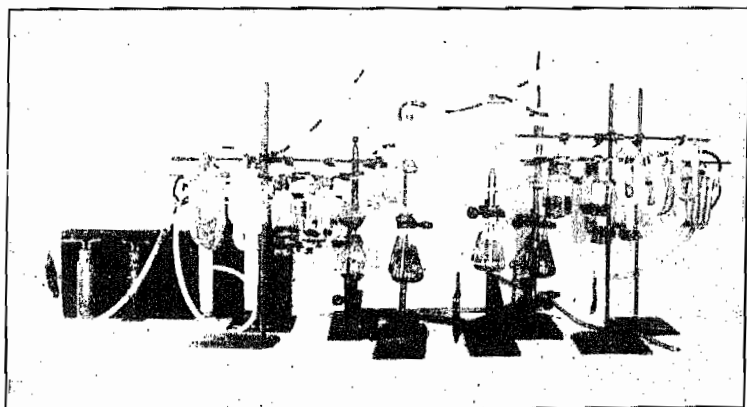


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SOIL CARBONATES
A NEW METHOD OF DETERMINATION

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SOIL CARBONATES

A NEW METHOD OF DETERMINATION

The necessity of rapidly and accurately determining soil carbonates in a comprehensive set of field experiments involving the use of light and heavy applications of lime, and lime supplemented by both light and heavy manure treatments, was responsible for investigations leading to the adoption of the method described in the latter part of this paper.

Hall, states, "In the analysis of a soil, without doubt the most important figure is the proportion of calcium carbonate." There has been proposed, however, no method sufficiently accurate and applicable to both light and heavy occurrences of carbonates to be adopted in detail as official by the Association of Official Agricultural Chemists. Lipman, reporting, in 1908, as Associate Referee for Soils to the above mentioned Association, states, "Unfortunately, there is no unanimity of opinion among chemists as to methods best adapted for the work."

The objects sought in this investigation were to determine: (1) The mineral acid least active upon soil organic matter and a concentration adapted to all occurrences; (2) whether the determination could be made by ordinary laboratory equipment without application of heat.

LITERATURE

METHODS FOR MISCELLANEOUS MATERIALS

Most of the methods advanced for the determination of CO_2 in miscellaneous materials are based upon the liberation of CO_2 by acids of different strengths, aided by application of heat. The acids usually suggested are sulphuric, hydrochloric or nitric. The liberated CO_2 is estimated volumetrically by titration of an absorbent solution or gravimetrically by gain or loss in weight.

Gooch, accomplished the determination by means of the test tube device of Kreider, the residual CO_2 being forced out of the few c.c. of solution by air. Fresenius, Treadwell and Hall, and Gossen, heat with an excess of HCl to determine CO_2 in minerals, while Olsen, for the same material specifies either HCl , HNO_3 or H_2SO_4 . Hillebrand, states that siderite and dolomite do not react completely with acids in cold and for total carbonates directs boiling with 1-1 HCl . Occurrences of CO_2 in substances such as bone are determined by Fresenius, quoting Scheibler, by the evolution of CO_2 at normal temperature and displacement through pressure resulting from the reaction, correcting for CO_2 absorption in the liberating acid. Dietrich, observed the necessity of correction for CO_2 absorbed by the acid in liberating flask, in the above method. J. Russ, first suggested the use of H_3PO_4 for determination of mineral carbonates and its use to differentiate between organic and inorganic carbon in steel work was noted by Morgan.

