously described for soil samples. Precaution was taken to ensure that all soil samples were treated identically during pH determination.

Results and discussion

The soils were selected from a collection of calcareous soils of different parts of Iraq, to give a wide range in carbonate (30 to 4967 g CaCO_3 kg soils. These soils were very low in organic matter (5.45 to 27.85 g organic matter kg soil) and free Fe – oxides and oxyhydroxide (1.13 to 9.57 g kg soil) content (Kassim *et al.*, 1993). The soils and their classification were given in Table (1).

Table 1. Location and classification of 21 soils profiles used in the study.

Profile numbers	Location	Classification
P1,P2	Al-Nassriah	Typic Fluvaquents
P3,P4	Al-Nassriah	Vertic Fluvaquents
P5,P6	Tikrit	Cambic Gypsiorthids
P7	Mosul	Cambic Gypsiorthid
P8,P9	Tikrit	Calcic Gypsiorthids
P10	Rabiah	Calcic Gypsiorthids
P11	South of Mosul	Calcic Gypsiorthid
P12,P13	Tikrit	Typic Torripsammen
P14,P15	Rabiah	Typic Calciorthids
P16,P17	Rabiah	Typic Calcixerolls
P19,20	Rabiah	Calcixerollic Xerochrepts
P20	Mosul	Calcixerollic Xerochrepts
P21	Aski Kalaic	Mollic Calciorthids

Eight two -soil samples were taken from different depths from 21 profiles. All samples were analyzed for lime (CaCO_3 equivalent) using three different methods. These methods were acid neutralization (HCl), calcimeter and acetic acid reaction (US Salinity Laboratory Staff, 1954, Allison and Moodie, 1965 and Loeppert *et al* 1974). In case of acetic acid method, an addition of a known amount of pure calcite (CaCO_3) was added to excess quantity of acetic acid and the pH of the reaction was experimentally determined. The pH vs. initial CaCO_3 weight is plotted and shown in Fig (1). The results indicated that the pH rang is 2.98 to 5.74 and the relative change in pH was great at low CaCO_3 , generally when it was > 75 mg CaCO_3 . The standard curve for soil samples was obtained by the procedure proposed by Loeppert *et al.*, (1974). A plot of pH vs. $\log [\text{mgCaCO}_3 / (\text{T} - \text{mg CaCO}_3)]$ was obtained to serve as standard curve for soil samples and was approximately linear with an $r = 0.996$ (Fig 2).

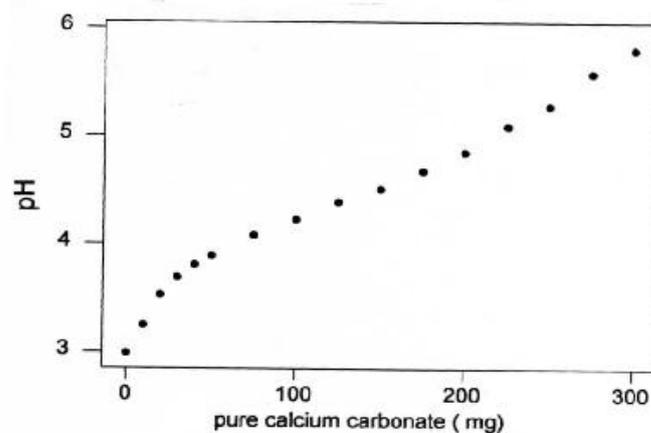


Fig 1: The effect of pure calcium carbonate on pH

In case of acetic acid method, the relative change in pH was great at low CaCO₃ levels and it was sensitive to small changes in CaCO₃ content. The errors due to consumption of protons by ion exchange complex were very high at low carbonate levels. It may be reduced by manipulating condition to result in an increase final equilibrium pH. It may be accomplished by increasing soil sample size and /or reducing concentration or volume of acid reactant. However, it was preferred increasing soil samples to reduce the error. Also, the soils under investigation showed that only few soil samples were low in carbonate content (Fig 3).

