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SUGGESTED MODIFICATION OF THE WINTON LEAD NUMBER, ESPECIALLY AS APPLIED TO MIXTURES OF MAPLE AND CANE SUGAR SIRUPS.

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APPLICATION OF THE ORIGINAL METHOD TO KNOWN MIXTURES.

The lead number as originally devised by A. L. Winton^a was intended to distinguish pure maple sirup from mixtures containing cane sugar sirup. The practice of adopting a standard lead number for pure maple sirups and then calculating the percentage present in a given mixture or compound sirup from the lead number obtained thereon is questionable. The value of the lead number for this purpose can be readily determined by tests made on mixed sirups of known composition.

At the suggestion of Doctor Winton, a preliminary test was made by the writer in the Chicago laboratory. The lead number was determined on two sirups: *A*, an alleged pure maple sirup, and *B*, a mixture of 50 per cent by weight of *A* and 50 per cent by weight of a cane sugar sirup of the same specific gravity. The lead number on *A* was 0.90 and on *B* only 0.29, instead of the theoretical 0.45. The apparent percentage of the maple sirup *A* in this mixed sample was, therefore, approximately 32 per cent instead of 50 per cent, which was actually present. The following study of this point was made at the Chicago laboratory:

Sirups *C* and *D*, containing 65 per cent of solids, were made from two supposedly pure samples of maple sugar. Another sirup, *S*,

^a J. Amer. Chem. Soc., 1906, 28: 1204.

was made to contain 65 per cent of cane sugar. Mixtures were made of *C* one part, *S* one part; *C* one part, *S* three parts; *D* one part, *S* one part; *D* one part, *S* three parts, all by weight. The lead numbers were then determined on the sirups *C* and *D* and on the mixtures in the usual manner, with the following results:

Winton lead numbers on known mixtures (Hendrickson).

Sirup.	Lead number.		Maple sirup content.	
	Actual.	Calculated.	Apparent.	Actual.
			<i>Per cent.</i>	<i>Per cent.</i>
C.....	1.20			100
C-S.....	.52	0.60	43.3	50
C-S.....	.08	.30	6.7	25
D.....	1.22			100
D-S.....	.55	.61	45.1	50
D-S.....	.19	.31	15.6	25

ERROR INTRODUCED BY CARBON DIOXID IN DISTILLED WATER.

Winton^a determines the standard of the lead subacetate solution in 25 cc by the lead sulphate method in the same way as in the test itself. On diluting 25 cc of the lead subacetate solution to 100 cc, precipitation of the lead occurs which varies from an opalescence to a decided turbidity, depending upon the quality of the distilled water. The distilled water used in the following experiments was either freshly boiled and the containing vessel connected with a soda lime tube while cooling, or redistilled from caustic potash. The water prepared by either method gave an opalescence or slight turbidity in the blank test, which turbidity appeared within five minutes after making the dilution but did not materially increase on standing in a stoppered flask for three hours. This time was adopted as the minimum, since one hour failed to give uniform results. To ascertain the amount of lead precipitated in the blank or standard, determinations were made upon 10 cc aliquots before and after filtering, with the following results:

Weight of lead sulphate from 10 cc—	Gram.
Unfiltered.....	{ 0.1673
	{ .1676
Filtered.....	{ .1645
	{ .1645

This difference is not so important on pure maple sirups, but on mixtures, especially those containing small percentages of maple, the error arising in the determination of the lead number is very marked

^a J. Amer. Chem. Soc., 1906, 28: 1205.

and gives zero or negative results, as indicated by the following comparisons of lead numbers on two series of sirups calculated from both unfiltered and filtered standards.

Comparison of lead numbers on two series of known mixtures, using unfiltered and filtered standards.