METHODS ADAPTED TO SOILS

In determining soil carbonates, Hopkins and Pettit,¹⁵ boil and estimate CO_2 evolved by absorption, noting change in volume of absorbent. Lincoln and Walton¹⁶ recommend boiling for 3 minutes. The Brown-Escombe double titration method was adapted to soils by Amos¹⁷, who boiled with 1-1 H_2SO_4 . Bowser¹⁸ studied the Amos method upon synthetic soils, boiling with HCl . Wiley¹⁹ recommends the Knorr method and also cites the Scheibler¹¹ method, using Bernard's calcimeter without heat, for approximations in chalky soils. Hall and Russell²⁰ use H_2SO_4 1-1 and liberate CO_2 at room temperature under vacuum, calculating CO_2 by means of formula. F. Sestini²¹ digested with boiling acetic acid and determined CO_2 by calculation from CaO found in solution, while F. Mortinotti²² suggested the use of neutral ammonium citrate solution. Mayer²³ used 1-2 glacial acetic acid because of its inactivity toward ferrous carbonate and Schütte²⁴ extracted with hot dilute HCl and determined CO_2 equivalent to dissolved lime. Distillation of ammonium carbonate formed by reaction of soil carbonates with added ammonium chloride was suggested by Stutzer and Harleb²⁵. Successive grindings of soil with small amounts of water and digestion for $1\frac{1}{4}$ - $1\frac{1}{2}$ hour with 30% acetic acid was proposed by Vant Kruijs²⁶. The Belgian²⁷ method quoted by Wiley²⁸ consists of working soil with water to expel CO_2 , washing soil into 300 c.c. flask, CO_2 being liberated by acid and collected, no reference to heat being quoted. Decrease in strength of acid and heating to 50°C under partial vacuum was advocated by Marr²⁹. The Marr method was investigated and recommended by Gaither³⁰ in a comprehensive study of Ohio soils, correlating the acid litmus test with negative evolutions of CO_2 by the Marr method.

Wiley³¹, quoting Van Bemmelen's³² method for humus by calculation from organic carbon, states that small charges of 3 to 5 grams are used in a small flask in determining mineral carbonates, sulphuric or citric acid being used at room temperature for liberation of the gas; and data are given to show action of dilute acids when heated in contact with organic matter, on three types of carbonate-free soil.

Schenke³³ ignited soil and then determined the amount of CO_2 taken up from contact with solution of ammonium carbonate.

 CO_2 EVOLUTION AS MEASURE OF SOIL ACIDITY

Tacke³⁴ in his method for soil acidity determines the amount of CO_2 evolved from an excess of suspended CaCO_3 , agitating at room temperature for 3 hours and displacing CO_2 by current of hydrogen. Wheeler, Hartwell and Sargent³⁵ modified Tacke's method by boiling the soil in contact with CaCO_3 . Süchting³⁶ modified Tacke's method by introducing a definite amount of CaCO_3 and determining the re-

sidual carbonate CO_2 by addition of acid, subsequent to removal of CO_2 liberated by action of soil acids upon added carbonate, the reaction being at room temperature and a current of hydrogen used as in Tacke's method.

COMPARISON OF ACTION OF DIFFERENT ACIDS ON CO_2 -FREE SOIL

During the winter of 1910, while at the Pennsylvania Station, the senior author adopted a suggestion from Dr. C. W. Stoddart and discontinued the use of HCl in favor of H_3PO_4 in the determination of soil carbonates, thereby simplifying the CO_2 apparatus by eliminating the silver sulphate tube.

The following table shows the comparative action of H_2SO_4 , HCl and H_3PO_4 of three strengths, upon boiling for periods of thirty minutes, the first minute's evolution being noted in each case. The soil used was a fairly fertile loam of decided acidity and with a CO_2 content of .0196% m. f. basis by the method described in this bulletin. Inspection of Table I shows the superiority of H_3PO_4 .

TABLE I—50 grams of moist soil dried at 40°C to remove CO₂ and digested at boiling—fairly fertile loam soil.

Acid	Strength	Gms. CO ₂ evolved 1st min.	Gms. CO ₂ evolved subsequent 29 min.	Total gms. CO ₂ evolved 30 min.	Per cent (on soil basis) evolved 1st min.	Percent (on soil basis) evolved subsequent 29 min.	Total per cent CO ₂ evolved 30 min.
HCl	1-5	.0452	.0164	.0616	.0904	.0328	.1232
	1-5	.0448	.0153	.0601	.0896	.0306	.1202
							.1216
HCl	1-10	.0386	.0210	.0596	.0772	.0420	.1192
	1-10	.0351	.0224	.0575	.0702	.0448	.1150
							.1171
HCl	1-15	.0295	.0241	.0536	.0590	.0482	.1072
	1-15	.0308	.0224	.0532	.0602	.0448	.1050
							.1061
H ₂ SO ₄	1-5	.0443	.0208	.0651	.0886	.0416	.1302
	1-5	.0420	.0259	.0679	.0840	.0518	.1358
							.1330
H ₂ SO ₄	1-10	.0461	.0210	.0671	.0922	.0420	.1342
	1-10	.0431	.0248	.0679	.0862	.0496	.1358
							.1350
H ₂ SO ₄	1-15	.0390	.0235	.0625	.0780	.0470	.1250
	1-15	.0369	.0237	.0606	.0738	.0474	.1212
							.1231
H ₃ PO ₄	1-5	.0378	.0114	.0492	.0756	.0228	.0984
	1-5	.0415	.0083	.0498	.0830	.0166	.0996
							.0990
H ₃ PO ₄	1-10	.0360	.0116	.0476	.0720	.0232	.0952
	1-10	.0358	.0120	.0478	.0716	.0240	.0956
							.0954
H ₃ PO ₄	1-15	.0281	.0170	.0451	.0562	.0340	.0902
	1-15	.0308	.0163	.0471	.0616	.0326	.0942
							.0922

