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A MANOMETRIC METHOD FOR THE DETERMINATION OF SOIL CARBONATES IN THE FIELD

by

N. A. Polyzopoulos

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Chemistry

Approved:

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Logan, Utah

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Nicholas A. Polyzopoulos

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INTRODUCTION

In soil survey work the method now generally used to evaluate the carbonate content of the soil in the field is to observe the amount of effervescence that takes place when the soil reacts with dilute acid. The four degrees of effervescence usually recognized are designated by the symbols eo, e, es, ev and correspond roughly to a lime content of 0-0.5, 0.5-3, 3-15, and above 15 per cent, respectively. This, or course, is a very rough estimate and therefore a method is needed for the quantitative determination of carbonates in the field with a fair degree of accuracy. If such a method were available it would be possible for the soil surveyor to follow accurately in the field the distribution of lime down the profile. It would also make possible the detection of lime "bulges," a consideration of primary importance in soil classification. The method would also be useful to agricultural advisers, especially in connection with the problem of lime induced chlorosis.

There is a large variety of methods for the determination of soil carbonate in the laboratory with varying degrees of accuracy but none of them is very suitable for field use as they either employ complicated apparatus, or in other ways require laboratory facilities. The present study is concerned with the development and evaluation of a rapid method for the determination of soil carbonate in the field. The apparatus used is very simple and easy to carry and to handle under field conditions. The results obtained are sufficiently accurate for the purpose intended,

their accuracy being above that of the semiquantitative effervescence test.

The proposed method is now rendered particularly useful by the availability on the market of small portable kits for the determination of soil moisture in the field which permit the expression of results on a dry basis.

REVIEW OF LITERATURE

Introduction

A great variety of methods have long been in use for the determination of soil carbonates. Some of them are very elaborate and time-consuming and yield results of a high degree of accuracy while others are much quicker and simpler and the degree of accuracy of their results is, accordingly, lower. The method to be used in each case depends, of course, on the purpose for which the determination is made. If very accurate results are required one of the more elaborate and precise methods must be used. If less accurate results are needed, as in the majority of cases, the quicker but less accurate methods are quite satisfactory. All of these methods make use of a dilute acid, most commonly hydrochloric, to decompose the carbonates in the soil and the CO_2 thus evolved is estimated by gravimetric, titrimetric, or gasometric procedures. Accordingly, these methods can be classified in three categories as follows.

Gravimetric methods

The CO_2 evolved is weighed either directly by the gain in weight of an absorbent such as potassium hydroxide or preferably Carboscorb, Ascarite, or some other solid absorbent, or indirectly by the loss in weight of the system. The direct procedures usually give more accurate results. The gas evolved from the reaction vessel is dried and purified by passing it through a suitable absorption train, purification usually

being achieved by passing the gas through "U" tubes containing syrupy phosphoric acid and CO_2-saturated $CaCl_2$ solution (or "Anhydrone").

In soil analysis it is more common to use the indirect procedure. Erickson, Li and Gieseking (5) described an "alkali-meter" consisting of a 50 ml. Erlenmeyer flask having a short 5 ml. pyrex tube fused to the inside wall. The flask is protected from atmospheric moisture by two U tubes containing Anydrone. The sample is placed in the bottom of the flask and 5 ml. of a mixture of trichloroacetic acid (CCl_3COOH) and water are added to the tube. After the reaction of the acid with the carbonates of the soil, for which a 12 hour interval is allowed, H_2O-free air is drawn through the flask for 10 minutes to displace all of the CO_2 evolved. The difference in weight of the alkalimeter before and after the reaction is taken as the amount of CO_2 evolved. The $CaCO_3$ equivalent of the sample is calculated from the CO_2 data. This method is notable for using trichloroacetic acid instead of the universally used hydrochloric acid. The authors claim it to be preferable to the latter as it has a low vapor pressure and no oxidizing power; it does not reduce MnO_2 to give volatile substances but is strong enough to decompose the carbonates ($pK = 0.7$) and is very soluble in water. Provided that other gaseous products are not derived from the sample (for example H_2S from sulfides), accurate results are secured if due precaution is taken to prevent loss of water from the system.

Also well known is an indirect procedure used at the U. S. Regional Salinity Laboratory (20). As in this procedure inadequate care is taken to prevent vapor losses from the system, the results are of a lower degree

of accuracy, the relative error being of the order of ± 10 per cent.

Titrimetric methods

In these methods the CO_2 evolved by the reaction with acid is absorbed in an excess of standard alkali, usually NaOH or $Ba(OH)_2$ which is then back-titrated with standard acid. These methods differ somewhat in the form of the reaction vessel, the means of absorption, and the mode of titration. One of the oldest is that proposed by Amos (1) in which the soil sample was boiled with a solution of approximately 2N HCl. The CO_2 after passing through a condenser, was absorbed by standard 0.5 N NaOH solution, the excess of which was titrated with standard HCl in two stages, the first to the phenolphthalein end point and the second to that with methyl orange. The difference between these two titration values represents bicarbonate. Nowadays boiling is never used in the decomposition of the carbonates in soil samples as it often gives high results due to decomposition of organic matter, especially uronides and to the formation of chlorine by oxidation when manganese oxides are present. In this category belong the Schollenberger method, that of A.O.A.C. and that of Hutchinson and MacLennan. Here also belongs a procedure due to Tinsley and his collaborators. They are the most accurate methods available for determining the carbonate content of the soil.

In Schollenberger's method (15, 16, 17) CO_2 is liberated by boiling in vacuo at a comparatively low acid concentration and low temperature (30° C) and in the presence of an effective reducing agent ($FeCl_2 \cdot 4H_2O$). The sample containing not more than the equivalent of 0.25 g. of $CaCO_3$ is placed in a 200 ml. reaction flask which is connected through an

upright condenser with a one-litre absorption flask. After evacuating the system by means of a pump to about 20 mm. of mercury, 50 ml. of standard 0.2N $Ba(OH)_2$ solution is admitted to the absorption flask and dilute acid is sucked into the reaction vessel. The contents are heated so that a steady rate of boiling at about 30° C is maintained. Decomposition is generally completed within a few minutes and absorption of the CO_2 is practically concurrent with its evolution. A slow stream of CO_2-free air is admitted into the reaction flask, which sweeps the last traces of the CO_2 into the absorption vessel so that it is quantitatively absorbed. With normal soils there is no error from absorption of other acids. Finally the excess of hydroxide is titrated with standard 0.1N HCl using phenolphthalein or thymolphthalein as indicators. Although the method has undergone minor modifications since it was first described in 1930 (4), its essential features remain unchanged in the latest description (6). The major improvement over the originally used apparatus is the substitution of a condenser tube with eight oval bulbs for the straight tube first described, thus eliminating the danger of the acid in the reaction flask being shot during boiling into the absorption vessel.

In the A.O.A.C. method (2) the reaction vessel, a 300 ml. Erlenmeyer flask, is fitted with a top funnel containing the acid (approximately 1N HCl) and connected through a rubber tubing to the lower end of an absorption tower. This tower is at least 25 inches long and 1 inch in diameter and contains alternating pockets of solid glass rods and small glass beads. It can be connected at its upper end to a vacuum pump and at its lower end to a 500 ml. volumetric flask. The sample is introduced into the

reaction flask and the system evacuated. After releasing the suction, a suitable exactly measured volume of 0.5N NaOH or KOH is introduced into the absorption tower and the acid (1 + 9 containing 5 per cent $SnCl_2$) slowly let into the reaction flask. The CO_2 evolved is aspirated into the tower where it is absorbed by the alkali which, then, is washed into the volumetric flask connected at the lower end of the tower.

For titration, 10 ml. of a neutral 25 per cent solution of $BaCl_2$ is added to precipitate barium carbonate and after dilution and mixing, the flask is set aside for 4 hours before the excess of hydroxide is titrated with standard acid, phenolphthalein being used as indicator. For soils containing resistant carbonates, the reaction vessel is heated with a condenser inserted in front of the absorption vessel. This is a rather lengthy procedure and in the United States has been largely supplanted by the Schollenberger method.

Hutchinson and MacLennan's method (8) makes use of very simple apparatus and, in addition, it requires but little attention during operation. A slight modification of their method is described by Piper (18). It gives very accurate results and has been used in the present study to afford a standard basis of comparison. The reaction vessel, a 150 ml. round bottomed spherical flask, is connected to the absorption vessel, a one-litre filtering flask, containing 50 ml. of standard 0.1N NaOH solution. The soil sample, containing not more CO_2 than the equivalent of 0.2 g. of $CaCO_3$, is placed in the reaction flask and the system is evacuated as completely as possible by a pump or a water aspirator before admitting into the flask about 50 ml. of approximately 0.5N HCl from a

tap funnel fitting onto it. For soils high in organic matter or containing MnO_2, the acid contains 3 per cent w/v of $FeCl_2 \cdot 4H_2O$. No heating is required. The apparatus is shaken intermittently for 20 minutes and then a slow stream of CO_2-free air is admitted through the tap funnel. The shaking is repeated for another 20 minutes to complete absorption of carbon dioxide and then 10 ml. of a saturated $BaCl_2$ solution is added to the absorbend before titration with 0.1N HCl using phenolphthalein (or thymolphthalein) as indicator.

The apparatus was further simplified by Van Slyke (19) who combined in a single vessel a 500 ml. filter flask, the decomposition of the carbonate, and the absorption of CO_2. He used it for carbonate determinations in powdered bone and other biological materials but the same apparatus and procedure was used by Robinson (13) for soils, limestones, and marls.

In all the above cases the soil sample is finely ground to ensure both uniformity of subsampling as well as complete decomposition of carbonates by the dilute acid. Furthermore, a blank for the reagents and apparatus is always run with each batch of determinations and its value subtracted from the actual titration value.

The author found in his own experience that the results of the Hutchinson and MacLennan method are highly accurate but reproducible only when great care is exercised to secure uniformity of procedure.

Tinsley and his coworkers (19) modified this method further mainly with respect to the mode of titration. They used perchloric acid ($HClO_4$) 20 per cent weight by weight (w/w) (approximately 3N) for the decomposition of the carbonate and absorption was effected by 20 ml. of standard 0.05-

0.2N NaOH solution contained in a second tube within the same reaction and absorption vessel, a thick walled 500 ml. conical flask. After weighing the soil sample (0.5-5.0 g. depending on the carbonate content) into the flask, 10 ml. of $HClO_4$ are placed into the smaller of two short tubes placed in the flask and 20 ml. of standard alkali into the larger. The flask then is stoppered and evacuated immediately through a tube inserted in the rubber stopper, until small gas bubbles emerge in the surface of the hydroxide solution--this point corresponding, according to the above workers, to a pressure of about 50 mm. of mercury. The acid is then tilted out of the smaller tube and thoroughly mixed with the soil by swirling the flask which then is set aside for 18 hours to allow complete absorption. The vacuum is then released, the flask opened, and the absorbent in the large tube immediately titrated within the same tube, using a 10 ml. or 25 ml. burette with a rubber tube and pinchcock connected to an elongated fine jet reaching to the bottom of the tube. This jet is also used to stir the solution during the titration.