Maple sirup content.	Lead number.			
	Unfiltered.	Filtered.	Unfiltered.	Filtered.
<i>Per cent.</i>				
100.....	1.073	0.997	1.521	1.444
50.....	.438	.362	.673	.597
25.....	.133	.057	.221	.145
10.....	.042	— .034	.062	— .013

On another lead subacetate solution the standard was obtained in three ways. First, on the unfiltered blank; second, on the filtered blank; and, third, on a blank to which 25 grams of a cane sugar sirup were added prior to the addition of the 25 cc of lead subacetate solution. The weights of lead sulphate obtained from 10 cc aliquots were respectively 0.1701 gram, 0.1660 gram, and 0.1685 gram. If the filtered blank is taken as the standard, one would apparently obtain more lead from the cane sugar sirup blank than was actually added, which discrepancy is corrected by the use of the unfiltered blank. To avoid the possibility of obtaining an incorrect aliquot on the turbid unfiltered blank, add 5 cc of 10 per cent acetic acid to the blank flask prior to the addition of the 25 cc of lead subacetate solution, which insures a clear blank for the determination of the standard.

Acetic acid should be added only to the blank, since this reagent dissolves the maple lead precipitate. Otherwise the procedure was the same as given by Winton with the exception that after addition of lead subacetate the mixture was allowed to stand three hours prior to filtering; 2 cc of 20 per cent sulphuric acid were used to precipitate the lead. The results were calculated by subtracting the weight of the lead sulphate obtained from 10 cc of the clear filtrate from that obtained from 10 cc of the acidified blank or standard. The remainder expressed in grams multiplied by 27.325^a equals the lead number or percentage of lead precipitated by the sirup.

FURTHER STUDY OF KNOWN MIXTURES, USING THE ACID BLANK.

The lead number was determined on four straight sirups, and on four series of mixtures made by combining with each sirup various percentages by weight of *S* (cane sugar sirup, 66 per cent sucrose

^aThis factor is obtained by dividing the lead factor (0.68312) by the number of grams of sirup in the 10 cc used (2.5 grams) and multiplying by 100.

content). The first three samples (*E*, Ohio; *F*, Vermont; and *G*, Canada) were authentic. The fourth sample (*H*) was unknown, but was used to illustrate the variation of the lead numbers obtained on mixtures made from a sirup having a low lead number. All of the results given in the following tables are on the basis of the acid blank:

*Winton lead numbers on known mixtures, using the acid blank.**

Sirup.	Lead number.		Maple sirup content.	
	Actual.	Calculated.	Apparent.	Actual.
			<i>Per cent.</i>	<i>Per cent.</i>
E.....	1.424			100
E-S.....	1.005	1.068	70.5	75
E-S.....	.601	.712	42.2	50
E-S.....	.221	.356	15.5	25
E-S.....	.044	.142	3.1	10
F.....	1.322			100
F-S.....	.959	.991	72.5	75
F-S.....	.604	.661	45.7	50
F-S.....	.235	.331	17.8	25
F-S.....	.057	.132	4.3	10
G.....	1.521			100
G-S.....	.673	.761	44.2	50
G-S.....	.221	.380	14.5	25
G-S.....	.062	.152	4.0	10
H.....	1.073			100
H-S.....	.438	.537	40.8	50
H-S.....	.133	.268	12.4	25
H-S.....	.042	.107	3.9	10

These results show conclusively that the lead number thus obtained is not proportional to the amount of maple sirup present in a mixture. Theoretically a pure maple sirup, which gives a copious precipitate when treated in the usual manner, should yield one-tenth the volume of the original precipitate if it is first diluted with 90 per cent of inert cane sugar sirup. But in several instances it was observed that these 10 per cent maple content sirups gave no precipitate or at most an opalescence, which would be reported as "no precipitate" or "slight precipitate," and the sirup would be declared ordinarily to contain little or no maple sirup.

INFLUENCE OF SUCROSE AND LEAD SUBACETATE ON THE MAPLE LEAD PRECIPITATE.

