A COMPARATIVE STUDY OF SOIL ACIDITY METHODS ON ILLINOIS SOILS

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INTRODUCTION

Much effort has been spent by agricultural investigators in determining the so-called lime-requirement or acidity of soils. That much of this effort is justified will be conceded, when it is recognized that the major portion of all agricultural land in the humid regions of the United States is "acid," and that on such lands the correction of this condition is fundamental to the establishment and maintenance of crop production at a reasonably high level.

Under humid weathering conditions the decomposition of soil minerals is accompanied by the liberation of basic elements in the form of soluble compounds, largely through the action of water and carbonic acid. The soluble bases are removed, partly in the ground-water and, in tilled soils, in the crops harvested from the land. The continual removal of basic elements at a more rapid rate than that at which the acidic elements are removed produces several conditions in the soil, which taken together, make it an unfavorable substrate for the growth of many of the most important farm crops. In soils which have developed a very high degree of acidity, practically all plants refuse to grow. Some of the more important factors of soil acidity may be enumerated as follows:

(a) The presence of hydrogen-ions, indicating true acidity in the chemical sense.

(b) Insoluble acids and acid salts.

(c) Colloids, both organic and inorganic, most of which absorb basic ions, rather than acid.

(d) Aluminum compounds which are either soluble or in a combination sufficiently "active" as to be rendered soluble by reaction with neutral salts, or to affect unfavorably the growth of plants.

Each of these factors taken separately may not be necessarily toxic to growing plants; indeed corn, wheat, rye and many other crops grow best in a soil containing a low concentration of hydrogen-ions. However, since these and other factors contribute in varying degrees to the results obtained by the application of various acidity methods to soils, these various methods can not be expected to give concordant results.

It is the purpose of this paper to record the results obtained in a comparative study of five different soil acidity methods, as applied to a number of Illinois soils which vary rather widely in type and in lime-requirement.

THE METHODS

Three of the methods used, those of Hopkins, Veitch and Jones, are recognized as *quantitative.* The Comber and Truog methods, which were designed primarily as *qualitative* tests for field use, furnish also a rough index of the degree of acidity.

The Hopkins method consists essentially in shaking 100 grams of soil continuously for three hours with 250 cc. of normal potassium nitrate solution. After settling has taken place, 125 cc. of the solution are decanted and titrated with standard alkali, after boiling to remove carbon dioxide. From the titration value and a factor proposed by Hopkins, the lime-requirement is computed in terms of calcium carbonate equivalent.

In the Veitch method, separate 10 gram samples of soil are treated with increasing amounts of standard calcium hydroxide solution and evaporated slowly to dryness. Then, after a short digestion on the steam bath with distilled water, a portion is filtered off and boiled down nearly to dryness and tested with phenolphthalein. From the amount of $Ca(OH)_2$ used in the sample which is neutralized, is computed the lime requirement.

The Jones method consists in grinding a small sample of soil, dry, in a mortar with a weighed quantity of calcium acetate. When thorough mixture is effected, distilled water is added, the whole stirred for one minute, filtered and titrated with standard alkali solution.

It will be noted that the Hopkins and Jones methods depend upon reaction with a neutral salt for liberation of acid-reacting compounds from the soil, while the Veitch method measures the absorption capacity of the soil for a free base.

In the Comber test, advantage is taken of the fact that iron and aluminum occur in acid soils in a combination that can be broken up by reaction with a salt, as KCNS, and it is essentially a test for ferric iron in such form. To 2 or 3 grams of soil in a test tube is added an excess of 4 per cent KCNS in 95 per cent alcohol. After shaking thoroly and allowing to settle, the supernatant liquid becomes red within 15 minutes if the soil is acid. The red color is due to the formation of ferric thio-cyanate.

The Truog test, like those of Jones and Hopkins, relies upon reaction with a neutral salt to liberate acid-reacting substances. The soil is mixed with zinc sulfide and barium chloride. Distilled water is then added and the mixture boiled. A strip of filter paper, saturated with lead acetate, is held over the flask and is blackened by the formation of PbS from the H_2S liberated from the flask. The intensity of blackening is presumably proportional to the acidity of the soil.

