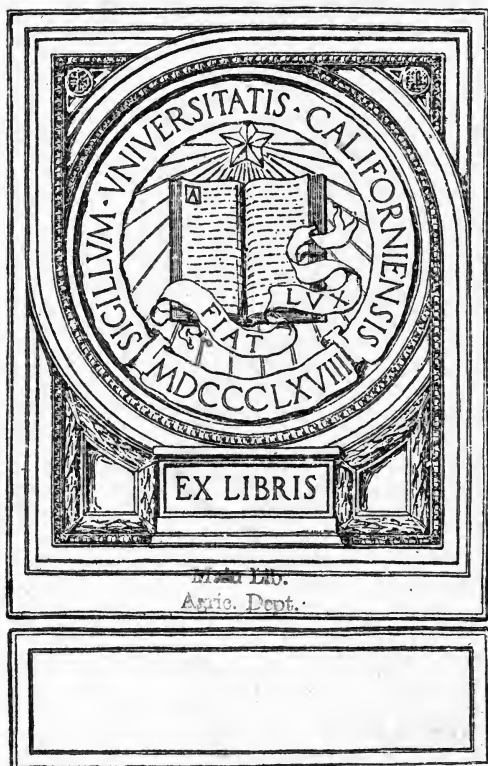


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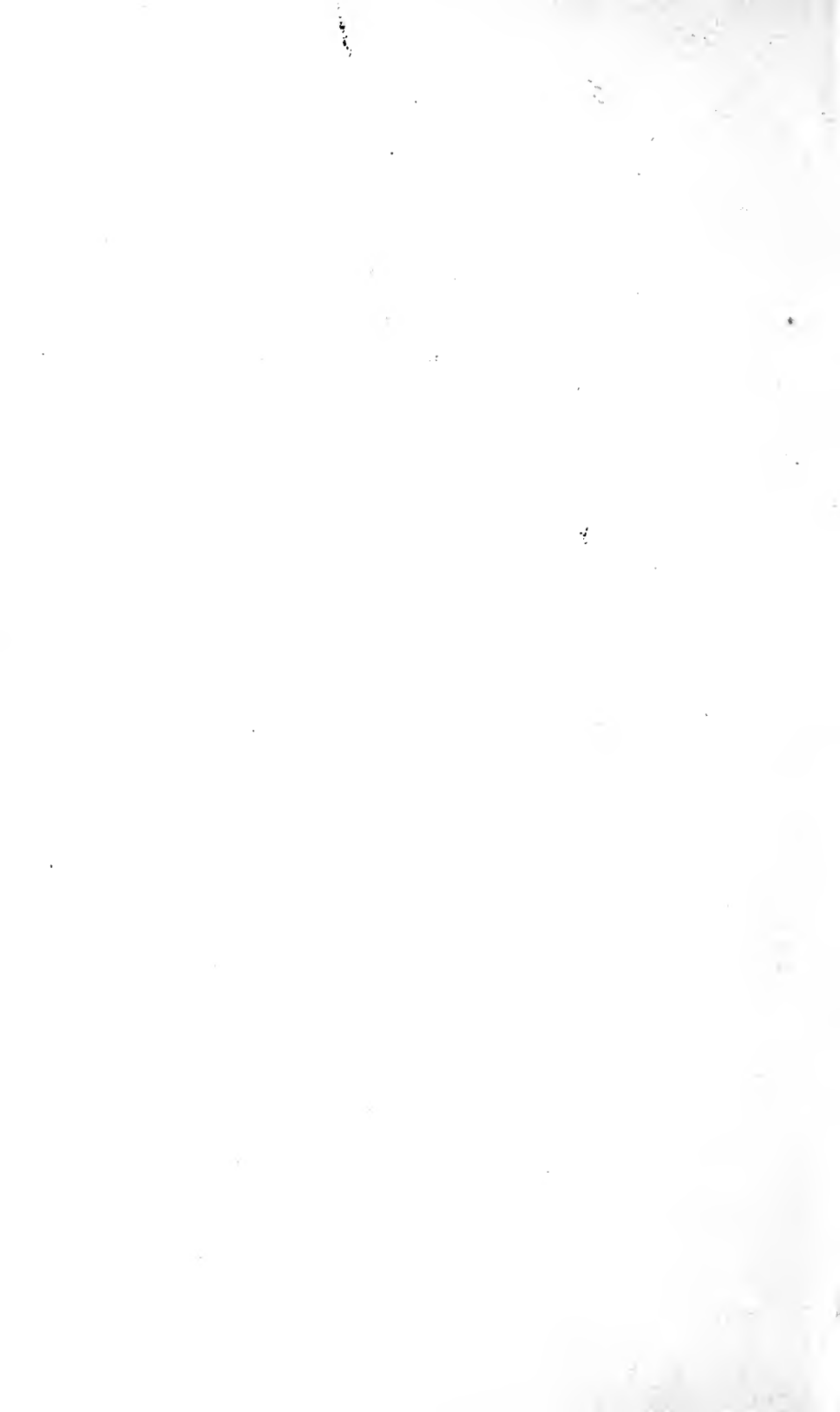