As a deduction from these experiments, it was inferred that the nonproportional result obtained on a mixed maple and cane sugar sirup was due to the solvent action of the sugar solution which partially inhibited the formation of the maple lead precipitate. Doolittle and Seeker^a judged that this discrepancy was due to a great

^a U. S. Dept. Agr., Bureau of Chemistry Bul. 122, p. 198.

excess of basic lead acetate. To determine the relative effect of the sucrose and the excess of basic lead acetate in the formation of the maximum maple lead precipitate, five series of determinations were made, using less lead in each successive series. In the first determination of each series 25 grams of a pure maple sirup were used. In the second determination of each series 5 grams of the same pure maple sirup plus 20 grams of a pure cane sugar sirup were used. In the third determination of each series 5 grams only of the maple sirup were used. In the second and third determinations there were present, therefore, equal amounts of maple sirup, and the difference in the amount of the precipitate formed was due to the solvent action of the 20 grams of cane sugar sirup present in the second but omitted in the third.

Method of Procedure and Results.

Introduce the quantity of sirup, maple or both maple and cane sugar sirup as indicated in the table, into a 100 cc volumetric flask; add distilled water, leaving room for subsequent addition of the lead subacetate solution, which then add in the amount indicated; make up to the mark, shake well and allow to stand three hours. Filter, and determine the amount of lead in 10 cc of the clear filtrate by the usual lead sulphate method. Standardize the lead solution in the same way but omit the sirup and add 5 cc of 10 per cent acetic acid (see p. 3).

The lead subacetate solution was introduced into the flasks from 25, 20, 15, 10, and 5 cc pipettes. In a given series the same amount was added to each subtest but, since the pipettes were not calibrated exactly or standardized among themselves, the quantity (25 cc) of lead solution introduced into *A* was approximately but not absolutely five times the quantity (5 cc) introduced into *E*, which explains the apparent slight discrepancy in the column giving the amounts of lead added.

Since the flasks were filled with water, leaving only sufficient room for the addition of the lead subacetate solution, of the strength specified by Winton, the results are comparable with those of Doolittle and Seeker, who added smaller amounts of lead by first diluting the strong solution and then adding 25 cc of the dilute solution.

Each determination was made in duplicate, the average result only being given. The maximum difference in the weight of the lead sulphate on duplicates was 0.5 mg and the minimum 0.0 mg; mean difference on 20 sets, 0.2 mg.

Determinations showing the relative effect of the sucrose and the excess of lead subacetate in the formation of the maximum maple lead precipitate.

Series.	Sub-test.	Maple sirup.	Cane sugar sirup.	Lead subacetate.	Ratio of lead to sirup. ^a	Lead-metal in 100 cc flask.				Lead number.	
						Added.	Precipitated.	Apparent excess.		Empirical. ^b	Actual. ^c
		grams.	grams.	cc.		grams.	grams.	grams.	per cent.		
A.....	1	25	0	25	1:1	1.1825	0.3682	0.8143	221.1	1.473	1.473
	2	5	20	25	1:1	1.1825	.0342	1.1483	3,357.6	.684	.137
	3	5	0	25	1:0.2	1.1825	.0697	1.1128	1,596.6	1.394	
B.....	1	25	0	20	1:1.25	.9461	.3757	.5704	151.8	1.503	1.503
	2	5	20	20	1:1.25	.9461	.0417	.9044	2,168.8	.834	.167
	3	5	0	20	1:0.25	.9461	.0779	.8682	1,114.5	1.558	
C.....	1	25	0	15	1:1.66	.7077	.3497	.3580	102.4	1.399	1.399
	2	5	20	15	1:1.66	.7077	.0526	.6551	1,245.4	1.052	.210
	3	5	0	15	1:0.33	.7077	.0799	.6278	785.7	1.598	
D.....	1	25	0	10	1:2.5	.4755	.2849	.1906	66.9	1.140	1.140
	2	5	20	10	1:2.5	.4755	.0594	.4161	700.5	1.188	.238
	3	5	0	10	1:0.5	.4755	.0861	.3894	452.3	1.722	
E.....	1	25	0	5	1:5	.2309	.1441	.0868	60.2	.576	.576
	2	5	20	5	1:5	.2309	.0601	.1708	284.2	1.202	.240
	3	5	0	5	1:1	.2309	.0833	.1476	177.2	1.666	

^a Volume (cc) of lead to weight (grams) of total sirup.