The titration is carried out in two stages: The first stage is to the thymol blue end point (pH = 8.25); the second stage is to the (screened) methyl orange end point pH = 3.8). Only the second titration value is recorded as it represents the CO_2 content as can be seen from the following equations:

$$NaOH + Na_2CO_3 + 2HCl \longrightarrow 2NaCl + NaHCO_3 + H_2O \qquad pH\ 8.3 \qquad (1)$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3 \qquad pH\ 3.8 \qquad (2)$$

From equation(2) it follows that 1 ml. of N HCl is equivalent to 44 mg. of CO_2. Then if z is the average number fo ml. of acid for the blank,

y the number of ml. of acid for the second stage only, and x is the normality of the acid we have:

$$\text{mg. of } CO_2 \text{ in the sample} = 44 \times (y-z)$$

This titration is fully described and discussed by Kolthoff and Stenger (10). As can readily be seen from equations (1) and (2), since the total amount of alkali in the absorbent tube is accurately known, the titration needs only to be carried to the first end point, the value of the second titration y being easily calculated (see for example Table 18, p. 146 in reference 20). This method of carbonate determination is, according to the authors, capable of a high degree of accuracy and reproducibility. It is used mainly in Great Britain.

In concluding the discussion of titrimetric methods for carbonate determination we should also mention the method described by Shaw and MacIntire (14) which is much quicker and of a satisfactory degree of accuracy. The reaction flask is fitted with a stopper carrying a steam inlet tube and a tap funnel for introducing the acid. The exit tube is a Liebig condenser leading through a gas-scrubbing bottle to the absorption vessel, a 500 ml. suction flask, containing dilute NaOH solution and provided with a special reservoir tube that can be moved vertically in the neck of the flask while maintaining an air-tight joint with a rubber sleeve. HCl or $HClO_4$ (approximately normal) containing 5 per cent w/v of stannous chloride ($SnCl_2 \cdot 2H_2O$) is used for decomposition which is aided by passing steam through the flask for about 2 minutes and shaking it for another minute. The absorbent is then titrated with standard HCl using phenolphthalein as indicator with or without addition of $BaCl_2$.

Some decomposition of organic matter, and therefore release of organic CO_2 takes place during the operation and this is attributed to the higher temperature of the steam as compared with the boiling in vacuo temperature in Schollenberger's method.

Finally we could classify with the titrimetric methods a widely used direct titration procedure in which the carbonates in the soil sample are decomposed by a measured amount of standard acid, with heating, and the excess of acid is back titrated in the same vessel and in the presence of the soil, with standard alkali. Edson (4) has suggested the use of a 1 per cent solution of resazurin as indicator for obtaining sharper and more easily perceptible end points which are often obscure in the presence of soil (especially in the case of ferruginous or organic soils).

Gasometric methods

In these methods the CO_2 liberated by the action of the acid is measured in a closed system either volumetrically at known temperature and pressure, or manometrically at known temperature and volume.

Of the volumetric devices well known is the Scheibler apparatus (21) which has been extensively used in Germany.

A more modern modification of the Scheibler apparatus is the Collins calcimeter (24) which has been exclusively used at the Rothamsted Experiment Station and the Macaulay Institute in Scotland as well as for advisory work all over Great Britain. It consists mainly of a small reaction flask connected to a gas burette both being jacketed in a wide-bodied cylinder full of water which, during operation of the apparatus is stirred by

bubbling air to keep its temperature uniform throughout. This temperature is read on a sensitive thermometer also immersed in the water in the cylinder. After decomposition of the carbonate and equalization of its pressure with the barometric pressure the percentage CO_2 in the soil sample is given by the expression:

$$CO_2\% = \frac{g\left(1 + \frac{as}{f - g - a}\right)(B - T)}{760\ (1 + \delta t)} \times 0.001964 \times \frac{100}{w}$$

where:

f = volume of decomposition flask in ml.
a = volume of acid used in ml.
g = volume of gas measured in burette in ml.
s = number of ml. of gas dissolved in 1 ml. of water
B = height of barometer in mm. of mercury
t = temperature in degrees centigrade
T = tension of aqueous vapor in mm. of mercury
w = weight of soil sample in g.
δ = coefficient of expansion of gas
0.001964 = weight of 1 ml. of CO_2 at N.T.P. in g.

The expression 760 $(1 + \delta t)$ as well as T and s are all functions of temperature and are taken from tables. The quantities f, a, w are known and g, t and B are measured. Calculations are facilitated by the use of a special slide rule accompanying the instrument.

The Van Slyke apparatus (19) is also a widely known instrument for the volumetric determination of carbonates. However it is mainly used for biological materials such as bones. All of these devices give rather accurate results and their operation requires short time.

A simple apparatus known as "calcimetre de Bernard" and consisting of a reaction flask connected to a gas burette equipped with a leveling bulb is widely used in continental Europe. If corrections due to temperature changes as well as to water vapor pressure and solubility of CO_2

in the water of the gas burette are made, the results are of a fair degree of accuracy.

Of the manometric procedures perhaps the simplest is Passon's method as modified by H. R. Skews (12). In this method CO_2 is liberated by the action of HCl on the soil in a closed system and the increase in pressure is measured in an open mercury manometer connected to the system. The apparatus is calibrated with known amounts of carbonate added to a carbonate-free soil so that the total weight of the sample and assumingly its volume, remain constant. Temperature is kept constant or, according to Piper, corrections can be made by subtracting for each increase of 1° C above the calibration temperature one-eightieth of the amount of $CaCO_3$ found. As stated by Piper, for soils containing 0.2 to 1 per cent of $CaCO_3$, the average error of this method varies from 10 per cent to 4 per cent of the total carbonate present, decreasing as the amount of carbonate increases.

Singh and Mathur (18) described an apparatus analogous to the Collins calcimeter, in which the pressure developed by decomposing an amount of carbonate in a detachable tube (a modification of Thunberg tube) is measured by connecting the tube to the apparatus which is essentially an open manometer enclosed in a water jacket. Uniform temperature during experimentation is secured by stirring the water in the jacket. The manometer liquid is Brodie's solution, the composition of which is: 500 ml. of water, 23 g. NaCl, 5 g. sodium tauroglycocholate, and a few drops of an alcoholic solution of thymol. One atmosphere is approximately equivalent to 10,000 mm. of Brodie solution. Since the amount x of CO_2 evolved

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in the reaction, in ml. at N.T.P. (dry) is proportional to the increase in pressure h, in mm. of Brodie solution: $x = kh$

The value of the constant k is calculated from the formula:

$$k = \frac{Vg \frac{273}{t + 273} + Vf\ CO_2}{P_o} + A \frac{273}{t - 273} \quad \text{where:}$$

Vg = volume of gas in ml.
Vg = volume of acid in ml.
α_{CO_2} = Bunsen absorption coefficient of CO_2 at t^o C
P_o = pressure of one atmosphere expressed in mm. of Brodie solution
A = area of cross-section of manometer tube in cm^2 (0.75 cm^2)

Tables give the value for k for temperatures from 15° to 35° C. Then the amount of CO_2 in a soil sample weighing w g. is $\frac{x \cdot 0.1977 \text{ mg.}}{w}$ The authors state that the accuracy of the apparatus is $\pm$ 1.25 per cent. It is noted that the apparatus presents many similarities to the well known Warburg apparatus used so frequently for the analysis of gases in connection with biological materials.

D. E. Williams (23) in his method makes use of an ordinary wide-mouthed, 8 ounce bottle, taking a screw-on bakelite cap, as the reaction vessel. By using a rubber gasket an air-tight joint between bottle and cap is secured. The soil sample containing not more than the equivalent of 0.5 g. of $CaCO_3$ is placed in a small plastic cup and lowered into the bottle after addition of 25 ml. of 2N HCl. After screwing on the cap and tightening it, a 24 or 25 gauge hypodermic needle is inserted through one of three or four small holes drilled in the cap in order to equalize internal and external pressures. Then the needle is removed (the rubber gasket is self-sealing), the bottle shaken, and the increase in pressure

measured by plunging into the bottle (in a second hole) another needle which is connected with rubber tubing to an open mercury manometer. The pressure in several bottles can be measured at one time and the $CaCO_3$ content of the samples read from a graph. This graph is plotted by calibrating a bottle with known amounts of carbonate; it is a straight line passing through the origin, implying ideal behaviour of the CO_2 gas within the pressure range of the experiment. Temperature is kept constant throughout. Williams (23) recommends . . .

> . . . running a standard with each set of determinations thus eliminating possible difficulties arising from slight changes in atmospheric pressure or room temperature between different sets of determinations.

However, although changes in temperature are certainly important, it is not seen how changes in atmospheric pressure, if not taking place within the very short time interval between pressure equalization and pressure measurement--which is highly improbable--can have any effect.

Martin and Reeve (11) in a critical study of Williams' method found that it was not possible to obtain consistent readings during calibration and attributed it to the failure of pressure equalization due to the hypodermic needle becoming blocked by droplets of liquid. In a preliminary study of the method, aiming at modifying it for field use, it has not been possible to obtain consistent readings during calibration. However, as the efficiency of the needles to equalize internal and external pressure was unquestionable, the failure to obtain consistent readings was attributed to small temperature changes occurring between the times of pressure equalization and measurement. These small changes in the temperature of the bottle contents can not be avoided even when working in

a constant temperature room, and are the result of manipulating the bottles and the heat of the reaction. Their effect is discussed more fully in a later section.

Martin and Reeve have modified Williams' procedure and they connect the bottles to the manometer with a short brass tube passing through the cap and secured tightly on it. Further, instead of using a calibration graph, they calculate the CO_2 evolved in a reaction from the formula:

$$v = \frac{h}{760}\left(\frac{273\ V}{T} + \alpha V_\alpha\right) \qquad \text{where:}$$

v = volume of CO_2 in vml. at N.T.P.
V_α = net volume of the system in ml.
T = absolute temperature
α = Bunsen absorption coefficient of CO_2 in HCl
h = pressure in mm. of mercury

In the above equation V_α is known and h and T are measured. V also can be measured directly but it must also include the attachments to the bottle (such as the tubing). Therefore the value of V is obtained from the above equation using a known quantity of calcium carbonate. The value of V, once obtained for each bottle, is then used for the calculation of v. The value of α is taken from Table 9.