EXPERIMENTAL

Fifty-seven samples of surface soil (0″—6⅔″) were selected from the stock samples collected in various parts of the state, representing twenty-six soil types. These were selected to represent a wide range of lime-requirement as previously determined by the Hopkins method. For the presentation of data, these soils were classified into five groups, each group containing soils similar in physical and textural characteristics. These groups are as follows:

I. Sandy soils (8 types.)

II. Light colored silt loams (5 types).

III. Dark colored silt loams (4 types).

IV. Clay loams and clays (5 types).

V. Black soils, high in organic matter (4 types).

The results of the tests by each of the five methods are presented in Tables I to V inclusive, each value representing the average of closely agreeing duplicate determinations. The content of total organic carbon and of calcium are included also in the tables. For the sake of convenience in studying the relative values obtained, the soil numbers are arranged in order of increasing values as determined by the Hopkins method.

The results are graphically expressed in Figs. 1 to 5, inclusive.

TABLE I.

SANDY SOILS.

Lab. No.	Soil Type	Total Org. C. lbs. per 2,000,000	Total Ca lbs. per 2,000,000	$CaCO_3$ requirement lbs. per 2,000,000			Comber Number	Truog Number × 1.3
				Hopkins	Veitch	Jones		
36	Dune sand	....	7,160	40	210	300	4	5.07
38	Dune sand	9,780	3,920	40	210	400	5	8.45
60	Yellow gray sandy loam...	29,320	5,980	40	630	1,100	14	5.2
41	Brown sandy loam........	9,980	7,340	40	300	400	6	6.76
23	Yellow gray fine sandy silt loam	13,860	7,220	60	700	500	4	1.69
43	Brown sandy loam	10,160	8,700	60	210	400	5	11.83
30	Brown sandy loam........	44,040	7,500	100	1,260	1,700	11	10.14
26	Yellow sandy loam	....	11,140	120	500	320	21	13.52
44	Brown fine sandy loam....	39,480	9,540	120	400	1,400	10	16.9
48	Yellow sandy loam.......	17,860	3,980	300	1,260	800	8	13.5
11	Brown sandy loam........	50,140	14,720	320	120	100	15	1.69
33	Brown sandy loam........	18,700	4,680	360	630	800	8	16.9
34	Brown gray sandy loam on tight clay	47,670	10,280	400	1,260	1,100	8	5.07
31	Yellow gray sandy loam...	18,360	6,080	460	500	500	6	8.45
24	Gray sandy loam.........	16,880	6,280	800	300	800	15	16.9

TABLE II.

LIGHT COLORED SILT LOAM SOILS.

Lab. No.	Soil Type	Total Org. C. lbs. per 2,000,000	Total Ca lbs. per 2,000,000	$CaCO_3$ requirement lbs. per 2,000,000			Comber Number	Truog Number × 1.3
				Hopkins	Veitch	Jones		
19	Yellow gray silt loam.....	27,880	7,240	40	1,260	2,400	10	11.83
29	Yellow silt loam..........	14,320	5,040	120	420	600	5	6.76
17	Yellow silt loam..........	18,440	8,840	240	1,890	900	10	16.9
1	Yellow gray silt loam.....	....	7,900	260	900	300	7	10.14
32	Yellow gray silt loam.....	70,580	14,480	260	300	500	2	3.38
28	Light gray silt loam on tight clay	12,860	2,560	380	630	1,100	6	10.14
27	Yellow gray silt loam.....	19,460	4,340	500	1,890	1,350	10	10.14
15	Yellow silt loam..........	16,160	8,360	540	480	500	4	8.45
14	Yellow gray silt loam.....	26,780	10,380	580	1,890	1,200	9	10.14
22	Deep gray silt loam.......	18,680	4,220	1,020	2,940	1,400	12	18.59
2	Gray silt loam on tight clay	....	2,520	1,380	3,990	2,200	14	20.28
6	Light gray silt loam on tight	29,060	6,340	2,420	1,890	1,900	17	20.28
49	Yellow silt loam..........	15,640	3,580	3,600	5,250	2,300	14	22.10
4	Yellow silt loam..........	....	3,860	5,680	3,360	4,750	14	22.10
5	Yellow silt loam..........	9,560	4,480	4,000	3,570	2,100	10	15.2

TABLE III.

DARK SILT LOAMS.