^b Per cent of lead precipitated by the maple sirup, i. e., the weight of lead in grams precipitated by 100 grams of the maple sirup under conditions given.

^c Per cent of lead precipitated by the total sirup, i. e., the weight of lead in grams precipitated by 100 grams of the total sirup under conditions given.

The relative effect of the sucrose and the excess of lead subacetate in the formation of the maple lead precipitate may readily be seen by referring to the following summaries from the main table:

Comparison of empirical lead numbers on subtests 2 and 3 showing differences due to the solvent action of the sugar.

Series.	Lead subacetate added.	Empirical lead number on—		Difference.
		Subtest 2 (5 grams of maple and 20 grams of cane sugar sirup).	Subtest 3 (5 grams of maple sirup only).	
	cc.			
A.....	25	0.684	1.394	0.710
B.....	20	.834	1.558	.724
C.....	15	1.052	1.598	.546
D.....	10	1.188	1.722	.534
E.....	5	1.202	1.666	.464

Comparison of empirical lead numbers on series A and E, showing differences due to the solvent action of an excess of lead subacetate.

Subtest.	Empirical lead number on—		Difference.
	Series A (25 cc lead added).	Series E (5 cc lead added).	
2.....	0.684	1.202	0.518
3.....	1.394	1.666	.272

Discussion of Results.

It is evident that while both the sucrose and the lead subacetate had a marked effect, that of the sugar was greater. By reducing the amount of lead subacetate solution from 25 cc to 5 cc it was not possible to attain on subtest 2 the empirical lead number 1.473 or 1.503 obtained on the straight maple sirup in tests *A*-1 and *B*-1, respectively, which numbers should have been very closely approached to permit the quantitative use of the Winton lead number.

In the writer's modification, given on page 8, the solvent action of the sugar appears to be satisfied in preventing the precipitation of the lead sulphate, which would naturally precipitate on the addition of the lead subacetate solution subsequent to the addition of the potassium sulphate solution. The maple lead compound is then free to precipitate and under the conditions specified appears to give proportional results.

In the determination of the actual lead number on 25 grams of the straight maple sirup the maximum number (1.503) was obtained in series *B*, in which there was present in the filtrate 151.8 per cent excess of lead. The corresponding lead number in series *C* was 1.399 with 102.4 per cent apparent excess of lead. In the latter case 0.7077 gram of lead was added and, using the weight (0.3757 gram) precipitated in series *B* as the basis for calculation, there was present 88.4 per cent excess of lead, yet a decidedly low result was obtained. It would therefore appear that to obtain the maximum precipitation on straight sirups at least 150 per cent excess of lead should remain in the filtrate.

When 5 grams only of maple sirup were used, i. e., subtest 3, a maximum precipitation was obtained in series *D*, in which an empirical lead number 1.722 was obtained with 452.3 per cent excess of lead. In *E*-3 a lead number 1.666 was obtained with 177.2 per cent excess of lead, which was a slight drop from the previous test and would further indicate that at least 150 per cent excess of lead should be present for maximum precipitation.

On the mixed sirup in test *D*-2 the ratio of lead to sirup was 1:2.5 and an actual lead number 0.238 was obtained with 700.5 per cent excess of lead. In *E*-2 the ratio was 1:5 and an actual lead number 0.240 was obtained with 284.2 per cent excess of lead. With a reduction of 416 per cent excess of lead the increase in the actual lead number is scarcely perceptible, and, from the results obtained on the straight sirup, it would not seem that a further reduction in the excess of lead would give a further increase in the actual lead number on mixed sirups.

With respect to the desired excess of lead it appears that on all sirups, both straight maple and mixed cane sugar and maple sirups,

at least 150 per cent excess of lead is required to obtain the maximum precipitation and, further, that 250 per cent excess of lead has practically a negligible effect in preventing the maximum precipitation.

In analyzing a series of unknown sirups it would be impracticable to ascertain by preliminary trial the desirable amount of lead to be added and then to introduce these varying amounts into each test; furthermore, proportional values are not obtained even by varying the amounts of lead. The modified method, however, as given in the following section appears to give satisfactory proportional results on sirups of varying composition.