The weight of CO_2 in g. is given by the expression: $w = \frac{v \times 44}{22,400}$ and the percentage of the $CaCO_3$ in a sample of weight W by:

$$CaCO_3\% = \frac{w \times 100}{44 \times W} \times 100$$

It can readily be seen that, since α is not a constant but a function of T, the relation between v and T is not linear.

Dixon and Williams (3) make use of an identical technique for the determination of (inorganic) CO_2 mainly in absorbent liquors or other

carbonate solutions (the method can, of course, be used for insoluble carbonates as well) but their calculations are slightly different. According to these authors, when using an open manometer the weight in grams of $CaCO_3$ (provided that no change occurs in the barometric pressure or the volume of the gases) is given by the expression:

$$W = \left(\frac{V \times 0.001965 \times 273}{760}\right) \times \left(\frac{P - p}{T_2} - \frac{P}{T_1}\right) \qquad (3)$$

or, if a_1 is substituted for the expression $\frac{V \times 0.001965 \times 273}{760}$

$$W = a_1 \frac{P}{T_2} - \frac{PD}{T_1 T_2} \qquad (4)$$

where:

W = weight of CO_2 in g.
V = volume of gases in ml. in reaction vessel and connection
T_1 = absolute temperature of gases before reaction
T_2 = absolute temperature of bases after reaction
$D = T_2 - T_1$
p = manometric pressure in mm. of mercury
P = barometric pressure in mm. of mercury, which in practice is unchanged during the determination

Equation (4) can be simplified if $T_1 T_2$ is taken as $(293)^2$ and $P = 760$. Then if we substitute b for $\frac{760 \times a_1}{293^2}$ equation (4) becomes:

$$W = \frac{a_1 p}{T_2} - bD \qquad (5)$$

They further introduce two correction factors F_1, F_2 for the amount of CO_2 dissolved in the mixed liquids and for the change in volume of the CO_2 due to displacement of the mercury in the manometer, respectively. The solubility of CO_2 in the mixed liquid (viz. 5 per cent H_3PO_4 partially neutralized with up to 3 per cent of base) was found to be 0.01 g. per

10 ml. at 760 mm. partial pressure of CO_2. Substituting a for $a_1F_1F_2$, equation (5) becomes:

$$W = \frac{ap}{T_2} - bD \qquad (6)$$

which is their working equation.

It is remarked that their correction factor F_1 is taken as a constant, while actually it is a function of temperature. By this approximation the linearity of equation (5) is not affected and equation (6) represents a straight line too. According to the authors, a mechanical pressure gauge can only be substituted for the manometer if the gauge is of such a type that the gases enclosed in the instrument do not change appreciably in volume.

In an alternative procedure, using a closed manometer, the reaction vessel is evacuated by means of a pump to about 10 mm. of mercury. If p_1, p_2 are the pressures before and after the reaction, the equation giving the value of W is:

$$W = \left(\frac{V \times 0.001965 \times 273}{760}\right) \times \left(\frac{p_2}{T_2} - \frac{p_1}{T_1}\right)$$

This can be simplified to:

$$W = \frac{a_1 \Delta}{T} \quad \text{where } \Delta = p_2 - p_1 \text{ and } T = \text{avg. temperature}$$

In this procedure volume changes are insignificant and Δ needs only to be corrected for the solubility of CO_2 by introducing the factor F_1 (taken again as a constant) if $a_1F_1 = K$, $W = \frac{a_1 \Delta}{T}$ becomes

$$W = \frac{K \Delta}{T} \qquad (7)$$

which again represents a straight line. In this case any accurate pressure

gauge can replace the manometer; a, b, and K are apparatus constants.

The authors in their paper give nomographs for the graphical solution of equations (6) and (7).

Horton and Newson (7) have described a rapid gas-evolution method for the determination of $CaCO_3$ equivalent in liming materials. In this method the carbonate in the sample is decomposed in a 125 ml. Erlenmeyer flask and the CO_2 evolved led through a glass tube into a graduated cylinder filled with water. The gas displaces a volume of water equal to its own volume z under the conditions of the experiment, which can be readily measured in the cylinder. The experiment is repeated under identical conditions using 1 g. of pure $CaCO_3$. If the volume of gas evolved in this case, as measured by the water displaced from the cylinder is y, the $CaCO_3$ equivalent x of the sample is given by the expression:

$$x = \frac{z}{y} \times 100$$

It is to be noted that in this method too, a linear relationship is found to exist between the amount of CO_2 and its pressure. It is obvious that the method can be used with soils if their carbonate content is sufficiently high.

Wilde and Voigt (22) in their book Analysis of Soils and Plants for Foresters and Horticulturists, published in 1955, propose a manometric method making use of an aneroid manometer for the determination of soil carbonates in the field. However, their discussion is too brief; no details are given and no evaluation of the method is made.

The literature on methods for the determination of soil carbonates is exceedingly large and no attempt has been made in this review to be

exhaustive. The author has briefly discussed the methods of general interest and presented in some detail only those methods of particular interest to the present study.

METHOD AND APPARATUS

Preliminary trials

As has become evident from the foregoing review, only gasometric methods hold promise for field use. They require neither complicated apparatus, use of laboratory facilities, or standard solutions. Manometric methods in particular seem to be the most adaptable for use under field conditions. However, the use in the field of a liquid manometer, either open or closed, is evidently objectionable and the only alternative seems to be a suitable mechanical pressure gauge.

It was originally intended to use Williams' hypodermic needle modification (23) of Passon's method (12) by further substituting a mechanical gauge for the mercury manometer. Therefore a large number of trials were carried out using 8 or 16 ounce ordinary wide-mouthed bottles as the reaction vessel and three commercial types of gauges. During these trials it was impossible to obtain any reproducible results when using known amounts of pure $CaCO_3$. This was attributed to the following three causes: 1) The gauges used were neither sufficiently accurate nor sensitive enough. In addition they were of the receding type, thus rendering impossible an accurate reading as well as detection of small leakages of the gas. 2) Even small temperature changes were found to have an appreciable effect on the pressure of the CO_2 evolved. 3) Clamping pressures (that is, the small pressures developed on screwing on the lid and gasket) were not completely released by plunging in a hypodermic needle, thus introducing a variable

error for which no consistent correction could be applied. This failure of releasing the clamping pressure has been explained by Martin and Reeve (11) as caused by liquid droplets blocking the needles. These authors calculated[1] the pressure required to overcome the liquid tension for a 25-gauge needle having an approximate internal diameter of 0.33 mm. to be 6.6 mm. of Hg. On the other hand, by direct experimental measurement, they found that the maximum pressure required to overcome interfacial tension of liquid drops within these needles was 9.3 mm. of Hg. This fair agreement lends support to the validity of their suggestion that the errors obtained are due to the effect of liquid trapped in the bore of the needle. However, even with perfectly clean needles, it was found when using a mercury manometer that small pressure differences were often recorded without any carbonate being decomposed in the bottle. This was attributed to vapor pressure building up to maximal values in the originally unsaturated atmosphere in the bottle.

As it was also considered that the handling of hypodermic needles and vaseline (used to obtain an air-tight joint between the gasket and the bottle) in the field is very inconvenient, Williams' technique was abandoned as not being adaptable under field conditions.

Laboratory experiments

Apparatus.--An accurate laboratory-type pressure gauge was obtained with reading range 0-60 mm. of mercury (Fisher Cat. No. 11-281) and a

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[1]By using the equation $h = \frac{2T}{rdg}$ where T = surface tension, d = density of water, g = acceleration of gravity, and h = capillary rise in cm.

simple apparatus was assembled as shown in Figure 1. "A" is an ordinary 2-litre bottle (an empty reagent bottle) which can take a No. 13 rubber stopper. Through two holes in this stopper are inserted a Weston metallic thermometer (Model 2261) graduated in halves of degrees centigrade, the stem of which was sprayed with "Krylon" to be protected from acid corrosion and a glass tube "B" equipped with a ground glass stopcock. The gauge "G" is connected to the glass tube through a short length (approximately 30 cm.) of rubber tubing. "C" is a small, flat-bottomed plastic cup to hold the soil sample.

Procedure.--An amount of soil containing not more than the equivalent of 0.6 g. of $CaCO_3$ is weighed into the plastic cup. By means of a small graduated cylinder a measured volume of approximately 2N HCl is added to the bottle and then the cup containing the soil is carefully lowered into it by means of a pair of tongs. The volume of acid added is 25 ml. minus the volume occupied by the soil sample, calculated as recommended by Williams, on the assumption that the real density of soil particles is 2.5. The stopper is placed in position, tightly secured, and the bottle left to attain temperature equilibrium with the top on the glass tube partially or totally removed so that internal and external pressures equalize. In the laboratory this may take a few minutes. Then the stopcock is restored to its position, the temperature recorded, and the bottle violently shaken to tilt the soil out of the cup and mix it with the acid. Manual shaking is repeated intermittently for a period of 10 minutes during which time the carbonates of most soils are completely decomposed. After allowing another two or three minutes for the gases in

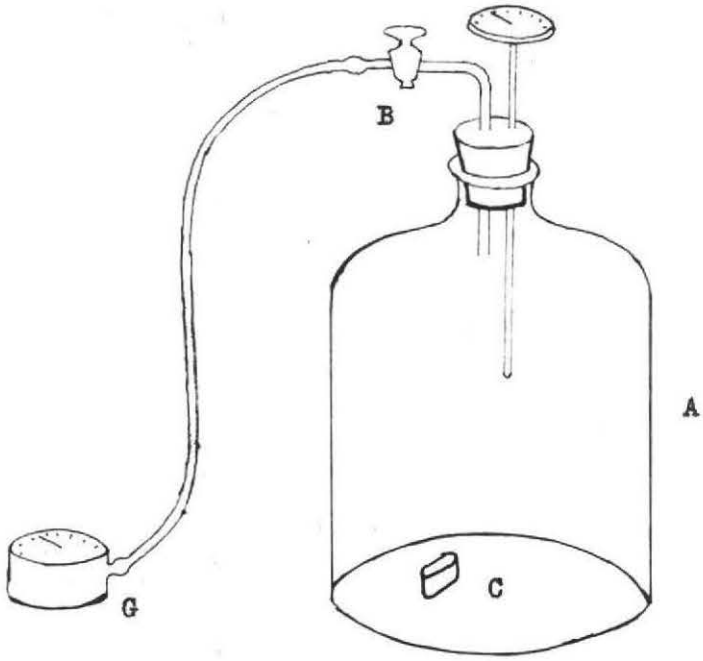

Figure 1. Apparatus for the determination of carbonates

the bottle to attain temperature equilibrium, the temperature is recorded and the pressure of CO_2 measured on the gauge to approximately 0.1 of a mm. of mercury.

