

Determination of Soil Carbonates by a Rapid Gasometric Method

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A technique using a portable, unbreakable, easy to assemble apparatus was designed for rapid determination of calcium carbonate equivalent of calcareous soils in the laboratory and in the field. CO₂ evolved was measured gasometrically within a few minutes, and the calcium carbonate equivalent was obtained by comparison with a standard. The method gave reproducible results which were comparable in accuracy to the titration method. The accuracy of the new method was not affected by increasing contents of lime in the soils tested. Fifty soil samples from 12 calcareous soil profiles were tested by the gasometric method, and results were reported. The rapid gasometric method appears to be useful in determining both lime contents of calcareous soils and calcium carbonate equivalents of high lime materials.

THE LIME CONTENT of soil is an important factor in agriculture because it has a significant bearing on physical and chemical properties of soils as well as on growth and production of crops. In addition, the distribution of lime content in soil profiles tells a story of soil genesis and has been used as a criterion for soil classifications.

On an ordinary field study trip or a soil survey tour, a few drops of HCl on a soil profile from an acid bottle would usually serve the purpose of distinguishing calcareous soils or horizons from non-calcareous ones. But this simple and widely used technique does not give quantitative information.

Considerable work has been done with development of better methods for lime determination. Edson (2), who titrated calcium carbonate equivalent, found that a 30-minute digestion period was required and that results were only accurate within 10%. Pierce and Haenisch (7) described a carbon dioxide evolution method which employed a carbon dioxide absorption material such as NaOH. This method was time-consuming since CO₂ had to be evolved slowly for complete absorption. The evolved CO₂ may be collected and weighed in soda-lime (6). Inorganic carbonates may also be determined gasometrically in the laboratory by measuring the volume of CO₂ evolved according to the method of Horton and Newson (4), but their apparatus could not be employed conveniently in the field. Piper (8) described the Passon's

manometric method for determining carbonates as modified by Skewes. This method was later improved by Williams (11), Martin and Reeve (5), Skinner and Halstead (9), and most recently by Skinner, Halstead and Brydon (10).

A rapid and accurate test for soil carbonates which could be employed in both the laboratory and field would greatly facilitate soil work, especially in the prairie regions of Canada and the United States where calcareous soils are predominant.

Methods and Materials

One gram of soil was carefully placed in a plastic vial of 25- to 35-ml. capacity (Figure 1). If some soil particles stuck to the wall of the vial, a stream of distilled water about 1 to 2 ml. from a polyethylene wash bottle could be used to wash them down to the bottle. The vial was then set in place, as shown in Figure 1, and covered with a rubber stopper to which a dropper of 1.5-ml. capacity filled with concentrated HCl was inserted. A rubber (or plastic) tube was then connected between the vial and a 100-ml. plastic measuring cylinder filled to the 100-ml. mark with water (or with a dilute HCl solution) into which a pigment could be added for better reading. After the connections were secured, the air outlet of the system was blocked by clamping the rubber tube, and pressure was applied on the rubber bulb of the dropper to release the HCl. The rubber bulb was released first and then the rubber tube. The volume of CO₂ produced replaced the water in the measur-

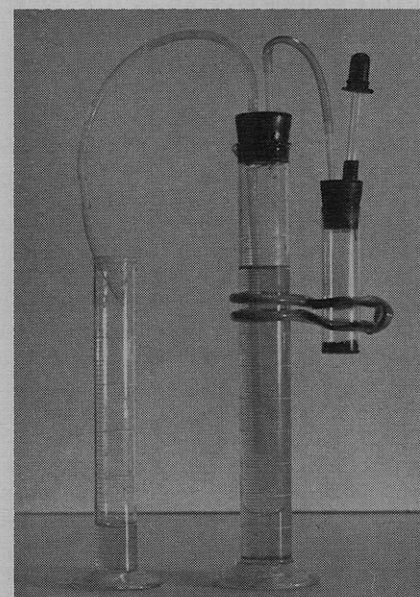


Figure 1. Apparatus for rapid determination of CaCO₃ equivalent of soils by volume of CO₂ evolved

ing cylinder, and the amount of water which overflowed was measured in another cylinder. The volume of CO₂ evolved from 0.1 gram of pure CaCO₃ was determined by the same procedure. The calcium carbonate equivalent of the soil tested was calculated as follows:

$$\text{Soil Carbonate } \% = \frac{\text{Volume of CO}_2 \text{ evolved by 1 gram soil}}{\text{Volume of CO}_2 \text{ evolved by 0.1 gram CaCO}_3 \times 10} \times 100$$

