	Conductivity Value	Canadian Lead No.	Volumetric Lead No.
Maximum.....	189	7.55	6.6
Minimum.....	108	1.72	4.8
Difference.....	81	5.83	1.8
Mean.....	134	3.22	5.77
Range, per cent of mean.....	60	181	31
Range, per cent of minimum.....	75	339	37.5

MEASUREMENTS ON NON-MAPLE SYRUPS—We have applied the method to 5 of the non-maple and compound maple syrups referred to in Paper I, *viz.*, Nos. 7 and 13 of Table VIII—a golden syrup and a syrup made from a pale brown commercial sugar—the latter of which had given a conductivity value within the limits for maple syrup—and Nos. 11, 31 and 33 of Table IX. All five of these syrups gave smooth curve plots.

A compound syrup, a syrup sold as pure but known to be adulterated, and 5 syrups made from raw cane sugars by dissolving in water, boiling to 219° F., and filtering, gave smooth curves. Two other syrups made from raw cane sugars and a sample of raw beet sugar gave breaks at 3.4, 4.1 and 4.2, respectively,—all outside the limits for maple syrups. Two of these syrups had conductivity values (143 and 210) within the limits found in maple syrups. In 3 samples of cane molasses no material change in the electrical resistance (which, of course, was much lower than with maple syrup) was produced by the addition of the 10 cc. of lead subacetate solution.

TIME REQUIRED FOR THE TEST—The time required to reboil, filter and cool the syrup and to make the test is about half an hour. The time consumed in the test itself is less than 5 minutes.

SUMMARY

I—The volumetric lead subacetate test consists in diluting the syrup to 10 times its original volume and titrating with lead subacetate solution of sp. gr. 1.033, obtaining the end-point by measurements of electrical resistance.

II—The volumetric lead number is the abscissa of the point of intersection of two straight lines on the plot of volumes as abscissae with resistances as ordinates.

III—Seventy genuine Quebec 1914 and 1915 syrups gave volumetric lead numbers ranging from 4.8 to 6.6—a range of 37.5 per cent of the minimum, as compared with 97 per cent for the conductivity value. In 28 of these syrups, the ranges of volumetric lead number, conductivity value and Canadian lead number were, respectively, 37.5, 75 and 339 per cent of the minima.

IV—Seventeen out of 20 syrups containing 30 per cent of sucrose syrup gave smooth curve plots: 18 out of 20 containing 40 per cent sucrose syrup gave smooth curves and the remaining two gave intersections outside the limits for genuine syrups.

V—Of 18 adulterated and non-maple syrups, 12 gave smooth curve plots, 3 gave intersections outside the limits found in genuine syrups and in the remaining 3 (cane molasses) the electrical resistance remained constant.

CONCLUSION

If future work by ourselves and others corroborates our experience of its reliability, we believe that, com-

paring as it does the merits of rapidity, narrow range of values in genuine maple syrup and rapid falling off or early disappearance as the syrup is adulterated with cane sugar syrup, this test will prove the most useful single test for purity of maple products yet proposed.

MACDONALD COLLEGE, PROVINCE OF QUEBEC

COMPARISON OF LIME REQUIREMENT METHODS

By J. W. AMES AND C. J. SCHOLLENBERGER

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The results presented have been obtained in the soil investigations pertaining to the effects of lime treatment being conducted at the Ohio Experiment Station. An estimation of the lime requirement in relation to effectiveness of applications of lime under different conditions of fertilizer treatment has been made, using several of the methods proposed for this determination.