If the two temperatures differ, as is usually the case, a temperature correction, generally negative, must be made on the pressure reading for the change in pressure of the atmospheric air within the bottle (Table 1). On the other hand, if the temperature at the time of measurement differs considerably from the temperature of calibration, a second temperature correction has to be made on the pressure of CO_2 (Table 2).

The carbonate content of the sample, expressed as its $CaCO_3$ equivalent, is then read from a calibration curve prepared with known amounts of pure calcium carbonate (Figure 2).

Using this procedure determinations of carbonate on 44 air-dried, ground and sieved soil samples of widely varying textures and carbonate content, which varied from a few tenths of a unit up to 80 or more per cent, were made in duplicate. Carbonate determinations using both Hutchinson and MacLennan's method and Williams' hypodermic needle technique were also run on the same soil samples for comparison. The reproducibility of the method was also tested by making duplicate determinations on 10 randomly selected soil samples by both Hutchinson and MacLennan and the method proposed.

Field experiments

In order for the manometric method, as it has been described above, to be conveniently used in the field, it was found that some modification of the apparatus was necessary.

Table 1a. Positive corrections in mm. of Hg for the atmospheric pressure inside the bottle for temperature decreases between pressure equalization and measurement (for use in laboratory experiments)

Temp. °C at pressure equalization	Positive corrections in mm. of Hg for the temperature decreases given below in °C														
	1.5	1.4	1.3	1.2	1.1	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
22	3.3	3.1	2.8	2.6	2.4	2.2	2.0	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2
23	3.3	3.0	2.8	2.6	2.4	2.2	2.0	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2
24	3.2	3.0	2.8	2.6	2.4	2.2	2.0	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2
24.5	3.2	3.0	2.8	2.6	2.4	2.2	1.9	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2
25	3.2	3.0	2.8	2.6	2.4	2.2	1.9	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2
25.5	3.2	3.0	2.8	2.6	2.4	2.2	1.9	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2
26	3.2	3.0	2.8	2.6	2.4	2.2	1.9	1.7	1.5	1.3	1.1	0.9	0.7	0.4	0.2

Table 1b. Negative corrections in mm. of Hg for the atmospheric pressure inside the bottle for temperature increases between pressure equalization and measurement (for use in laboratory experiments)

Temp. °C at pressure equalization	Negative corrections in mm. for Hg for the temperature increases given below in °C														
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
22	0.3	0.4	0.7	0.9	1.1	1.3	1.5	1.7	2.0	2.2	2.4	2.6	2.8	3.1	3.3
23	0.2	0.4	0.7	0.9	1.1	1.3	1.5	1.7	2.0	2.2	2.4	2.6	2.8	3.0	3.3
24	0.2	0.4	0.6	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.4	2.6	2.8	3.0	3.3
24.5	0.2	0.4	0.6	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.4	2.6	2.8	3.0	3.3
25	0.2	0.4	0.6	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.4	2.6	2.8	3.0	3.2
25.5	0.2	0.4	0.6	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.4	2.6	2.8	3.0	3.2
26	0.2	0.4	0.6	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.4	2.6	2.8	3.0	3.2

[a]Calculated on the basis of a barometric pressure of 645 mm. of Hg.

Table 2. CO_2 pressure corrections in mm. of Hg for small deviations from the calibration temperature 25 °C (for use in laboratory experiments)

Positive corrections of the CO_2 pressure for negative deviations from the calibration temperature - Deviations in °C				CO_2 pressure mm. Hg	Negative corrections of the CO_2 pressure for positive deviations from the calibration temperature + Deviations in °C			
2.0	1.5	1.0	.5		.5	1.0	1.5	2.0
-	-	-	-	5	-	-	-	-
0.1	-	-	-	10	-	-	0.1	0.1
0.1	0.1	0.1	-	15	-	0.1	0.1	0.1
0.1	0.1	0.1	-	20	-	0.1	0.1	0.1
0.2	0.1	0.1	-	25	-	0.1	0.1	0.2
0.2	0.2	0.1	0.1	30	0.1	0.1	0.2	0.2
0.2	0.2	0.1	0.1	35	0.1	0.1	0.2	0.2
0.3	0.2	0.1	0.1	40	0.1	0.1	0.2	0.3
0.3	0.2	0.2	0.1	45	0.1	0.2	0.2	0.3
0.3	0.3	0.2	0.1	50	0.1	0.2	0.3	0.3
0.4	0.3	0.2	0.1	55	0.1	0.2	0.3	0.4
0.4	0.3	0.2	0.1	60	0.1	0.2	0.3	0.4

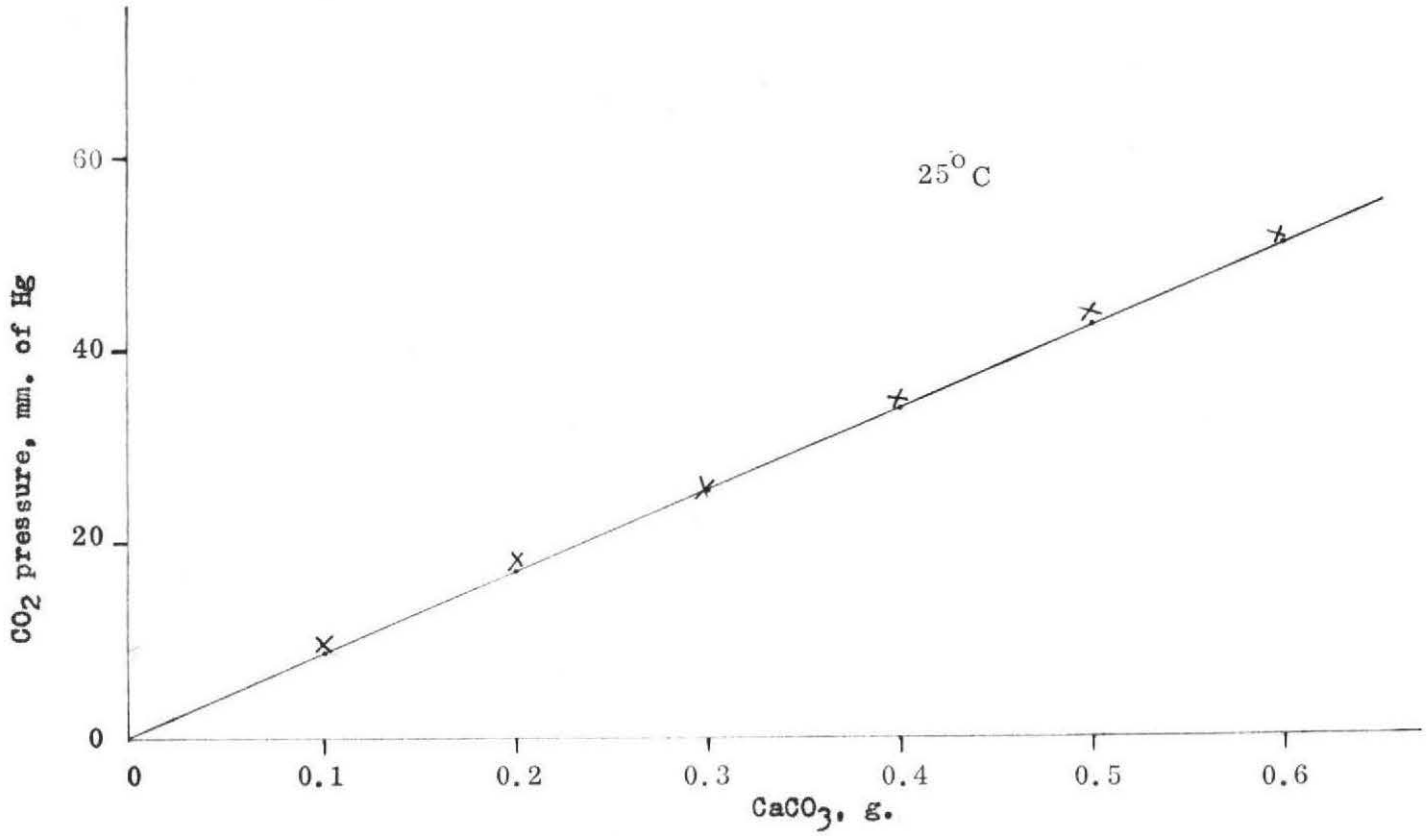

Figure 2. Calibration graph for the laboratory experiments using a 2000 ml. bottle and known amounts of $CaCO_3$

In the first place, a 2-litre bottle is too big for field use so it was necessary to use smaller bottles and after trying a few different sizes it was finally decided to use hard polyethylene bottles (tall shaped, Boston round) of about 900 ml. capacity. These bottles can take a No. 12 rubber stopper; they do not deform when pressure is uniformly applied on them from inside and there is no indication that, at least in the time taken by any experiment, the CO_2 derived from the sample diffuses through the walls. Besides, they are unbreakable and of a much lighter weight than glass bottles of the same size.

With smaller bottles and considering that in the field, where the soil sample can be neither accurately weighed nor ground, a much larger soil sample would have to be used, it would be necessary to use a gauge covering a much wider range of pressures, and yet which would be accurate enough. Such a laboratory-type pressure gauge is manufactured by Fisher (Cat. No. 11-281) and covers the range 0 to 300 mm. of Hg. This instrument is of the same type as that used in the laboratory experiments, the only difference being the wider range it covers, and accordingly, its smaller sensitivity. It is graduated in 5 mm. divisions which makes it possible to take, by estimation, readings down to 1 mm. of pressure.

As to the way in which the sample is to be measured, in the field it was found that measuring it by volume instead of taking its weight must be ruled out as it introduces a very large error. Eighty-four soils, ranging from a few tenths of a unit up to 80 per cent or more in carbonate content, were used to test this possibility. A small plastic scoop was successively filled with each of these soils which then was lightly

pressed with the thumb, stricken level with a spatula, and its weight measured with a torsion balance; this was done in duplicate and the results averaged. Although reproducibility of the weight of the same sample was very good, different soil samples measured by volume in this way had widely different weights. Table 3, summarizing the results of these measurements, shows that even within the same textural class the weights of soil thus measured showed deviations from an average value sometimes as high as 18 per cent. It is thus obvious that the sample could not be measured by volume and has by some means to be weighed. A small hand balance (Fisher Cat. No. 2-140) was found suitable for the purpose. It is sensitive to about 0.01 g.

Further, as in the field the range of temperatures encountered is much wider than that observed in the laboratory, Tables 1 and 2, for the correction of pressures due to temperature changes, were extended to cover the expected range; they were reproduced as Tables 4 and 5. The bottles were also calibrated in two temperatures, 15° and 25° C (Figure 3).

