A STUDY OF THE REACTIONS
BETWEEN
SOLUTIONS OF MAPLE SYRUP
& BASIC LEAD ACETATE
WITH PARTICULAR REFERENCE
TO THE CANADIAN LEAD NUMBER

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A STUDY OF THE REACTIONS BETWEEN SOLUTIONS OF MAPLE SYRUP AND BASIC LEAD ACETATE WITH PARTICULAR REFERENCE TO THE CANADIAN LEAD NUMBER.

A thesis
Presented as partial Requirement for the
Degree of Master of Science
at
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by
Donald Eugene Fowler
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Corrections.

Page 25, line 7. Insert after "water", "were used in place of 2 c.c. of the original (1.25 Sp.Gr.) solution."

Page 46, Table V. Omit the last column.

Page 51, fourth line from bottom. Change "undoubtedly" to "probably".

Page 80, line 14. Insert after "were treated with 10 c.c.", "of $\frac{N}{2}$ oxalic acid, the precipitate allowed to settle, and the mixture filtered. The filtrate was titrated with..."

Page 76, Table XXI. In heading, column 5, change "malic" to "malate radical".

Table of Contents.

A Study of the Reactions between Solutions of Maple Syrup and Basic Lead Acetate with Particular Reference to the Canadian Lead Number.

THE LEAD SUBACETATE PRECIPITATE.

When a solution of Basic lead acetate is added to a maple sugar or syrup solution, a copious precipitate is formed, which varies in colour from a deep brown to a pale buff or almost white. The basic lead salt precipitates malic and other organic acids, and their salts, as well as sulphates, chlorides, carbonates, colouring and other organic matter (U).

By a quantitative examination of the lead subacetate precipitate, several of the most important tests for adulteration in maple products have been devised.

HISTORICAL.

The first results on the Analysis of Maple Products by the lead subacetate method were published in 1904 by C.H. Jones of the Vermont Agricultural Station. Jones' method was devised as a quick method to sort out samples that had been seriously adulterated and was dependent on the volume of precipitate produced.

(G) He dissolved 5 grams of syrup in 10 c.c. of water; placed this in a Purdy sediment tube. 2 c.c. of standard (Sp.Gr. 1.26) lead subacetate solution were added, the solution mixed and whirled in a Babcock machine at a speed of 1400 R.P.M. for 4 minutes, and the volume of the ppt. read.

The following general results were recorded (G).

Pure maple goods - average quality 1.5 - 3 c.c.

Pure, high grade, carefully filtered maple products rarely less than 1.2 c.c.

Dark syrups, with much malic acid, up to and sometimes above 5 c.c.

Cane sugars - trace of precipitate.

Adulterated maple samples - 0.1 to 1 c.c. reading. Samples showing a reading of 1 c.c. were regarded with suspicion, if below that were considered as adulterated, but syrups with readings slightly above 1 c.c. were not always accepted as pure.

During the following year Jones made a large number of analyses on pure and adulterated maple products, using the lead subacetate method as descibed above, as well as other analytical methods.

(H) The following is a summary of his results on the pure products:

	Jones Lead Number.		
	Max.	Min.	Av.
1. Pure Maple Syrup.	2.60	0.90	1.51
2. Pure Maple Sugar.	3.80	2.60	3.03
3. Syrups in (1) Expressed on Dry Matter Basis.	4.00	1.38	2.32
4. Sugars in (2) Expressed on Water Free Basis.	4.22	2.89	3.37

While Jones was working on the maple lead subacetate precipitate at the Vermont Station, Julius Hortvet was independently devising a similar method. Hortvet had noticed that when lead subacetate was added to a maple syrup solution in order to clarify it for polariscopic examination, a heavy precipitate was formed. He also observed that in many cases of known or suspected adulteration of the syrup with cane sugar, the precipitate was slight, sometimes equivalent to a mere cloudiness. A method was devised whereby the volume of the precipitate under fixed conditions could be measured. Hortvet's Method (F) consisted in reducing the precipitate to a fixed mass at the bottom of a graduated tube by the use of a centrifuge machine and expressing the volume of the precipitate in cubic centimeters and tenths. The apparatus consisted of a special glass tube somewhat suggestive of an inverted Babcock cream test bottle, 15 cm. in total length and 3 cm. in diameter, while the neck was 2 cm. in diameter and graduated to 5 c.c. in tenths. The tube was provided with a special holder. A 5 c.c. sample of the syrup or 5 grams of sugar were placed in the tube, 10 c.c. of water were added, and the sample completely dissolved. 10 drops of alumina cream were added and 1.5 c.c. lead subacetate and the contents well shaken. The mixture was occasionally rotated to facilitate settling. It was then placed in a centrifuge and run for six minutes at a speed producing a centrifugal force of 519,363 dynes. The tube was removed and any particles of the precipitate adhering to the wide part of the tube were loosened and the tube was again whirled for six minutes at the same speed and the volume of the precipitate observed. A blank determination using water was also made and subtracted from the first reading. The results in the case of syrup were calculated to the 5 g. basis, by multiplying the results by the specific gravity of the sample.

The following summary of the Hortvet numbers on twenty-two samples of genuine syrups and eighteen genuine sugars determined by Hortvet himself illustrates the variations of the method. (U).

	Max.	Min.	Average.
Syrups.	1.82	0.94	1.26
Sugars.	4.41	1.18	2.25

The errors involved in making this determination were so great that it was almost impossible for different chemists to obtain concordant results on the same sample and it was sometimes quite difficult to get duplicates that would agree. The results obtained by seven collaborators are as follows: (U).

	Syrup I.	Syrup II.	Sugar I.	Sugar II.
Average.	0.95	1.79	2.38	1.83
Maximum.	2.15	2.50	3.70	2.90
Minimum.	0.40	1.23	1.41	0.89

Such a method could be of very little value except to give very approximate results, but it might be used along with other analytical values to point out serious adulteration.

The Winton Lead Number and the Ross Modification.

Although the Jones and Hortvet methods might serve the purpose for which they were intended, the results were not always reliable and were quite indefinite. It is impracticable to convert the volume of solid precipitates into percentages; this is made all the more indefinite since the precipitate is not a pure substance but rather a mixture of substances and the volume of the precipitate also depends on the speed of the centrifuge and the time, and other details of manipulation.

A.L. Winton and J. Lehn Kreider sought an analytical method which would be more exact and more reliable than the previous methods, by determining the amount of lead in the precipitate. This might be determined directly in the precipitate itself, or the amount of lead remaining unprecipitated from a standard lead subacetate solution by a known quantity of the maple solution might be determined in the filtrate and the lead in the precipitate found by difference. The new method follows the latter possibility.

The details of the Winton method (V) were published in the Journal of the American Chemical Society in 1906 and as accepted by the Association of Official Agricultural Chemists as a tentative method are as follows: (A)

Lead Number (Winton) - Tentative. (VIII) 61. Standard Basic lead acetate solution - Boil 430 grams of neutral lead acetate and 130 grams of litharge for thirty minutes, or boil 560 grams of Horne's dry basic lead acetate with 1 litre of water, cool, allow to settle and dilute the supernatant liquid to 1.25 sp. gr. To a measured amount of this solution add 4 volumes of water and filter if not perfectly clear. The solution should be standardized each time a set of determinations is made.

62. Determination of lead in the blank.- Transfer 25 c.c. of the standard basic lead acetate solution to a 100 c.c. flask, add a few drops of acetic acid and make up to the mark with water. Shake and determine lead sulphate in 10 c.c. of the solution as directed under 63. The use of acid is imperative in this case to keep the lead in solution when diluted with water.

63. Determination. Transfer 25 grams of the sample to a 100 c.c. flask by means of water. Add 25 c.c. of the standard basic lead acetate and shake, fill to the mark, shake and allow to stand for at least 3 hours before filtering. Pipette 10 c.c. of the clear filtrate into a 250 c.c. beaker, add 40 c.c. of water and 1 c.c. of concentrated sulphuric acid, shake and add 100 c.c. of 95% alcohol. Allow to stand overnight, filter on a tared Gooch, wash with 95% alcohol, dry in water oven and ignite in a muffle, or over a Bunsen burner applying heat gradually at first and avoiding the reducing flame. Cool and weigh. Subtract the weight of lead sulphate so found from the weight of lead sulphate found in the blank, 62. Multiply by the factor 27.33. This gives the lead number directly. The Winton lead number is the number of grams of lead precipitated by 100 grams of the sample.

As different lead subacetate solutions may vary somewhat in composition, on account of impurities in the materials used and irregularities in the process of preparation, it was thought that a difference in the amount of lead precipitated might result. Winton tested three lead subacetate solutions of different composition with pure and adulterated samples and obtained virtually the same results with all. He also found that by allowing the precipitate to stand one hour he got practically the same results as by allowing it to stand 18 hours and concluded that one hour was sufficient time for complete precipitation and any increase in the precipitate after one hour was due to some foreign substance as atmospheric carbon dioxide, and could be justly disregarded. A number of analyses were made on both pure and adulterated samples. (V) The Winton lead numbers ranged in pure samples from 1.61 to 2.03 and in adulterated samples from 0.02 to 0.93.

The following variations of the Winton Lead Number in pure maple syrups have later been recorded:

Date.	Observer.	Ref.	No. of Analyses.	Max.	Min.	Av.	Remarks.
	McGill.		47	2.38	1.05	1.75	
1910.	Bryan.	B.	481	4.41	1.76	2.70	U.S. and Canada.
1910.	Bryan.	B.	86	3.92	1.85	2.55	Canada only, included in above.
1917.	Bryan.	C.	363	4.95	1.85	2.76	U.S. and Canada. Sugars.
1917.	Bryan.	C.	80	4.14	1.86	3.04	Canadian Maple Sugars.
1913.	Snell & Scott.	P.	126	4.09	1.41	2.30	

S.H. Ross (N) investigated the possibilities of the Winton Lead Number as an analytical method to determine the percentage of maple sugar in adulterated and compound syrups. A number of mixtures of cane and maple sugar syrups as well as the pure syrups were examined by this method, and it was found that the lead numbers were not proportional to the percentage of maple, but that they dropped off rapidly as the percentage of cane sugar was increased. The following Winton lead numbers were obtained on two pure maple syrups C and D and their mixtures with a 66% sucrose solution S.

Syrup.		Lead Number.		Maple Syrup Content.	
		Actual.	Calculated.	Apparent.	Actual.
C	100:0	1.20			100
C.S.	50:50	.52	0.60	43.3	50
C.S.	25:75	.08	.30	6.7	25
D.	100	1.22			100
D.S.	50:50	.55	.61	45.1	50
D.S.	25:75	.19	.31	15.6	25

Ross found that an error was introduced into the Winton Lead Number by carbon dioxide in the distilled water used. On diluting 25 c.c. of the lead subacetate solution to 100 c.c., precipitation of the lead occurs which varies from an opalescence to a decided turbidity depending on the quality of the distilled water. This error is most effective in the blank determination and is great enough to give even a negative lead number when only a small percentage of pure maple is present. The precipitation should be reduced to the minimum by using carbon dioxide free water, and in the blank the precipitate should not be filtered off, and a few drops of acetic acid may be added to dissolve the cloudiness and insure the taking of an even aliquot. Acetic acid must not be added to the maple syrup solution as it dissolves the maple-lead precipitate.