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United States Department of Agriculture,
BUREAU OF CHEMISTRY.—Circular No. 23,
WASHINGTON, D. C.

WASHINGTON, D. C., *March 24, 1905.*

SIR: I desire to submit for your approval a paper on the methods for the examination of maple products, by Mr. Julius Hortvet, associate referee on saccharine products, Association of Official Agricultural Chemists. Credit should also be given to Mr. C. H. Jones, chemist of the Vermont Agricultural Experiment Station, Burlington, Vt., who by his helpful suggestions has been of material assistance to the associate referee in outlining the methods for collaborative work. These directions were prepared for distribution among those chemists who had indicated their intention to participate in the work planned by the Association of Official Agricultural Chemists for the coming year. Owing to the widespread interest in this matter, however, it was deemed advisable to print a circular which would not only be of service to collaborators in the field but would also meet the requests which are received for information relative to methods for detecting the adulteration of maple products.

Respectfully,

W. D. BIGELOW,
*Referee on Food Adulteration, A. O. A. C.,
Chief, Division of Foods.*

Dr. H. W. WILEY,
Chief, Bureau of Chemistry.

METHODS FOR THE EXAMINATION OF MAPLE PRODUCTS.¹

Four samples will be sent out to collaborators, viz, two known-pure sirups and two known-pure sugars. In sampling the sirups for analysis the clear liquid should be taken, avoiding the sedimentary material. In sampling a sugar a portion of the mixed shavings obtained from several pieces should be taken.

The following determinations are to be made upon all samples:

- (1) Lead subacetate precipitate.
- (2) Ash.
 - (a) Total, per cent.
 - (b) Soluble, per cent.
 - (c) Insoluble, per cent.
 - (d) Alkalinity of soluble ash, expressed as cubic centimeters of tenth normal hydrochloric acid for ash of 1 gram of sample.
 - (e) Alkalinity of insoluble ash, expressed as cubic centimeters of tenth normal hydrochloric acid for ash of 1 gram of sample.
 - (f) Ratio of insoluble ash to soluble ash: $b \div c$.
 - (g) Alkalinity of 1 gram soluble ash: $\frac{d \times 100}{b}$
 - (h) Alkalinity of 1 gram insoluble ash: $\frac{e \times 100}{c}$
 - (i) Ratio 1 gram insoluble alkalinity to 1 gram soluble alkalinity: $g \div h$.
- (3) Manganese, calcium, sulphates, and potassium.
- (4) Malic acid value.

(1) LEAD SUBACETATE PRECIPITATE.

The wide variation in the volumes of the precipitates formed when clarifying maple sugar and sirup solutions with subacetate of lead has often been noted. It has been observed that more or less copious precipitates are associated with samples of known purity, while in very many cases of known or suspected adulteration with cane sugar the precipitates are slight or only equivalent to a mere cloudiness. A year ago a method was devised by which these precipitates could be made to occupy definite volumes under fixed conditions. The method, in brief, consists in reducing the precipitate to a compact mass at the bottom of a graduated tube by the use of a centrifugal machine, noting the reading on the tube, applying necessary corrections, and expressing the volume of the precipitate in cubic centimeters and tenths. By means of this method it has been shown that valuable data are readily obtainable regarding the character of suspected samples.

