THE ESTIMATION OF SOIL ACIDITY AND THE LIME REQUIREMENTS OF SOILS.

BY F. P. VEITCH.

WITHIN the past few years, it has been definitely shown that the reaction of a soil exerts a marked influence on its crop-producing power. While the reaction affects the chemical and the physical condition of the soil to a considerable extent, the growth of plants is more directly affected by the action of the acids on the plant roots, and upon the micro-organisms of the soil.

The importance of the matter has led to the elaboration of several methods for determining the amount of acids in soil, but, owing to the exceedingly small amount usually present in ordinary arable soils, the influence of other material, and the constant changes taking place in the soil, none of these methods has shown a close relation between crop production and the amount of acidity as determined by any of the methods. Wheeler, Hartwell, and Sargent[1] have recently made a critical examination of the methods which have been proposed for this purpose, checking the chemical methods by field experiments. The investigators were unable to correlate the chemical results obtained by any of the methods examined with the field results, but regarded as promising the titration of dilute ammonia which had been in contact with the soil for some time, and also a method based on the evolution and estimation of the carbon dioxide freed from calcium carbonate by the acid soil on boiling them together in water.

It has not seemed advisable to the writer to give more study to either of these methods, because any solution placed in contact with a soil, no matter whether acid or alkaline, will be decreased in strength through adsorption or physical reaction between the solution and the soil; and we have no certain means of measuring the amount thus adsorbed. Further, owing to the deflocculating power of ammonia, it is practically impossible to get even an approximately clear filtrate or supernatant liquid, and the amount of acid as determined is more or less affected by this fact. With regard to the evolution and estimation of carbon dioxide, the

[1] This Journal, 22, 153.

evolution continues indefinitely, and whether it is due to reaction between the soil and the carbonate or to the oxidation of the organic matter of the soil is not definitely known, though it is probable that it is more largely due to the first-mentioned reaction.

After a great deal of experimenting the writer has devised a method in which lime-water is used to neutralize the acid material in the soil.   The method is based on the fact that the small excess of lime-water present, after the neutralization of the acid material, is converted into carbonates and bicarbonates, the boiling solution of which gives an alkaline reaction with phenolphthaleïn.

No effort has been made to secure great refinement or close duplication of results, because the problem is a practical one in which the application of several hundred pounds of lime, more or less, per acre has but little economic or agricultural significance. It may be said, however, that the writer has reason to believe that the method will give duplicate results accurate to one hundred pounds of lime per acre foot of 3,500,000 pounds.   The method is as follows :

For the preliminary test, to three portions of 10 grams each of the soil in platinum dishes add 50 to 60 cc. of distilled water, and different amounts of standard lime-water. For example, to the first 10 cc., to the second 20 cc., and to the third 30 cc. of lime-water are added.   Dry down at once on the steam-bath, transfer to a stoppered Jena flask with 100 cc. of distilled water, allow to stand over night, with occasional shaking, filter (the filtrate should be clear or but faintly turbid), take 50 cc. in a Jena beaker, add a few drops of phenolphthalein solution, and boil until the appearance of the pink color, or in the case where no color is developed to a volume of about 5 cc.   Then with the two portions of treated soil, one of which has been rendered alkaline by the added lime-water and the other of which is still acid, as guides, prepare three fresh portions of 10 grams each, and add lime-water as before, except that the amount added to a dish differs from that added to another, by only one or two cc.   Dry, allow to stand, filter, and treat exactly as before ; the smallest amount of lime-water which gives the characteristic pink with phenolphthaleïn is taken as the acidity equivalent of the soil.   From the data thus obtained, the acidity and lime requirements of the soil may be calculated.

The results which have been obtained with this method are given in Table I. The amount of lime (CaO) required to neutralize the acids in an acre foot of 3,500,000 pounds is also included. 1 cc. of calcium hydroxide to 10 grams of soil is approximately 450 pounds of lime per acre.

TABLE I.