The performance of the method in the field was tested in the following way: A soil pit was dug or an undisturbed soil core obtained by the core sampler and the lime content in each of its horizons determined on a representative sample in the field. This sample was obtained by taking small amounts of soil with a spatula, placing it into a can (those used for soil moisture determinations), mixing it by shaking the can with the lid on, and using a part of this quantity of soil, of an appropriate size, for the lime determination. The remainder was taken to the laboratory for moisture determination. The size of the sample used was from 2 to 10 g.

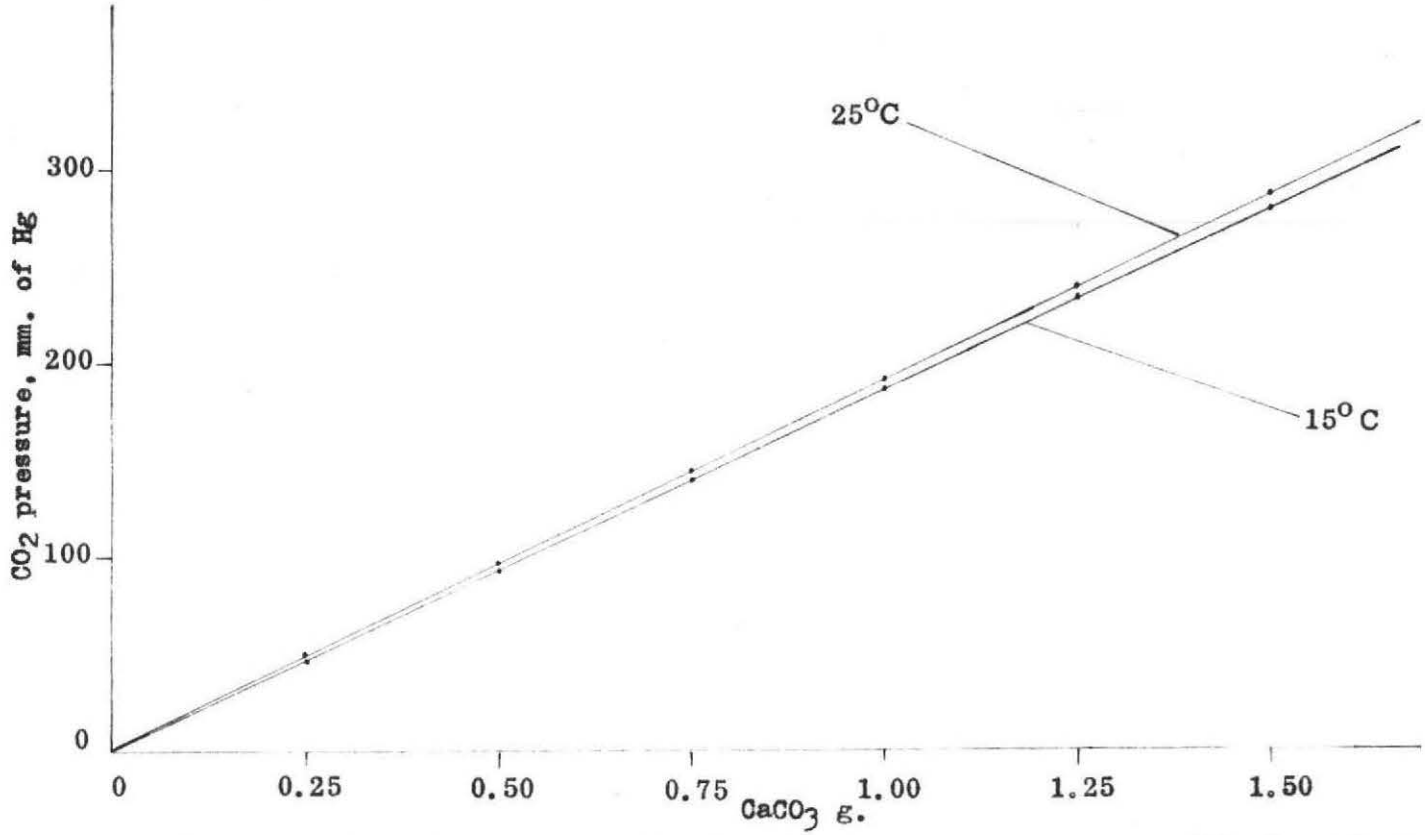

Figure 3. Calibration graphs for the field experiments using a 900 ml. polyethylene bottle and known amounts of $CaCO_3$

Table 3. Variation in weight of equal volumes of various soil samples[a]

Textural classes	Number of samples	Range of carbonate contents[b]	Average weight of samples	Range of sample weight	Coefficient of variation[c]
			g.	g.	
Sands	5	1.1 - 53.7	4.84	0.25	2.11
Loamy sands	10	0.7 - 65.5	4.77	0.60	5.11
Sandy loams	9	3.5 - 62.0	4.56	0.79	6.09
Loams	10	0.4 - 74.7	4.04	1.03	9.59
Silty loams	7	5.5 - 87.6	3.54	0.86	8.57
Silty clay loams	10	4.9 - 55.8	3.71	1.22	10.42
Sandy clay loams	7	2.2 - 56.6	4.35	0.64	2.00
Clay loams	13	3.8 - 78.4	3.83	1.40	11.91
Silty clays	5	13.8 - 50.3	3.95	0.65	6.99
Clays	8	1.6 - 52.9	4.08	0.51	4.32

[a]Summary of the results of duplicate measurements on 84 soils of widely varying texture and carbonate content.

[b]Expressed as $CaCO_3$ per cent.

[c]$\frac{S}{\bar{Y}} \times 100.$

Table 4. Corrections in mm. of Hg of the atmospheric pressure inside the bottle for temperature changes between pressure equalization and measurement (for use in the field experiments)

Positive correction in mm. for the temperature decreases indicated below (in deg. C)						Temp. at time of pressure equalization	Negative correction in mm. for the temperature increases indicated below (in deg. C)					
3.0	2.5	2.0	1.5	1.0	0.5		0.5	1.0	1.5	2.0	2.5	3.0
6.8	5.7	4.6	3.4	2.3	1.1	10	1.1	2.3	3.4	4.5	5.7	6.8
6.8	5.7	4.5	3.4	2.3	1.1	11	1.1	2.3	3.4	4.5	5.6	6.7
6.8	5.7	4.5	3.4	2.3	1.1	12	1.1	2.3	3.4	4.5	5.6	6.7
6.8	5.6	4.5	3.4	2.3	1.1	13	1.1	2.3	3.4	4.5	5.6	6.7
6.7	5.6	4.5	3.4	2.3	1.1	14	1.1	2.2	3.4	4.5	5.6	6.7
6.7	5.6	4.5	3.4	2.2	1.1	15	1.1	2.2	3.3	4.5	5.6	6.6
6.7	5.6	4.5	3.3	2.2	1.1	16	1.1	2.2	3.3	4.4	5.5	6.6
6.7	5.6	4.5	3.3	2.2	1.1	17	1.1	2.2	3.3	4.4	5.5	6.6
6.6	5.5	4.4	3.3	2.2	1.1	18	1.1	2.2	3.3	4.4	5.5	6.6
6.6	5.5	4.4	3.3	2.2	1.1	19	1.1	2.2	3.3	4.4	5.5	6.6
6.6	5.5	4.4	3.3	2.2	1.1	20	1.1	2.2	3.3	4.4	5.5	6.5
6.6	5.5	4.4	3.3	2.2	1.1	21	1.1	2.2	3.3	4.4	5.4	6.5
6.6	5.5	4.4	3.3	2.2	1.1	22	1.1	2.2	3.3	4.3	5.4	6.5
6.5	5.5	4.4	3.3	2.2	1.1	23	1.1	2.2	3.3	4.3	5.4	6.5
6.5	5.4	4.3	3.3	2.2	1.1	24	1.1	2.2	3.2	4.3	5.4	6.4
6.5	5.4	4.3	3.3	2.2	1.1	25	1.1	2.2	3.2	4.3	5.4	6.4
6.5	5.4	4.3	3.2	2.2	1.1	26	1.1	2.2	3.2	4.3	5.3	6.4
6.4	5.4	4.3	3.2	2.2	1.1	27	1.1	2.1	3.2	4.3	5.3	6.4
6.4	5.4	4.3	3.2	2.1	1.1	28	1.1	2.1	3.2	4.3	5.3	6.4
6.4	5.3	4.3	3.2	2.1	1.1	29	1.1	2.1	3.2	4.2	5.3	6.3
6.4	5.3	4.3	3.2	2.1	1.1	30	1.1	2.1	3.2	4.2	5.3	6.3
6.4	5.3	4.3	3.2	2.1	1.1	31	1.1	2.1	3.2	4.2	5.3	6.3
6.3	5.3	4.2	3.2	2.1	1.1	32	1.1	2.1	3.2	4.2	5.2	6.3
6.3	5.3	4.2	3.2	2.1	1.1	33	1.1	2.1	3.1	4.2	5.2	6.3
6.3	5.3	4.2	3.2	2.1	1.1	34	1.1	2.1	3.1	4.2	5.2	6.2
6.3	5.2	4.2	3.1	2.1	1.1	35	1.1	2.1	3.1	4.2	5.2	6.2

Table 5. CO_2 pressure corrections in mm. of Hg for deviations from the calibration temperatures, 15° and 25° C (for use in the field experiments)

Pressure corrections in mm. for temperatures other than the calibration temperature and for the pressures given below													
	Calibration temperature 25° C Pressure measured, mm.						Calibration temperature 15° C Pressure measured, mm.						
	°C	60	120	180	240	300	°C	60	120	180	240	300	
Positive corrections	20	1.0	2.0	3.0	4.0	5.0	10	1.0	2.0	3.0	4.0	5.0	Positive corrections
	21	0.8	1.6	2.4	3.2	4.0	11	0.8	1.7	2.5	3.3	4.0	
	22	0.6	1.2	1.8	2.4	3.0	12	0.6	1.3	1.9	2.5	3.0	
	23	0.4	0.8	1.2	1.6	2.0	13	0.4	0.8	1.3	1.7	2.0	
	24	0.2	0.4	0.6	0.8	1.0	14	0.2	0.4	0.6	0.8	1.0	
	25	0	0	0	0	0	15	0	0	0	0	0	
Negative corrections	26	0.2	0.4	0.6	0.8	1.0	16	0.2	0.4	0.6	0.8	1.0	Negative corrections
	27	0.4	0.8	1.2	1.6	2.0	17	0.4	0.8	1.2	1.7	2.0	
	28	0.6	1.2	1.8	2.4	3.0	18	0.6	1.2	1.9	2.5	3.0	
	29	0.8	1.6	2.4	3.2	4.0	19	0.8	1.7	2.5	3.3	4.0	
	30	1.0	2.0	3.0	4.0	5.0	20	1.0	2.0	3.0	4.0	5.0	

according to its lime content. For each 2.5 g. of sample, 1 cc. of acid was deducted from the amount of acid used in calibrating the bottles, namely, 25 cc.