After it was determined that H_3PO_4 is the least active of the three most adaptable acids, the activity of 1-15 H_3PO_4 toward organic matter on an original loam soil was compared with the action on the carbonaceous material in the same soil subsequent to treatment with 1 per cent HCl and carbonated water to remove any carbonates. The data given in Table II and the contents of Table I show that there is decided action at the boiling point, even by boiling only one minute.

TABLE II— CO_2 evolved from 50 grams original soil by boiling for 30 minutes with H_3PO_4 , 1-15, and the same subsequent to elimination of carbonates

Treatment	Grams CO_2 evolved	Per cent CO_2	Average per cent CO_2
Original soil air-dried	.0428	.0856	.0862
	.0428	.0856	
	.0430	.0860	
	.0438	.0876	
Extracted with 1% HCl in cold, air-dried	.0402	.0804	.0841
	.0422	.0844	
	.0438	.0876	
Extracted with 1% HCl in cold, dried at 40°C	.0427	.0854	.0874
	.0447	.0894	
Extracted with 1% HCl and then with carbonated water by agitation for 5½ hours, dried at 40°C	.0437	.0874	.0841
	.0404	.0808	
Extracted with carbonated water by agitation for 4 hours, dried at 40°C	.0335	.0670	.0784
	.0454	.0908	
Extracted with carbonated water by agitation for 16 hours, dried at 40°C	.0400	.0800	.0896
	.0496	.0992	

As a further check upon the data of Table II the soil was extracted with carbonated water and the carbonates determined in the extractant.

TABLE III—Fifty grams moist soil agitated with current of CO_2 , filtered and washed with carbonated water. Filtrate acidified with N-140 H_2SO_4 and excess acid titrated after boiling

Time of contact	Grams CaCO_3 liberated	Grams CO_2 liberated	Per cent CO_2
30 min.	.0129	.0057	.0114
	.0132	.0058	.0116
2 hrs.	.0146	.0064	.0128
	.0159	.0070	.0140
4 hrs.	.0262	.0115	.0230
	.0255	.0112	.0224

According to Cameron³⁶, a portion of the carbonates recovered would be the result of hydrolyzation of alkali silicates. The data of Tables I and II indicate that the evolution of CO_2 by heat is many times that accounted for by the aggregate of natural and synthetical mineral carbonates. Marr³⁷, studying the action of heat upon organic matter, presents the following table:

TABLE IV— CO_2 evolved by boiling 10 grams CO_2 -free soil, H_2SO_4 1-1, three successive 20-minute periods

Origin of soil	1st 20 min.	2d 20 min.	3d 20 min.	Total CO_2 evolution from organic matter
	Grams	Grams	Grams	Grams
Ohio.....	.0422	.0224	.0211	.0857
Transvaal.....	.0316	.0171	.0136	.0623

The data presented in the foregoing tables prove beyond doubt the fallacy of boiling a soil with mineral acids for carbonate determinations.

Wiley³⁸ states, and quotes Veitch to the effect, that the boiling of alkaline soils with water will evolve CO_2 . To the same effect Gaither³⁹ presents data upon a large number of soils, both acid and alkaline.

The acid loam soil of Table II was dried at 40°C to remove atmospheric CO_2 and boiled with CO_2 -free water with the following results (50 gms. charge):

$$\left. \begin{array}{l} .0037 \\ .0065 \\ .0027 \\ .0044 \\ .0054 \\ .0026 \end{array} \right\} .0042 \text{ grams } \text{CO}_2.$$

This shows either action of heat upon the soil organic matter or reaction between minute localized occurrences of soil acids and carbonates.

PREPARATION OF SOIL PRIOR TO ANALYSIS

Subsequent to determining the superiority of H_3PO_4 , data were secured to learn the most favorable treatment of the soil samples prior to digestion. Moist soil freed of atmospheric CO_2 by suction gave identical results with air drying, while samples oven-dried at $40^\circ C$ gave somewhat greater CO_2 evolution.