Even when the acid blank was used and the carbon dioxide error eliminated, the lead numbers were found not to be proportional to the amount of pure maple in the syrup. It seemed probable that the sugar solution exerted some solvent action on the maple lead precipitate. It was also suggested by Doolittle and Seeker (E) that the discrepancy was due to a great excess of basic lead acetate. The following extract from Ross's work confirms both of these suggestions.

Series.	Lead Subacetate Added. c.c.	Empirical lead No. on		Difference due to Solvent Action of Sucrose.
		(Subtest 2) 5 g. Maple Syrup 20 g. Cane.	(Subtest 3) 5 g. Maple only.	
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

Subtest.	Empirical Lead No.		Difference due to Solvent action of excess lead subacetate.
	Series A. 25 c.c.lead subacetate.	E. 5 c.c. lead subacetate.	
2. 5 g. maple syrup - 20 g. cane syrup soln.	0.684	1.202	0.518
3. 5 g. maple syrup only.	1.394	1.666	0.272

It is evident that while both sucrose and lead subacetate in excess have a marked effect on the precipitate, the error due to the solvent action of sucrose is the greater. The lead subacetate error could be reduced to the minimum by adjusting the quantity of this reagent to be added to that producing maximum precipitation. An excess of at least 150% of lead over that precipitated was found necessary to produce maximum precipitation, and an excess of 250% has practically a negligible effect in preventing the maximum precipitation. The sucrose error Ross found might also be removed. The solvent action of the sucrose solution can be satisfied by preventing the precipitation of lead sulphate, as well as by the lead maple compound. If just enough lead sulphate is present to saturate the sucrose solution with the lead compound, the lead maple compound will be left free to completely precipitate. This may be accomplished by adding potassium sulphate to the syrup solution before the addition of lead subacetate.

No account of Ross's experimental work to substantiate this theory was available. There seems to be no reason for assuming that the sucrose would dissolve lead sulphate in preference to the lead maple compound, or that, even if the sucrose were saturated with lead sulphate, it might not take up a quantity of the lead-maple substance and reprecipitate lead sulphate.

If the solubilities of the two substances in a sucrose solution were about equivalent, however, the common ion effect would allow only a constant weight of lead to remain dissolved by the sucrose. It would, then, make no difference whether the solubility of the sucrose were satisfied with lead as sulphate, as the maple compound or as a mixture of the two, for in any case an equivalent amount of lead would be taken up, and the Winton lead number would not be diminished by the precipitate dissolving in sucrose, nor would it be increased above the theoretical by the addition of the right amount of potassium sulphate, as for any lead precipitated as sulphate an equivalent amount will be dissolved by the sucrose in the form of the lead-maple compound.

Ross determined the amount of potassium sulphate required to correct for the solvenent action of the sucrose. A modification of the Winton method was devised in which this amount of potassium sulphate viz: 10 c.c. of a 7% solution was added to the syrup solution, before the addition of the 25 c.c. of lead subacetate. The time that the precipitate was to stand in contact with the solution was increased to 3 hours. The blank was run in exactly the same way, substituting 25 g. of a 66% cane sugar solution for the maple syrup. The lead numbers obtained by this method were slightly higher than those by the original Winton method, but the results obtained on mixtures of maple and cane sugar syrups were proportional to the amount of maple in the solution.

Snell and Scott (P) found that the Ross method gave results on mixtures of cane and maple syrups much closer to the calculated than the original Winton method. In most cases the estimated results by the Winton method were lower than the actual maple content and by the Ross method slightly higher. They also state that it is preferable to use 25 g. of a cane sugar solution as a clarifier in the Winton blank instead of acetic acid. The results found in this way are slightly lower, but the conditions under which the maple lead precipitate is formed are more thoroughly duplicated.

The directions must be very closely followed in the Winton lead number determination to insure concordant results. The sugar solution must not be warm, nor can it be poured into the lead subacetate. The following results on a pure syrup illustrates this point. (S)

WINTON LEAD NUMBER	
Regular method	2.49
Syrup added to 25 c.c. lead subacetate solution in a flask	2.69
Diluted syrup heated to 60° C.	2.26

SULPHATE AND CHROMATE METHODS FOR LEAD.

Thus far the sulphate method for the determination of lead in the Winton and Ross lead numbers has always been used. The sulphate method is more costly, involving the use of a quantity of alcohol as well as requiring more time for the determination than other methods, particularly the chromate method.

C.A. Clements (D) compared the sulphate, chromate, molybdate and phosphate methods of determining lead with particular reference to the Winton and Ross lead numbers. The chromate and molybdate methods were found to give concordant values for the Winton lead number which were slightly higher than the values given by the sulphate method. In other words the sulphate method gave higher results for lead than either of the other two. This irregularity was investigated. The three methods were found to give concordant results on the lead subacetate containing a few drops of acetic acid, and even when sucrose was added, but when potassium acetate was added the lead by the sulphate method was increased while that by the chromate and molybdate methods remained unchanged. It seems that potassium acetate in some way contaminates the lead sulphate precipitate. Clements' recommends the substitution of the chromate for the sulphate method in the determination of the Ross and Winton lead numbers and has written directions for the chromate method in this application. (D) The phosphate and molybdate modifications offered difficulites and were not so satisfactory

THE CANADIAN LEAD NUMBER.

The Canadian Lead number was originated in the laboratory of the Inland Revenue Department, Ottawa, in 1906 as a rapid and convenient method of determining the value of the maple lead precipitate. The method is as follows:-

Canadian Lead number:

Weigh such a quantity of the syrup as contains 25 grams of dry matter; transfer to a 100 cc volumetric flask; cool to 20°C, and dilute to mark. Pipet 20 cc. into a large test tube; add 2 cc. of the standard basic lead acetate solution and mix; allow to stand for 2 hours; filter on a weighed Gooch crucible having an asbestos mat at least 3 m.m. thick; wash four or five times with boiling water, dry at 100°C., and weigh. Multiply the weight of the dry precipitate by 20.

The error involved in making this determination, as found by studying the variations in duplicates, was very great, and frequently as high as 0.2, (i.e. 10% on a syrup showing a lead number of 2.0.) The average differences between duplicates found on a number of syrups by two operators were 0.10 and 0.09. The results must not, therefore, be interpreted closer than 0.2, and for example, if 2.0 was found to be the minimum lead number in genuine maple products, a lead number of 1.8 must not be interpreted as proof of adulteration. (M).

McGill found that only 59 out of 2000 samples showed a Canadian lead number of less than 2.5 and at first recommended that this be set as the Canadian standard, but after considering the objections advanced by a number of dealers in maple products and considering the great error in making the determination, the minimum lead number was reduced to 2.2, and this came into effect by Order in Council, April. 1911. Continued objections were received from the dealers and at the same time analyses were being made on about 450 samples at the Inland Revenue Department laboratory, and as a result new standards for maple products were introduced including the official minimum of 1.7 for the Canadian lead number.

The following tables show the range in variation of the Canadian lead number on genuine maple syrups and sugars.

Observer.	Ref.	Date	Analyses	Max.	Min.	Av.	Remarks.
McGill		1911	456	6.56	1.37	2.83	25g Sugar used calculated to dry basis.
Scott	P	1913	126	7.50	1.74	3.48	
Lancaster	I	1924	198	10.29	2.20	5.09	Sugar as delivered at reprocessing factories.
"	J	1925	186	12.29	2.19	5.90	
Fowler		1927	51	5.42	2.19	3.19	

Observer	Date	Below 200.	2.00- 2.24	2.25- 2.49	2.50- 2.74	2.75- 2.99	3-4	4-5	5-6	6-7	7
Scott	1913	4	7	7	7	10	61	21	5	2	2
McFarlane	1914	0	0	1	1	4	1	1	0	0	1
Van Zoeren	1915	4	2	2	4	0	3	4	1	0	0
Fowler	1927	0	3	6	12	4	18	5	3	0	0

In mixtures of maple syrup and cane sugar, the Canadian lead number drops off much more rapidly than the actual percentage of maple, and practically vanishes when this percentage is small. Ten or twenty percent of pure syrup often gives merely a turbidity or cloudiness when lead subacetate is added. This behaviour gives the Canadian method an advantage so far as it is concerned with the detection of adulteration with cane sugar, but the method would be of no value in determining a small quantity of maple syrup in compound maple products. The great variability of the Canadian Lead No. in genuine maple syrups adds a disadvantage to the method in that syrups with high lead numbers could be seriously adulterated without falling below the minimum for genuine maple syrups.

It was found in the laboratory of the Inland Revenue Department where the Canadian method was originated that the results by this method were not so exact as those obtained by the Winton method. The same observation was made by Snell and Scott (P). The mean error for the Canadian method (M) was found to be 0.16, while that for the Winton method was only

0.04. This difference would be less, however, if the errors were expressed as percentages of total error since the total value for the Canadian Lead Number is greater than that for the Winton.

For convenience in weighing the samples in the Canadian Lead No. determination it was recommended that 25 grams of syrup be taken and the results calculated to the dry basis, as is done in the determination of the Winton lead number. The results, however, by this short cut method were found to be materially lower than those obtained when the amount of syrup containing 25 grams of dry matter was used. The range in variation of the Canadian Lead Number on genuine syrups is increaded by this modification which is an objection.

Canadian Lead Number on Wet and Dry Basis

	Wet Basis	Dry Basis.
Average	1.91	2.83
Maximum	4.68	6.56
Minimum	0.89	1.37
Diff.	3.79	5.19
Range % of Average	198	183
Range % of Minimum	426	379

Similar results are seen in the case of the Winton lead No. In this, however, the variation on pure syrups is less when 25 grams of syrup is used as the sample, and the results calculated to dry matter then when the amount of syrup containing 25 grams of dry matter is used.

Winton Lead Number on Wet and Dry Basis.

	418 Samples Average Bryans Samples.		McGill's Samples	
	Wet Basis.	Dry Basis.	Wet Basis.	Dry Basis.
Average.	1.78	2.70	1.17	1.75
Maximum	2.70	4.41	1.53	2.38
Minimum	1.15	1.76	0.70	1.05
Diff.	1.55	2.65	.83	1.33
Range % of Average	.87	98	71	76

The irregularities in the lead numbers when determined by the wet and dry methods must depend on the solubility of the precipitate which Ross illustrated both in sucrose and excess of lead subacetate.

Experiments were made by Snell and Scott (P) which investigated the effect of the temperature and the volume of the wash water on the weight of the lead maple precipitate as obtained by the Canadian Lead Number. It was found that the wash waters at 80° and 100°C. gave identical results. Higher results were obtained with 50 c.c. of wash water (applied in 5 portions) while there was no material difference between the results obtained with 100 c.c. and 150 c.c. of wash water.

The Composition of Lead Maple Precipitate.