The time allowed for the reaction of the acid with the soil was about 20 minutes with intermittent shaking. For some soil samples containing carbonates resistant to decomposition, the reaction was not completed within this time, as it was indicated by a slowly increasing pressure recorded by the gauge. The reaction was considered complete when the rate of further increase of the pressure became very small. For some soils this required one hour or an even longer period.

Six polyethylene bottles and two rubber stoppers fitted with metallic thermometers and glass stopcocks were used in these trials and it was found that a batch of six determinations could be completed within 75 to 90 minutes. With such an arrangement a period of about 30 minutes is allowed to each sample for the reaction with the acid.

Temperature corrections on the pressures read on the gauge were made, if it were considered necessary, using both tables. In most cases these corrections needed not to be made. For example, if a 5 g. sample were analyzed and the temperature at the time of pressure equalization was 22° while that at the time of measurement was 24° C, a pressure of 110 mm. read on the gauge should be corrected by subtracting 4.3 mm. according to Table 4, and by adding about 1.1 mm. according to Table 5, or by a net positive correction of about 3 mm. corresponding to 15.8 mg. of $CaCO_3$ or 0.3 per cent of lime. However, for larger temperature differences and especially if these corrections are both positive or both negative,

the pressure measured is relatively high and the sample used small, the error thus introduced may be appreciable and the corrections must be made. For example, for a sample of 2 g. and temperatures at the times of pressure equalization and measurement 15° and 11° C respectively, a pressure of 250 mm. must be corrected by +9 mm.[1] according to Table 4 and by another +3.3 mm. according to Table 5. If these corrections are neglected an error of -3.3 g. of lime per 100 g. of wet soil is introduced, which, if the moisture of the sample is 20 per cent, becomes -4.7 per cent, representing a percentage of -6 of the amount of lime present. Although such large temperature fluctuations are, in general, not common they are sometimes observed as a result of the bottles being exposed, even for short time periods, to direct sunlight or wind. Therefore some kind of protection of the bottles from them is required. In order to validly apply temperature corrections sufficient time must be allowed for the contents of the bottle to attain temperature equilibrium. Considering the other sources of error and mainly sampling as well as estimation of moisture, it may be concluded that in the majority of cases temperature corrections are unnecessary. Such a conclusion almost renders obsolete the use of a thermometer, but it is advisable that the bottle stoppers be fitted with a thermometer in order to make sure that no such temperature changes as to make it necessary to correct the pressure for them have taken place.

In these trials both calibration graphs at the two temperatures, 15° and 25° C, were used according to the temperature of the atmosphere at the time of measurement. It was found convenient to compute the lime

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[1]Extrapolated value.

content of the sample from the slope of the corresponding graph (5.38 and 5.26 mg. of $CaCO_3$ per mm. of Hg, respectively) rather than determining it graphically.

The moisture content of the soils tested in the field varied within very wide limits so that expressing the lime content on a moist soil basis was almost meaningless. Therefore, in order to express the lime content on a dry soil basis, the moisture content of the soil was roughly estimated and the lime content corrected accordingly. As it was mentioned earlier, this field estimation of the moisture was checked with a moisture determination made later in the laboratory.

The soil samples tested in the field were taken from the horizons of 10 profiles representing 8 established soil series in Cache Valley[1] and varied widely as far as both texture and lime content are concerned. Bulk samples from these horizons were taken to the laboratory, processed in the usual manner, and a lime determination run on them with the adopted laboratory method for comparison.

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[1]These soil series are the following: Syracuse, Parley, Greenson, Timpanogos, Logan, Trenton, Warm Springs, Mendon.

RESULTS AND DISCUSSION

Theoretical considerations

For the pressures and temperatures within the working range of the method the relationship between the amount of a simple gas like CO_2 and its pressure when its volume is kept constant is accurately represented by the ideal gas law:

$$pv = 760\ nRT \qquad (8)$$

Where: p = pressure of the gas in mm. of mercury
v = volume of the system in litres
n = number of moles of the gas
R = the gas constant = 0.08205 litre-atmosphere
T = the absolute temperature in degrees

At it was seen in the Review of Literature, this linear relationship between the amount of CO_2 evolved and its pressure, if its volume were kept constant, or its volume when its pressure is kept constant, was found to hold and is the basis of all gasometric methods discussed. Manometric carbonate determinations on materials other than soils are also based on this linear relationship (see for example reference number 6).

In the present method the effective volume of the apparatus is considered as constant. However, small changes, i.e. such as those occurring when using a larger soil sample without allowing for its volume by reducing correspondingly the amount of acid used, or those due to differences in the depth to which the stopper is inserted, or else to the expansion of the bas within the gauge, are always possible. According to equation (8), changes in volume will be reflected in the pressure developed. The

difference in pressure $\pm$ p due to a change in volume $\mp$ v can be calculated from the relation pv - (p $\pm$ p) (v $\mp$ v) from which

$$\pm \triangle p = p \frac{v}{v \mp \triangle v} = \frac{1}{1 \mp \frac{v}{\triangle v}} \qquad (9)$$

which means that the changes in the pressure of the gas due to changes in volume of the system are directly proportional to the value of the pressure. In this point a very important distinction must be made: if the change in volume takes place before the pressure in the bottle is equalized with the atmospheric pressure (as for example when using an amount of acid different from that used for the calibration) the only component of the system which is affected is the pressure of CO_2, as the atmospheric air within the bottle (as well as any water vapors) will have a change to equalize its pressure with that of the atmosphere. In this case p is given by equation (9) if we substitute the pressure of CO_2 evolved (which is 60 mm.) for p. If, on the other hand, the change in volume takes place after pressure equalization, both compoents, i.e., pressure of the atmospheric air within the bottle as well as CO_2 pressure, are affected and p in equation (2) must take a value equal to the sum of atmospheric plus CO_2 pressure. In this last case the error caused is much greater than in the first case. An arithmetical example will make it clear: if we use a 25 g. sample of soil containing 0.6 g. of carbonate, without reducing the amount of acid by 10 ml. (the volume taken by the soil particles, having a density of 2.5) the error in the CO_2 pressure thus caused will be:

$$+ \quad p = p \frac{1}{\frac{v}{\triangle v} - 1} = 50 \frac{1}{\frac{2000}{10} - 1} \simeq 0.25 \text{ mm. Hg}$$

If, on the other hand, in the same determination, after pressure equalization and evolution of CO_2, the volume of the system increases by 10 ml., as for example when the stopper is pushed a little outwards by the pressure from inside, the error thus introduced is $\Delta p = (650 + 50) \frac{1}{\frac{2000}{10} - 1} \simeq 3.5$ mm. of Hg. In these calculations the pressure developed from 0.6 g. of carbonate in a volume of approximately 2 litres is taken from the calibration graph (Figure 2) as 50 mm. and the atmospheric pressure as 650 mm. of Hg.

The above discussion emphasizes the need for a secure fitting of the stopper, a non-expanding rubber connection, as well as a gauge within which the gas does not expand appreciably. On the other hand, it follows that one does not have to be accurate in measuring the acid for the decomposition or in allowing for the volume of soil particles. Thorough drying of the bottle, after washing it for the next determination, is also unnecessary.[1]

At this point it might be remarked that in most manometric methods no correction is made for the change in volume of the system resulting from the displacement by the gas of the mercury in the manometer.

Changes in temperature are significant sources of error but corrections can easily be made for them. Here again it is necessary to draw the following important distinction. As we mentioned before, the pressure in

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[1]It was found that as a check on the correct position of the rubber stopper in the neck of the bottle, it is possible to use the pressure developed on stoppering the bottle which can be read on the gauge. When the same reading on the gauge is obtained, the stopper has been inserted to the same depth in the neck of the bottle (small temperature changes or barometric fluctuations have no measurable effect).

the bottle is due to two components: The atmospheric air which is the major component and whose pressure is equal to the atmospheric pressure at the time of pressure equalization and the pressure due to CO_2 evolved. If the temperature after the pressure equalization changes this will result in a change in pressure of the atmospheric air enclosed in the bottle and this change will be added (or subtracted) to (or from) the measured CO_2 pressure. On the other hand, if the temperature of measurement differs significantly from the temperature of the calibration of the apparatus, CO_2 pressure must be corrected for this difference. Two corrections are therefore necessary: one for the change in pressure of the atmospheric air in the bottle for the temperature change, if any, between pressure equalization and measurement, and another for the CO_2 pressure for the difference between the temperatures of measurement and of calibration. Under laboratory conditions where pressures only up to 60 mm. of Hg are measured and the temperature fluctuates but little, the first correction is the more important, as it concerns the major pressure components; the second can be safely neglected.

These corrections are calculated from the relation $P_1/P_2 = T_1/T_2$ and, for convenience are tabulated in Tables 1 and 2. Values in Table 1 have been calculated using a value of 645 mm. of Hg for the atmospheric pressure which seems to be very close to the average barometric pressure in Logan, but it should be noted that barometric fluctuations of ± 15 mm. of Hg or even more have no appreciable effect on the values of the table.

It should be noted that, in the case of the pressure of CO_2 (Table 2), these temperature corrections theoretically should not be extended

over a wide temperature range since in such a case the relationship $P_1/P_2 = T_1/T_2$ can not be validly applied due to differences in the solubility of CO_2 in HCl at widely different temperatures. Some idea of the magnitude of error thus introduced can be gained from the values of α, the Bunsen absorption coefficients of CO_2 in HCl given in Table 6 (taken from "International Critical Tables" Vol. VI, 1926) (23).

Table 6. Bunsen absorption coefficients α of CO_2 in HCl solutions[a]

Gram equivalents of HCl per litre of solution	$\alpha \times 10^3$	
	At 15° C	At 25° C
0.5	989	738
1.0	974	732
2.0	968	728

[a] α = ml. of CO_2 at NTP, which, at the indicated temperatures, dissolves in 1 ml. of the solvent when the partial CO_2 pressure is 760 mm.

It is readily seen that in the laboratory experiments where the maximum CO_2 pressure measured is 60 mm., the difference in volume of CO_2 dissolved in 25 ml.[1] of 2N HCl at 15° and at 25° C is not greater than $\frac{25 \times (0.968 - 0.728) \times 60}{760} = 0.474$ ml. of CO_2 at NTP which is negligibly small. In the field experiments the maximum CO_2 pressure measured is 300 mm. and by applying the relationship $P_1/P_2 = T_1/T_2$ over the temperature

[1]In the above calculation the volume of acid is taken as 25 ml. but it should be remembered that it is even smaller since the acid is partially neutralized by the carbonate of the sample.

range 15° - 25° C the error thus introduced is not greater[1] than 2.37 ml. of CO_2 at NTP or 2.37 x 1.965 = 4.65 mg. of CO_2 which is equivalent to 4.65/0.44 = 10.5 mg. of $CaCO_3$ or (from the graph on page 31) to 1.75 mm. of pressure. The error is again very small. However, by calibrating the apparatus at two temperatures, for example 15° and 25° C it can be rendered even smaller.

