When employing the scheme outlined below the following results were obtained:

No.	8.6% alcohol Cc.	Phenol added Grams	Alcohol found Per cent	No.	20.0% alcohol Cc.	Phenol added Grams	Alcohol found Per cent
1	50	1	8.6	4	50	1	20.0
2	50	3	8.6	5	50	3	20.0
3	50	10	8.6	6	50	10	20.0

In testing the method the phenol was dissolved in 50 cc. strong NaOH solution in the distilling flask to which the known alcohol solution was then added.

METHOD

Pipette 50 cc. of sample into a 300 cc. flask containing 30 cc. water. Make strongly alkaline with an excess of strong NaOH solution so that the final volume is about 100 cc. and the odor of phenol is absent. Add glass beads and distil into a 50 cc. graduated flask containing 1 or 2 cc. water. The end of the condenser or adapter should almost touch the surface of the distillate in the receiver, especially at the beginning of a distillation. A drawn-out thistle tube is serviceable in this connection. The flask is lowered as distillation proceeds.

When nearly 50 cc. of distillate have been collected, remove the receiver, dilute with water to mark, shake thoroughly and pipette 25 cc. into another 300 cc. flask containing 30 cc. water. Precipitate the phenol as its tribrom-derivative by adding bromine water, drop by drop, to slight excess while rotating flask. Without delay add normal "hypo" solution (a few drops will be sufficient) to decolorize (*i. e.*, to remove the free bromine excess) and finally add enough strong NaOH solution to dissolve the white tribromphenol as its phenate, and then a decided excess of alkali. The final volume will be less than 100 cc. After the addition of glass beads distil into the 50 cc. flask as before, dilute to mark and determine density by weighing. The percentage of alcohol in this last distillate multiplied by 2 gives the required figure.

For high concentrations of alcohol a 100 cc. receiving flask may be substituted in the above method and 50 cc. of distillate treated and redistilled. For high concentrations of phenol the method is directly applicable since the amount of phenol which passes over during the first distillation is small. If the original phenol content is low, the first distillation may be omitted. In this case the 50 cc. sample plus 30 cc. water in the 300 cc. flask is treated directly with bromine water to slight excess as shown by color; then add "hypo," alkali, etc., as above and distil into a 50 or 100 cc. flask according to alcohol concentration. Samples high in phenol cannot be treated directly in this manner because the bulky precipitate of tribromphenol prevents thorough mixing while adding the bromine water, making it impossible to perceive when an excess of bromine is present.

The hydrobromic acid formed by the action of bromine on the phenol is neutralized and retained by the alkali.

CONCLUSION

The method is seen to be not only accurate in result but extremely simple in manipulation, no filtration or separation being required. The results obtained

demonstrate that a low concentration of bromine acting during a short period of time has no appreciable effect on aqueous ethyl alcohol at room temperature.

The behavior of methyl alcohol when present in phenolic ethyl alcohol mixtures will be investigated in the same way.

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THE ANALYSIS OF MAPLE PRODUCTS, VI¹

A Volumetric Lead Subacetate Test for Purity of Maple Syrup

By J. F. SNELL, N. C. MACFARLANE AND G. J. VAN ZOEREN

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The fact that lead subacetate produces a heavy precipitate in genuine maple syrup has been utilized in various ways for the detection of adulteration.² In the method here communicated a more dilute solution of this reagent than is employed in any of the older methods is gradually added to the diluted syrup from a burette and the end-point of the titration is determined by means of measurements of electrical resistance in the manner suggested by van Suchtelen and Itano.³ The method in detail is as follows:

SOLUTION

A filtered solution of Horne's lead subacetate of specific gravity 1.033.⁴ This solution is to be kept in a bottle connected with a burette and protected from atmospheric carbon dioxide by a soda-lime tube.

METHOD

Dilute the syrup with water, boil until the temperature reaches 219° F., and filter through cotton wool. After cooling, dilute 10 cc. to 100 cc. with distilled water and measure 60 cc. of the diluted syrup into a 100 cc. beaker.