METHODS—The methods used included the Veitch, Hopkins, Hutchinson-MacLennan,¹ MacIntire² and Vacuum³ methods. The Veitch and the Hopkins, which are two of the more generally used methods, are entirely different in principle. The Hutchinson-MacLennan method and that proposed by MacIntire, two of the more recent of the numerous methods which have been published, are somewhat similar, a solution of calcium bicarbonate being the carrier of base in the two latter-mentioned methods. In the Hutchinson method the soil is kept in contact with the bicarbonate solution for 3 hours and a portion of the filtrate is titrated against *N*/10 acid, using methyl orange as indicator, to obtain a figure for the amount of calcium absorbed. The MacIntire method differs in that the bicarbonate solution is evaporated in contact with the soil to a thin paste; after transferring to a suitable flask, the excess of calcium carbonate is determined by addition of acid and estimation of liberated carbon dioxide.

SOILS—These five methods were compared on soils from a number of variously treated plots from one of the fertility sections of the Wooster farm, located on silt loam soil which is largely derived from sandstones and shales. So far as its history is known, it contains no natural supply of calcium carbonate, and each year it becomes increasingly difficult to secure a satisfactory growth of clover unless lime is applied. The west half of the plots had been treated with 1875 lbs. per acre of calcium oxide in 1903, and 2000 lbs. of limestone in 1909. The composition of the lime materials applied was such that the equivalent of 5700 lbs. of calcium carbonate had been applied to the limed halves of the plots previous to the time samples were taken from the plots, which was 3 years after the last treatment with lime.

From determinations of calcium carbonate which

¹ *Chem. News*, 110, No. 2854, Aug. 7, 1914.

² *Am. Fert.*, 41, No. 11, Nov. 28, 1914.

³ This method was proposed by E. W. Gaither, formerly of this laboratory, and is essentially a modification of the Tacke procedure for estimation of degree of acidity of peat soils. Instead of boiling the mixture of soil and calcium carbonate at 100°, the soil was heated in contact with finely divided calcium carbonate under reduced pressure as in the Marr (*Jour. Agr. Science*, 3, Part 2, p. 155) procedure for determination of soil carbonates; the carbon dioxide liberated by decomposition of the calcium carbonate by the soil is taken as a measure of the lime requirement.

are available for several of the differently fertilized plots on which lime requirement determinations were made, it is evident that the greater portion of the lime applied has disappeared or no longer exists in the carbonate form.

QUANTITIES OF CALCIUM CARBONATE PRESENT IN THE LIMED HALVES		
Plot	FERTILIZER	Lbs. per acre
0	None.....	150
2	Acid phosphate.....	225
3	Muriate potash.....	450
5	Sodium nitrate.....	575
11	Complete.....	300
24	Complete, including ammonium sulfate as carrier of nitrogen	None
26	Complete, including bone meal as carrier of phosphorus.....	250
29	Complete, including basic slag as carrier of phosphorus.....	300

When tested with litmus paper, all of the soils—the limed soils containing a small amount of lime carbonate residual from application made, as well as the unlimed soils—gave a decided acid reaction. The amounts of CaCO_3 required for 2,000,000 lbs. (approximately) per acre 6 in. of soil are stated in Table I.

TABLE I—LBS. CaCO_3 INDICATED FOR 2,000,000 LBS. SOIL

Plot	FERTILIZER	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
0	None.....	3440	2000	3550	2925	7300
	None + Lime.....	100	Alk.	2250	1700	4900
2	Acid Phosphate.....	2640	2000	3850	2700	7800
3	Acid Phosphate + Lime.....	80	Alk.	2400	975	3800
	Muriate Potash.....	3240	2000	3550	3025	
	Muriate Potash + Lime.....	200	Alk.	2650	1600	
5	Sodium Nitrate.....	3640	1200	3550	2550	6200
	Sodium Nitrate + Lime.....	120	Alk.	2500	1250	4225
11	Acid Phos. + Mur. Pot. + Sod. Nitr.....	3080	1800	3850	2825	7100
	Acid Phos. + Mur. Pot. + Sod. Nitr. + Lime.....	80	Alk.	2500	1375	5900
24	Acid Phos. + Mur. Pot. + Amm. Sulf.....	4240	3000	4000	2700	8300
	Acid Phos. + Mur. Pot. + Amm. Sulf. + Lime.....	260	200	2850	1475	5700
26	Bone Meal + Mur. Pot. + Sod. Nitr.....	2940	2000	3700	2250	7350
	Bone Meal + Mur. Pot. + Sod. Nitr. + Lime.....	360	Alk.	2900	1325	4050
29	Basic Slag + Mur. Pot. + Sod. Nitr.....	2560	1200	3600	2250	6600
	Basic Slag + Mur. Pot. + Sod. Nitr. + Lime.....	150	Alk.	2100	1075	4050
18	Manure.....	2760	2600	4200	3100	8500
	Manure + Lime.....	120	Alk.	2950	1950	5200