The small temperature changes in the laboratory result from the manipulation of the bottle as well as from the heat of the reaction.

Changes in barometric pressure have no effect on the results of the method unless they take place at the short time interval between pressure equalization and measurement but this is highly improbable. Differences in barometric pressure between calibration and actual determinations have no effect either.

In the present method the carbonate content of the sample is read off a calibration graph rather than calculated. Therefore, since uniformity of procedure is followed in both calibration as well as in actual determinations consistent errors, if any, are automatically corrected.

Results of laboratory experiments

Figure 2 shows the calibration graph[2] obtained in the laboratory with known amounts of pure $CaCO_3$ at 25° C. It is a straight line passing through the origin, as would be expected.

Table 7 gives the results of the determinations of carbonate on the

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[1]It is usually much smaller than this.

[2]The points marked x show the pressures not corrected for temperature changes.

Table 7. $CaCO_3$ equivalent of 44 soils as determined by: (a) Williams' hypodermic method; (b) Hutchinson and MacLennan's method; and (c) the proposed manometric method

Soil no.	$CaCO_3$ equivalent % Williams' hypodermic	Hutchinson-MacLennan	Manometric	Soil no.	$CaCO_3$ equivalent % Williams' hypodermic	Hutchinson-MacLennan	Manometric
468	0.4	0.54	0.5	1718	32.1	30.57	30.1
477	0.4	0.54	0.5	473	31.9	31.71	32.7
485	1.6	1.71	1.7	4470	35.0	35.04	34.2
484	2.2	2.61	2.6	1837	35.5	35.58	34.9
480	4.0	3.75	3.8	2154	39.3	38.37	39.5
1593	4.1	3.84	4.0	3134	39.7	38.51	38.2
4478	4.9	4.73	4.4	831	36.5	35.79	36.4
1295	5.4	5.28	5.5	2148	41.0	40.96	40.9
1289	5.5	6.14	5.9	1358	42.4	41.17	41.2
4507	6.7	6.66	6.6	1907	40.2	41.50	39.0
1583	9.7	6.66	6.8	838	45.3	44.05	43.6
483	7.4	7.09	7.0	1513	45.0	45.99	46.4
2222	9.8	8.09	7.9	3409	52.9	51.8	52.3
1261	9.8	9.46	9.0	2184	51.5	51.64	51.0
1296	9.7	10.51	10.5	1744	50.3	52.44	52.5
1508	14.2	13.44	13.9	2185	53.7	54.34	53.9
1362	15.5	15.40	15.0	1745	56.6	58.97	59.6
1096	19.8	19.69	19.1	2125	59.4	59.02	59.9
1341	19.7	19.97	21.0	3404	65.5	63.3	64.0
1838	24.1	24.38	24.3	1514	74.7	74.2	74.9
1839	28.2	26.12	26.0	1831	78.4	78.21	79.6
1695	33.3	30.07	29.9	1742	87.6	87.34	87.9

soils chosen. It is readily seen that the results obtained with this method agree very closely with those obtained with Hutchinson and MacLennan's method. A linear regression equation $Y = 0.240375 + 0.991708X$ fits the data and both hypotheses: $a = 0$ $b = 1$ can be accepted at the 0.01 level. ($Y = CaCO_3$ per cent by Hutchinson and MacLennan method; $X = CaCO_3$ per cent with the manometric method.)

Table 8 gives the results obtained in duplicate determinations, using both Hutchinson and MacLennan's and the present method on 10 randomly selected soils. A pooled estimate of the variance gives $\sigma_1^2 = 0.4168$ for Hutchinson and MacLennan's method, and $\sigma_2^2 = 0.6680$ for the proposed method; while an F test shows that the hypothesis that these two variances are equal can be accepted at the 1 per cent probability level. The two methods therefore can be considered as virtually of equal reproducibility.

Results of field experiments

The procedure finally adopted for the determination of $CaCO_3$ in the field can be outlined as follows.

A representative soil sample is obtained by taking small amounts of soil from different points of the horizon to be tested and from 2 to 10 g. are weighed into the plastic cup. The amount of acid added is 25 ml. minus 1 ml. for each 2.5 g. of soil used. The stopper is placed in position and the stopcock opened to equalize external and internal pressures. After thermal equilibrium is reached as indicated by the thermometer, the temperature is recorded, the stopcock closed, and the bottle shaken to effect decomposition of the carbonates. Shaking is repeated intermittently

Table 8. Reproducibility of the manometric method as compared to that of Hutchinson and MacLennan's method

Sample no.	$CaCO_3$ equivalent % by Hutchinson-MacLennan's method			$CaCO_3$ equivalent % by manometric method		
	1st determination	2nd determination	Average	1st determination	2nd determination	Average
2184	50.22	51.64	50.93	51.8	50.4	51.1
1583	6.56	6.76	6.66	6.9	6.7	6.8
839	27.65	26.30	26.975	27.7	26.4	27.05
1318	59.18	59.95	59.565	62.1	63.4	62.75
1700	31.63	32.40	32.015	30.1	30.9	30.5
1695	30.17	29.97	30.07	29.2	29.0	29.1
1745	58.52	59.42	58.97	60.9	58.4	59.65
1424	63.28	64.67	63.975	64.6	65.3	64.95
1296	10.16	10.87	10.51	10.5	10.5	10.5
3397	19.7	19.7	19.70	19.6	19.6	19.6

for about 20 minutes or longer if necessary. Then the CO_2 pressure is read on the gauge and the temperature of the contents of the bottle noted. If it differs significantly from that at the time of pressure equalization the pressure is corrected using Table 4. Moreover, the CO_2 pressure is corrected, if necessary, for deviations from the temperature of calibration using Table 5. The amount in mg. of $CaCO_3$ in the sample is found by multiplying the pressure in mm. by 5.38 or 5.26 according to the temperature at the time of measurement, the higher coefficient being the slope of the 15° C calibration graph and the lower that of the 25° C calibration graph. The percentage of $CaCO_3$ in the moist soil is obtained by dividing this figure by 10 w, where w is the weight of the sample in grams. Then the moisture content of the sample is roughly estimated and the $CaCO_3$ percentage corrected accordingly.

Table 9 summarizes the results of the field experiments and Figure 4 and Figure 5 show graphically how the results obtained in the field compare with those found in the laboratory.

In Figure 4 the lime content of the dry soil has been computed from that of the moist soil and from an estimated soil moisture percentage. Although large errors were made in estimating the moisture content of the soil in the field, as it is seen from the table, the error thus introduced in the percentage of lime is not excessive. Indeed, in many instances, the errors in the lime determination and in the estimation of soil moisture may be compensated. The rather close arrangement of the points around the 45° straight line, together with the value of $r = 0.900$, show that the results obtained in the field are in satisfactory agreement with those

Table 9. Comparison of the results of the field and the laboratory methods

Soil series or location	Depth of horizon (inches)[1]	Moisture % Estimated	Moisture % Determined	Lime % (dry soil basis) Laboratory method	Lime % (dry soil basis) Field method: Estim. moisture basis[2]	Lime % (dry soil basis) Field method: Determined moisture basis	Error introduced[3]
Timpanogos	6-10	18	20.8	3.7	3	3.0	0
	10-16	17	21.0	8.4	8	8.4	- 5
	16-22	16	20.1	20.9	16	17.1	- 6
	22-34	14	15.5	31.6	31	32.0	- 3
	34-40	10	12.9	20.9	17	17.5	- 3
	40-49	8	10.3	29.9	29	29.6	- 2
	49 +	7	13.0	28.8	24	25.0	- 4
Warm Springs	0-10	24	18.9	1.5	1	1.1	- 10
	10-16	26	22.5	0.7	1	0.6	+ 67
	16-20	28	20.8	0.7	1	0.7	+ 43
	20-24	29	19.5	2.7	3	2.4	+ 25
	24-27	30	22.4	12.5	14	12.3	+ 14
	27-32	30	23.5	20.4	25	22.2	+ 13
	32-38	30	25.1	28.1	31	28.8	+ 10
	38-47	32	27.5	21.0	24	22.1	+ 9
	47-56	32	26.1	18.6	19	17.5	+ 7
Evans Farm	0-8	11	18.2	31.7	33	35.7	- 8
	8-11	13	20.7	33.0	31	33.5	- 7
	11-19	17	23.6	42.7	44	46.7	- 4
	19-28	20	24.2	40.6	38	39.6	- 4
	28-33	23	21.0	43.1	40	38.4	+ 4
	33-41	25	21.8	39.5	36	34.4	+ 5
	41-54	27	22.3	37.1	37	33.6	+ 10
	54-60	28	22.7	33.7	31	29.2	+ 6
	60-72	30	23.3	27.8	31	28.3	+ 10
Logan I	0-10	18	25.4	1.7	2	1.8	+ 11
	36-40	22	22.9	13.2	10	10.4	- 4
	40-47	16	20.7	36.9	36	36.2	- 1
	47-65	19	23.8	38.0	40	39.8	- 1
Logan II	0-10	30	36.6	2.1	2	2.5	- 20
	34-46	20	23.9	14.0	16	16.9	- 6
	46-52	18	17.0	27.0	34	33.6	+ 1
	52-65	15	14.9	39.0	37	36.9	0

Table 9. (cont'd)

Soil series or location	Depth of horizon (inches)[1]	Moisture % Estimated	Moisture % Determined	Lime % (dry soil basis) Laboratory method	Lime % (dry soil basis) Field method: Estim. moisture basis[2]	Lime % (dry soil basis) Field method: Determined moisture basis	Error introduced[3]
Trenton	14-17	24	29.2	8.7	8	8.4	- 5
	17-24	21	27.0	30.1	31	33.5	- 7
	24-34	20	20.8	45.0	43	43.6	- 1
	34-48	25	24.7	23.5	26	26.2	- 1
	48-60	35	28.1	21.9	32	28.5	+ 12
Parley	11-22	13	21.2	4.1	4	4.2	- 5
	22-25	17	18.5	8.1	9	8.7	+ 3
	25-28	15	16.1	23.3	19	19.5	- 3
Greenson	0-8	22	27.8	10.0	8	8.4	- 5
	8-16	19	22.6	35.0	32	33.1	- 3
	16-27	17	22.7	39.2	34	36.4	- 7
	27-38+	16	18.2	48.7	47	48.3	- 3
Mendon	28-37	23	26	18.6	17	17.7	- 4
	37-45	15	20	28.0	23	24.2	- 5
	45-52	14	18.8	28.0	25	24.8	+ 1
Syracuse	0-12	18	13.4	0.6	1	0.5	+ 50
	35+	30	24.6	8.2	11	10.9	+ 1

[1]In the table are listed only horizons containing lime.

