Pressure calcimeter as a simple method for measuring the $CaCO_3$ content of soil and comparison with Scheibler calcimeter

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Abstract

A pressure calcimeter was made as an alternative to Scheibler calcimeter which is the conventional method of soil $CaCO_3$ content analyses. Since the measurement of $CaCO_3$ content of soil with Scheibler calcimeter is a slow and labor intensive method, the accuracy and presicion of the results are based on labor experience. The pressure calcimeter gives fast and accurate results by eliminating these disadvantages. The measurement of $CaCO_3$ by pressure calcimeter, as in Scheibler, is done by measuring pressure of CO_2 gas produced from reaction of soil with HCl. The gas pressure, formed by the chemical reaction in a gasproof chamber was measured by a digital manometer on the cap. The results were converted to % $CaCO_3$ by calculations. Excellent correlation (R^2=0,998) was obtained in calibration carried out with pure $CaCO_3$. 46 soil samples contain $CaCO_3$ between % 1–30 were analysed by Scheibler calcimeter and the results were compared with pressure calcimeter. It can be concluded that pressure calcimeter has given satisfactory results and can be used as an alternative to conventional Scheibler calcimeter in soil $CaCO_3$ content analysis.

Key Words: Pressure calcimeter, Calcium carbonate ($CaCO_3$), soil analysis, Scheibler calcimeter.

INTRODUCTION

One of the most important parameters in determining soil chemistry is $CaCO_3$ content. There are many $CaCO_3$ measurement methods available in literature (Loeppert and Suarez, 1996). In many of these methods, $CaCO_3$ percentage is decided by calculating the gas pressure of CO_2 resulting from the reaction of HCl with soil lime ($CaCO_3$). Generally, Scheibler calcimeter is used in determination of soil lime content. The percentage of the soil $CaCO_3$ content can also be found with special calculations by measuring the CO_2 volume formed in Scheibler calcimeter.

One of the most conventional methods applied is the measurement of the amount of $CaCO_3$ in soil by Scheibler calcimeter. Although this analysis can get accurate results, it is a slow, old and labor intense method. It takes lots of time and has multi-step calculations such as use of complex tables including temperature corrected barometric pressure values, measuring the water vapor pressure, equalizing the water level in calcimeter in order to measure the gas volume after each reaction. On the other hand, it is very easy to measure soil $CaCO_3$ content with pressure calcimeter. The gas pressure formed by the reaction between $CaCO_3$ and HCl is measured in one step, and the soil $CaCO_3$ content is calculated.

There are many methods used in pressure calcimeter available in literature (Williams, 1948; Martin and Reeve, 1954; Woodward, 1961). Wagner et al. (1998) developed computerized inorganic carbon analyses system with a pressure transducer. Although the method is fast and sensitive, it is so complex and expensive.

MATERIALS AND METHODS

In this study, MIR calcimeter prototype was used as the pressure calcimeter.

150 ml screw-capped test tube was used as a reaction vessel. Silicone o-ring was used on the joint surface of the vessel and cap in order to gasproof. Three holes were bored in cap. A manometer was placed in the hole. To the second hole, a valve was placed in order to bleed off. To the third hole, a three way valve was placed. HCl was taken by an injector passing through this valve to the reaction vessel. There was also a support table on the magnetic stirrer to the reaction vessel stands. Images of all the system components are shown in Figure-1.

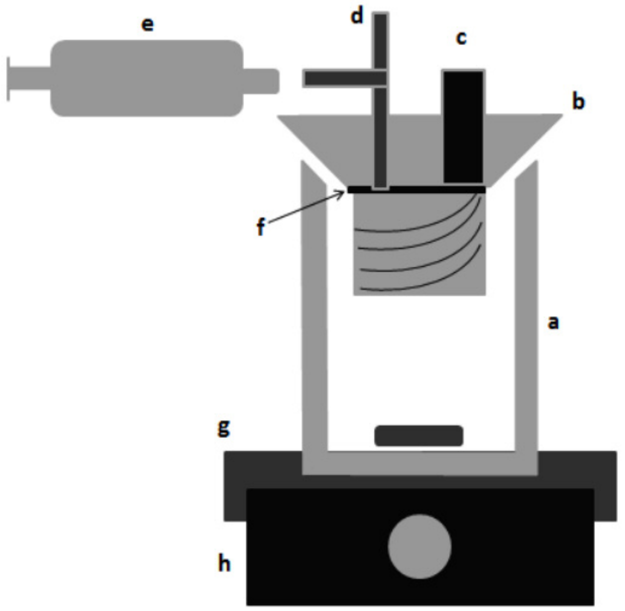

Figure 1. Components of MIR calcimeter (a: reaction vessel, b: screwed cap, c: digital manometer, d: three way valve, e: injector, f: o-ring, g: support table, h: magnetic stirrer)