Lab. No.	Soil Type	Total Org. C. lbs. per 2,000,000	Total Ca lbs. per 2,000,000	$CaCO_3$ requirement lbs. per 2,000,000			Comber Number	Truog Number × 1.3
				Hopkins	Veitch	Jones		
37	Brown silt loam..........	37,420	6,160	40	840	1,100	9	11.83
57	Brown silt loam..........	....	10,200	40	2,300	1,600	8	16.9
16	Brown silt loam..........	....	9,760	60	2,100	2,200	9	16.9
55	Brown silt loam..........	53,380	5,620	80	1,260	2,000	9	18.59
59	Brown silt loam..........	55,560	8,980	80	1,890	1,500	6	10.14
45	Brown silt loam..........	48,620	6,720	100	630	1,825	13	6.76
56	Brown silt loam..........	62,440	9,480	120	1,680	1,800	10	6.76
20	Brown silt loam..........	....	7,240	160	1,260	4,700	13	16.9
21	Brown silt loam..........	75,240	6,120	180	1,470	4,400	10	13.5
52	Brown silt loam..........	49,840	8,040	260	6,300	2,100	14	18.59
47	Brown gray silt loam on tight clay	36,680	4,700	400	1,420	1,750	16	18.59
35	Mixed loam	42,000	12,880	420	840	700	7	8.45
8	Brown silt loam..........	71,520	18,180	600	820	1,700	8	13.52
9	Brown silt loam..........	59,900	10,320	600	2,840	1,975	13	15.21
13	Brown gray silt loam on tight clay	50,900	12,110	960	1,260	1,200	8	11.83
3	Brown loam	90,500	3,940	3,540	6,310	3,200	17	21.97

TABLE IV.

CLAY LOAMS AND CLAYS.

Lab. No.	Soil Type	Total Org. C. lbs. per 2,000,000	Total Ca lbs. per 2,000,000	$CaCO_3$ requirement lbs. per 2,000,000			Comber Number	Truog Number × 1.3
				Hopkins	Veitch	Jones		
54	Black clay loam..........	64,300	19,120	20	420	400	2	1.69
39	Drab clay loam...........	39,020	10,820	40	420	700	8	6.76
53	Black clay loam..........	68,120	16,900	40	630	700	3	5.46
40	Drab clay	40,280	11,940	60	400	600	9	6.76
42	Sandy drab clay loam.....	53,740	12,240	60	1,260	3,750	7	13.52
10	Drab clay loam...........	51,000	14,220	400	630	1,200	8	6.76
7	Clayey muck	220,100	13,940	1,620	5,250	3,000	16	18.59

TABLE V.

BLACK SOILS, HIGH IN ORGANIC MATTER.

Lab. No.	Soil Type	Total Org. C. lbs. per 2,000,000	Total Ca lbs. per 2,000,000	Hopkins	Veitch	Jones	Comber Number	Truog Number × 1.3
50	Peaty loam	229,760	25,560	40	1,050	1,100	3	8.45
46	Black silt loam..........	44,480	7,060	160	2,310	1,350	13	13.5
12	Black mixed loam.........	90,480	19,180	560	630	300	2	1.69
25	Medium peat	....	9,080	580	4,500	2,750	6	10.4

Sandy soils.

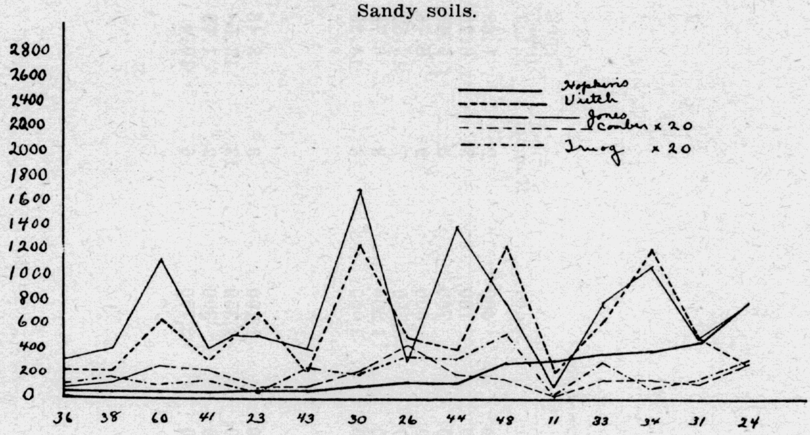

Fig. 1

Light silty soils.