As it was known that salts of malic acid were present in maple syrup, and that salts constituted the greater part of the solids-not-sugar, it was thought that the lead-maple precipitate was largely a lead malate.

The percentage of lead in the Canadian lead precipitate was determined by Scott (0). The precipitate was dissolved with concentrated nitric and hydrochloric acid, and the lead reprecipitated with sulphuric acid, and determined as sulphate. Scott's results show percentages of lead varying from 66.95 to 70.11, and the conclusion was drawn that the lead maple precipitate is not entirely normal lead malate, which contains 61.07% of lead.

A basic lead malate of the formula $C_4H_4O_5(PbOH)_2$ which would contain 71.38% of lead would appear to be the most likely substance as major constituent of the precipitate, as the reagent used was of a basic nature and as this compound corresponds more closely to the composition found by Scott than does the normal malate. In any case the precipitate cannot be considered as any one pure substance.

An unsuccessful attempt was made by Scott (0) to isolate the organic acids in the precipitate, by decomposing it with hydrogen sulphide, and recovering the acids from the filtrate.

A Volumetric Lead Number.

A volumetric lead number was devised by Snell, MacFarlane and Van oeren (2) in which the syrup solution is treated with a lead subacetate solution and the electrical resistance measured during the titration. The volumes of the reagent added are plotted as the abscissae against the resistance as ordinates. The determination is carried out as follows:-

Reagent: A Filtered solution of Horne's lead subacetate of specific gravity 1.033.

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

Measure the electrical resistance by using a dip electrode. Maintaining the temperature constant add 1c.c. of the lead subacetate solution from the burette, stir well and again measure the electrical resistance. Continue the addition of lead subacetate in this manner, 1 c.c. at a time, until 10 c.c. have been added. Plot the resistance found against the quantities of reagent used.

In the case of pure maple syrup, two straight lines are obtained which intersect between 4.8 and 6.6 c.c. Thirty percent adulteration with cane sugar gives a smooth curve in the great majority of cases, and when two lines are obtained the intersection is usually below 4.8.

This method has the advantage of being more rapid and having a narrower range of variation in genuine syrups than any of the other analytical methods. A range of variation of 31.9% of the mean was found as compared with 113% for the Canadian lead number. The method, however, is sometimes quite indefinite, as it is often difficult to differentiate between two intersecting straight lines and an unbroken curve in the graphs. The method has never been adopted officially.

The Lead Subacetate Solution.

The standard lead subacetate solution as used in the lead number determinations described in this paper, and as used to clarify sugar solutions for polariscopic examination, was formerly prepared by boiling litharge with a solution of normal lead acetate. This method of preparation was largely discarded when Horne's salt, from which the solution could be more conveniently prepared, was introduced.

The preparation of the lead subacetate solution by both of the above methods is described in connection with the Winton lead number determination on page 5.

COnsiderable variation in the composition of the solutions prepared by either of the above methods was known to exist, and slight differences in the results of the determination made by both the Winton and Canadian methods were noted, when different solutions of the reagent were used. This was especially noticed when the results found by using the ligharge solution and the solution from Horme's salt were compared. Winton, himself, however, was unable to detect any practical difference in results when different litharge - lead acetate solution were used.

In 1917 a comparison was made of the lead numbers obtained with different solutions of lead subacetate, by A.O. A.C. collaborators under Dr. J. F. Snell. (S)

Lead subacetate solutions were prepared both from Horne's salt, and from litharge and lead acetate, and were analyzed. The alkalinity of the solution and the total lead were determined and, from these, the ratio of neutral to basic lead was calculated.

It was found that horne's salt yielded solutions a little more variable in lead content, but much more uniform in basicity than the litharge and lead acetate.

The extreme variations among the five collaborators are as follows:-

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Range of Variation in Composition of Basic Lead Acetate Solution.

Solution	Grams per c.c. Total Lead	Ratio of Neutral to Basic Lead
Horne's salt	0.214-0.237	1.50-1.83
Litharge and lead acetate	0.215-0.233	1.33-2.75 Usually about 2.0.

Determinations were made by both the Canadian and Winton methods on a number of selected samples of pure and adulterated syrups, using the prepared lead subacetate solutions.

It was found that although the differences were small the solutions prepared from Horne's salt gave higher results than those prepared from litharge and lead acetate.

Exceptions were noted when very basic litharge lead acetate solutions were used.

The solutions prepared from Horne's salt were usually more alkaline than those from litharge and lead acetate.

These observations seem to indicate that the amount of precipitation is, to a small extent, dependent on the amount of basic lead in the solution, or, at least, on the ratio of neutral to basic lead.

Additional A.O.A.C. collaborative work was done under Lancaster (I) as associate referee. The samples and a lead subacetate solution were supplied from the Departmental of Health laboratories, Ottawa. The collaborators were instructed to make Canadian lead number determinations on the samples, using the reagent supplied, as well as a reagent prepared by themselves, a part of which was forwarded to Ottawa for examination.

The hydrogen ion concentration of the solution was determined colorimetrically in the Ottawa Laboratory using phenol red as indicator, while Canadian lead number determinations were made by M. E. Whalley on a sugar syrup, using each of the lead subacetate solutions, with the following results:-

Solution prepared in	PH	Canadian Lead Numbers			& Average
Winnipeg	7.7	1.36,	1.29,	1.30	1.32
Montreal	7.5	1.25,	1.22,	1.26	1.28
Ottawa	7.5	1.25,	1.20,	1.21	1.22
Halifax	7.35	1.23,	1.35,	1.14,	
		1.27,		1.14	1.19
Vancouver	7.3	1.06,	1.08,	1.03	1.05

The hydrogen ion concentration of the reagent is found to vary between the limits indicated by pH. 7.3 and pH. 7.7. The variation in the Canadian lead number was between 1.36 and 1.03 in this particular sample, and larger values were found when the more basic lead subacetate solution were used and vice versa.

The range of the Canadian lead numbers as found by the eight collaborators on two pure and one adulterated syrups is shown in the following summary:-

CANADIAN LEAD NUMBERS.

Reagent	Prepared in Ottawa	Locally Prepared.	Prepared in Ottawa	Locally Prepared	Prepared in Ottawa	Locally Prepared.
Max.	1.59	1.52	3.78	3.79	5.09	5.00
Min.	1.22	1.24	3.24	3.18	4.43	4.52
Av.	1.38		3.48		4.75	

It is noticed that the variation in values as found by using the various locally prepared solution, and which might be ascribed to differences in the composition of the reagent, was not greater than that found when the same reagent (that prepared in Ottawa) was used. This difference must be due to irregularities in mannipulation. Lancaster is under the impression that the importance of the slight differences in the reagent have often been somewhat exaggerated.

The Causes of Error in the Canadian Lead Number Determination

The great error experienced in making this determination has been already referred to.

Valin (s) has suggested that the variation in duplicates was due to actual differences in the amount of lead precipitated rather than to irregularities in manipulation. He substantiates his theory by experiment work with a modification of the Canadian lead method in which 5 c.c. of a solution made by diluting the 1.25 sp.gr. lead subacetate solution to five times the volume with water. The time of standing was extended to 3 or 4 hours. Valin determined the weight of the precipitate as well as the weight of lead not precipitated, as is done in the Winton method. Slight differences were found in the amount of lead in the filtrates from duplicate determinations and Valin infers that the differences between duplicates are not due to washing but to the actual amount of precipitate produced by the reagent.

Lancaster (I) on the other hand is of the opinion that the differences are due largely to irregularities in washing and suggests the method of washing be standardized.

The Analytical Values of Reprocessed Syrups.

A large proportion of the maple syrups on the market are prepared or reconstructed from maple sugar. As maple sugar is more easily transported than the syrup, a number of factories purchase the maple sugar from the individual producers and reprocess this into a commercial maple syrup. The reprocessing consists essentially in redissolving the sugar in water, removing the insoluble solids and removing excess of water by evaporation. This process is usually supplemented by various processes of clarification, sedimentation and filtration in order to improve the appearance of the product.

In a great many cases it was found that the ash value and Canadian lead number of the products turned out by the reprocessing factories was amazingly less than would be expected from the composition of the raw materials used. This lead to an investigation under Lancaster (J,K). The Canadian lead number and ash values were determined on the sample taken before and after each of the reconstructing processes, and it was found that none of the processes, in the presence of the inspectors, altered, either the ash value or the Canadian lead number appreciably.

Description of Materials Used in Experimental Work.

The Solution of Lead Sub-acetate used in the experimental work was prepared from Horne's salt, as manufactured by the Baker and Adamson Chemical Company.

560 grams of Horne's dry lead subacetate were boiled with 1000 c.c. of distilled water. A considerable amount of insoluble residue remained. The solution, when cool, was filtered off and diluted to a Specific Gravity of 1.25 at 20°C. with recently boiled distilled water. The solution was placed in a bottle connected with an automatic burette, and protected from atmospheric carbon dioxide by a soda-lime tube.

Composition of the Lead-Subacetate Solution. The total lead was determined as lead sulphate. The basic lead was determined volumetrically, by treating a portion of the solution with N/2 oxalic acid, filtering, and titrating the filtrate with N/10 soda. This method was suggested by Snell.(T).

One cubic centimetre of the solution was found to contain

0.2243 grams of Total Lead.
0.0779 grams of Basic Lead.
0.1465 grams of Neutral Lead (by difference)

and the ratio of neutral to basic lead was 1.88.

The hydrogen ion concentration of the solution was determined colorimetrically, using phenol red as indicator, and was found to be equivalent to a pH of 7.4.

After some time, a white sediment collected on the sides and bottom of the bottle containing the solution. This, however, is a common occurrence in lead subacetate solutions.

The solution was reexamined after the experimental work had been completed, and it was found that the ratio of neutral to basic lead had not changed.

Preparation of the Maple Syrup Samples.

The maple syrups, as received, were first examined with the Abbé refractometer and the percentages of total solids recorded.

Each syrup was then placed in a large beaker, a quantity of distilled water added, and the solution boiled over a flame until a reading of 104°C. was shown by a thermometer dipping in the syrup. The hot syrup was then filtered through a plug of cotton wool in the stem of a large funnel and collected in a bottle. A few drops of toluene# were added, and the solutions set aside to cool.

The toluene forms a layer on the surface of the syrup, and protects it from molds. No molds developed on the surface of any of the syrup protected with toluene, while those not protected, and kept under the same conditions, were attacked by surface molds in a few weeks. The toluene does not dissolve in the syrup, or affect its properties.

The maple sugars were first dissolved in hot water, and the samples prepared as in the case of syrups.

Description of the Samples.

Syrups Nos. 2, 3, 10, 11, 12, and 13 were prepared from old samples of maple sugar, which had been in the laboratory for several years in stone jars, and which had molded slightly.

Syrups Nos. 4, 5, 6, 7, 8, and 9 were prepared from samples of pure maple sugar supplied by Mr. Valin of the Food and Drugs Laboratories, Montreal.

The rest of the samples were all received as maple syrups, presumably sap syrups.