The digital manometer measures the CO_2 gas pressure forming as a result of the reaction. According to the measured values, the soil $CaCO_3$ content is found as percentage with special calculations. The digital manometer is highly sensitive and has the advantage of the transparent readibility of the measured pressure value. Analog manometers are based on observation, so reading errors can be made easily. The technical features of the digital manometer are given in Table 1.

Table 1. Features of digital manometer

Pressure range	-1….3 bar
Resolution	1 mbar
Accuracy RT (room temperature)	< 0.1 %FS
Total Error Band (0…50 C)	< 0.2 %FS
Storage / Operating Temperature	-20…70 C / 0….50 C
Supply	3 V pil, type CR 2430

As in the classic Scheibler calcimeter, 10% (v/v) HCl is needed for the reaction. 10% HCl solution was prepared by taking 225 ml of HCl with 37 % purity (d = 1.19) and completing it to 1000 ml with deionized water (Kacar, 2012).

The chemical reaction equation used for the measurement of the soil $CaCO_3$ content is the same with the Scheibler calcimeter method (1):

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \qquad (1)$$

The mole of CO_2 formed by the reaction in closed vessel can be found by using the CO_2 gas pressure value in ideal gas equation. According to the stoichiometry, the mole of CO_2 is equal to the mole of $CaCO_3$. The mole is found by using the measured pressure value, the volume of the chamber which reaction takes place, and the ambient temperature in the ideal gas equation (2):

$$P * V = n * R * T \qquad (2)$$

By multiplying the number of moles with 100 ($CaCO_3$ molecular weight; 100 g/mole), the total amount of reacting $CaCO_3$ is calculated. When this amount is proportioned with the amount of soil that is used in the reaction, and multiplied with 100, the amount of % $CaCO_3$ is calculated. In this equation, P is the atm-unit pressure value which is measured at the digital manometer, V is the litre-unit volume of the chamber in which the reaction has occurred, T is the value of the ambient temperature in K, R is 0.082.

The pressure resistance of the reaction vessel was tested. In this test, pure $CaCO_3$ and 10% of HCl was used. In practice, the pressure resistance of the reaction vessel was set as 1.5 bar.

For the analysis, 4 grams of soil sample was reacted with 30 ml of 10 % HCl. After closing the reaction vessel, the digital manometer was reset. In this way, the reaction ambient was completely separated from the outside atmosphere ambient. Through being isolated from outside ambient, digital manometer eliminates the need for complicated calculations where water vapor pressure, atmospheric pressure factors are used as in Scheibler calcimeter. When the pressure value that is measured on digital manometer has exceeded 1.5 bar, the analysis was repeated by using 2 grams of soil sample and 15 ml %10 HCl.

RESULTS AND DISCUSSION

In order to determine the linear working range of the digital manometer, firstly, analyses were carried out with pure $CaCO_3$ and %10 HCl. Because the %10 HCl was used in two different volumes and the volume value effects the result of the analysis directly, two separate linear working range were set. In the first study, 15 ml of 10% HCl was used. Considering that 1 gram of soil was used in the analysis, pure $CaCO_3$ was used according to its rates in the soil. Pure $CaCO_3$ was analyzed from 0.8 g to 0.01 g; that is to say, the soil can be considered as being analyzed from 80 % content to 1% content (Table 2). In practical application, the exact measurement results of theoretical calculations are not obtained. In order to prevent the deviations between the theoretical and practical value, a correction function was applied. The correction function is a correction method which is applied to the practical (measured) pressure value. With the point spread graphic of practical pressure results, the linear trend line and with the correction function that is formed through equation of the graphic, the practical pressure value was approximated to the theoretical pressure value. (Figure 2).