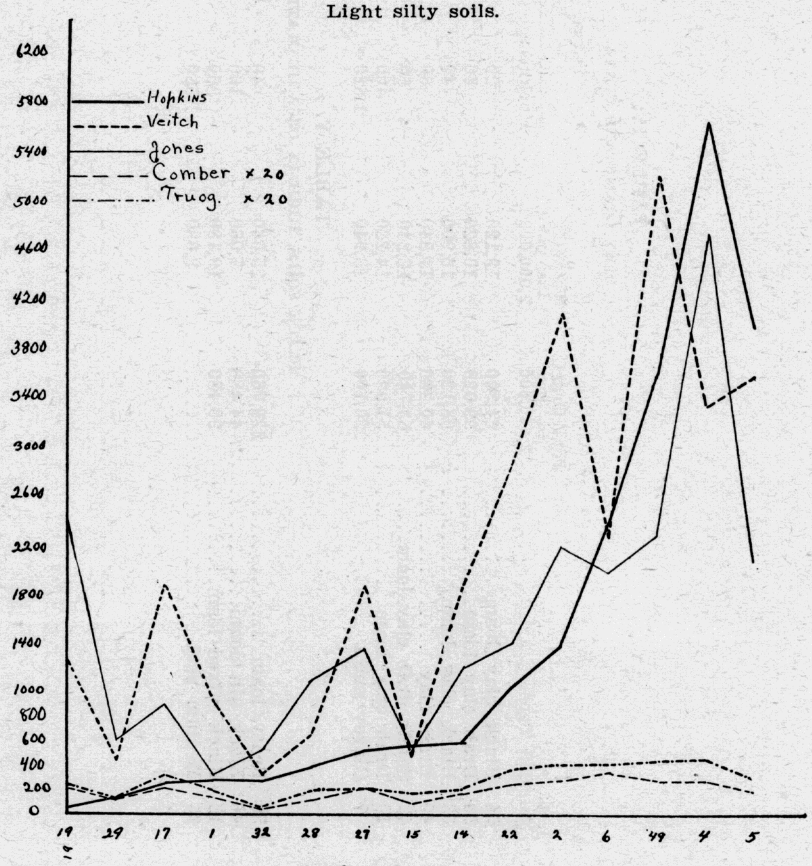

Fig. 2.

DISCUSSION OF RESULTS

The two outstanding results of this study are first, the lack of agreement of the three quantitative methods studied, and second, the low values obtained by the Hopkins method as compared with the other two. The only

Dark Silt Loams.

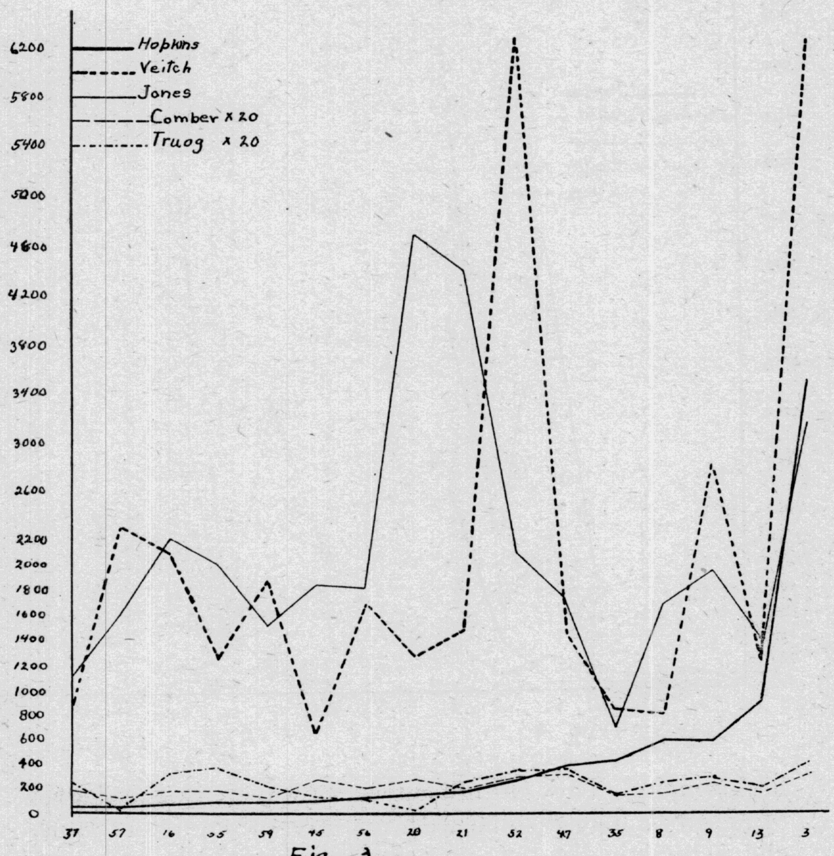

Fig. 3

semblance of a correlation is in the group of light colored silt loams. In only three cases are the results by the Hopkins method higher than by the Jones; in one case they are greater than the results by the Veitch method, and in three other cases they are higher than the results by both the Jones and Veitch methods. These seven soils showing relatively high Hopkins values are for the most part low in organic matter, being yellow silt loams or sandy soils, although one is classified as black mixed loam. There are six soils having a lime-requirement of more than 1000 pounds per acre by the Hopkins method and the other methods agree in showing these soils to be