Samples 20 to 54 were collected by "Agronomes", or District Representatives of the Provincial Department of Agriculture throughout the provinces of Quebec and Ontario, who were instructed to choose samples of various qualities, the purity of which could not be questioned.

As complete a description of the samples as could be obtained is given,as follows:-

No.	Producer, Name,	Address.	Sample as prepared. % solids.	Canadian Lead No.	Remarks.
1	L.L.Jenne, Co.	Sutton, Que.	65.13	2.31	#
2	L.B.Parker	Lennoxville	66.7	2.74	1924
3	Ben Hammond	Lachute	64.2	2.40	1924
4			66.2	3.39	#8744
5	Laurent Gagnon	W.Broughton	66.0	4.49	#4467
6			65.8	5.42	#4499
7	Maple Tree Producers Assoc'n.	Montreal.	65.64	4.64	#4592. Sugar very hard, boiled to 250°
8			69.4	4.70	#4496
9			54.7	4.83	#4466
10	Roy Lowry	Cookshire	66.2	3.2	1924
11	Woodward	Lennoxville	66.00	2.3	1924
12	Arthur Pollock	Lachute	65.45	2.7	1924
13	Harry Robinson	Cookshire	66.07	3.3	1924

No. of Syrup	Name & Address of Producer.	Producers Description.
20	Geo Halliday, Sawyerville.	
21	F. C. Caswell, Sandhill.	
22	Eudore Dion, Sawyerville	
23	Philippe Paré Cookshire	
24	Damase Roy, Ste.Rose de Dorchester	Grimm evaporator, 30 March
25	Mathias P. Begin, Ste.Prosper de Dorchester	Grimm evaporator, 15 April
26	Mathias Rodrigue, Ste.Germaine de Dorchester	Grimm evaporator, 15 April
27	Francois Godbout, Ste.Justine de Dorchester.	Grimm evaporator, 15 April
28	C.Elder, Cargill, Bruce Co.Ont.	Pan, hard maples, mid season
29	Wes.Abell, Walkerton, Ont.	Evaporator, hard maple, mid season
30	Jas.Garland, Cargill, Bruce Co Ont.	Evaporator, hard maples, Late, 10 April
31	Jas.Garland, Cargill, Ont.	Evaporator, hard maples, Last of March.
32	Ed.Campbell, Eden Grove, Bruce Co. Ont.	Tin pan; hard maples; 2 April
33	C. Smith, Carlsruhe, Bruce.Co. Ont.	Pot; hard maple; early season
34	J. A. Pollock, Lachute.	Grimm ev.; Last runs.
35	W. D. Hume, Lachute.	Evaporator; Last runs.
36	W.T.Jackson, Lachute.	Grimm evaporator; Early runs
37	Erskine Rodger, Lachute	Corrugated evaporator; Early run
38	Jas.T.Gagnon, Ste.Marguerite, Dorchester Co.	Old iron evaporator; Early run
39	Mme.Cyrille Seguil, Ste.Claire, Dorchester Co.	Champion evaporator; Last runs
40	Joseph Roy, Ste.Hinédéne	Champion evaporator; Mid season
41	Louis Mercier, St.Hinédéne	Old iron evaporator; Mid season
42	Megantic County	
43	" "	
44	" "	

As Received. % Solids, by Abbe Refractometer.	Sample as prepared. % Solids, by Refractometer	Canadian Lead Number	Colour
65.25	67.65	2.74	6
69.15	66.18	3.08	6
60.56	69.19	3.76	13
69.4	66.18	3.25	9
64.8	66.20	2,834	13+
68.5	67.15	3.712	9
69.7	65.85	2.700	9
69.1	65.85	3.092	8
67.25	65.54	3.372	14
68.85	65.54	2.600	12
67.8	64.69	3.078	13
66.8	66.16	2.236	8
68.9	66.09	3.304	13
69.1	66.69	2.520	10
70.3	65.37	3.386	18
66.0	65.79	2.802	12
67.0	65.14	2.190	5
65.0	64.93	2.616	7
67.3	65.16	3.798	13
66.4	64.87	3.936	8
67.1	65.39	5.145	19
67.7	65.44	3.096	8
67.6	66.94	2.994	13
68.0	66.64	2.466	8
61.6	65.14	3.228	8

No. of Syrup	Name & Address of Producer.	Producers Description.
45	Megantic County.	
46	" "	
47	" "	
48	St. Ephrem	
49	" "	Champion evaporator
50	" "	
51	Orangeville District, Ont.	Evaporator, hard maple, First runs.
52	Orangeville Town, Ont.	Copper boiler in house; hard maple, early
53	Orangeville District, Ont.	Open pans; hard maple; Early run.
54	Shelburne District, Ont.	Iron kettle; hard maple; Early run.

Received % Solids by be Refractometer.	Sample as prepared. % Solids by Refractometer.	Canadian Lead Number.	Colour
64.2	65.89	2.736	9
67.65	66.19	2.426	7
61.9	64.94	3.004	7
53.2	65.22	4.312	12
68.5	66.72	2.724	9
69.6	67.07	2.550	8
65.7	65.32	2.670	9
68.0	66.08	2.910	8
70.0	66.48	2.420	9
66.2	66.25	2.236	13

Experimental.

As no record of any preliminary work on the Canadian Lead Number had been published by the originator of the method, and as very little work has since been done in the way of investigating this method, it was suggested that first a study be made of the conditions under which the precipitate is formed, and that the effects which the variations of these conditions had on the results, be recorded.

The general method of proceedure first adopted, was to make the determination, varying one of the conditions at a time, and to compare the results with those found when the conditions described in the method were all closely adhered to.

The Time Required for Maximum Precipitation.

An attempt was made to determine whether it was necessary to allow the precipitate to stand for two hours in order to produce complete precipitation.

Canadian Lead Number determinations were made on three syrups, varying the time the precipitate was allowed to stand in contact with the solution before filtering. Except for the time of standing the prescribed method was closely adhered to. The results are recorded in table I.

TABLE I.

Time	Syrup 2.			Syrup 11			Syrup 13		
Hours	A	B	Average.	A	B	Average.	A	B	Average.
½	2.54	2.64	2.59	2.41	2.37	2.39	3.19	2.99	3.09
1	2.79	2.78	2.79	2.35	2.41	2.38	3.20	3.34	3.27
1½	2.69	2.73	2.71	2.44	2.46	2.45	3.34	3.26	3.30
2	2.74	2.84	2.79	2.42	2.28	2.35	3.35	3.46	3.40
2½	2.78	2.90	2.84	2.38		2.38	3.31	3.10	3.20
3	2.81	2.91	2.86	2.37		2.37	3.03	3.14	3.08
5				2.24	2.28	2.26	3.16	3.29	3.22

A slight increase in the lead number can be noted in Syrup 2 as the time is increased. In the case of the other syrups, however, this cannot be observed. If there is an actual difference in the weight of the precipitate formed, the experimental error experienced in making the determination is so great that such a difference cannot be detected. Even in the case of syrup 2 all the values, except A at ½ hour, fall within the range of variation in duplicate determinations.

The time that the precipitate is allowed to stand in contact with the solution before filtering does not seem appreciably to affect the results as determined by this method.

Precipitation at Various Temperatures.

The lead-maple compound was precipitated at 20°, 40°, 60°, 80°, and 100° C. in duplicate on four syrups.

The aliquot sample was heated to the required temperature on a water bath. The lead subacetate was then added and the temperature maintained for two hours. In no case was the temperature allowed to vary more than one or two degrees from the stated temperature during this time. The determination was completed in the usual way.

The results are recorded in table II. All the results are averages of duplicates.

TABLE II. Canadian Lead Numbers.

Temp. °C.	Syrup 9	Syrup 11	Syrup 12	Syrup 13
100° C	2.826	1.590	2.174	2.386
80°	3.284	1.512	2.240	2.500
60°	3.620	1.539	2.139	2.800
40°	4.484	2.230	2.696	3.500
20°	4.630	2.640	2.840	3.676

The precipitates formed at 100° C. were at first a light brown in colour and at once became coagulated. After two hours the precipitates had changed in colour to a deep chocolate brown and were lumpy. At 80° C. the precipitates were formed and became curdy almost immediately. A clear syrupy layer later formed at the surface, in which a fine secondary precipitate developed, similar to that formed at room temperature. After two hours the precipitates were yellow, more like those formed at room temperature than at 100°.

In all cases, much lower results were obtained at 60°, 80°, and 100° C. than at 20°, while the precipitates formed at 40° were intermediate and closer to those formed at 20° C. In syrups 9 and 13 a steady increase in the lead number was found with decreasing temperature from 100° to 80° C. and from 80° to 60°, while in syrups 11 and 12 this could not be observed. In all cases, however, there was a great change in the values between 60° and 40° C. and a smaller change between 40° and 20°.

These results may indicate either that the precipitate itself is much more soluble in hot solution than in cold, or that an entirely different substance is precipitated at higher temperatures. The observations made on the physical nature of the precipitate at higher temperatures would seem to comfirm the latter supposition.

Varying the Amount of Lead Sub-Acetate.

Canadian Lead Number determinations were made on five syrups using amounts of the lead sub-acetate solution varying from 0.5 to 5. c.c. The results are shown in table III.

Table III

Canadian Lead Numbers. Averages of Duplicates.

Volume of Lead Sub-Acetate.	Syrup 1	Syrup 2	Syrup 3	Syrup 4.	Syrup 7.
0.5 c.c.	2.066	1.936		2.368	2.506
0.75 c.c.		2.442			
1.0 c.c.	2.633	2.710	2.508	3.074	4.136
1.5 c.c.	2.594	2.727	2.470	3.152	4.658
2.0 c.c.	2.577	2.744	2.408	2.962	5.042
2.5 c.c.	2.453	2.594	2.250	2.852	4.916
3.0 c.c.	2.150	2.343	2.132	2.728	4.928
4.0 c.c.	1.674	1.978	1.593	2.442	4.722
5.0 c.c.	1.121			1.918	4.294

The amount of precipitation was found to increase from the value with 0.5 c.c. of lead sub-acetate to a maximum when from 1 to 2 c.c. had been added, and then decrease rapidly as the amount of lead sub-acetate was increased.

In no case did the lead number nearly represent the total lead in the system, even when only 0.5 c.c. of the reagent had been added.

Assuming that the precipitate contains 70% of lead (P. 19) the largest precipitate found when 0.5 c.c. of lead sub-acetate were added, i.e. the precipitate from syrup 7, would represent.

$$\frac{2.506}{20} \times \frac{70}{100} = .08771 \text{ grams of lead.}$$

while the precipitate from syrup 2 would contain.06776 gms. of lead. The lead subacetate solution used contained 0.2243 grams of total lead per c.c. or 0.1122 grams of lead in the volume of the reagent added.

The difference between the amount of lead added and the amount of lead precipitated is 0.0245 grams in syrup 7 and 0.0444 grams in syrup 2. This would represent values of 0.700 and 1.270 respectively in the Canadian Lead Number, and cannot, in the opinion of the author, be accounted for by the solubility of the lead maple compound in the water of the system or in the wash water. It would seem that the sucrose present exerted some solvent influence on the maple-lead precipitate.