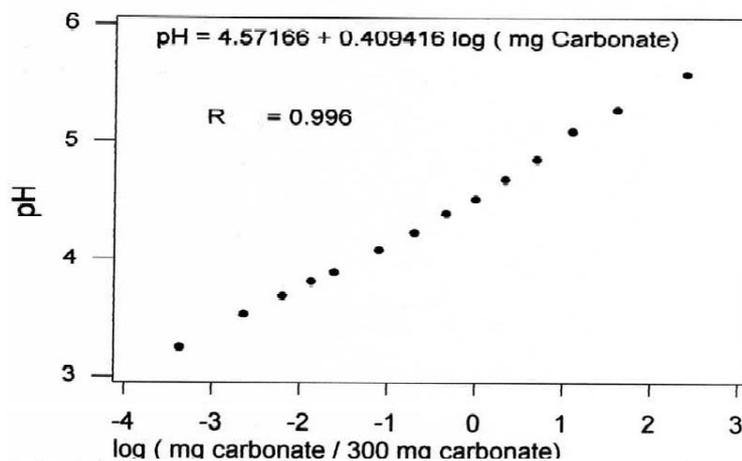


Fig 2: The relationship between the log amount of pure calcium carbonate and pH

The major sources of error in the procedure for determination of soil carbonates were clay minerals, organic matter, incomplete dissolution of CaCO₃ and error in pH determination. Addition of acetic acid to different quantity of CaCO₃ in the presences of different levels of clay minerals, the CaCO₃ level was experimentally determined. The results were shown in Table (2). It was indicated that the levels of experimentally determined CaCO₃ were higher in presences of clay minerals especially at lower added CaCO₃. Upon addition of 25 mL of 0.40 M acetic acid to 25.0 of pure CaCO₃ in presence of 0.250, 0.500, 1.00 and 1.50 g of kaolinite or smectite, the experimentally determined CaCO₃ levels were approximately 26,26, 28, and 29; 26,28,30 and 32 respectively (Table 2).

Table 2- Influence of Ca-saturated clay on determination of CaCO₃ equivalent by acetic acid

Actual CaCO ₃	Kaolinite	Experimentally determined CaCO ₃	Bentonite (smectite)	Experimentally determined CaCO ₃
mg	mg	mg	mg	mg
	250	26	250	26
	500	26	500	27
25	1000	28	1000	39

	1500	29	1500	31

	250	50	250	51
	500	52	500	53
50	1000	52	1000	53
	1500	53	1500	56

	250	100	250	101
	500	102	500	104
100	1000	102	1000	106
	1500	107	1500	107

	250	150	250	150
	500	154	500	156
150	1000	155	1000	158
	1500	153	1500	158

	250	200	250	200
	500	203	500	206
200	1000	204	1000	207
	1500	204	1500	207

Also, the experimentally determined CaCO_3 was higher in the presence of smectite than kaolinite. Therefore it is evident that the clay mineral consumed protons predominantly via a mechanism of ion exchange onto the clay surface or interlayer. So, it could be concluded that relative experimental or actual error generally increased as the clay contents were increased for a given CaCO_3 level. For example with actual CaCO_3 quantity of 25, 50, 100 and 200 mg, relative percentage errors in presence of 1.50 g of kaolinite were 16, 6, 4.7, 3 and 2 respectively. But the relative percentage errors in the presence of 1.50 of smectite were 24, 13, 7, 5.3 and 3.5 respectively. It was well known that the dissolution of CaCO_3 , Ca^{+2} was released into the reaction mixture. The proportion of H^{+1} on the exchange complex was controlled largely by $\text{Ca}^{+2} / \text{H}^{+1}$ exchange equilibrium relationships.

The amount of adsorbed H^{+1} being influenced by the quantity and cation exchange capacity of the clay. Therefore, at low carbonate levels and high clay levels, errors due to retention of H^{+1} on the exchange complex were greatest especially in presence of smectite.