Calibration Tests. TEST WITH PURE CALCIUM CARBONATE. The new tech-

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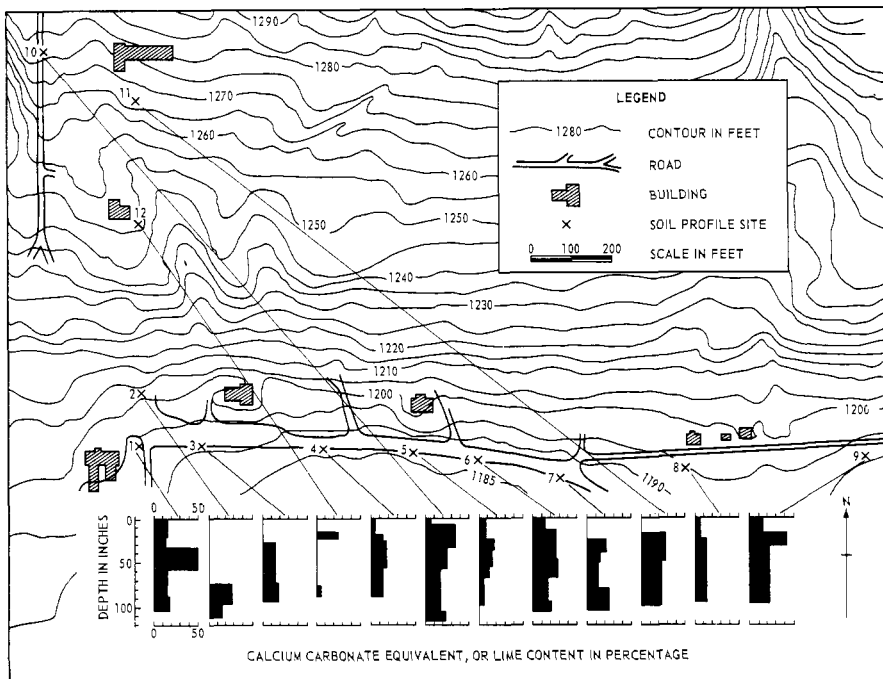


Figure 2. Map showing sites of soil profiles at the Experimental Farm, Brandon, Manitoba, Canada, and their carbonate contents as determined by the gasometric method

Table II. Gasometric Determination of CaCO_3 in Artificially Prepared Calcareous Soils Containing Known Concentrations of CaCO_3

(1 Gram of Soil Tested)

CaCO_3 Added, %	CaCO_3 Determined, %			Recovery, %
	Trial 1	Trial 2	Av.	
0	0	0	0	0
10	9.7	9.7	9.7	97.0
20	20.0	20.0	20.0	100.0
30	29.2	29.4	29.3	97.7
40	40.4	40.2	40.3	100.8
50	52.0	51.6	51.8	103.6

—e.g., Fisher Scientific Company Catalog No. 1-3689 or a similar type with plastic parts for metal accessories for acid resistance. If the pipettor is used, the volume of CO_2 obtained minus the amount of HCl used will be the actual volume of CO_2 .

Determination of Carbonates in Field Soils. After the gasometric method was calibrated, 50 soil samples and two limestone samples from 12 calcareous soil profiles were taken to a depth ranging from 7 to 10 feet at the Experimental Farm, Brandon, Man. (Figure 2), and tested in duplicate for their carbonate contents by the method described. The sampling sites, located on the north bank of the Assiniboine River valley, had varying soil characteristics. Soil color and textures were used as criteria for separating various soil horizons in the soil profiles. The descriptions of the soil profiles are listed in Table III. The soil analyses were conducted in the laboratory, but with their possible field applications in mind.