The decrease in the lead numbers, when the quantity of the reagent is increased beyond that amount required to produce maximum precipitation, appears to be due to some action exerted by the reagent itself in dissolving the precipitate.

Experiments to Confirm the Assumption that the Precipitate is Soluble in Excess of Both Sucrose and Basic Lead Acetate.

Excess of Sucrose. Four aliquot samples were prepared from each of three syrups as in the Canadian Lead method. Two c.c. of lead sub-acetate were added and the mixture set aside. After one hour (which time is sufficient to produce complete precipitation P34) an additional 3 c.c. portion of the reagent was added to two of the determinations from each of the three syrups, and all were allowed to stand for one hour longer before filtering. The determinations were completed and calculations made by the usual method. The results are recorded in table IV.

Table IV

Canadian Lead Numbers.	Averages of Duplicates.		
	Syrup 13:	Syrup 40:	Syrup 36:
Check determination,usual method.	3.324	5.280	2.216
As above,with 3 c.c. PbOAc soln. added.	1.860	4.440	1.216

Excess of Sucrose.

A. A sample was prepared from syrup 11 and four aliquots were precipitated as in the Canadian Lead Number. After the precipitate had stood for two hours in contact with the solution as much of the supernatant liquor, as could be poured off, was decanted onto the Gooch crucible.

In two of the determinations this was replaced with an equal volume of a 25% sucrose solution while in the other two, cold distilled water was used. The substances were stirred and allowed to settle. This was repeated three times. The precipitates were then filtered and washed with hot water as in the usual method.

Syrup 11	Lead Number.
A. Additional sucrose solution added.	1.932
B. Check determination, water replacing sucrose	2.138

B. To 20 c.c. aliquots of a solution from syrup 13 containing 5 g. of dry matter, 20 c.c. of a 60% sucrose solution and two c.c. of the standard lead subacetate solution were added. A check determination was run in which the sucrose solution was replaced by an equal volume of cold water. The remainder of the determination was carried out in the usual way.

Canadian Lead Number,	Average of Duplicates.
Check determination.	3.786
With sucrose solution added.	2.672

The solubility of the precipitate in excess both of sucrose and basic lead acetate, is well marked.

The amount of precipitate required to saturate the sucrose solution, and therefore dissolved by the sucrose, would be constant in all determinations since the quantity and dilution of the sucrose is always the same. The amount of the lead maple compound lost by dissolving in sucrose would, therefore, not affect the accuracy of the method in detecting adulteration in maple products, once the range of values for pure maple products had been established.

The amount of precipitate dissolved by excess of the reagent, on the other hand, would not be a constant value, even though a constant quantity of lead sub-acetate were added. The amount of precipitate formed varies from syrup to syrup, so the amount of the reagent left to dissolve the precipitate would be variable, and the amounts dissolved also would be variable.

In the case of syrups with low lead number, that is where small amounts of precipitable matter are present, a smaller portion of the lead subacetate would be used up, and a greater excess would remain to exert its solvent influence on the lead-maple precipitate than in syrups with a higher lead number. The Canadian lead number would be rendered even lower than that corresponding to the low amount of precipitable matter. Syrups with high lead numbers are in contact with a much smaller excess of the reagent, so the precipitates would not be reduced to the same extent by their dissolving in the reagent.

This action would tend to cause an even wider range in the Canadian Lead Number on genuine maple products than would correspond to the range of values of the substances in the maple syrup on which the lead number determination depends.

This effect might be eliminated to some extent, and the range of lead numbers somewhat narrowed, by using a smaller quantity of the lead sub-acetate solution.

It is noted in table III that with syrups showing a low lead number, the precipitation, when 1 c.c. of the reagent is used, is as great as or greater than that with 2 c.c.. In the case of syrups with high lead numbers there may not be sufficient lead present in the solution to produce maximum precipitation, but this would make no difference in the value of the method, as it is the syrups with small lead values which might be considered of doubtful purity, while those with higher lead values would pass in either case.

Regulation of the Washing.

In an attempt to detect the causes of the great error experienced in making the determination, and of the differences found between duplicates, attention was first directed to the methods of washing the precipitate.

By the usual method the precipitate is washed four or five times on the crucible with hot water. By the directions, neither the temperature nor the volume of the wash water is strictly defined.

When the solution carrying the precipitate is poured onto the Gooch and suction applied, the precipitate forms a compact mass at the bottom of the crucible, and the solution runs through the filter very slowly. As soon as the solution has passed through the filter, the precipitate on the asbestos mat cracks into cakes of varying sizes, and the wash water now applied, runs through quite rapidly.

This would seem to show that the mass of precipitate was penetrated with difficulty and that after cracking the wash water rapidly ran through the cracks between the cakes of precipitate rather than percolate through the precipitate itself.

As the time of contact of the wash water with the precipitate is thus greatly shortened and the surface of contact greatly reduced, the wash water would probably not be saturated with the substance of the precipitate, and the amount of the precipitate dissolved would depend on the rapidity with which the water ran through the filter as well on the size of the particles exposed to the water.

The following observations were made on the rate of filtration and the time and apparent conditions of the cracking.

The solution carrying the precipitate when poured onto the Gooch began to filter through quite rapidly. The precipitate, however, soon formed a mass on the asbestos filter, and filtering proceeded much more slowly.

The cracking occurred just as the last of the solution ran through the filter and the precipitate was exposed to the air. Cold wash water was now found to run through much more rapidly than the original solution. A 25% sucrose solution, which would have about the same viscocity as the solution itself was found to run through after cracking almost as rapidly as the distilled water, and much more rapidly than the original solution had run through.

As exposure to the air seemed to have something to do with the cracking in the precipitate, it was thought that this might be prevented by adding the wash water before the last of the solution had run through the filter.

When hot wash water was added in this way, the cracking was found to take place very much as it had done when the precipitate was exposed to the air.

It was found that if cold wash water was used, the water being added before the liquid, covering the precipitate layer in the crucible, had all run through, no checking took place. A number of portions of wash water were added, and no cracking occurred provided each portion was added just before the preceeding portion had all run through. Once the precipitate becomes exposed to the air, it cracks and the wash water runs through much more rapidly.

The comparative speed of filtration was estimated by counting the drops of liquid which fell from the stem of the Gooch funnel.

Filtration, in one case, was found to be very rapid just as the solution was added to the Gooch. This speed soon decreased to about 36 drops per minute. The first portion of wash water, added before the filter went dry, and before cracking, showed about 38 drops per minute, and the second, third, and fourth portions, about 40 drops per minute. The fourth portion was allowed to run completely through and cracking occurred immediately. Another portion of wash water ran through at a rate of about 130 drops per minute.

The cracking of the precipitate is very irregular, and particles of very different sizes are formed so, even in duplicate precipitates, a great difference in the total surface of these particles is possible. The rate of filtration also is noticed to vary considerably even in duplicates, depending on the nature of the asbestos mat in the crucibles used, or on the number or size of the perforations in the individual crucibles. The surface of contact as well as the time may vary considerably from one determination to another so if the solubility of the precipitate in hot water were great enough, a difference even in duplicate determinations might be expected.

The fact that the weight of the Canadian Lead Number precipitate formed at high temperatures was found to be much less than that at ordinary temperatures, in spite of the fact that all were washed with boiling water (table II), would seem to be in line with this theory, as well as to indicate a considerable solubility of the precipitate in hot water.

The solubility of the well-washed precipitate in hot water was determined by boiling the precipitate with 250 c.c. of distilled water, filtering, and determining the weight of the total solids in aliquot portions of the hot filtrate by evaporation. The details of this method are later described.

The precipitates from three syrups were examined in this way with the following results:-

Table V. Solubility of Lead Maple Precipitate in Hot Water.

Syrup.	Canadian Lead Number.	Total Solids in 100 c.c. aliguots.	% of ppt. dissolved in 250 c.c.	% of ppt. dissolved in 100 c.c.
36	2.2	0.0173	38.05	15.22
40	5.2	0.0373	34.12	13.65
41	3.1	0.0277	43.50	17.30

These three syrups cover a wide range as far as the Canadian Lead Numbers are concerned, and are considered as representative of maple syrups in general. In all cases the solubility of the precipitate is quite considerable.

If some method could be devised whereby these irregularities in washing could be largely eliminated, a better agreement in duplicate determinations would be expected.

Washing by Decantation.

A modification of the Canadian lead number method was devised in which the washing was done mostly by decantation, using a carefully measured volume of water.

By this modification, the time of contact of the precipitate with the wash water could be regulated, and the surface of contact maintained at the maximum.

It was found that the precipitate, even after standing two hours, had usually not settled sufficiently to make it possible to pour off any quantity of the supernatant liquid, and the use of centrifugal force had to be introduced in order to make the precipitate settle.

Precipitation was done in centrifuge tubes, After the precipitate had stood for two hours the tubes were whirled for a few seconds in a Babcock centrifuge. The supernatant liquid was then decanted onto the Gooch, and a portion of hot water was added from an automatic pipette delivering 17.4 c.c. of water. (The tubes connecting the pipette with the flask of boiling water were insulated with asbestos to avoid loss of heat). The precipitate was mixed with the hot water, allowed to stand a few seconds, again whirled in the centrifuge and the supernatant liquid decanted off. This was repeated until the precipitate had been washed four times by decantation. The use of the centrifuge was usually unnecessary after the second portion of wash water had been added, as the precipitate is then more granular and settles more rapidly. A fifth and sixth portion of wash water were used to wash the precipitate onto the filter, making in all 104.4 c.c. of wash water.

A number of aliquots from 3 syrup solutions were precipitated as in the Canadian lead number determination and in some, the washing was done by decantation, in others, by the ordinary method.

The following tables show a comparison of the values as found by the two methods as well as the variations in results on parallel determinations.

Table VI

Canadian Lead Number.	Washing by Decantation.		
	Syrup 31	Syrup 44	Syrup 48
1	2.336	3.648	4.736
2	2.360	3.744	4.752
3	2.316	3.632	4.730
4	2.376	3.688	4.730
5	2.356	3.712	4.696
6	2.372	3.668	4.684
Average.	2.353	3.682	4.721
Max.Variation from Average	.037	.062	.037
Max.Variation from Average in per cent of average	1.61 %	1.68 %	0.78 %
Variation,Max. to Min.	.060	.112	.068
Variation, max. to min. as per cent of average	2.61 %	3.04 %	1.44 %

Table VII

Canadian Lead Number,	Washed in Crucible.		
	Syrup 31	Syrup 44	Syrup 48
1	2.144	3.460	4.352
2	2.104	3.548	4.324
3	2.120	3.484	4.344
4	2.072	3.360	4.328
5	2.176	3.556	4.292
6	2.076	3.488	4.344
7	2.112	3.532	4.368
8	2.054	3.352	4.252
Average.	2.107	3.472	4.325
Max.Variation from Average.	.069	.120	.073
Max.Variation from average in per cent of average.	3.28	3.46	1.69
Variation-max. to min.	.122	.204	.116
Variation-max. to min. as per cent of average	5.79	5.88	2.68

The following table compares the variations as found by the two methods.