Measure the electrical resistance using a dip electrode.⁵ Maintaining the temperature constant, add 1 cc. of the lead subacetate solution from the burette, stir well and again measure the electrical resistance. Continue the addition of the subacetate in this manner, 1 cc. at a time, until 10 cc. have been added. Plot the resistances found against the quantities of subacetate solution used. If the syrup is genuine the results of the plot will be two intersecting straight lines. In the 70 genuine maple syrups,⁶ to which the

¹ Presented at the 51st Meeting of the American Chemical Society at Seattle, August 31-September 2, 1915. Previous papers of this series: *THIS JOURNAL*, **5** (1913), 740, 993; **6** (1914), 216, 301; **8** (1916), 144. An account of the preliminary experiments leading to the volumetric test is given in Paper V, *THIS JOURNAL*, **8** (1916), 144.

² Hortvet, *J. Am. Chem. Soc.*, **26** (1904), 1543; Bureau of Chem., U. S. Dept. Agric., *Circ.* **23** (1905); Jones, Vermont Agr. Expt. Sta., *18th Ann. Rept.*, 1904-5, p. 322; Thos. MacFarlane, Laboratory Inland Revenue Dept., Ottawa, *Bull.* **120** (1906); Winton and Kreider, *J. Am. Chem. Soc.*, **28** (1906), 1204; McGill and Valin, Laboratory Inland Revenue Dept., Ottawa, *Bull.* **140** (1907); **228** (1911); Ross, Bureau of Chem., U. S. Dept. Agric., *Circ.* **53** (1910); Department of Inland Revenue, Ottawa, *Circ.* **G 994**.

³ van Suchtelen and Itano, *J. Am. Chem. Soc.*, **36** (1914), 1793.

⁴ We make a cold, saturated solution of the subacetate, dilute to approximately the correct density, filter and adjust to exactly 1.033, as measured by a hydrometer.

⁵ A suitable form of electrode is described in a paper by Van Zueren, published in the *Journal of the American Chemical Society*, March, 1916. The rest of the apparatus used by us for the measurements of electrical resistance is described in Paper I of this series (*THIS JOURNAL*, **5** (1913), 740).

⁶ These syrups were all collected from the makers in the Province of Quebec, 62 in the season of 1915 and 8 in that of 1914.

method has been applied, the intersections have all fallen between 4.8 and 6.6 cc.

SPECIMEN PLOT—The accompanying diagram is a typical specimen of the plots obtained with a pure syrup and with mixtures of the same syrup of equal density made from commercial white sugar.

THE EFFECT OF TEMPERATURE—Measurements at 20°, 25° and 30° C. with five of the syrups indicate that the particular temperature at which the measurement is made is of no consequence as long as the temperature remains constant during the measurements. The resistances were uniformly higher the lower the temperature but the intersection points did not change.

EFFECT OF ADULTERATION WITH SUCROSE SYRUP

Table I gives the results of determinations of, respectively, (1) the "volumetric lead number," viz., the abscissa of the point of intersection of the two straight lines, and (2) the Canadian lead number, upon 20 syrups (10 of which were dark-colored, late-run prod-

TABLE I—VOLUMETRIC AND CANADIAN LEAD NUMBERS OF 20 PURE MAPLE SYRUPS AND THEIR MIXTURES WITH CANE SUGAR SYRUP OF EQUAL DENSITY