The fact that no residual carbonate is present in the soil, and the poor growth of clover on the plot which received ammonium sulfate as the nitrogen carrier, is in accord with the lime requirement indicated by the Veitch and Hopkins methods, since the figures for the unlimed end of this plot are higher than those obtained for any of the other plots, by either of these methods, while the MacIntire, Hutchinson and Vacuum methods each show the highest lime requirement in the case of the manure-treated plot.

A comparison of the figures for the soils where three different carriers of phosphorus (acid phosphate, bone meal and basic slag) have been used, shows a higher lime requirement for the acid phosphate-treated soil by the Hopkins, MacIntire and Hutchinson methods. The Veitch and Vacuum methods give slightly higher results for the bone meal plot, while the Hutchinson method gives the same figure for both the bone meal and basic slag plots. With this one exception, all the methods indicate a lower requirement for the basic slag plot. The figures by those methods which show a lower requirement for the basic slag and bone plots agree with the growth of clover on the unlimed ends of these plots, since a more satisfactory stand of clover is secured on these plots than on the plot where acid phosphate is the carrier of phosphorus.

The variations shown by several of the methods

indicate the possible usefulness of some of these methods for comparative purposes where different soil treatments have been made. For the soils which have been limed, but with amounts which were evidently too small, since the growth of clover on the limed halves of the plots indicates that they will be benefited by additional quantities, the MacIntire, Hutchinson and Vacuum methods have, no doubt, given a better indication of the optimum quantity of lime necessary to make conditions satisfactory for the growth of leguminous plants.

If either the Hopkins or the Veitch test were used to obtain a figure for the limed soil's requirement, the results would lead to erroneous conclusions, because the Veitch method indicates that the limed halves of all the plots are alkaline, excepting the one where ammonium sulfate has been used; and the Hopkins test has shown a very small requirement for the limed halves of the plots, the largest amount of calcium carbonate required, according to this test, being 360 lbs. per acre. The results obtained by the Hutchinson, MacIntire and Vacuum methods are much higher than those by either the Hopkins or Veitch test for the soil which has been limed.

While the figures obtained for the unlimed soil by the several methods do not exhibit the wide variation that is found for the limed soil by the Veitch and Hopkins methods as compared with the other methods, there are appreciable differences indicated. Excepting the ammonium sulfate-treated plot, the results for the unlimed soil are uniformly lower by the Veitch test. In some instances there is a very close agreement between the Hopkins and MacIntire results, although in the majority of cases the Hopkins and Hutchinson methods agree more closely. The results by the Veitch method for Plots 24 and 26, which have received different carriers of phosphorus and nitrogen, correspond to those secured by the Hutchinson method. In the case of the manure-treated soil, the results by the Veitch and Hopkins methods are practically the same.

The Vacuum method shows a much larger amount of lime required than is indicated by the other methods, and it may be that for non-calcareous soils the figures closely approximate the actual amount of calcium carbonate required. However, for many soils naturally supplied with calcium carbonate and which gave an alkaline reaction with litmus, results by this method indicate a further need of lime, the amount required in many cases being considerably in excess of the amount of calcium carbonate present. This would seem to indicate that the results obtained for lime requirement are probably too high and that the method would not be applicable to soils in general.