Table I. Comparison of the Gasometric Procedure with the Titration Method, Using Pure CaCO_3 for the Determination of CaCO_3

Wt. of CaCO_3 , Grams	Recovery of CaCO_3 (2 Methods)							
	Gasometric				Titration			
	Trial 1, grams	Trial 2, grams	Av., grams	Recovery, %	Trial 1, grams	Trial 2, grams	Av., grams	Recovery, %
0.1000	0.0980	0.0980	0.0980	98.0	0.1032	0.1027	0.1030	103.0
0.2000	0.2040	0.2040	0.2040	102.0	0.2015	0.2038	0.2097	101.4
0.3000	0.3040	0.3080	0.3060	102.0	0.3031	0.2962	0.2997	99.9
0.4000	0.4000	0.4000	0.4000	100.0	0.3997	0.4045	0.4021	100.5
1.0000	1.0060	1.0100	1.0080	100.8	1.0075	1.0072	1.0074	100.7

nique and the standard titration method (6) were compared by using duplicate samples of 0.1, 0.2, 0.3, and 0.4 gram of pure CaCO_3 . In the new method, the measured volumes were divided by the gram molecular volume of gas computed under laboratory conditions according to gas laws.

TEST WITH ARTIFICIAL CALCAREOUS SOILS. A lime-free soil was mixed with pure CaCO_3 to make up calcareous soils consisting of 0, 10, 20, 30, 40 and 50% CaCO_3 . Each mixture was wetted, stirred, air-dried, crushed, and mixed again to ensure sample uniformity. The soil samples so prepared were measured for their CaCO_3 contents by the new method. The recovery of the CaCO_3 contents was calculated.

Alternative Procedures for Field Tests. When the test is to be carried out under field conditions, a "pocket" balance—e.g., Fisher Scientific Company Catalog No. 2-136 or a similar type—and alcohol moisture content devices (7)

or tin boxes for soil moisture samples should be carried along. If no alcohol moisture content device is available for moisture correction in the field, the carbonate content of soil obtained is an approximate value and can be converted to an oven-dry basis afterwards. If only an estimation of carbonate is required, a soil measuring spoon, of 1-gram capacity, could be used in the place of a balance (3). Sampling errors in the field test would be larger.

The CaCO_3 standards can be pre-weighed and stored in ready-to-use vials, and enough empty plastic vials can be brought along. By so doing, no washing of soiled vials is necessary in the field.

The water which overflows from the measuring cylinder can be received with another plastic cylinder of desired size, and the water can be replaced and used over and over again.

As an alternative for the rubber dropper for transferring HCl , a continuous pipettor can be substituted

Results and Discussion

Results of the calibration test with pure chemical calcium carbonate are shown in Table I. Both the gasometric method and the titration method gave similar results with little difference between trials. Over-all recovery of the former method was 100.8% while that of the latter was 100.7%. This is comparable to the results of Horton and Newson (4). The data also revealed that increases in the amount of CaCO_3 did not reduce the accuracy of the proposed technique.

Results of analyses of the artificial calcareous soils by the new method are listed in Table II. The contents determined by the new method were close to the corresponding known percentages. Since the over-all recovery of 12 determinations of the soil samples was 100.7, and duplicates of each sample were nearly identical, the accuracy of the gasometric method was once again dem-

Table III. Description and Lime Contents of 12 Calcareous Soil Profiles by the Gasometric Procedure