Table VIII. Canadian Lead Numbers.

Method of washing precipitate	Syrup 31		Syrup 44		Syrup 48	
	Average	% Variation,max. to min.	Average	% Variation.max. to min.	Average.	% Variation.max. to min.
Decantation	2.353	2.61 %	3.682	3.04 %	4.721	1.44 %
In Crucible	2.107	5.79 %	3.472	5.88 %	4.325	2.68 %

Lead number determinations were made in duplicate on nine syrups, the washing being done by decantation, with the following results which illustrate the variations of the method.

Table IX Canadian Lead Numbers, Washed by Decantation.

No.of Syrup.	A	B	Average.	Difference in Duplicate
31	2.336	2.360	2.348	0.024
36	2.296	2.280	2.288	0.016
38	4.132	4.100	4.116	0.032
40	5.680	5.716	5.698	0.036
44	3.632	3.682	3.657	0.050
47	3.544	3.528	3.536	0.016
48	4.608	4.600	4.604	0.008
49	2.936	2.992	2.964	0.056
50	2.688	2.692	2.690	0.004
Average				0.027

The results, when the washing is done by decantation do not show so great a range of variation in parallel determinations as those when the washing is done in the crucible. The largest difference between maximum and minimum values, found when washed by decantation was 0.112 on syrup 44 (Table VI). The difference thus found would undoubtefly have been much less had only duplicate determinations been made. The variations found by the original method were greater in all cases than by the new method.

The mean difference in duplicates as found by the new method on nine syrups (Table IX) is 0.027. This may be contrasted with the mean difference of 0.16 as was found by McGill (M) when the original method was used.

The author has found that the increase in accuracy of the method by this modification is not as great as the above comparison might indicate, a difference of 0.1 in duplicates is still not infrequent. The improvement, however, is considerable, and the method is rendered delicate enough to detect irregularities which escape the original method, as will be later illustrated.

Volume of Wash Water.

To determine whether it was necessary to carefully regulate the volume of water used in washing the Canadian Lead number precipitate, a number of aliquots from solutions of syrups 38 and 54 were precipitated, allowed to stand for two hours, and washed by decantation using 3, 6, 9, and 12 portions of hot water from the 17.4 c.c. automatic pipette, making an approximate total volume of 50, 100, 150 and 200 c.c. respectively. The results are recorded in the following table.

Table X Canadian Lead Numbers, Washed by Decantation.

Volume of Wash Water.	Syrup 38		Syrup 54	
	Individual Determinations.	Average.	Individual Determinations.	Average
50 c.c.	4.320	4.320	2.456 2.536	2.496
100 c.c.	4.024 4.028	4.026	2.276 2.328 2.232	2.279
150 c.c.	3.848 3.900	3.874	2.148 2.104 2.148	2.133
200 c.c.	3.724 3.772 3.812	3.769	1.820 1.864 1.844	1.843

A steady decrease in the lead number is noted when the amount of wash water is increased, and must be due to the precipitate dissolving in the wash water. This difference could not be detected by Scott (P) who used the original method in a similar series of experiments.

and who stated that it made no difference in the results, whether 100 or 150 c.c. of wash water were used.

It was thought that the time that the precipitate is allowed to stand in contact with the solution before filtering, might be shortened without affecting the results. In the ordinary method, a little time seems to be necessary for the very fine particles of the precipitate to collect together into somewhat larger particles which are more easily filtered; but by the modified method, the hot wash water collects the particles together and the precipitate could be filtered almost immediately.

Six aliquots from each of three syrup solutions were precipitated with lead subacetate by the usual method. Three of the aliquots were allowed to stand only ten minutes before washing by decantation and filtering. The other three were allowed to stand the full two hours, and the determination was completed in the usual way. The results are compared in Table XI.

Table XI Canadian Lead Numbers Washed by Decantation

	Syrup 35		Syrup 38		Syrup 54		
	10 minutes	2 hours	10 minutes	2 hours	10 minutes	2 hours	
A.	2.668	2.744	3.748	3.876	2.076	2.156	
B.	2.632	2.796	3.688	3.940	2.172	2.124	
C.	2.716	2.764	3.894	3.816	2.092	2.136	
Av.	2.673	2.768	3.777	3.877	2.113	2.139	

An increase in the weight of the precipitate is indicated. As the test tubes containing the precipitate were not corked in this experiment, there was a possibility that the increase during the two hours might be due to the absorption of carbon dioxide from the air, and the precipitation of lead as a carbonate. This point was next investigated.

The Effect of Atmospheric Carbon Dioxide on the Canadian Lead Number.

Six aliquots from each of the syrups used in the preceeding experiment were precipitated with the usual volume of lead subacetate. The test tubes containing three of the precipitates were tightly corked while the others were left uncorked and exposed to the air. All were allowed to stand for two hours before washing and filtering. The results in Table XII do not show any appreciable difference due to the action of carbon dioxide while the precipitate is standing in contact with the solution.

Table XII Canadian Lead Numbers, Washed by Decantation

	Syrup 35		Syrup 38		Syrup 54	
	Corked.	Not Corked.	Corked.	Not Corked.	Corked.	Not Corked.
A.	2.716	2.772	3.948	3.876	2.112	2.080
B.	2.764	2.772	3.988	3.888	2.104	2.020
C.	2.792	2.780	3.864	3.872	Det'n lost	2.116
Average	2.757	2.775	3.933	3.879	2.108	2.072

Time Required for Complete Precipitation.

In order to determine how much time was necessary for complete precipitation in the Canadian Lead Number, determinations were made on three syrups, and the time that the precipitate was allowed to stand in contact with the solution before filtering was varied. Determinations were made after standing 10 minutes, ½ hour, 1, 2, and 5 hours with the following results.

Table XIII : Canadian Lead Numbers : Washed by Decantation

Syrup 35

	10 minutes	½ hour	1 hour	2 hours	5 hours
A.	2.632	2.560	2.688	2.772	2.784
B.	2.588	2.656	2.688	2.740	2.772
C.	2.534	2.608	2.680	2.744	-
Av.	2.581	2.608	2.685	2.752	2.778

Syrup 36

	10 minutes	½ hour	1 hour	2 hours	5 hours
A.	1.988	2.056	2.088	2.088	2.116
B.	1.960	2.016	2.080	2.080	2.156
C.	1.932	2.000	2.060	2.072	2.168
Av.	1.960	2.024	2.076	2.080	2.147

Syrup 25

	10 minutes	½ hour	1 hour	2 hours	5 hours
A.	3.340	3.408	3.506	3.494	3.544
B.	3.300	3.488	3.532	3.498	3.552
C.	3.332	3.504	3.452		3.636
Av.	3.324	3.467	3.496	3.496	3.577

Table XIV is a summary of the results shown in Table XIII.

Table XIV Canadian Lead Numbers, Washed by Decantation
Averages of Triplicates.

No of Syrup	10 minutes	½ hour	1 hour	2 hours	5 hours
35	2.581	2.608	2.685	2.752	2.778
36	1.960	2.024	2.076	2.080	2.147
25	3.324	3.467	3.496	3.496	3.577

A steady increase in the lead number is noticed on all three syrups as the time of standing is increased.

This difference in results could not be observed when the original Canadian method was used in a similar series of experiments (Table I). Valin (T) also has stated that allowing the precipitate to overstand does not render the results high.

The positive results found by this series of experiments, as well as those found by varying the volume of the wash water (Table V), when compared with the results of similar experiments in which the original method was used, illustrate well the increase in accuracy of the Canadian Lead number when the washing is regulated.

Washing with Cold Water.

Solutions were made up from syrups 42, 43 and 48, and eight aliquots from each were precipitated, and after standing two hours the precipitates were poured onto Gooch crucibles, and washed with cold water. The crucibles were filled four times with wash water, and each portion was added just before the last of the liquid in the crucible filtered through. In this way, cracking of the precipitate was avoided, or at least reduced greatly.

Table XV. Canadian Lead Numbers : Washed with Cold Water.

	Syrup 42	Syrup 43	Syrup 48
1.	3.116	2.948	4.468
2.	3.260	2.928	4.512
3.	3.288	2.952	4.568
4.	3.296	2.948	4.516
5.	3.264	2.992	4.516
6.	3.284	2.888	4.468
7.	3.380	2.904	4.460
8.	3.396	2.902	4.456
Average	3.310	2.933	4.495
Max. Variation from Average.	0.086	0.059	0.073
Max. Variation from Av. in Per cent of average.	2.58 %	2.01 %	1.62 %
Variation-Maximum to minimum	.136	.104	.112
Variation-Maximum to minimum as per cent of average.	4.11 %	3.55 %	2.49 %

A similar set of determinations was made on the same three syrups, using the original Canadian Lead method.

Table XII Canadian Lead Numbers, Ordinary Method.

	:Syrup 42	:Syrup 43	:Syrup 48
1.	2.996	2.668	4.152
2.	3.256	2.772	4.312
3.	3.204	2.764	4.388
4.	3.112	2.656	2.252
5.	3.164	2.700	4.372
6.	3.348	2.718	4.324
7.	3.168	2.664	4.524
8.	3.188	2.740	4.308
Average	3.180	2.710	4.329
Max. Variation from Average.	.184	.062	.195
Max. Variation from Average in per cent of average.	5.79 %	2.30 %	4.50 %
Variation-Maximum to minimum.	.352	.116	.372
Variation-Maximum to minimum as per cent of average.	11.07 %	4.30 %	8.59 %

The results, when the washing is done as described with cold water, show a somewhat wider range of variation in parallel determinations, than was found when the washing was done by decantation (Table VI), but not nearly so great as the variations commonly found in duplicate determinations by the ordinary method, and as illustrated by the results in tables VII and XVI.

The method of washing by decantation has proved itself of great value in making it possible to study the Canadian Lead Number on certain points, which could never have been satisfactorily studied by the original method.

The Canadian Lead method, including the modification, whereby the washing is done by decantation, is somewhat more difficult than the original method. It involves a careful standardization of the volume of the wash water, as well as the use of centrifugal force to make the precipitate settle. Although the time required to make the determination is not increased materially, it is doubtful whether the increase in accuracy of the method is great enough to warrant the introduction of this modification to the method as now used as a test for the purity of Maple products.

The method of washing with cold water, in which the precipitate is not allowed to crack, increases the accuracy of the method considerably, and involves practically no more care than the original method. The volume of the wash water probably need not be so carefully standardized as there is evidence that the precipitate is much more insoluble in cold water than in hot. The introduction of such a modification into the general method seems to be worthy of careful consideration.

The Solubility of the Lead-Maple precipitate in Hot Water.

Two of the weighed precipitates from the syrups under investigation were combined and placed, with the asbestos mat, in a one litre flask. Exactly 500 c.c. of water was added, a part of which was used to rinse out the Gooch crucibles which contained the precipitates. The flask was connected with a reflux condenser, and heated on a steam bath for five hours. The contents of the flask were then boiled for a few seconds over a flame, and filtered quickly through a hot water filter into a flask standing in a beaker of hot water.