		50 cc. filtrate boiled.		Lime (CaO) required per acre foot of 3,500,000 pounds.
		Acid with cc. Ca(OH)$_2$.	Alkaline with cc. Ca(OH)$_2$.	
No. 1	Summit, R. I	20	25	11,250
No. 2	Jamestown, R. I	..	8	3,600
No. 3	Harrisville, R. I	10	15	6,750
No. 4	Foster Center, R. I	25	32	14,300
No. 5	Niantic, R. I	6	8	3,600
No. 6	South Portsmouth, R. I	30	35	15,750
No. 7	Hamilton, R. I	17	18	8,100
No. 8	Slocumville, R. I	54	56	25,200
C	Coarse sand used in greenhouse	3	4	1,800
No. 1 A. O. A. C. sample 1900		9	{ 10 { 10	4,500
No. 3 A. O. A. C. sample 1900		50	{ 52 { 52	22,500
No. 4 A. O. A. C. sample 1900		..	1	450
No. 3 A. O. A. C. sample 1901		8	9	4,050
No. 4 A. O. A. C. sample 1901		1	2	900
No. 5 A. O. A. C. sample 1901		1	2	900
5118	Leonardtown loam, Md	4	{ 5 { 5	2,250
5127	Leonardtown loam, Md	8	10	4,500
5112	Norfolk loam, Md	4	5	2,250
5131	Norfolk sand, Md	0	1	450
4244	Conowingo Barrens, Md	4	5	2,250
3624	Fine sandy soil, Fla. (much organic matter)	7	8	3,600
A	Gabbro soil, Md	10	{ 12 { 12	5,400
O	Lime Expt. plot, Md. Station, 60 bushels per acre	1	2	900
B	Lime Expt. plot, Md. Station, no lime	5	{ 1 6 { 6	3,150
D	Md. phosphoric acid plots	1	{ 2 { 2	900

The samples from Rhode Island Nos. 1 to 8 are samples kindly furnished by Dr. Wheeler, and are the same upon which he worked in the investigation previously referred to. Owing to the

scarcity of material, closer readings than those given in the table could not be made, on these samples; but the readings made on other samples show that much closer readings could probably have been made here.

A summary of Wheeler's results on these soils, field and laboratory, is given in Table II. To this has been added the results obtained by the lime-water method on these same samples by the writer. For a more satisfactory comparison, the lime-water results have been calculated to their nitrogen equivalents, and the acidity of the samples as expressed in pounds of lime (CaO) per acre foot of 3,500,000 pounds has been included.

These results, while somewhat unsatisfactory, are not so surprising when we consider the different soils and the number of factors involved in plant production which are influenced and modified by the addition of lime to a soil, even though that soil may be liberally supplied with available plant food. It is of interest to note that soils Nos. 6, 8 and 9 produced such large crops of beets after liming, although the soils still remained very acid. In other words, after liming, beets were not as sensitive apparently to an acidity equivalent to 20,000 pounds of lime per acre as they were to half this amount on unlimed, but different soils, a fact which possibly indicates that the toxic effect of acids is not so great in the presence of large quantities of soluble lime-salts.[1] This fact is highly important practically and may explain why small applications of lime are often as beneficial as large. It may also explain why slightly acid soil will often produce certain crops, clover, for instance, which will not grow on other soils which are even less acid.

It is also interesting to note that the relative acidity of these soils is the same, whether determined by treatment with ammonia, as was done by Wheeler, or by treatment with lime-water, as was done in this laboratory.

Perhaps the most striking point brought out in the table is the apparent relation of alkali neutralized by the soil to the total humus of the soil. While this relation does not seem to be exceedingly close, it is clearly apparent and is very suggestive in lending support to the hypothesis that the acidity of soil is gener-

[1] *Vide* Ninth Annual Report R. I. Expt. Station p. 309; also Report 71, Bureau of Soils, U. S. Dept. of Agriculture.

F. P. VEITCH,

TABLE II. —COMPARISON OF THE AMMONIA WATER, AND THE LIME-WATER METHODS.

Summarized from Wheeler's results.