APPARATUS.

The apparatus consists of a glass tube somewhat suggestive of an

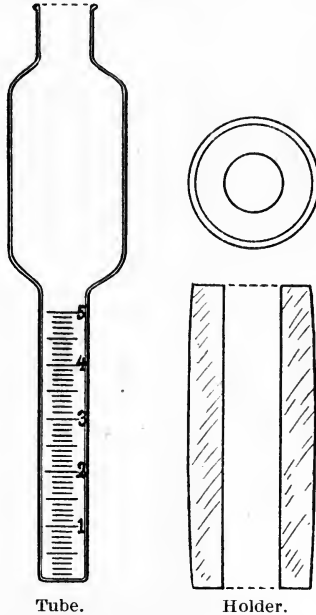
¹ Hortvet, J., Amer. Chem. Soc., 1904, 26: No. 11, p. 1523. Further details and analytical results in full will be found in this article entitled The Chemical Composition of Maple Sirup and Maple Sugar.

inverted Babcock cream test bottle, as shown in the illustration, and is described as follows:

	Cm.
Total length	15.2
Diameter (wide part)	3.0
Diameter (neck)	2.0
Stem graduated to 5 cc and tenths; 5 cc division line 5 mm below beginning of wide part.	
Ground area on wide part for use in numbering. Made of pine or white wood.	

The tube is provided with a holder having the following dimensions:

	Cm.
Length	7.7
Diameter	3.2 to 3.5
Diameter of center hole, to fit stem	1.3



Apparatus for the determination of lead subacetate precipitate.

The tube and holder constitute a couple and weigh together about 50 grams. They should be so constructed that when fitted together the bottom end of the tube will be exactly even with the lower surface of the holder. In order to prevent mixing the pieces belonging to a set, each tube should bear a number corresponding with the number of its holder. Also, in a set, each couple, i. e., tube and holder, should be made to balance every other. There should be, as nearly as possible, a balanced load carried at the circumference of the wheel of the centrifuge.

CONDUCT OF DETERMINATION.

Five cubic centimeters of sirup or 5 grams of sugar are introduced into the tube, 10 cubic centimeters of water added, and the contents thoroughly mixed. Time is given in the case of sugar for complete solution.

One-half cubic centimeter (10 drops) of alumina cream (prepared as described in Bulletin No. 46¹), and 1.5 cubic centimeter of lead subacetate are then added and the contents well shaken. The mixture is allowed to stand from forty-five to sixty minutes, occasionally giving the tube a twisting motion to facilitate the settling of the precipitate.

The tube with its holder is then placed in the centrifugal machine and run six minutes (see conditions given below). At the end of six minutes the contents of the tube are examined, and if any material adheres to the side of the wider portion it is loosened by means of a small wire provided with a loop at the end. The tube is returned to the centrifuge and run six minutes longer at the same rate. The volume of the precipitate is noted, estimating 0.01 cubic centimeter as closely as possible. A blank, using water² and the reagents named above, is run as often as necessary in order to be certain of its value. The blank reading is subtracted from the reading given by the precipitate in each case. In the case of a sirup the result is reduced to the 5-gram basis by dividing by the specific gravity of the sample. If the sugar content of the sample is known, the specific gravity may be found from tables.³ Usually 1.330 has been found very nearly correct for maple sirup.

DISCUSSION.

The centrifugal machine used in this laboratory has a radius of 18.5 cm, and a speed of 1,600 revolutions per minute has been adopted. Calling M unity in the formula

$$F = \frac{Mv^2}{r}, \text{ then } F = \frac{v^2}{r}, \text{ and } v = \sqrt{Fr}.$$

From the above a numerical expression for F can be computed, and having measured r for a given machine, the value of v and the required number of revolutions per minute can be found.

The results obtained by the author⁴ show why a total run of twelve minutes was adopted. Such results can possibly be made to agree more closely under more perfect conditions. The results were obtained on 5-cc samples and have not been reduced to results on the 5-gram basis. The mean blank at the end of twelve minutes was 0.44 cc.