The relative errors may be reduced by manipulating conditions to results in an increase in final equilibrium pH. Increasing soil sample size and /or reducing concentration or volume of acetic acid reactant could be accomplished this. Also, the errors in experimentally determination of actual CaCO_3 in presence of kaolinite and smectite by the two other methods (acid – base titration and calcimeter methods). The results in Table (3) showed that the relative percentage errors were the highest in acid base titration than the other methods. For example with actual CaCO_3 quantity of 25, 50, 100 and 200 mg the relative percentage errors in presence

of 1.5 g of kaolinite or smectite were 24,16,13,6.6 and 4.5 for kaolinite and 40,28,18,12 and 8 for smectite respectively in acid base titration method. But they were negligible in the calcimeter method even in the presence of high percentage of clays. So, it is evident that the clay consumed protons predominantly via mechanism of ion exchange on the clay surface. Also, it could be due to decomposition of the clay mineral especially in acid base titration methods. Generally, the relative experimental error increased as the clay content was increased for a given CaCO₃ level. Another error may be due to presence of organic matter especially at high organic matter (Martin, 1955), which may be attributed to large number of potential proton binding sites. But these errors could be negligible simply because the studied soils were very low in organic matter content (Al – Janbi *et al.*, 1989 a,b and Kassim *et al.*, 1989). These results are in agreement with the results reported by Hassan and Al – Tawil (1973) that organic matter could not be considered are limiting factor for application especially for calcimeter methods.

Table 3 - Influence of Ca-saturated clay on determination of CaCO₃

Actual CaCO ₃	Acid titration				Calcimeter			
	Kaolinite	Experimentaly determined CaCO ₃	Bentonite (smectite)	Experimentaly determined CaCO ₃	Kaolinite	Experimentaly determined CaCO ₃	bentonite (smectite)	Experimentaly determined CaCO ₃
mg	mg	mg	mg	mg	mg	mg	mg	mg
25	250	27	250	27	250	25	250	26
	500	27	500	29	500	25	500	26
	1000	31	1000	35	1000	26	1000	26
	1500	32	1500	36	1500	26	1500	27
50	250	54	250	57	250	50	250	50
	500	56	500	60	500	50	500	52
	1000	56	1000	63	1000	51	1000	52
	1500	58	1500	64	1500	51	1500	52
100	250	103	250	108	250	100	250	100
	500	104	500	109	500	100	500	100
	1000	109	1000	116	1000	101	1000	102
	1500	113	1500	119	1500	101	1500	103
150	250	152	250	153	250	150	250	150
	500	154	500	155	500	150	500	150
	1000	157	1000	166	1000	150	1000	151
	1500	160	1500	168	1500	151	1500	151
200	250	201	250	204	250	200	250	200
	500	202	500	208	500	200	500	201

200	1000	207	1000	212	1000	201	1000	202
	1500	209	1500	216	1500	201	1500	202

The soils under investigation were high in carbonate content and the results were shown in Fig (3). The histograms showed that more than 80% of these soils were high in carbonate exceed 200 g CaCO₃kg soil. It had been found that the rate of reaction of CaCO₃ was linearly and inversely related to pH within the range 3.00 to 5.00 (Berner and Morse, 1974). The condition employed in these experiments i.e. addition of 25 mL of 0.40 M acetic acid to 2.0 g soil samples. It has been found that the maximum working limit is 200 g CaCO₃ kg soil, which results in final equilibrium pH of approximately 4.85. So, if the soil carbonate minerals (Kassim and Haba, 1989), it would not be preferred increasing the acid concentration especially with soil containing readily decomposable minerals example soil chlorite may be subjected to severe errors due to decomposition of soil components. On the other hand, contact time must be sufficient to allow for complete dissolution of solid phase CaCO₃.

The distribution of soil carbonate contents are summarized in Fig 3 and present values of CaCO₃ equivalents determined by three methods. The acid neutralization method gave significantly higher estimates of total carbonate (p 0.001) than the other methods. But the calcimeter method gave the lowest estimates value of total carbonate. Also, it is interesting to note that the 5% CaCO₃ equivalent as the lower limit for calcareousness (Hodgson, 1976) only 7 out of the 82 soil samples could not be classified as than 5% CaCO₃ equivalent. On the other hand, the acid neutralization was the only method calcareous soil by the calcimeter method, while none of the other methods gave values less gave values 40% CaCO₃ equivalent and 25 soils samples were CaCO₃ values above 350 mg CaCO₃ kg soil. The acetic acid and / or calcimeter methods gave only 7 and 3 soils have values of 350 mg CaCO₃ kg soil respectively. The results showed that the majority of soil samples were within the range of 200 to 300 mg CaCO₃ kg soil. The mean CaCO₃ content for all soil samples studied were 209, 246, and 287 mg CaCO₃ kg soil estimated by calcimeter, acetic acid and acid neutralization methods respectively. The mean values indicated that the results of acid neutralization method were significantly different from each other and gave the highest mean values for CaCO₃ content. This could be attributed to the fact that the acid neutralization method suffers from the reaction of acid with soil constituents other than carbonate and the consumption by the exchange complex that lead to overestimate of carbonate. These results were in agreement

with results found by many workers (Bundy and Bremmer, 1972; Nelson and Summer, 1982; Loeppert *et al.*, 1984 and El Mahi *et al.*, 1987).