Soil Profile No.	Depth, Inches	Munsell Color Reading ^a		Description	CaCO ₃ Content, %		
		10 YR	Soil color		Run 1	Run 2	Av.
1	0-20	4/1	Dark gray	Sandy loam, blocky, friable	16.4	16.4	16.4
	20-32	2/1	Black	Fine sandy loam, structureless, friable	14.8	14.4	14.6
	32-58 ^b	7/1	Light gray	Fine sandy loam, concrete-like, plastic when wet	49.6	49.6	49.6
	58-87	5/3	Brown	Fine sand, structureless, gravelly	15.6	15.6	15.6
	87-103	6/6	Brownish yellow	Structureless, stony till	18.0	18.8	18.4
2	0-42	Gravel fills
	42-72	3/1	Very dark gray	Sandy loam, blocky structure	0.0	0.0	0.0
	72-96	8/2	White	Loamy texture	27.2	27.6	27.4
	96-115	6/3	Pale brown	Fine sand with rusty mottling	14.4	15.2	14.8
3	0-24	3/1	Very dark gray	Sandy loam, blocky structure, breaking easily	0.0	0.0	0.0
	24-72	6/3	Pale brown	Fine sandy loam, structureless, stony	13.6	15.2	14.1
	72-92	6/4	Light yellowish brown	Coarse sand, rusty and mottling, structureless	18.4	18.4	18.4
4	0-18	2/1	Black	Sandy loam, blocky structure	4.4	4.4	4.4
	18-24	4/2	Dark grayish brown	Sandy loam	13.6	12.8	13.2
	24-54	5/8	Yellowish brown	Sand, stony, structureless	17.2	16.8	17.0
	54-90	6/8	Brownish yellow	Fine sandy, stony, structureless	12.8	12.8	12.8
5	0-24	5/1	Gray	Sandy clay loam, blocky structure, friable	9.6	8.8	9.2
	24-33	6/3	Pale brown	Sandy clay loam, platy structure	17.2	17.2	17.2
	33-51	5/1	Gray	Clay loam	15.2	15.2	15.2
	51-67	6/3	Pale brown	Clay loam, shining breakage, hard	11.6	11.6	11.6
	67-97	7/3	Very pale brown	Clay, hard when dry	4.8	4.8	4.8
6	0-12	3/1	Very dark gray	Sandy loam, with black organic matter stains	2.6	2.2	2.4
	12-43	6/5-8/2	Gray white	Gray sandy clay loam with white lumps	16.8	16.8	16.8
	43-67	5/1	Gray	Fine sandy loam, with whitish stone	17.0	17.0	17.0
	67-91	7/1	Light gray	Clay with decayed root	7.6	7.6	7.6
	91-105	8/3	Very pale brown	Very fine sand	10.0	10.0	10.0
7	0-24	3/1	Very dark gray	Sandy loam, blocky structure	0.0	0.0	0.0
	24-39	5/2	Grayish brown	Sandy clay loam	20.4	20.4	20.4
	39-48	6/4	Light yellowish brown	Sandy loam, structureless	16.0	15.8	15.9
	48-59 ^b	6/3	Pale brown	Coarse sand, rusty mottling, stony	14.4	14.0	14.2
	58-79	7/3	Very pale brown	Fine sand, rusty, mottling, structureless	12.4	11.4	14.9
8	0-24	4/1	Dark gray	Sandy clay loam, blocky structure	6.4	6.4	6.4
	24-54	6/2	Light brownish gray	Clay, concrete-like	12.4	12.0	12.2
	54-93	6/3	Pale brown	Sand with clay pockets, structureless	10.8	11.2	11.0
9	0-17	3/1	Very dark gray	Sandy loam, blocky structure	15.2	15.4	15.3
	17-30	6/1	Light gray	Sandy loam, granular	40.8	40.4	40.6
	30-96	6/3	Pale brown	Sandy clay loam, concrete-like with clay pockets	22.6	22.6	22.6
10	0-8	4/1	Dark gray	Sandy loam, blocky structure	7.8	7.3	7.6
	8-32	7/3	Very pale brown	Sandy clay loam, hard when dry	33.5	33.1	33.3
	32-55	6/4	Light yellowish brown	Sandy clay loam with clay pockets	24.9	24.1	24.5
	55-106	7/6	Yellow	Very fine sand with clay pockets	19.2	19.8	19.5
	106-120	6/4	Light yellowish brown	Sand with small rusty mottling, stony, structureless	22.0	21.0	21.5
11	0-18	3/1	Very dark gray	Sandy loam, friable	0.0	0.0	0.0
	18-48	7/4	Very pale brown	Sandy loam, clay, stony, hard when dry	28.2	28.2	28.2
	48-104	7/3	Very pale brown	Sandy clay with clay pockets	22.7	22.9	22.8
12	0-12	4/1	Dark gray	Sandy loam, blocky	0.0	0.0	0.0
	12-20	6/3	Pale brown	Sandy clay loam with grayish pockets	24.9	24.3	24.6
	20-34	2/1	Black	Loam, blocky, hard	0.0	0.0	0.0
	34-58	4/2	Dark grayish brown	Sandy clay loam	0.0	0.0	0.0
	58-73	6/2	Light brownish gray	Sandy clay loam	0.0	0.0	0.0
	73-85	5/4	Yellowish brown	Sand, stony, structureless	5.5	5.5	5.5

^a Color reading when samples were dried. ^b Where limestone was tested for CaCO₃ equivalent.

onstrated. This also indicates that there was no interference of soil on CaCO₃, as tested by the proposed method.

The above tests showed that the new method had several merits. Since CaCO₃ is used as a standard, a correction for changes in volume of CO₂ evolved due to variation in atmospheric pressure and in temperature is not required. If, in a series of determinations, the atmospheric pressure and air temperature remain nearly unchanged, only one CaCO₃ standard would be sufficient.