The precipitates vary in the pure sirups from 0.94 to 1.82 cc, and in the pure sugars from 1.18 to 4.41 cc. The highest results, especially among the sugars, are apt to occur in samples which have not been properly clarified. In well clarified samples the precipitates will be found, as a rule, between 1.00 and 1.20 cc for sirups, and between 1.20

¹ U. S. Dept. Agr., Bureau of Chemistry, Bul. 46, Methods of Analysis, p. 39.

² Cane-sugar solution of sp. gr. 1.330 is suggested; the blank would be a trifle higher.

³ U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, Table VI, p. 139.

⁴ Am. Chem. Soc., 1904, 26: No. 11, p. 1523.

and 2 cc for sugars. Dilution by adding cane sugar brings the precipitate values down. The precipitates given by the pure samples were commonly white or very light gray in color, while the supernatant liquid, in practically every case, was clear and colorless. Distinct dark colors have often been observed when making tests on adulterated samples, and these colors have been shown to be due to the presence of caramel.

Duplicate determinations on each sample should be made and the mechanical conditions prescribed are to be very strictly followed.

(2) ASH.

(a) TOTAL ASH.

The determination of ash is of especial value both as a means of deciding upon the general character of a sample and in detecting adulteration. Unclarified samples are much less uniform in composition than clarified samples, hence the percentages of ash among the former will show wider variations than among the latter. The ash results obtained on pure clarified maple sirups and sugars should vary within narrow limits. The tabulated results obtained by the author¹ show a variation among the pure sirups from 0.52 to 1.01 per cent, and among the pure sugars from 0.65 to 1.30 per cent. An inspection of these tables, however, shows that the variation among pure clarified samples is not so great, that the proper range for sirups is from 0.52 to about 0.75 per cent, and for sugars from 0.65 to about 1 per cent. Percentages of ash furnish, also, fairly definite values upon which to base estimates of the extent of adulteration with cane sugar, and in making such estimates, say in the case of sirups, it is very fair to assume 0.50 per cent as the minimum for ash. A safe estimate could be made in the majority of cases, using 0.60 per cent as representing the ash of an average pure maple syrup.

The color of the ash of a maple sirup or sugar is an interesting property. An almost constant indication is a more or less distinct green color, the intensity of which varies partly with the degree of purity of the sample. The characteristic green color is doubtless due to the presence of manganates formed by the fusion of manganese with the potash. The green mass dissolves in a small quantity of cold water to a green solution. When this solution is either acidified, or warmed, or even highly diluted with water, its color changes from green to pink, owing to the conversion of manganate to permanganate.

Weigh 10 grams of the sample in a flat-bottomed platinum dish, heat carefully over an asbestos plate until near the point of charring, then ash until nearly decarbonized, at faint redness in a muffle furnace. Remove remaining particles of carbon by cooling, adding a few drops

¹ Ibid.

of water and evaporating over an asbestos plate, then heating at dull redness. Cool in a desiccator and weigh the total ash.

Note the color and general appearance of the ash.

(b) AND (c) SOLUBLE AND INSOLUBLE ASH.

Add water to the ash in the platinum dish, heat nearly to boiling, filter through ash-free filter paper, wash with hot water until the filtrate and washings amount to about 60 cc. Return the filter paper and contents to the platinum dish, carefully ignite, and weigh. Compute percentages of water-insoluble ash and water-soluble ash.

(d) ALKALINITY OF SOLUBLE ASH.

Allow the filtrate from the above determinations to cool, then titrate with tenth normal hydrochloric acid, using methyl orange as an indicator.

(e) ALKALINITY OF INSOLUBLE ASH.

Add excess of tenth normal hydrochloric acid (usually 10 to 15 cc) to the ignited insoluble ash in the platinum dish, heat to the point of boiling over an asbestos plate, allow to cool, and titrate excess of hydrochloric acid with tenth normal sodium hydrate, using methyl orange as an indicator.

Express the alkalinity in each case as the number of cubic centimeters of tenth normal acid used on the ash of 1 gram of sample.

(3) MANGANESE, CALCIUM, SULPHATES, AND POTASSIUM.