COMPARISON OF MARR METHOD WITH BOILING AND ROOM TEMPERATURE

Substituting H_3PO_4 for H_2SO_4 , the Marr method was studied, as compared with digestion at room temperature and at boiling, using 25 grams of loam soil freed from carbonates by cold digestion with 1 per cent HCl .

TABLE V—*Effect of temperature upon action of H_3PO_4 on soil organic matter*

25-gram charge 30-min. aspiration, 1-50 H_3PO_4 , 4 in. vac., room temperature	25-gram charge 30-min. aspiration, 1-15 H_3PO_4 , 4 in. vac., room temperature	25-gram charge Marr method H_3PO_4 , 1-15, $50^\circ C$, 4 in. vac., 30 min.	25-gram charge Boiling 30 minutes H_3PO_4 , 1-15
Grams	Grams	Grams	Grams
.0028	.0046	.0128	.0326
.0026	.0046	.0118	.0340
.0028	.0044	.0186	
	.0058	.0156	
		.0106	
		.0168	
Av. .0027	Av. .0049	Av. .0144	Av. .0333
P. ct. .0104	P. ct. .0196	P. ct. .0576	P. ct. .1332

The above results show considerably less action on organic matter at 50° than that effected by boiling, but appreciably more than at room temperature. The same results were also found in the case of well-rotted barnyard manure and of barnyard soil. The addition of 48 tons per acre of manure was found to cause no increase in CO_2 evolution by treatment with 1-15 H_3PO_4 in the cold. Phosphoric acid 1-15 by volume in several trials on substances rich in organic matter gave but very slightly higher results than H_3PO_4 , 1-50, while it was found that for pure carbonates of calcium and magnesium the greater strength was necessary for complete liberation of CO_2 within 30 minutes. *It should be noted that CO_2 evolutions from the usual charge of 5 gms. gave unweighable quantities of CO_2 evolved from 3 acid soils by 1-15 H_3PO_4 at room temperature.*

CARBONATE DETERMINATIONS IN SOILS, WITHOUT APPLICATION OF HEAT

In preparing soils for determinations of humus Grandeau¹⁰, Hilgard¹¹, Huston and McBride¹², Pasturel¹³, A. O. A. C. Official Method¹⁴, Wiley¹⁵, and Fraps¹⁶ direct the use of a dilute HCl solution at room temperature to eliminate carbonates of calcium and magnesium prior to digestion with ammonia. This agreement as to evolution of all calcium and magnesium carbonate CO₂ by dilute HCl, simplified the authors' problem to ascertaining whether dilute H₃PO₄ would liberate carbonates and if the CO₂ could be freed from solution without use of heat, most methods being hypotheticated upon the necessity of heat to expel the last traces of CO₂. Folin¹⁷ describes a method for the determination of NH₃ in urine by freeing NH₃ with soda, without heat, and aspirating off the gas into standard acid. The method was further studied and modified by Steel & Giess¹⁸ and Howe and Hawk¹⁹. The accuracy obtained in the manipulation of this method indicated that CO₂ might be aspirated under similar conditions. After preliminary work it was determined that 2 gms. of calcium carbonate and 2 gms. of magnesium carbonate were easily dissolved in 100 c. c. 1-15 H₃PO₄ and that *agitation with aspiration* would remove all CO₂. Four residues were tested for CO₂ subsequent to 30 minutes' agitation and aspiration with 1-15 H₃PO₄ at room temperature by boiling, with negative results. The following CO₂ results were obtained gravimetrically from Kaulbaum's C. P. calcium carbonate and Iceland spar, with constant agitation and aspiration for 30 minutes under slight vacuum without soil.

TABLE VI.—*Analysis of C. P. CaCO₃*

Taken		Found
Grams CaCO ₃	Grams CO ₂	Grams CO ₂
.4000	.1760	.1739
.4000	.1760	.1761
.4000	.1760	.1781
.4000	.1760	.1783
.4000	.1760	.1780
.2054	.0904	.0894
.1678	.0728	.0742
Average	.1492	.1497

Average difference = .0005 grams.

After the foregoing data were secured the work was duplicated by introducing three distinct types of surface soil and a red clay subsoil from a cellar digging. In view of the fact that Findlay and Creigh-

ton₂₀ observed that suspended silt increases solubility of CO₂ at normal pressure, one very silty soil was included among the surface soils.