[2]Figures rounded to the nearest integer.

[3]As percentage of total lime present.

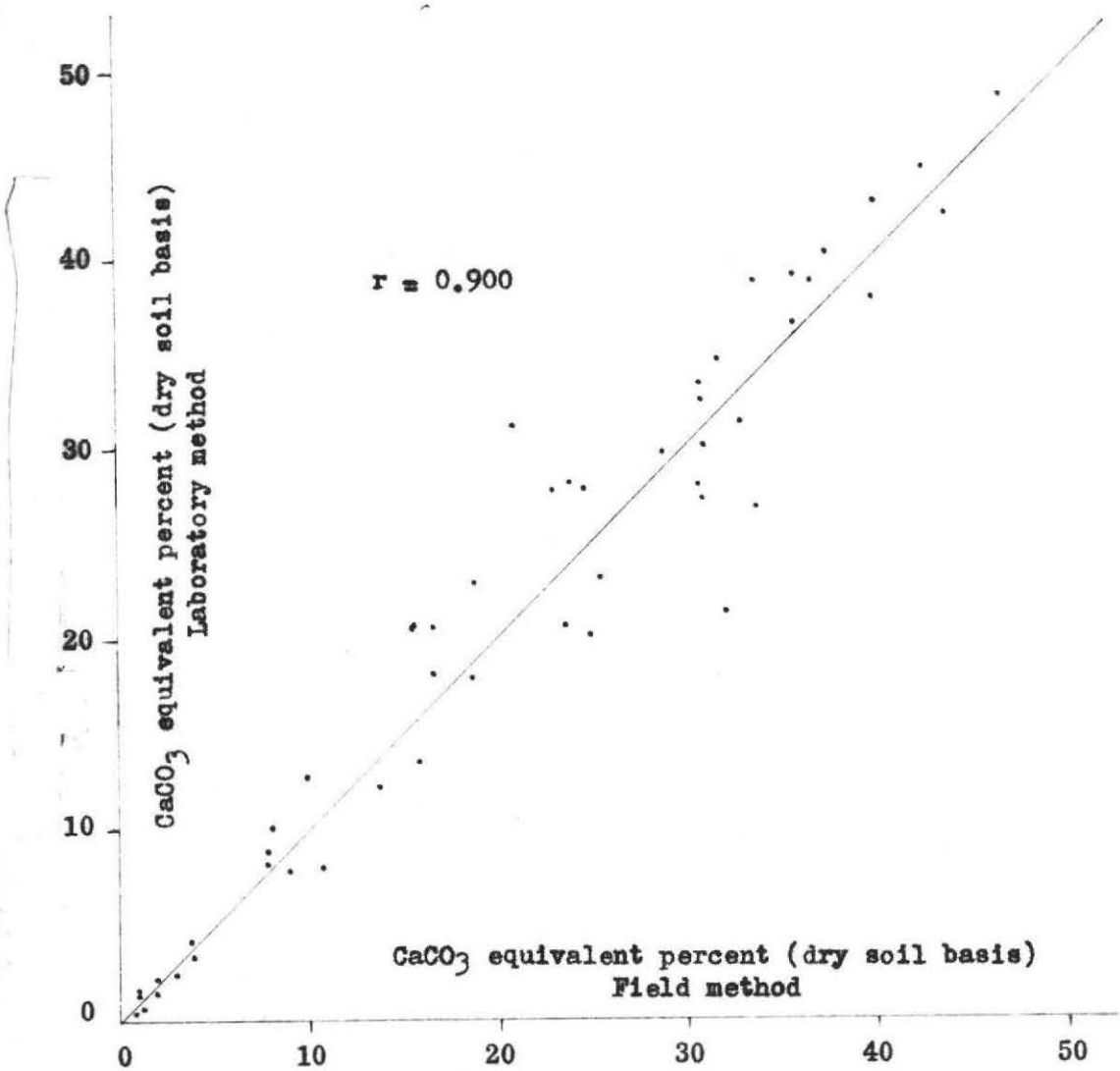

Figure 4. Comparison between field and laboratory methods for lime determination (soil moisture estimated).

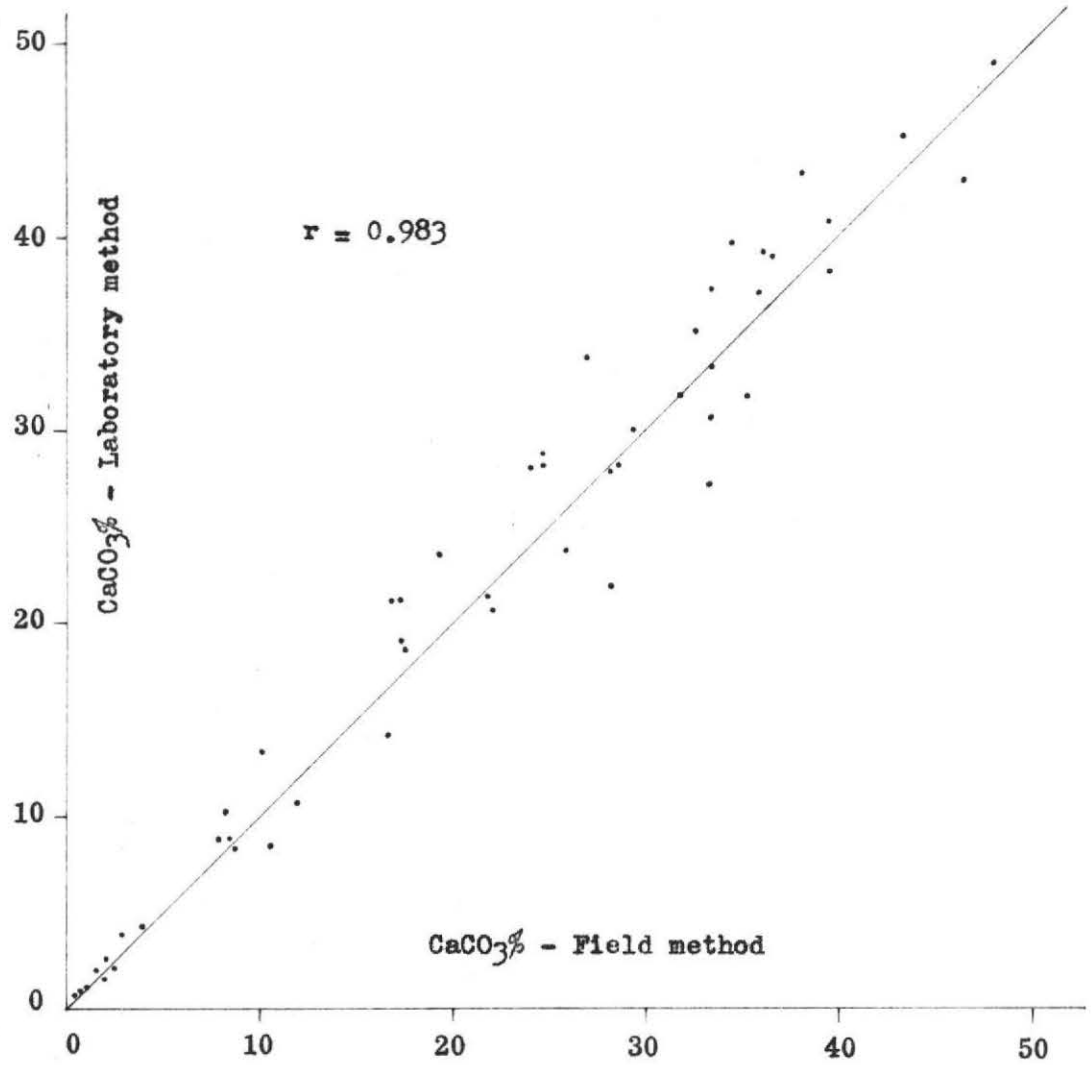

Figure 5. Comparison between field and laboratory methods for lime determination (soil moisture determined)

given by the usual procedure of obtaining bulk samples from each horizon, taking them to the laboratory and after processing them in the usual manner, analyzing them by a laboratory method.

The agreement in Figure 5, where the lime content is expressed on a dry soil basis by determining the soil moisture instead of estimating it, is, of course, better as it is shown by the closer arrangement of the points around the 45° straight line and by the value of $r = 0.983$. However, the method would be of no use as a field method if one had to determine the moisture content of the soil in order to express the lime content on a dry soil basis. On the other hand, differences in moisture content from one horizon in a profile to another or, in general, from one soil to another, are so large that expressing the lime content on a moist soil basis would be almost meaningless.

Estimating the soil moisture in the field requires, of course, some experience but even without much experience, as in the present case, the error thus introduced in the percentage of lime is not too large.[1] It is expected that working with soils in a drier condition than those used in these experiments would reduce the errors due to this cause. Necessary criteria for estimating the moisture of the soil are its texture and organic matter content and helpful reference points are the permanent wilting percentage, the field capacity, and the saturation percentage.

It is to be expected that, at least for some soils containing

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[1]It is interesting in this connection to mention that "Soil Test Inc." manufactures portable apparatus for the determination of soil moisture in the field. It is based on the measurement of the pressure of the acetylene gas produced when carbides react with moisture.

resistant carbonates, elimination of grinding the sample and of mechanical shaking would lead to low results. This is the case of some horizons in the profile of the Evans Farm where it was found that the reaction of the acid with the soil required long time periods, well over one hour, in order to be completed. With most soils, however, this reaction is completed within the 20 minute period of the experiment as indicated by no further increase in the pressure.

On the other hand, positive errors are caused by sampling the soil profile or core with a spatula as it is thus possible to include with the sample pieces of solid calcareous material in proportion larger than its actual proportion in the bulk of the soil.

This method is found to be capable of detecting changes in lime content at the various depths of the soil profile as it is seen from the table. Therefore it is useful to the soil surveyor for making decisions on matters of soil classification based on the distribution of lime throughout the profile, which decisions sometimes have to be made in the field.

SUMMARY AND CONCLUSIONS

A method for the quantitative determination of soil carbonates in the field has been developed and evaluated. This method makes use of very simple apparatus and does not require any laboratory facilities or standard solutions. It yields results of a fair degree of accuracy even though it depends on an estimation of the moisture content of the soil, which frequently involves large errors.

It is believed that the method represents a definite improvement over the old semi-quantitative method of estimating the lime content of the soil by the degree of its effervescence with acid and therefore, it might prove useful to soil surveyors and agricultural advisers.

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