Clay loams and clays. Soils very high in organic matter

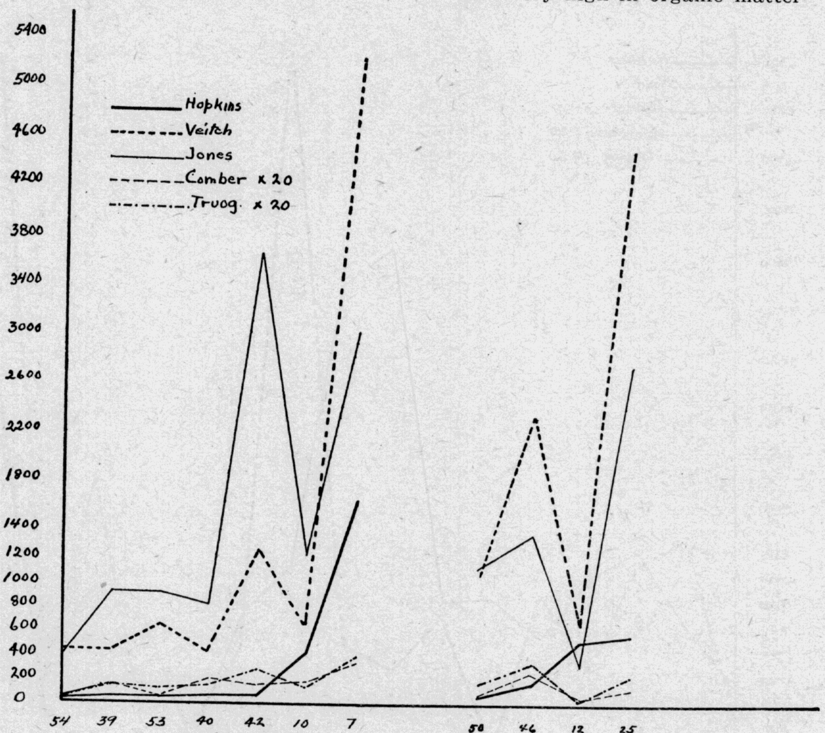

Fig. 4. Fig. 5

highly acid. They do not agree, however, in the degree of acidity. These soils, with one exception, are of types characteristically low in organic matter. It has been generally observed that the majority of Illinois soils actually need considerably larger applications of limestone in order to grow the more acid-density crops than are indicated by the results obtained by the Hopkins method.

A considerable number of soils which are high in organic carbon content were found to give high lime-requirements by the Veitch and Jones methods. On charting all the results in order of increasing content of organic carbon, however, no indication was observable of a causal relationship. When all the results were similarly charted in order of increasing total calcium content of soil, no relationship whatever was found between total calcium and lime-requirement as determined by any method.

The wide divergence between the Hopkins method on the one hand, and the Veitch and Jones methods on the other, is in accordance with what one might expect when the principles involved in the methods are considered. The Veitch method measures essentially the total absorbing power of the soil for the free base, since $Ca(OH)_2$ is the reagent used. The absorbing capacity of the soil is a lesser factor in the Jones calcium acetate method, the calcium ions being in equilibrium with those of a weak acid, while in the Hopkins method absorption phenomena are more largely excluded. Potassium ions, which under similar conditions are absorbed more readily by most soils than are calcium ions, are here combined with a strong acid into one of the most stable salts. It is altogether probable that absorption plays some part in the exchange of bases which occurs in this determination, as a result of which aluminum salts are brought into solution. These undergo hydrolysis, yielding an acid solution which may be titrated until all the aluminum is precipitated as the hydroxide. It is of interest to note that Dr. Veitch criticized the Hopkins method when it first appeared on the ground that it was essentially a method for the determination of soluble aluminum in soils. At that time aluminum was not recognized as a factor in the toxicity of acid soils to crops. The discovery of aluminum toxicity has converted this objection into an advantage for the method.