Trials upon C. P. CaCO₃ with 50 gms. of soil without agitation and with agitation at 5-minute intervals, gave repeatedly low results.

TABLE VII—CO₂ recovered from .3000 gram Kalbaum's C. P. CaCO₃ aspirated for 30 minutes, slight vacuum, with constant vigorous agitation, 1-15 H₃PO₄

Soil	Gms. CO ₂ original soil	Gms. CO ₂ added	Gms. CO ₂ theory	Gms. CO ₂ found	Gms. CO ₂ difference	Difference per cent CO ₂ soil basis
50 gms. loam soil	.0091	.1320		.1405		
	.0085	.1320		.1421		
	.0078	.1320		.1408		
	.0109	.1320		.1400		
	Av.0091	Av.1320	Av.1411	Av. .1409	— .0002	— .0004
50 gms. silty Ford soil	.0056	.1320		.1384		
	.0043	.1320		.1364		
	.0050	.1320		.1383		
	.0045	.1320		.1370		
	Av.0049	Av.1320	Av.1369	Av. .1375	+ .0006	+ .0012
50 gms. red sandy Keffer soil	.0033	.1320		.1347		
	.0014	.1320		.1354		
	.0027	.1320		.1332		
	.0021	.1320		.1335		
	Av.0024	Av.1320	Av.1344	Av. .1342	— .0002	— .0004
50 gms. red clay subsoil	.0006	.1320		.1315		
	.0009	.1320		.1325		
		.1320		.1338		
	Av.0008	Av.1320	Av.1328	Av. .1326	— .0002	— .0004

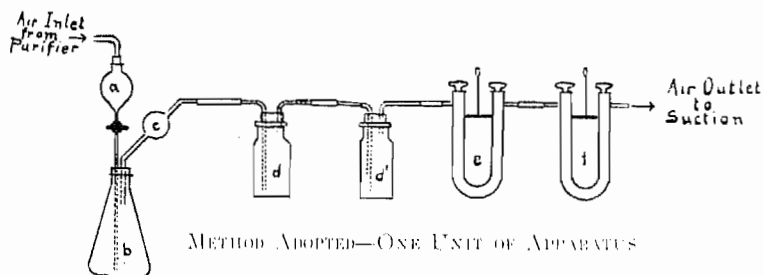
Referring again to Table V, it will be noted that the 1-15 H₃PO₄ gave slightly higher results on the CO₂-free soil than 1-50 H₃PO₄. In practice it was found that the 1-15 was required for very heavy occurrence of carbonate. Very slight action was found, however, upon well-rotted manure and barnyard soil from H₃PO₄ acid, 1-15. The action of H₃PO₄ 1-15 in the cold is much less than would be permitted as laboratory error of duplication in routine investigational work. However, in view of the results above stated and the results of Marr, Wiley and Gaither, previously cited, the authors advance and strongly advocate the following suggestion: Where two or more soils are to be studied comparatively, or when the *absolute* carbonate CO₂ content be desired, blank determinations be run upon the soil, after treatment as suggested by Fraps₁₀, for humus, increasing the strength of the HCl to 2 per cent where the carbonate occurrence is

heavy and filtering by suction on a 9 cm. filter with Bächner funnel, which is very rapid. The blank obtained from this chlorine-free acid-washed soil should be deducted from the determination on the untreated soil, as measuring the degree of activity of the acid upon soil organic matter.

ACTION OF H_3PO_4 ON OTHER CARBONATES

Frear³, studying action of various strengths of HCl , with and without heat upon dolomite and siderite, notes inactivity of the two minerals named and cites the surprising fact in the case of siderite that when in contact in the cold for 10-15 minutes the evolution of CO_2 is 2.6 times that secured from boiling for one minute. He makes reference to the need of vigorous agitation. Samples of siderite secured from the collection of Dr. Wait, of the University of Tennessee, were analyzed and gave with 1-50 H_3PO_4 and 30 minutes digestion, and agitation, at room temperature, .0023 gm. CO_2 , which was increased to .0258 gm. on boiling, using a charge of .5 gm. while .1650 gm. CO_2 were secured from the same charge by heating with HCl 1-5. A 1-per cent HCl aspirated with agitation at room temperature for 30 minutes gave .0044 gms. CO_2 and .0658 gm. upon boiling. On testing the siderite used, considerable calcium was found, and it is quite possible that trace of CO_2 found could be attributed to that source, making the action of the acid on the iron carbonate entirely negative.