In Table II the differences between the results obtained for the limed and unlimed soil of the several fertilized plots is expressed in percentages of the figures for the unlimed soil. Considering to what extent the soils lime requirement has been satisfied following the lime treatment, the results obtained by the Hopkins and Veitch methods exhibit a marked uniformity, although the lime requirement for the un-

limed soil by the Hopkins test is considerably in excess of the amount shown by the Veitch test. The figures show that the decrease in lime requirement as measured by either the Hopkins or Veitch test is quite uniform for all the plots.

TABLE II—PERCENTAGES OF THE ORIGINAL LIME REQUIREMENT SATISFIED BY LIME TREATMENT

SOIL TREATMENT	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
None.....	97	100	36	41	32
Acid phosphate.....	97	100	37	60	51
Muriate of Potash.....	94	100	25	47	..
Sodium Nitrate.....	96	100	29	50	31
Acid Phos. + Mur. Pot. + Sod. Nitr.....	97	100	35	51	17
Acid Phos. + Mur. Pot. + Amm. Sulf.....	94	93	28	45	31
Bone Meal + Mur. Pot. + Sod. Nitr.....	87	100	21	41	45
Basic Slag + Mur. Pot. + Sod. Nitr.....	94	100	41	52	38
Manure.....	95	100	29	37	39

The MacIntire and Hutchinson methods exhibit a variation between the soils variously fertilized, the figures by the MacIntire procedure for the majority of the soils showing that a smaller percentage of the lime requirement has been satisfied by the lime treatment previously given the plots.

CHANGES IN LIME REQUIREMENT DURING 16 YEARS

A comparison of the lime requirement figures for soil sampled in 1896 and again in 1912 is of interest in relation to changes which have taken place in soil during a period of 16 years. By inspection of results grouped in Table III, it will be noted that, as measured by the Hopkins method, the requirement of the unlimed soil at the earlier period is markedly lower than that obtained by the other methods, while the same soil at the latter date of sampling has a higher requirement by the Hopkins method than by the other methods, excepting the Vacuum method, and in one case the MacIntire method.

The Veitch results being lower at the latter sampling as compared with the earlier sampling are just the reverse of those by all the other methods which have indicated a decidedly increased lime requirement for the soil after a period of 16 years. Although all the methods excepting the Veitch show an increase

TABLE III—COMPARISON OF LIME REQUIREMENT OF SAME SOIL SAMPLED IN 1896 AND 1912

FERTILIZER	Sampled	Hop-kins	Veitch	Mac-Intire	Hutch-inson	Vacuum
Ammonium Sulfate.....	1896	750	4000	3000	1750	5500
Ammonium Sulfate.....	1912	4240	3000	4000	2700	8300
Ammonium Sulfate + Lime.....	1912	260	200	2850	1475	5700
None.....	1896	625	4000	2700	1575	6100
None.....	1912	3440	2000	3550	2925	7300
None.....	1912	100	Alk.	2250	1700	4900

in the lime requirement for the soil at the latter date as compared with the earlier sampling, the Hopkins method indicates a much greater increase than the other methods. In direct contrast to the lower results by the Veitch method for the soil at the later date compared with results by the same method for the first sampling, is the fact that for the soil when first sampled, the Veitch method gave higher indications than the Hopkins, MacIntire or Hutchinson methods.

It should be stated that the determinations on the soil collected in 1896 and that in 1912 were made by each of the methods used, at the same time, so that the differences found cannot be attributed to factors introduced by variations in the procedure employed.

Many changes have taken place in the soil during 16 years. Following the deeper plowing and better cultivation the soil has received since the 1896 sampling, the physical condition of the soil and its organic content will have been affected to an extent sufficient to cause the variations observed in the lime requirement of the old and new soil by the several methods.