Four 100 c.c. aliquots of the hot filtrate were taken, two of which were placed in weighed platinum evaporating basins, and two in 250 c.c. beakers. The remainder of the filtrate was measured to show whether the total volume of the solution had been decreased materially. This portion was allowed to cool, and, in all cases, a white precipitate settled out, showing that the solution had been saturated.

The portions in the platinum basins were evaporated to dryness on a steam bath, dried at 100°C. in an electric oven, and the total solids weighed.

The portions in the beakers were acidified with acetic acid and the total lead determined as lead chromate.

Syrups 36, 40 and 41 were treated in this way.

The total filtrates measured 490, 492 and 482 c.c. respectively. The rest of the 500 c.c. might be easily accounted for by that amount adhering to the sides of the flask, or absorbed by the asbestos or the filter paper, so any portion lost by evaporation would be extremely small, and may be disregarded.

In all cases, when the aliquots were evaporated in the platinum dishes, two distinct solid substances separated out. One was a light brown or yellow substance and the other a creamy white powder.

The following results were obtained.

Table XVII First Water-Soluble Extract.

Number of Syrup.		36	41	40
Total solids found in 100 c.c. aliquots	A.	0.0164 g	0.0278	0.0372
	B.	0.0182	0.0276	0.0374
	Average	0.0173	0.0277	0.0373
Weight of precipitate in 250 c.c		0.04325	0.06925	0.0932
Original weight of precipitate#		0.1136	0.1592	0.2733
Per centage of total ppt. dissolved in 250 c.c.		38.05	43.50	34.12
Weight of ppt. in undissolved residue		0.0704	0.08995	0.1801
Weight of lead chromate found in 100 c.c. aliquots	A.	0.0146	0.0258	0.0336
	B.	0.0148	0.0254	0.0348
	Average	0.0147	0.0256	0.0342
Average equivalent in lead		0.00942	0.01641	0.02192
Weight of lead in original ppt.		0.08252	0.1115	0.1847
Weight of lead in residue		0.05896	0.07048	0.1299
Percentage of lead in Water-Soluble portion		54.47	59.24	58.78
Percentage of lead in original precipitate.##		72.64	70.04	67.58
Percentage of lead in residue		83.75	78.35	72.13

Average weight of the two precipitates used. Calculations are made on the basis of one ppt. in 250 c.c. water instead of two in 500 c.c. as was actually used in the experiment.

Table XIX

The residues from the above experiment were again treated in the same way with 500 c.c. of water, and the total solids determined. An attempt was made to determine the amount of lead in this second water-soluble extract, but concordant results could not be obtained. The results for the total solids are as follows:-

Table XVII A. Second Water-Soluble Extract.

Number of Syrup.		: 36	: 41	: 40
Total solids found in 100 c.c. aliquots.	A.	:0.0088 g.	0.0100	0.0182
	B.	:0.0094	0.0118	0.0176
	Average.	:0.0091	0.0109	0.0179
Weight of ppt. dissolved in 250 c.c.		:0.02275	0.02725	0.04475
Weight of ppt. in residue		:0.04765	0.06272	0.13535
Percent of total ppt. in 2nd 250 c.c. portion		: 20.03	17.12	16.37
Percentage of total ppt. dissolved in 500 c.c.		; 58.08	60.62	50.49

An examination of the residues left in the platinum dishes showed, in all cases, a creamy white substance, apparently the same as that found in the residues from the first water soluble extract. In numbers 40 and 41 the brownish substance could be detected but in much smaller proportions than in the first residues. In number 36 this second substance could not be seen at all.

From 34 to 44 per cent of the entire precipitate was found to be dissolved in 250 c.c. of hot water. The actual amount of the lead-maple substance dissolved, however, shows a much wider variation representing solubilities from 0.0173 to 0.0374 grams in 100 c.c. of water. The amount of the precipitate dissolved seems to increase with the weight of the precipitate itself. This shows either that the precipitates from the three sirups are of different composition, or that the precipitates are composed of two or more substances with different solubilities.

If several such substances were present in the precipitates as formed from all three sirups, and even in the same proportions, the washing of the precipitates with hot water would dissolve out a quantity of the more soluble substances. This would tend to remove the more soluble substances more completely from the smaller than from the larger precipitates, and would leave a larger proportion of these substances in the larger precipitates. In the precipitates as weighed, therefore, the proportion of the more suluble substances would vary with the weight of the precipitate itself.

When these precipitates are digested with hot water the larger ones, which have a greater proportion and a much greater amount of the more soluble substances, would naturally show a higher solubility.

The much smaller solubility of all the precipitates as found when they were treated with a second portion of hot water, shows that the greater part of the more soluble substances had been removed in the first treatment.

The brown substance was observed in the residues in the platinum dishes when the first water-soluble extract was evaporated. This was present in much smaller proportions in the residues from the second water-soluble extract from syrups 40 and 41 and not at all in the residue from syrup 36. This would seem to be one of the more soluble substances.

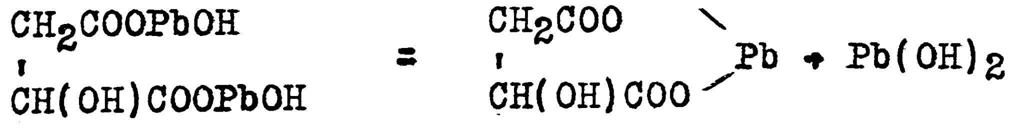
The creamy white portion of the residue was present in all cases and is undoubtedly a much less soluble constituent of the precipitate.

The percentage of lead in the substances dissolved out by the water is considerably less than that known to be present in the original precipitate. It follows, therefore, that the percentage of lead, in the portion not dissolved, is higher than that in the original precipitate. The precipitate has been separated into two portions of different composition and different solubility.

These results may indicate, either that the precipitate is composed of several substances, or that it is hydrolyzed by the hot water and a more soluble substance is formed.

Assuming that a basic lead malate is present in the precipitate the hydrolysis may take place thus.

(1)

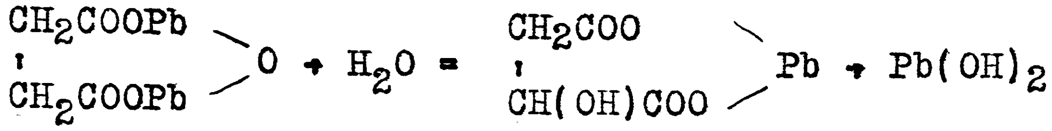


$$\begin{array}{l} CH_2COOPbOH \\ \vert \\ CH(OH)COOPbOH \end{array} = \begin{array}{l} CH_2COO \\ \vert \\ CH(OH)COO \end{array} \!\!\!\! > Pb + Pb(OH)_2$$

Insoluble — Slightly soluble — Insoluble

71.38% Pb — 61.06% Pb — 85.89% Pb

(2)



$$\left.\begin{matrix}CH_2COOPb\\ |\\ CH_2COOPb\end{matrix}\right> O + H_2O = \left.\begin{matrix}CH_2COO\\ |\\ CH(OH)COO\end{matrix}\right> Pb + Pb(OH)_2$$

Insoluble

73.66 % Pb

$$Pb(OH)_2 = PbO + H_2O$$

Insoluble Very insoluble

85.89% Pb 92.82% Pb

The percentage of lead in the precipitates, after the first treatment with hot water, is higher than that of either of the basic lead malates represented; and must indicate the presence, or the formation by hydrolysis, of even more-basic compounds of lead.

The percentage of lead in the soluble substance is slightly lower than that corresponding to the normal malate, and still lower than would be expected if small portions of the more basic lead compounds are dissolved. These low results must be accounted for by the presence of slightly soluble lead compounds in the precipitate, which contain lower percentages of lead than even the normal malate.

It is possible that some hydrolysis does take place when the precipitate is treated with hot water, but there is no doubt in any case that the precipitate is composed of more than one distinct compound.

Composition of the Maple-lead Precipitate.

For the determination of the composition of the precipitate in the Canadian Lead method, three syrups were chosen: Syrup 41 was an average syrup, showing a lead number of about 3.1; syrup 36 was very light in colour, and had a low lead number, 2.2; while syrup 40 was very dark, the lead number being 5.1. These three samples represented as wide a range in lead values as was represented in our collection, and the results, found by the examination of the precipitates from these three samples, are considered as representative of all types of pure maple syrups.

A number of precipitates from these three syrups were prepared and weighed, as in the Canadian Lead method, the washing being done by decantation. These were analyzed for total lead, carbon, and hydrogen, basic lead, and total acid equivalents.

Total Lead.

Determination: - The precipitate was removed with the asbestos from the Gooch crucible, placed in a 100 c.c. beaker, about 25 c.c. of dilute (2N.) nitric acid added and boiled gently until solution was complete.

The solution was filtered into a 250 c.c. volumetric flask. The Gooch was rinsed out with hot, dilute nitric acid and the rinsings poured onto the filter. The residue was washed, first with hot acidified water and then with hot distilled water in small portions until the volume of the filtrate was about 200 c.c., and the washings gave no reaction with potassium chromate. The filtrate was cooled to room temperature, and made up to volume with distilled water.

(To show that the precipitate had been completely dissolved, the residue was boiled with concentrated nitric acid, filtered, and the filtrate neutralized with sodium hydroxide, reacidified with acetic acid, and tested qualitatively for lead with potassium chromate. Negative results were obtained in all cases.)

A 100 c.c. aliquot of the solution was placed in a 250 c.c. beaker. To this a saturated sodium hydroxide solution was added, drop by drop, until a slight precipitate of lead hydroxide remained after stirring. The precipitate was then dissolved and the solution acidified with acetic acid.

The solution was heated to boiling and 2 c.c. of a 10% potassium chromate solution run in. This gave a distinct excess of potassium chromate. The solution was boiled for a few minutes to collect the orange precipitate, and after cooling was filtered onto a weighed Gooch crucible, washed with cold water, dried at 100° over night and weighed.

The percentage of lead was determined in duplicate on two precipitates from each of the three syrups.

The following results were obtained:-

Table XVIII Lead Content of the Precipitate.

Syrup 36

Weight of $PbCrO_4$ in ppt			Average equivalent in lead	Total lead in original ppt.	Weight of original ppt.	% of lead in original ppt.
A.	B.	Average				
1:0.0530g	0.0526	0.0528	0.03385	0.08462	0.1162 g	72.82
2:0.0490g	0.0510	0.0500	0.03205	0.08014	0.1106 g	72.46
Average.						72.64

Syrup 40

Weight of $PbCrO_4$ in ppt			Average equivalent in lead	Total lead in original ppt.	Weight of original ppt.	% of lead in original ppt.
A.	B.	Average				
1:0.1152g	0.1150	0.1151	0.07379	0.1845	0.2728	67.62
2:0.1146	0.1148	0.1147	0.07358	0.1839	0.2724	67.53
Average.						67.58

Syrup 41

Weight of $PbCrO_4$ in ppt			Average equivalent in lead	Total lead in original ppt.	Weight of original ppt.	% of lead in original ppt.
A.	B.	Average				
1:0.0700	0.0706	0.0703	0.04507	0.11267	0.1602	70.32
2:0.0704	0.0684	0.0694	0.04449	0.11122	0.1572	70.75
Average						70.53

The following is a summary of the foregoing tables.