A Knox dolomite found to have 44.10 per cent CO_2 , as calculated from CaO and MgO determinations of W. H. MacIntire, and 44.22 per cent from CO_2 determination with heat by L. G. Willis, gave 42.4 per cent CO_2 by aspirating 30 minutes with constant shaking, using 1-15 H_3PO_4 at room temperature. A further aspiration of 15 minutes gave a full recovery of CO_2 . A 5-gm. charge of manganese spar aspirated at room temperature for 30 minutes with 1-per cent H_3PO_4 gave .0141 gm. of CO_2 and .0687 gm. when boiled with the same acid. This mineral showed an absence of calcium carbonate when tested.



METHOD ADOPTED—ONE UNIT OF APPARATUS

METHOD ADOPTED

The following method as used in this laboratory has given entire satisfaction, having been used upon 135 soil samples which were under absolute laboratory control and covering light and heavy occurrences of CO_2 . Where evolution of CO_2 is not greater than .2000 gm., 50 gms. of soil may be used, the amount of soil for the charge being decreased with an increasing percentage of CO_2 . The evolution is kept to this amount in order that the soda-lime tubes may be effective for more determinations. A separatory funnel (a) connected with purifying apparatus leads through a two-holed rubber stopper to the bottom of a 300-c. c. Erlenmeyer flask (b). Through the second hole is inserted a bulb tube (c) leading to two purifying bottles (d and d) containing concentrated H_2SO_4 . To the second acid bottle is attached U tube (e) containing soda lime and this attached to tube (f) containing pumice stone saturated with concentrated H_2SO_4 . The tube used is the modification described by W. H. MacIntire, Jour. Am. Chem. Socy., March, 1911. If volumetric determinations be desired, a Folin absorption tube or a tower containing glass beads may be used. After purifying the atmosphere of the apparatus, 60 to 100 c. c. of H_3PO_4 , 1-15 CO_2 -free, is added through the funnel and CO_2 drawn off at a *very slow* rate, with *constant agitation*, for 10 minutes. The second 10 minutes the rate is slightly increased, and during the third 10-minute period purified air is drawn fairly rapidly through the system. Slight vacuum should be maintained.

The essentials of the method are *very slow aspiration* at first, *constant agitation* and slight vacuum.

When charges of as much as 25 gms. are used, or if the soil be highly carbonaceous, determine and deduct blank on the soil, after eliminating CO_2 , local citation 46.

It is good practice to have two soda-lime tubes in the train and discard the first when the second begins to gain. Experience has shown the inadvisability of using one tube alone after the heating phenomenon is noticed as far as the curve of the tube. In an endeavor to eliminate the labor incident to shaking by hand, the authors tried various schemes and different-shaped containers for charges, bringing air in through mercury and zinc bottoms, but none gave satisfactory results, save shaking by hand.

Due to the elimination of condensers and silver sulphate tubes, the apparatus can be made very compact, and as many units as desired may be used.

Mr. Willis has ingeniously coupled eight units together by clamping stands, and the entire eight can be shaken by one person with ease by means of glass tubing for rollers. The 8-unit system occupies but 50 inches of desk space and with it two men can easily make 32 gravi-

metric determinations daily, one person purifying apparatus and weighing charges, the other weighing two sets of tubes. Where several units compose a system, two Muencke's wash bottles should be used, followed by two tall soda-lime tubes, containing cotton at outlet, for air purification. The system is illustrated on the title page of this bulletin.

SUMMARY AND CONCLUSIONS

1. Phosphoric acid is, of the available mineral acids, the least active upon soil organic matter.
2. Phosphoric acid at room temperature acts but slightly on soils rich in organic matter.
3. Phosphoric acid 1-15 at room temperature liberates all of the CO_2 from CaCO_3 and MgCO_3 in soils, and the CO_2 evolved can be collected by aspiration with suction, either gravimetrically or volumetrically.
4. If *finely ground*, limestone and dolomite can be determined with or without soil, under the above conditions.
5. Constant agitation is essential to complete CO_2 liberation.
6. Dilute phosphoric acid in the cold is not appreciably active upon ferrous carbonate and but slightly so on manganese carbonate.
7. In comparative CO_2 studies, a blank should be run upon the soil subsequent to its being freed of carbonates, and as correction made for the action of the acid on organic matter.

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