Weigh 50 grams of the sample in a large platinum dish, heat over an asbestos plate to the point of carbonization, carbonize at low heat, dissolve the soluble salts in hot water, filter, and wash. Return the filter and residue to the dish, ignite until free from carbon, add the solution of soluble salts, evaporate the whole to dryness, and gently ignite. Remove the ash from the dish to a weighing bottle and keep in a desiccator. Weigh out about 0.25 gram of the dried ash, add dilute hydrochloric acid, heat gently for a few minutes, filter, wash, and make up to 100 cc.

MANGANESE (Mn_3O_4).

Take 50 cc of the solution, make slightly alkaline with ammonia, evaporate on a water bath to remove excess of ammonia, filter, wash with hot water until free from chlorids, concentrate the filtrate and washings to about 50 cc, then follow the directions given in Bulletin 46, page 73.

CALCIUM (CaO).

Concentrate the filtrate from the manganese determination to about 50 cc, heat to $70^\circ C.$, make alkaline with ammonia, add ammonium oxalate in slight excess, and allow to stand over night. Filter, wash thoroughly with hot water, thrust a glass rod through the apex of the

filter paper, and transfer the precipitate to a beaker by means of a stream of hot water from the wash bottle, remove the part remaining on the filter by allowing about 20 cc of warm dilute sulphuric acid to pass over, then again wash with hot water. To the solution in the beaker add 20 cc of concentrated sulphuric acid, then titrate with tenth normal potassium manganate solution.

SULPHUR (SO_3).

In the remaining 50 cc of the solution of ash determine sulphates, following the method given in Bulletin 46, page 75.

POTASH (K_2O).

In the filtrate from the sulphate determination proceed as in the Lindo-Gladding method.

Express all results on manganese, calcium, sulphates, and potassium, as per cent in ash of sample.

(4) MALIC ACID.

This determination affords interesting data, and is of great value in doubtful cases. The author's results¹ on the pure sirups range from 0.84 to 1.28 (excluding 1.76 obtained on sample No. 4 Penn.), and on the pure sugars from 0.98 to 1.67. When the results fall below these minimum values there is evidence of adulteration with cane or so-called brown sugar. It is safe to say that in the majority of cases the malic acid value furnishes absolute evidence as to whether a sample contains brown sugar. The malic acid values for the brown sugars, tabulated by the author,¹ vary from 0.08 to 0.18.

This determination is made by a modification of the calcium chlorid method of Leach and Lythgoe.² Six and seven-tenths grams of the sample are weighed into a 200 cc beaker, and water added to make a volume of 20 cc. The solution is made slightly alkaline with ammonia, 1 cc of a 10 per cent solution of calcium chlorid added, then 60 cc of 95 per cent alcohol. The beaker is covered with a watch-glass and heated for one-half hour on a water-bath, when the flame is turned off and the beaker allowed to stand over night. The material in the beaker is then filtered through good quality filter-paper, the precipitate washed with hot 75 per cent alcohol to freedom from soluble calcium salt, dried and ignited. From 15 to 20 cc of tenth-normal hydrochloric acid is added to the ignited residue, the lime thoroughly dissolved by careful boiling, and the excess of acid titrated with a tenth-normal sodium hydroxid, using methyl orange as an indicator. One-tenth of the number of cubic centimeters of acid neutralized expresses the result, which, for the present, will be called the "malic acid value."

¹ Ibid.

² Ibid., No. 4, p. 380.

It is not advisable to filter before adding the alcohol, nor has it been found necessary, as no precipitate appears at that point. Repeated trials have also shown that heating to boiling and filtering immediately after adding calcium chlorid and alcohol not only incurs a possible loss of material due to bumping, but gives results which are always lower and are seldom concordant. The method has given satisfactory results on a wide range of samples, yet it is not claimed at the present stage of the investigation that the results express absolutely the malic acid present; they are given only as "values" which are shown to be significant.

All of the methods should be subjected to careful criticism, and collaborating chemist are requested to point out defects and suggest improvements.

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Recommended for publication:

H. W. WILEY,
Chief of Bureau and Secretary A. O. A. C.

Approved:

JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *March 25, 1905.*



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