INFLUENCE OF VARIATIONS IN METHOD ON RESULTS

It may be pointed out that these methods for the determination of a "Lime Requirement" are empirical in nature, and comparatively slight variations in procedure affect the results obtained markedly. Thus, the Veitch method is much affected by the degree of clarity of the extract—the clearer the extract the lower the lime requirement, and a method of filtration removing every trace of suspended clay might possibly show a zero requirement in a great number of cases where the usual procedure indicates a considerable lime requirement. On the other hand, all soils do not settle to the same extent when allowed to stand over night, and a comparatively small amount of suspended clay will prevent any appearance of a pink color on boiling, although calcium hydroxide solution in quite measurable quantity is added directly to the boiling solution. For this reason, it was thought best to employ filtration.

Ten grams of soil were weighed into a porcelain dish, wet with sufficient water to give about 50 cc. of liquid after the standard lime water had been added and evaporated on the steam bath as rapidly as possible, stirring once or twice before the mass is dry. It was then washed into a 100 cc. Jena flask with 100 cc. water, shaken occasionally for 15 to 30 minutes, and allowed to stand over night. The contents of the flask were shaken and poured onto an S. & S. 18 cm. folded filter; the first 30 or 40 cc. were rejected, the next 50 cc. collected, a few drops of phenolphthalein added, and immediately boiled down to about 5 cc. in a Jena beaker. A distinct pink color was taken to indicate alkalinity, but in cases where the color was only faint, the result was recorded as doubtful and the experiment repeated.

The Hopkins method will not give the same indications if another salt is substituted for KNO_3 . In this work, 100 g. air-dry soil were shaken with 250 cc. N KNO_3 for 3 hours, using a shaking machine, then filtered immediately, 125 cc. pipetted off, boiled and titrated with $N/10$ NaOH , using phenolphthalein. The factor 2.5 was used.

The method proposed by MacIntire is quite sensitive in this respect; the directions call for evaporation "to a thin paste," but higher results are obtained

TABLE IV—LIME REQUIREMENT BY MACINTIRE METHOD. LBS. CaCO_3 PER 2,000,000 LBS. SOIL

G. in 100 cc.	TREATMENT	CaCO_3
10	Evaporated to thin paste immediately.....	7500
10	Evaporated to dryness immediately.....	8200
10	To thin paste immediately, to dryness next morning.....	8900
10	Let stand over night, to dryness next morning.....	8100
20	Evaporated to thin paste immediately.....	5750
20	Evaporated to dryness immediately.....	6300

if the evaporation is carried to dryness. The results also vary with the time required for the evaporation, even when it is carried to the same stage (see Table IV).

It should be noted that the soil used in this experiment had a rather high requirement, and that if the requirement as determined when using 10 g. soil to 100 cc. of solution was the correct figure, 20 g. of the soil should be more than sufficient to exhaust 100 cc. of the $\text{Ca}(\text{HCO}_3)_2$ solution. As a matter of fact, only about three-fourths of the total amount of CaCO_3 was decomposed by the 20 g. charge. The soils under investigation showed a requirement of about one-third the total calcium carbonate in 100 cc. bicarbonate solution when 20 g. of soil were used; the evaporations were carried to dryness as rapidly as possible, and stirred several times meanwhile. The residual CO_2 was determined by the Marr method.

The Hutchinson method seems to be affected to some extent by allowing the soil and $\text{Ca}(\text{HCO}_3)_2$ solution to remain in contact for a period longer than 3 hours. Thus, a determination in which 40 g. soil was shaken with 200 cc. $\text{Ca}(\text{HCO}_3)_2$ solution for 3 hours indicated a calcium absorption of 3025 lbs. per acre; 100 g. of the same soil shaken with 500 cc. of the same bicarbonate solution for 3 hours, then allowed to stand over night, on titration showed a requirement of 3600 lbs. per acre. The soil used for this experiment was from plot treated with muriate of potash. The bicarbonate extract of the soil showed but a faint trace of chlorine, no potassium, but traces of sodium and magnesium. The calcium in the bicarbonate extract by permanganate titration was only about 0.4 cc. lower than the figure obtained by direct titration with acid, both being on the $N/10$ basis. This shows that with the Hutchinson method interchange of bases plays but a very subordinate part and the chief factor is absorption. The method will sometimes show a lime requirement in the case of a soil which contains a great excess of carbonate.