It may be observed that the divergence between the Hopkins, and the Veitch and Jones methods is slightly greater in the soils represented in Figs. 3, 4, and 5, than in those of Figs. 1 and 2. The former three groups consist of soil types which ordinarily contain a larger proportion of combined organic and inorganic colloidal constituents than the soils shown in the latter groups. This statement can be taken as no more than a mere indication of a possible relationship between colloidal content and high results by the Veitch and Jones methods.

An attempt was made to compare the Comber and Truog field tests with the quantitative methods discussed. In studying Comber's test, 17 shades of color were prepared as standards for comparison of the colors obtained with the various soils. These were prepared by adding increasing quantities of $FeCl_3$ to an alcoholic solution of KCNS. The shades obtained in the Truog test were classified into 13 groups and numbered from 1 to 13. In order to have these "Truog numbers" comparable with the "Comber numbers" they were each multiplied by the factor 17/13 or 1.3. Again in order to increase the scale so that these results could be charted along with those from the quantitative methods, the results of both tests were further multiplied by 20.

The results obtained in these two tests appear to agree rather closely, but show no correlation with the quantitative methods used. Field observations with the Comber test indicate that in general soils which give a red or pink color will not grow sweet clover or alfalfa and will not grow red clover satisfactorily without the application of limestone. Further than this, quantitative deductions can not safely be made.

In another series of nearly 200 tests, not reported here in detail, the Comber test was compared with the Hopkins method on soils covering a wide range of types and degrees of acidity and alkalinity. The Comber test consistently gave negative results on those soils reacting neutral or alkaline to the Hopkins test, while a red color was produced invariably with those soils having a lime-requirement of 40 or more pounds per two million pounds of soil. In these tests, the color intensity was of no significance from a quantitative point of view.

In a further study of the Comber test, samples of a very acid soil (No. 2009) were extracted with water and alcohol respectively. These extracts were both distinctly acid, showing a Ph value of 5.0 to 3.5 by the colorimetric method. They were free from ferric iron, since they failed to respond to KCNS additions, although a positive reaction was secured by adding Comber's solution to the soil itself. The intensity of the color is reduced greatly by substituting an aqueous solution of KCNS because of the excessive ionization of the colored ferric salt.

Since the intensity of the red color is dependent upon the amount of iron which can react, the iron content of the soil might be expected to affect the results. It has been found, in fact, that this is true. Five soils (numbers 1620, 1717, 2015, 4471, 8153), showing a faint pink color with KCNS, were moistened and treated with iron filings. After standing two days they were dried and then taken up with KCNS as usual. The color was intensified considerably in each case.

It has been observed frequently that this test is not applicable to peat or peaty soils, no color being produced even by very acid peats. This was conceived to be due to a possible iron deficiency. Accordingly several peat soils ranging from alkaline to acid by the Hopkins method were treated with the Comber solution, both with and without the addition of iron filings. All those without iron filings were colorless. In each case the samples with iron filings and having a lime-requirement by the Hopkins method showed a red color, while the neutral and alkaline samples remained colorless. The iron filings were added to the dry soil immediately before adding the KCNS. It is suggested that this test may be made applicable to iron-deficient soils by means of this slight modification.

SUMMARY

1. The Hopkins, Veitch and Jones quantitative methods, and the Comber and Truog field tests were studied on 57 soils representing a wide range of Illinois soil types and degrees of acidity.

2. The three quantitative methods failed to show any consistent agreement with each other from a quantitative point of view.

3. The Veitch and Jones methods gave consistently higher results than the Hopkins, particularly on those soil types which ordinarily contain fairly large proportions of colloidal material, including organic and inorganic.

4. The comparatively low results obtained by the Hopkins method are due probably to the failure of this method to measure fully the absorption capacity of soils for bases.

5. The Comber and Truog field tests agreed fairly closely with each other in the comparative intensity of their respective colors with the various soils, but these graduations of color intensity are considered of but little significance as quantitative indications of the lime needs of soils.

6. Both the Comber and Truog tests are reliable as qualitative tests.

7. In the Comber test the alcoholic KCNS solution must be brought in contact with the soil mass. Neither water nor alcohol extracted ferric iron from the acid soils used in these tests.

8. By the addition of iron filings to the soil previous to applying the Comber test, it may be used for soils very high in organic matter, such as peats and peaty loams.

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