	Yield of beets unlimed. Pounds per 1:20 acre.	Yield of beets limed. Pounds per 1:20 acre.	Increase due to liming. Pounds.	Total humus. Per cent.	Mgs. N in NH4 retained by 10 grams soil.	Mgs. CaO retained by 10 grams soil lime-water method.	Mgs. N equivalent to CaO retained by 10 grams soil.	CaO required per acre foot to render the soil neutral. Pounds.	CaO still required per acre foot to render soil neutral after Wheeler's liming. Pounds.
No. 1 Summit, R. I	47.4	92.9	45.5	1.73	19.6	32.0	16.0	11,250	6,250[1]
No. 2 Jamestown, R. I	75.8	152.7	76.9	0.85	10.4	10.2	5.1	3,600	....
No. 3 Harrisville, R. I	151.5	207.3	55.8	1.46	14.1	19.2	9.6	6,750	1,750
No. 4 Foster Center, R. I	36.3	143.4	107.1	2.21	25.5	40.9	20.4	14,300	9,300
No. 5 Niantic, R. I	9.9	43.4	33.5	0.95	7.9	10.2	5.1	3,600	....
No. 6 South Portsmouth	26.0	153.0	127.0	2.63	27.2	44.8	22.4	15,750	10,750
No. 7 Hamilton, R. I	14.5	131.8	117.3	1.60	15.8	23.0	11.5	8,100	3,100
No. 8 Slocumville, R. I	1.0	101.8	100.8	5.08	43.8	71.5	35.75	25,200	20,200
No. 9 Kingston, R. I	6.6	161.4	154.8	5.15	36.1	66.6	33.3	23,400	18,400

[1] The figures in this column were obtained by subtracting the pounds of lime (CaO) applied to duplicate plots by Wheeler, from the figures given in the preceding column.

ally due to organic acids. In studying these figures, the fact should be borne in mind that neither the methods of determining acidity nor total humus are very exact, and there may be errors in these various determinations, which, if eliminated, would make the relation pointed out much more striking.

As with all other chemical methods used in soil work, the method must not only give accurate results, but these results must have an agricultural significance. Let us see how well the proposed method satisfies the conditions.

The development of the pink color with phenolphthaleïn in the boiled aqueous extract of a soil is doubtless only a question of the volume of extract which is boiled down; even very acid soils will, on long-continued treatment with much water, yield an extract which, on concentration, will give an alkaline reaction with this indicator. A great number of determinations made in this laboratory shows that a soil which gives an alkaline reaction with litmus paper also gives an aqueous extract which is alkaline to phenolphthaleïn when treated with water in the proportion of 1:10, and 50 cc. of the extract is boiled. Numerous determinations of the reaction of soils from all over the country indicate very strongly that those soils which are alkaline to litmus and to phenolphthaleïn under the conditions above described are always more productive soils than contiguous soils which are acid to these indicators. These are the reasons why the proportion of soil to water, and the amount of filtrate to be boiled, as given above, were adopted.

As has been said, we have no method by which we can determine how much of the lime taken up by the soil is actually neutralized by the acid material of the soil, and how much is simply adsorbed and held physically by the soil in such a manner that it does not pass into solution. This is the chief difficulty inherent in any titration method for determining soil acidity. Plus errors are thus introduced, and the acidity of a soil appears greater than it actually is. Experiments, in which soils of different nature were treated with known amounts of dilute ammonia ($N/20$), soda ($N/50$), and lime-water ($N/20$), and aliquot portions of the filtrate titrated both directly with acid, and also by adding an excess of acid and titrating back, showed in every instance that the amount of adsorbed alkali was greater than by the lime-water method. The figures in Table II show the same thing.

Theoretically, there is every reason to believe that adsorption is less under the conditions obtained in the lime-water method than in the titration methods, for, as we know, adsorption is actually greater from the more concentrated solution, and in the titration methods we must always expect to have more alkali present than is sufficient to neutralize the acid material of the soil, and to satisfy the soil's adsorptive power in the presence of such excess of alkali.

In the method above outlined, the amount of alkali which must be present is enough to neutralize the acid material plus a little more than the soil is able to hold against the solvent power of partially carbonated water. That this is so seems quite clear, and is strongly supported by the results in Table II, from which we see that in every case the lime equivalent to nitrogen retained by the soil is much less by the lime-water than by the ammonia-water method. The differences are much too large and regular to be accounted for either by errors or by differences due to neutralization of the acid material of the soil. Another point: It is more than likely that considerable reaction takes place between the non-acid material of the soil and ammonia, even in the cold. If there is any reaction between the lime-water and the material, it is reasonable to think that it is much less, because the very small excess of lime-water is immediately converted into carbonate and bicarbonate, as shown by the behavior toward phenolphthalein. Nevertheless we must regard all these methods as likely to give high results, owing to the probable combination of the alkalies with some silica and silica compounds, both reactions introducing plus errors. The smallest difference between the two methods occurs on No. 5, which is visibly a coarse sandy soil, and upon which adsorption would be expected to be at a minimum.