For this work, 20 g. soil to 200 cc. solution was the rule, the air in the bottle was displaced by CO_2 , the bottle securely stoppered, shaken for 3 hours, immediately filtered, and 100 cc. of the filtrate titrated with $N/10$ HCl , using methyl orange; 100 cc. of the original solution was titrated in the same way.

The Vacuum method, it will be noticed, invariably shows the highest figures for the lime requirement; this is doubtless because the conditions of the method are such that the decomposition of CaCO_3 by the soil can proceed to a maximum without hindrance.

OHIO AGRICULTURAL EXPERIMENT STATION
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THE ACTIVITY AND AVAILABILITY OF INSOLUBLE NITROGEN IN FERTILIZERS AS SHOWN BY CHEMICAL AND VEGETATION TESTS¹

By F. R. PEMBER AND BURT L. HARTWELL

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Since 1908 the Agricultural Experiment Station of the Rhode Island State College has conducted vegetation tests in pots under greenhouse conditions to ascertain the availability of the water-insoluble

¹ Contribution 217 of the Agricultural Experiment Station of the Rhode Island State College.

nitrogen of certain brands of commercial fertilizers collected in the state, and in various nitrogenous substances, such as Kanona tankage, rape meal, castor pomace, etc.

Until the season of 1910, this station had employed no means, except the vegetation test, for differentiating between the organic nitrogen of one brand of commercial fertilizer and that of another. In March, 1910, the directors of the New York, New Jersey and New England Stations adopted the alkaline permanganate method¹ as a means of distinguishing between the more or less active forms of the water-insoluble organic nitrogen of mixed fertilizers.

The Rhode Island Station, having already secured results by the vegetation method showing a wide variation in the availability of the water-insoluble nitrogen of certain commercial fertilizers, submitted to Mr. C. H. Jones, for activity tests by the alkaline permanganate method, some of the same nitrogenous materials as were used in the vegetation tests and he, without knowing the vegetation results, secured a close agreement.²

I—EFFECT OF SEASON ON PLANT GROWTH

In carrying on vegetation tests at different seasons of the year, it was felt that the season and different soil conditions might have a very important influence upon the relative growth of a plant or different kinds of plants. With this in view two experiments were conducted: the *first* from November 11, 1910, to February 15, 1911, and the *second* from February 23, 1911, to May 30, 1911: thus 96 days elapsed between planting and harvesting. In both experiments, 6-inch galvanized iron pots were used, each containing 1 lb. of soil and 6.5 lbs. of a medium fine, fresh-water beach sand. Oat and rye plants were grown in pots having the same mixture of sand and soil, and oats alone were grown in a mixture of the same sand and a different soil: otherwise the treatment of all the pots was the same, with the exception of the nitrogenous material which was added to furnish 0.1 g. of nitrogen per pot except where the amount of blood was doubled. All of the pots received 3 g. of potassium sulfate and 8 g. of acid phosphate. The mixture of sand and soil was changed in each pot for the second experiment so that the two were identical in every way except for the season of year in which they were conducted.

It will be seen from the weights of the dry tops as given in Table I that the plants growing from February 23rd to May 30th made a greater growth in every instance than those growing from November 11th to February 15th under late fall and early winter conditions. The per cent of nitrogen in the dry tops of the first experiment was enough larger, however, than that in those of the second experiment to make the total amount of nitrogen recovered in the tops much alike in the two experiments having the same treatment.

¹ Report on Nitrogen, C. H. Jones, Referee, Association of Official Agricultural Chemists. Proceedings of the Twenty-seventh Annual Convention, 1910.

² "The Availability of Insoluble Nitrogen in Certain Commercial Fertilizers," B. L. Hartwell and F. R. Pember, *THIS JOURNAL*, 3 (1911), 584.