Because concentrated HCl is used, the reaction between the acid and soil carbonates is completed within a few

minutes. No prolonged shaking is required as in manometric methods for complete reaction. The strong acid attacks soil carbonates vigorously; therefore, the fineness of soil samples is not critical as far as the completion of reaction within a short time is concerned. The effect of partial gas pressure of HCl fumes on the whole system is negligible, because there was no detectable volume change caused by blank samples.

The heat generated from the chemical reaction is most likely compensated by that of the standard CaCO₃ and by heat exchange of the whole system of the apparatus and surrounding air.

Since the volume of the vial used is rather small, and since the rubber bulb was pressed and released while the whole system was closed, no effect of dead space and no error caused by depressing the rubber bulb is expected.

The 100-ml. cylinder would be sufficiently large for most calcareous soils with up to about 50% calcium carbonate equivalent. For a soil with a higher lime content, either a larger cylinder or a smaller sample can be used.

The surface area of contact of CO₂ and water is rather small and the contact time very short. Therefore, the amount of CO₂ dissolved in the water is most

likely to be negligible. However, if desired, dilute HCl in which CO₂ is less soluble may be used as a substitute for the water in the measuring cylinder.

A few precautions should be pointed out here. The rubber stopper should be secured tightly enough to prevent a gas leak. The rubber tube connecting the vial and the measuring cylinder should be secured after the rubber stoppers are closed safely, so that there will be no air pressure changes in the system and the pressure inside and outside of the system will be equal before the chemical reaction takes place.

No attempt was made to distinguish between the calcite and dolomite. The technique gives only a calcium carbonate equivalent, or a total lime content.

The carbonate content of the 12 profiles as determined by this method is shown in Table III and also diagrammatically in Figure 2. The duplicate analyses of 26 of 50 soil samples were identical and the remainder had 0.28% variation from their means. There were great variations in concentration and distribution of lime contents in the soils both vertically and horizontally. The distance between two adjacent profiles was usually less than 200 feet. The range of

lime content of the soils tested was from 0 to 50%. The calcium carbonate equivalents of limestone from two profiles range from 70 to 100%. The wide variation in lime content within the soil catena studied is not unusual with the high heterogeneity of the soils in color, texture, structure, and horizon depth (Table III). However, most of the top soils were black when wet. It would be rather difficult for an individual, without a chemical test, to realize that there were such great differences in lime content among soil samples within such a small area of the farm. Agricultural experiments of a comparison nature, when carried out on soils with a similar characteristic, would expect considerable errors.

From the foregoing context it is concluded that the rapid method described herein for determining carbonates in calcareous soils and in liming materials appears to be satisfactory and useful.

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INSECTICIDE ACTIVITY IN MAN

Urinary Excretion of Paranitrophenol by Volunteers Following Dermal Exposure to Parathion at Different Ambient Temperatures

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The rate of absorption of parathion, as reflected by urinary excretion of paranitrophenol, was measured in human volunteers exposed to 2% parathion dust at different ambient temperatures. Rates of paranitrophenol excretion varied directly with temperature between 58° and 105° F. Maximum excretion occurred 5 to 6 hours following initiation of exposure. Neither depressions in cholinesterase activities nor clinical symptoms were observed following the exposures used.

THE ORGANIC phosphorus insecticide parathion is a useful material for controlling insects of economic and public health importance. It has a high toxicity to humans, however, and each year deaths are attributed to its use. In an effort to understand more fully the toxic hazards associated with parathion, studies have been made of factors that influence the mechanisms and rates of

absorption. Two methods have been used to measure parathion absorption. They are determination of activities of cholinesterases, enzymes that are inhibited by parathion, and quantitation of a urinary metabolite, paranitrophenol (3).

Excretion of paranitrophenol and depression of cholinesterase activities reflect different physiologic functions. Changes in enzyme activity ordinarily cannot be determined by the Michel method following brief light exposures, because normal variations in the method are greater than the changes produced by the compound (7). Paranitrophenol

assay is useful under these conditions however, since microgram quantities can be measured and the metabolite is absent from the urine of unexposed individuals. The quantity of paranitrophenol excreted indicates the magnitude of absorption and, less directly, the magnitude of exposure, but it does not necessarily measure the physiologic effects of the exposure. Changes in cholinesterase activities reflect physiologic effects resulting from parathion.

A direct quantitative correlation between changes in enzyme activities and paranitrophenol excretions has not been

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