Reference has been made to the fact that Wheeler regarded as particularly promising a method based on the evolution of carbon dioxide from a mixture of soil and calcium carbonate in boiling water. He found that after boiling such a mixture (40 grams of soil and 4 grams of calcium carbonate) until apparently the evolution had become constant and hence the evolution of carbon dioxide set free by the acid material in the soil had ceased, that two more boilings of the same mixture yielded 0.016

and 0.048 gram of carbon dioxide. These results indicate the decomposition of calcium carbonate equal to 20.8 and 16.6 mg. of lime to 40 grams of soil. These figures are equal to 4.4 and 3.4 cc. of lime-water to 10 grams of soil. From this it would appear that the possible errors would be greater by this method than by the lime-water method.

As has been pointed out, in all these methods the possible combination of the lime with silica and other inorganic soil constituents, without the release of an equivalent of some other base, is a source of error which increases the actual acidity of the soil. Any difference in the methods in this particular would probably be in favor of the lime-water method. As a matter of fact, the adsorption of the added alkali appears to introduce no error greater than the working limits of the method, a fact which was shown by determining the acidity of two soils in natural condition, and also after they had been powdered. On the other hand, adsorption phenomena certainly vitiates the results by those methods based on the titration of an aqueous extract of the soil or of an alkali which has been in contact with the soil. Nor does it seem probable that the water-insoluble material of an acid nature produces an appreciable error in the method, there being every reason to suppose that these materials will be neutralized by the lime. Further, it is believed that under the conditions of the method, the results are not complicated by the reaction of free carbonic acid or by bicarbonates.[1] Viewed in any light, this method or any method based on the use of lime-water or lime carbonate as the neutralizing agent, must appear to one as being along the right line, imitating as it does actual field conditions.

Analytically considered, the method appears to be sufficiently reliable for practical purposes, and appears to be the best now available for the end in view.

Agriculturally considered, we have no positive direct data showing that the acidity of a soil as determined by analytical methods has a definite ratio to the crop production of that soil. The fact that those soils which are universally regarded as fertile, have an alkaline reaction to litmus paper and to phenolphthaleïn, when their aqueous extracts are boiled, as in the previously de-

[1] The data upon which this view is based will be given in full in a publication soon to appear from the Bureau of Soils, U. S. Dept. of Agriculture.

scribed method, furnishes strong evidence as to the agricultural significance of the results thus obtained, but so far no one has been able to show a close agreement between crop yields and the lime requirements of soil as determined by laboratory methods.

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THE ANALYSIS OF VANILLA EXTRACT.

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HESS AND PRESCOTT, in papers published in this Journal,[1] have discussed the adulteration of vanilla extract and have described methods devised by them for the separation and determination of vanillin and coumarin, for the distinction of genuine from artificial extracts, and for the detection of artificial coloring-matter, all of which methods, with slight changes, are included among the "Provisional Methods for the Analysis of Foods", adopted by the Association of Official Agricultural Chemists.[2]

Preliminary to the examination of commercial extracts, under the Connecticut pure food law, we have subjected these methods to a critical investigation, the results of which, while substantiating in the main the accuracy of the methods, suggested certain modifications. The Hess and Prescott method for determination of vanillin and coumarin was found to be thoroughly reliable but susceptible of abridgment without diminishing its accuracy.

The methods as finally amended were employed in the analysis of five extracts made in the laboratory and sixty-two commercial extracts.[3]

METHODS OF ANALYSIS.

Determination of Vanillin and Coumarin. Modified Hess and Prescott Method.—The modified method differs from the original method in three details:

First. Two per cent. instead of 10 per cent. ammonia is used, and consequently a less concentrated ammonium chloride solution is obtained after neutralizing with hydrochloric acid, thus reducing the chance of carrying this salt into the extract.

[1] Vol. 21, 256, 721.

[2] Bulletin 65, U. S. Dept. Agr., Bureau of Chem., pp. 69-71.

[3] Conn. Agr. Expt. Sta., Rep. 1901, pp. 152-162.