Table 2. Results of linear working range studies.

$CaCO_3$ amount (g)	P(bar) (Practical)	P(bar) (Theoretical)	T (°C)	P (bar) (Calculate)
0.800	1.412	1.456	22.8	1.460
0.600	1.083	1.092	22.8	1.091
0.500	0.919	0.911	23.0	0.908
0.400	0.764	0.728	22.6	0.734
0.300	0.596	0.544	21.6	0.545
0.250	0.512	0.456	23.1	0.451
0.200	0.420	0.362	20.8	0.348
0.150	0.348	0.271	20.9	0.267
0.125	0.310	0.227	22.1	0.225
0.100	0.274	0.181	20.7	0.185
0.075	0.231	0.136	22.0	0.136
0.050	0.192	0.091	22.5	0.093
0.025	0.148	0.046	23.0	0.043
0.010	0.137	0.018	22.7	0.031

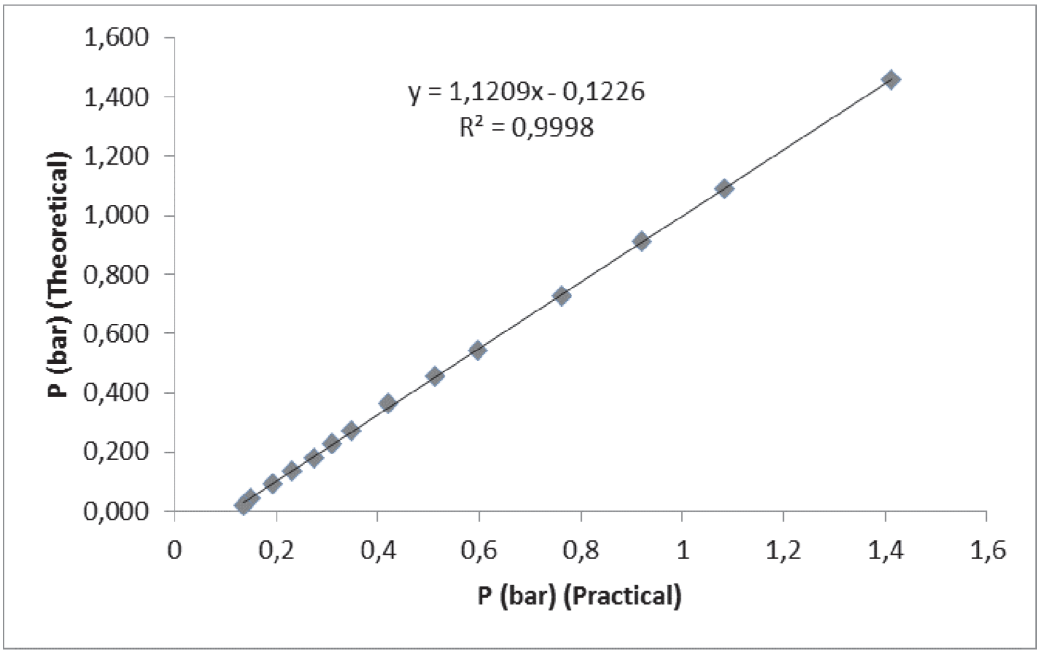

Figure 2. Relationship between practical and theoretical results of measurement

$$P\ (\text{theoretical}) = (n*R*T) / V \qquad (3)$$

In this equation, n (mole) value is the mole value of pure $CaCO_3$ amount which is used in the analysis. (n=m/ma). The P value which is measured by applying graphic equation calculation to P (theoretical) is approximated to the practical value (3). (4)

P (calculate) = (P(practical) * 1.1209)-0.1226 (1st Correction function)

If there is a change in the volume of reaction vessel which is measured except these measurements, this graphic and equation have to be re-calculated; in this case, when 2 grams of soil and 15 ml HCl reaction is executed, the equation does not change.