The acid neutralization method suffers from the reaction of the acid with soil constituent other than carbonates and the consumption of protons by the exchange complex. The latter error was corrected by assuming that protons occupied the entire exchange complex (El Mahi *et al.*, 1987). The corrected values of CaCO₃ equivalent using acid neutralization did not differ significantly from the other three methods.

On the other hand, the overall mean values (272 mg CaCO₃ kg⁻¹) were higher than those of the others, suggesting that the acid may be reacted with noncarbonated soil minerals.

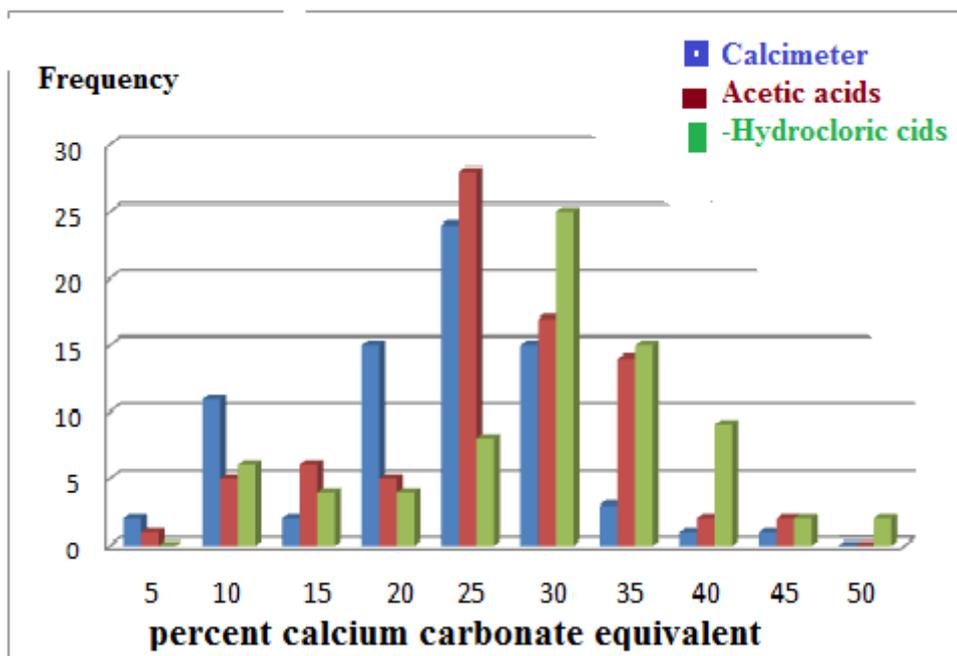


Fig 3: Frequency distribution of carbonate in soils determined by the calcimeter, acetic acids and hydrochloric acids

Generally, it may be concluded that the calcimeter method gave the lowest CaCO₃ equivalent estimate while the acid neutralization method gave the highest CaCO₃ equivalent content. The results in Table (4) shown that there were highly significant correlation between the methods. The acetic acid method was higher correlated with the calcimeter method (r = 95.1). Also, the acetic acid method may be reasonably used to determine CaCO₃ equivalent in the local soils of arid and semiarid. In addition to its simplicity, it required only a pH meter.

Table 4. Simple correlation coefficients(r values) between different methods of estimation of CaCO₃ equivalent

Methods	Calcimeter	Acetic acid
Acetic acid	0.975	
Acid neutralization	0.963	0.974
Corrected	0.963	0.973

A further investigation will needed to developed methods for evaluating the particle size distribution and reactivity of soil carbonate. Also, it is important to study carbonate mineralogy to quantify carbonate minerals phases present in local soils.

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