PROPOSED MODIFICATION.

To overcome the solvent or disturbing action of the sugar, it occurred to the writer that the addition of a precipitant, such as potassium sulphate solution, would allow a more complete formation of the maple lead precipitate and give proportionate results. Several series of experiments were made to ascertain the amount of potassium sulphate which should be added to correct the solvent action of the sugar, and the following method was adopted:

Transfer 25 grams of the sirup to a 100 cc flask, using about 25 cc of distilled water,^a add 10 cc of potassium sulphate solution (7 grams per liter); then 25 cc of lead subacetate solution of the strength specified by Winton. Make up to the mark, shake thoroughly and allow to stand three hours. Filter, rejecting the first portion of the filtrate. Pipette off 10 cc of the clear filtrate into a 250 cc beaker, dilute to 50 cc, add 2 cc of 20 per cent sulphuric acid and 100 cc of 95 per cent alcohol. Let stand overnight; filter off the lead sulphate on an ignited, weighed Gooch crucible, wash with 95 per cent alcohol, dry, ignite at low redness for three minutes in a muffle or over a burner, taking care to avoid reducing cone of the flame, and weigh. Run a blank in exactly the same way substituting 25 grams of a pure cane sugar sirup (66 per cent sucrose content) in place of the sirup to be tested.^b Subtract the weight of the lead sulphate, obtained from 10 cc of the sirup test filtrate, from that obtained from 10 cc of the cane sugar sirup blank filtrate. The remainder, expressed in grams and multiplied by 27.325 gives the modified Winton lead number.

The precipitate formed in the blank was very slight, little more than an opalescence, while in the mixed sirups the volume of precipitate was proportional and a marked flocculent precipitate was observed in the 10 per cent maple content sirup. The flasks should be rotated gently when water is added to make up to mark, otherwise the sugar solution becomes too weak. When water is floated on the contents of the flask a slightly increased precipitation of lead sulphate is produced, which is not redissolved on subsequent agitation.

The lead numbers obtained in this way on straight maple sirups are somewhat higher than by the original method, 1.8 to 3 instead of 1.2

^a Freshly boiled distilled water should be used throughout.

^b Do not use acetic acid in this blank; acidified blank is suggested for use only with original Winton method.

to 2.5, but the results obtained on the mixtures are proportional and more dependence can be placed on a fractional part of a higher constant. The modified lead number was determined on ten authentic samples ^a of maple sirup and also on each sample after adding 50 per cent, by weight, of a cane sugar sirup (66 per cent sucrose content) with the following results:

Modified lead numbers on authentic samples and mixtures containing 50 per cent of cane sugar sirup.

Source.	Modified lead number.			Apparent content of maple sirup in 50 per cent mixtures.
	Actual on 100 per cent.	Calculated on 50 per cent.	Actual on 50 per cent.	
				<i>Per cent.</i>
New York.....	2.44	1.22	1.21	49.6
Vermont.....	2.47	1.235	1.20	48.6
Do.....	2.74	1.37	1.48	54.0
Massachusetts.....	2.08	1.04	1.01	48.6
Do.....	2.73	1.365	1.36	49.8
New York.....	2.30	1.15	1.15	50.0
Do.....	2.17	1.085	1.15	53.0
Ohio.....	2.47	1.235	1.26	51.0
Do.....	2.99	1.495	1.64	54.8
New Hampshire.....	2.52	1.26	1.29	51.2
Average.....	2.49	1.245	1.275	51.1

In this work the effect of the addition of cane sirup or brown sugar sirup, which is very pronounced, has not been considered, only the determination of the maple content of sirups made by the admixture of cane sugar sirup. The points which the writer wishes to emphasize are the use of an unfiltered or acidified blank when following the original Winton method and the advantage of the proposed modified method in that it affords proportionate results on mixtures.

^a Samples furnished by A. H. Bryan, Sugar Laboratory, Bureau of Chemistry.
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