In analyses, in order to acquire clearer results under 0.15g which corresponds to 15% content level, by using more $CaCO_3$ and more 10% HCl, linear working range has been applied again (Table 3). In this application, by considering that 4 grams of soil is used, from 0.6g up to 0.04g pure $CaCO_3$ has been reacted with 30 ml of 10% HCl. That is to say, its amount has been measured from 15% to 1%. There was deviation on the practical and theoretical pressure values in the low $CaCO_3$ levels as well. Due to the change of volume in the CO_2 gas which occurs as a result of the reaction, these deviations are prevented with a new correction function application (Figure 3).

As a result of all studies, in soil measurement results whose content is over 15% 1st correction function (4), in soil measurement results whose content is %15 and lower values 2nd correction function should be applied (5). If it is not known in advance whether its content is over 15% or not, firstly, the 4 gram soil and 30 ml HCl reaction should be applied; if a measurement higher than 1.5 bar value is observed, 2 gram soil and 15 ml HCl reaction should be applied.

Table 3. Results of linear working range studies

% Soil $CaCO_3$ content	$CaCO_3$ amount (g)	P(bar) (Practical)	P(bar) (Theoretical)	T (°C)	P(bar) (Calculate)
15	0.60	1.211	1.224	21.7	1.231
8	0.32	0.737	0.654	22.2	0.636
5	0.20	0.56	0.409	22.3	0.414
2	0.08	0.362	0.164	22.4	0.166
1	0.04	0.298	0.082	23.2	0.085

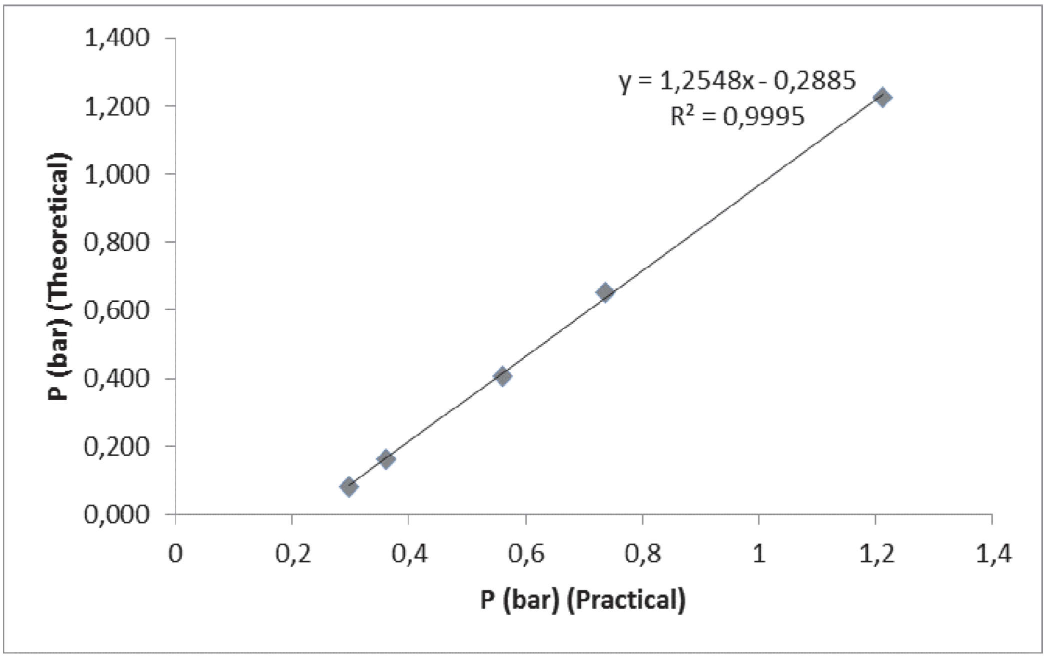

Figure 3. Relationship between practical and theoretical results of measurement (5)

P (calculate) = (P(practical) * 1.2548)-0.2885 (2nd Correction function)

The soil samples used in the analyses were dried in the air and sifted through a <2 mm sieve (<10 mesh). Another important point about the analysis is its duration. It is studied to determine an optimum duration in the analyses. As a result of the studies, it is determined that the optimum duration should be 2-3 minutes.

accurate method that can be used as an alternative to conventional Scheibler calcimeter in soil $CaCO_3$ content analysis.