No.	1—VOLUMETRIC LEAD NUMBERS					2—CANADIAN LEAD NUMBERS			
	100%	90%	80%	70%	60%	100%	80%	70%	60%
1	4.8	4.9	4.8	C	C	5.35	2.85	2.72	2.23
2	4.9	5.9	4.7	C	C	1.94	1.40	1.02	..
3	4.9	5.8	4.8	C	C	2.43	1.44	1.17	..
4	6.0	6.2	5.0	C	C	2.58	1.68	1.35	..
5	6.1	5.3	4.9	C	C	1.96	1.14	0.84	..
6	5.4	5.6	4.7	5.4	4.4	3.25	1.96	1.53	..
7	5.8	6.0	5.5	C	C	2.23	1.45	1.11	..
8	5.6	5.1	5.0	5.0	..	2.67	1.85	1.10	..
15	6.0	5.3	5.7	C	C	1.82	1.38	0.99	..
19	6.0	5.3	4.8	C	C	2.29	1.14	0.99	..
31	5.8	5.8	5.3	C	C	4.27	2.80	2.38	1.6
32	5.8	6.0	5.9	C	C	4.44	2.53	2.06	1.5
33	6.0	6.2	5.5	C	C	3.90	2.46	2.01	1.31
34	5.4	5.5	5.2	C	C	1.72	1.03	0.59	..
35	5.4	4.8	4.8	C	C	4.11	2.54	2.23	1.79
36	6.2	6.4	5.1	C	C	2.56	1.72	1.18	..
37	5.4	5.1	5.0	C	4.5	2.21	1.58	0.96	..4
38	5.9	5.9	..	C	..	4.76	1.96	1.29	..
39	6.0	5.7	5.9	C	C	3.70	2.59	2.15	1.65
40	5.3	6.0	..	5.5	C	2.54	1.95	1.31	..
	VOLUMETRIC					CANADIAN			
	Maximum for pure syrup.....					6.6			
	Minimum for pure syrup.....					4.8			
	Difference.....					1.8			
	Mean for pure syrup.....					5.64			
	Variation, per cent of mean.....					31.9			
	Variation, per cent of minimum.....					37.5			

ucts) and upon mixtures of these with a syrup of equal density made from commercial granulated sugar. In the table a smooth curve on the plot is represented by the letter "C." Such a curve is given by all but 2 of the mixtures containing 60 per cent of maple syrup and by all but 3 of those containing 70 per cent. The two exceptional 60 per cent mixtures give intersections outside the limits (4.8 to 6.6 cc.) found in genuine syrups.

The Canadian standard (minimum) for Canadian lead number is 1.7. Two of the 62 per cent and 6 of the 70 per cent mixtures attain to this standard.

The results of Snell and Scott¹ show (as well as can be shown by the study of so small a number of syrups) that the Canadian lead method has this advantage over all the other current tests, that its value falls off more rapidly than in proportion to the adulteration with cane sugar syrup. The basis of comparison employed by Snell and Scott in their paper appears scarcely applicable to the volumetric lead subacetate test, inasmuch as the 90 per cent mixture frequently,

and the 80 per cent mixture occasionally, gives a higher intersection point than the pure syrup itself. If, however, we assume as a provisional standard for the volumetric lead number the minimum value found in our 70 syrups (*i. e.*, 4.8) it is clear that this test condemns all the 60 and all but 3 of the 70 per cent mixtures, whereas the Canadian lead test, as we have seen, passes 2 of the 60 and 6 of the 70 per cent mixtures and it seems probable from Snell and Scott's work that the other tests, had they been applied, would have made a still poorer showing.

RANGE OF VARIATION IN GENUINE SYRUPS

The range of variation of the volumetric lead number among the 70 syrups (4.8 to 6.6) amounts to only 37.5 per cent of the minimum or 31.9 per cent of the

TYPICAL PLOTS FOR A PURE MAPLE SYRUP AND FOR MIXTURES CONTAINING 90 TO 60 PER CENT OF THE SAME WITH CANE SUGAR SYRUP OF EQUAL DENSITY. VARIATIONS IN ELECTRICAL RESISTANCE AS LEAD SUBACETATE SOLUTION IS ADDED

mean (5.64). In the same syrups the conductivity value shows a range of 97 per cent of the minimum or 74 per cent of the mean (125). The volumetric lead number, therefore, appears to have a narrower range than the conductivity value, which, as will be seen by reference to Table V of Paper III, excels all the older analytical values in this respect.

In 28 of the 70 syrups (8 of the season of 1914 and 20 of the season of 1915) the Canadian lead number has been determined. In these 28 samples the three values determined compare as follows:

¹ Paper II of this series, THIS JOURNAL, 5 (1913), 993.

	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.

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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.