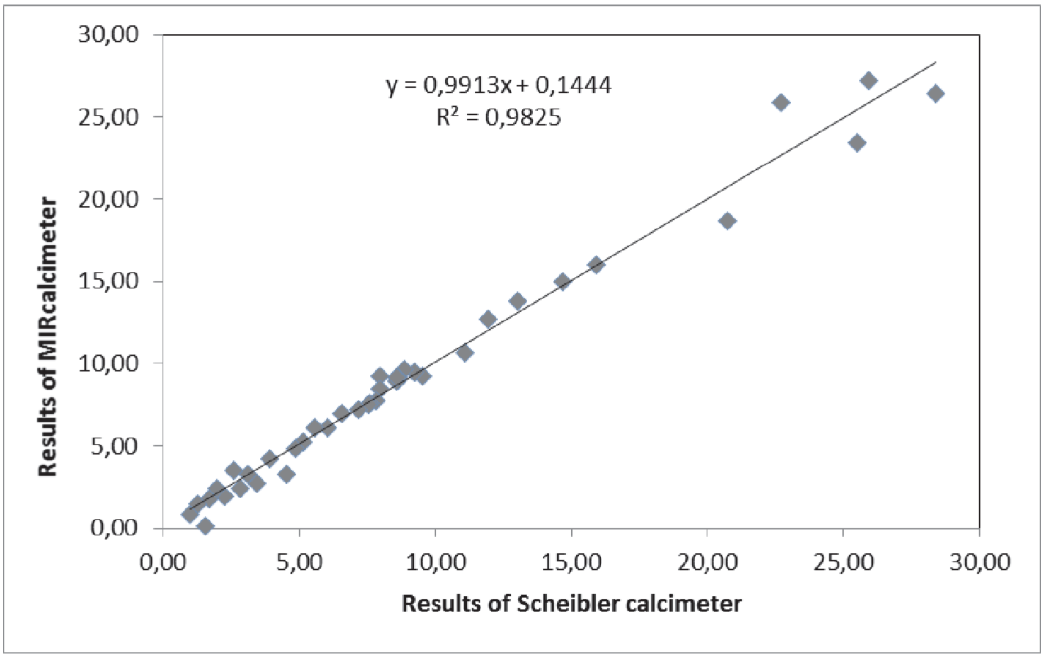

Figure 3. Relationship between results of Scheibler calcimeter and MIR calcimeter

After completion of the necessary data for an accurate method, correction functions were applied according to the measured pressure values. The results of Scheibler calcimeter and MIR calcimeter analysis were compared (Figure-4) and high regression coefficient was obtained (R^2= 0.9825). Since soil samples were used in analyses, the regression coefficient is lower than in pure $CaCO_3$ analyses.

CONCLUSIONS

In this study, a pressure calcimeter was developed as an alternative to Scheibler calcimeter. The soil samples contain $CaCO_3$ between % 1 – 30 were analysed by Scheibler calcimeter and the results were compared with MIR calcimeter. Excellent correlation (R^2=0.9825) was obtained between MIR calcimeter and Scheibler calcimeter. It can be concluded that MIR calcimeter is an

REFERENCES

Horvath, B., Opara-Nadi, O., Beese, F., 2005. A simple method for measuring the carbonate content of soil. Soil Sci. Soc. Am. J. 69, 1066-1068.

Kacar, B., 2012. Toprak Analizleri. Nobel Akademik Yayıncılık Eğitim Danışmanlık Tic. Ltd. Şti., Ankara. 43-53.

Loeppert, R.H., Suarez, D.L., 1996. Carbonate and gypsum. 437–475.In D.L. Sparks et al. (ed.) Methods of soil analysis: Part 3—Chemical methods. SSSA Book Ser. No. 5. SSSA and ASA, Madison, WI.

Martin, A.E., Reeve, R., 1954. A rapid manometric method for determining soil carbonate. Soil Sci. 79, 187–197.

Wagner, S.C., Hanson, D.J., Olness, A., Voorhess, W.B., 1998. A volumetric inorganic carbon analysis system. Soil Sci. Soc. Am. J. 62:690–693.

Williams, D.E., 1948. A rapid manometer method for the determination of carbonate in soils. Soil. Sci. Soc. Am. Proc. 13:127–129.

Woodward, L., 1961. A manometric method for the rapid determination of lime in soils. Soil Sci. Soc. Am. Proc. 25, 248–250.