Table XIX Comparison of Lead Numbers with Lead Content of Precipitates.

No. of Syrup.	Canadian Lead No.	Percentage of Pb in ppt.
36	2.2	72.64
41	3.1	70.53
40	5.6	67.58

These results are somewhat in agreement with those of Scott (See page 19) who found a percentage of lead varying from 66.95 to 70.11

CARBON AND HYDROGEN.

The carbon and hydrogen were determined in the precipitate by combustion analysis.

The well dried and weighed precipitate was entirely removed from the Gooch with the asbestos and placed in a combustion boat. This was at once placed in the combustion tube and the combustion carried out in the usual way. The oxygen, before entering the combustion tube, was purified by passing it through concentrated sulphuric acid, soda lime and calcium chloride in a gas tower. Copper oxide gauze and wire were both used in the combustion tube, and the absorption train consisted of, one calcium chloride U tube to collect the water and weighing about 40 grams; one soda lime and calcium chloride U tube to collect carbon dioxide, and weighing about 60 grams; a calcium chloride tube to protect the absorption tubes from moisture from the wrong direction, and a bottle containing baryta water, which acted as a bubble counter as well as a carbon dioxide indicator. This was protected from the air by a soda lime tube.

After combustion, small globules of metallic lead, and a yellow powdery substance, presumably litharge, remained in the boat along with the asbestos.

Table XX Combustion Analyses of Lead-Maple Precipitates.

Syrup	Wt. of ppt.	Weight H_2O	Weight H_2	% H_2	Weight of CO_2	Weight Carbon	% C
36	0.1054g	.0153	.00170	1.61	.0426	.0116	11.00
	0.1056	.0136	.00151	1.43	.0440	.0120	11.36
	0.1018	.0124	.00138	1.35	.0412	.01124	11.04
Av. 36				1.46			11.13
40	0.2578	.0246	.00273	1.06	.1156	.02728	12.23
	0.2616	.0278	.00309	1.18	.1194	.03257	12.45
	0.2616	.0284	.00315	1.20	--------CO_2 lost------		
Av. 40				1.15			12.34
41	0.1520	.0182	.00202	1.33	.0658	.01795	11.81
	0.1536	.0152	.00170	1.11	.0680	.01855	12.08
	0.1524	.0158	.00175	1.15	.0614	.01675	11.25
	0.1534	.0178	.00199	1.30	-----CO_2 partly lost-		
Av. 41				1.22			11.71

The values for hydrogen as shown are not absolute, a value having been subtracted to correct for the slight amount of water given off by the asbestos. The value of the correction is the average gain in weight in the calcium chloride tube found in blank determinations.

ORGANIC ACID EQUIVALENT IN THE MALPE LEAD PRECIBITATE.

Precipitates from syrups 36, 40 and 41 were prepared in the usual way, washed by decantation, dried in the Gooch crucibles, and their weights determined. These precipitates were then ground up as fine as possible in the crucible, and transferred completely, with the asbestos, to a flask. About 100 c.c. of water were added and hydrogen sulphide gas passed through the water to decompose the precipitate. A large precipitate of lead sulphide was formed. The solution was then boiled to expel the hydrogen sulphide, filtered, and the filtrate titrated with $\frac{N}{20}$ sodium hydroxide using phenolphthalein as indicator.

The results thus found were not concordant, and somewhat lower than would be expected. An examination of the residue showed particles of the original precipitate which had not been decomposed. Prolonged contact with the H_2S did not improve the results. The particles of the precipitate, which are very hard, and inaccessible, seem to be coated on the surface with a layer of black lead sulphide, which protects them from further action of the hydrogen sulphide. This layer, however, was found to be removed when the solution was boiled.

By passing the hydrogen sulphide through the solution, then boiling, and again passing the gas through until the solution was cool, and repeating this several times, the precipitate was entirely decomposed and concordant results were obtained.

Table XXI Organic Acid Equivalents of the Precipitate.

Syrup 40	c.c. $\frac{N}{20}$ NaOH.	Weight of ppt.	c.c. of NaOH for 1 g. ppt.	% organic acid as malic.	Equivalent of acid as Pb in,% of ppt.
A.	14.49	0.2582	56.12		
B.	14.59	0.2618	55.73		
Average			55.925	18.46	28.93 g.
Syrup 41					
A.	8.20	0.1594	51.44		
B.	8.02	0.1558	51.74		
Average.			51.59	17.02	26.70
Syrup 36					
A.	5.15	0.1020	50.49		
B.	5.23	0.1050	49.81		
Average.			50.15	16.55	25.95

The acid filtrate, after treatment with hydrogen sulphide was colourless. When this was neutralized a brown colour developed in the solution, which, however, did not seriously interfere with the end point. When the neutral solution was concentrated by evaporation the original maple odour could be detected, and the solution was brown in colour, very nearly like the maple syrup itself. When the solution was concentrated before being neutralized the maple odour did not develope.

This seems to be a possible way to separate the maple flavouring matter from the sugar in the maple syrup, which might be carried further towards the isolation and identification of this substance.

MALIC ACID DETERMINATION.

As a considerable quantity of malic acid must be present in order to make this determination with any degree of accuracy, a large number of precipitates would have to be combined, and it was not found possible to do this with the three syrups under examination. It was thought sufficient, to determine the ratio of malic acid to the total acids in the precipitates from a number of syrups, and to take this as usually general.

A large number (about 50) of the lead-maple precipitates, saved from previous experiments and representing a large number of syrups, were ground together in a mortar, placed in a 3 litre flask, water added, and Hydrogen sulphide passed through the solution, hot and cold, as in the total acids determination.

The solution (about 1500 c.c. vol.) was then boiled to expel the hydrogen sulphide , filtered, and evaporated to about 200 c.c., boiled with decolorizing carbon, and filtered.

Aliquots of the solution were titrated with $\frac{N}{20}$ NaOH to determine the total acids.

The malic acid was determined on this solution, according to the method prescribed by the Association of Official Agricultural Chemists for Malic Acid in fruit juices.

In this method the polarization is taken directly on the solution. The solution is then saturated with uranyl acetate, filtered and the polarization again taken. The algebraic difference in readings in degrees Ventzke, corrected for dilution and multiplied by the factor 0.036, corresponds to the number of grams of malic acid in 100 c.c. of solution.

The experiment was repeated in the same way using a different decolorizing carbon. The results from both determinations are recorded in Table XXII.

Table XXII Malic Acid by Polarization.

Decolorizing Carbon used.	"M" C.P. :	C.S.Co.P.775
Difference in polariscope readings before and after treatment with uranium acetate.	25.52°V	24.1°V
Percentage of Malic Acid in solution	0.919	0.8509
Percentage of total acids in solution calculated as Malic	0.958	0.8676
Percentage of total acid equivalents as Malic Acid.	95.93	98.08

These results indicate that Malic is practically the only acid present in the lead-maple precipitate. The last two or three percent not accounted for may be mineral aicds. Very small proportions of sulphates are known to be present in maple products, and would undoubtedly be found here as sulphuric acid . The solution was tested for sulphates with barium chloride and small quantities were found to be present.

BASIC LEAD IN THE LEAD-MAPLE PRECIPITATE.

The amount of basic lead in the lead maple precipitate was considered as the difference between the amount of basic lead in the lead subacetate solution used and that in the filtrate and washings from the precipitate, less an amount equivalent to any acidity, which might be present in the original solution, and which would neutralize its equivalent of basic lead.

Samples from syrups 36, 40 and 41 were precipitated in quadruplicate, as in the Canadian Lead Number determination and the weights of the precipitates were found. The lead subacetate solution was carefully measured in a 2 c.c. pipette, and the precipitate was washed with hot water by decantation. The filtrate and washings from each of these determinations, were treated with 10 c.c. of $\frac{N}{10}$ NaOH using phenolphthelein as indicator.

Blank determinations were run on 2 c.c. portions of lead subacetate. In these the maple syrup was replaced with 20 c.c. of a 25% sucrose solution. Distilled water was added until about the same volume was obtained, and the solution was treated with oxalic acid, filtered, and titrated as in the above determination.

Aliquots of the maple syrup solutions were titrated with $\frac{N}{10}$ NaOH and the acidity of the syrups determined.

The following readings were obtained, which demonstrate well the accuracy of this method.

Table XXIII   Readings in c.c. HaOH 0.1020N

	Syrup 36	Syrup 41	Syrup 40	Blank.
A.	38.80	40.90	45.30	34.60
B.	38.90	41.12	45.35	34.63
C.	38.85	41.00	45.20	34.65
D.	38.83	41.20	-	
Average.	38.85	41.05	45.28	34.63

10 c.c. of the oxalic acid alone was equivalent to 48.84 c.c. of the 0.102 N. NaOH, or had a normality of 0.497.

Table XXIV   Basic Lead in the Lead Maple Precipitates.

	Syrup 36	Syrup 41	Syrup 40
Acidity of 20 c.c. syrup - c.c. 0.1020 N NaOH	0.12 c.c.	0.36 c.c.	1.2 c.c.
Titration of filtrate (excess oxalic as 0.1020 N NaOH)	38.85	41.04	45.28
Titration-Basic lead acetate black (excess oxalic as NaOH)	34.63	34.63	34.63
Difference-corrected for acidity of syrup, i.e. basicity of ppt. as c.c. $\frac{N}{10}$ NaOH	4.18	6.18	9.64
Equivalent in grams PbO	0.04661	0.06891	0.1075
Equivalent in gms. Pb	0.04326	0.06396	0.09977
Weight of precipitate	0.1120	0.1660	0.2815
Equivalent in PbO as % of ppt.	41.61	41.51	38.18
Equivalent in Pb as % of ppt.	38.62	38.53	35.44

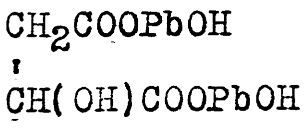
COMPOSITION OF PRECIPITATE. SUMMARY.

Table XXV is a summary of the results on the composition of the Canadian lead-number precipitate.

Table XXV Composition of the Maple Lead Precipitate.

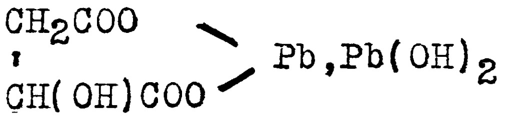
	Syrup 36	Syrup 41	Syrup 40
Canadian Lead Number.	2.2	3.1	5.6
Total lead	72.64 %	70.53 %	67.58 %
Total Carbon	11.13 %	11.71 %	12.23 %
Total hydrogen (approximately)	1.46 %	1.22 %	1.15 %
Oxygen (by difference)	14.77 %	16.54 %	19.04 %
Total Acids as Malate radical	16.55 %	17.02 %	18.46 %
Neutral lead (equivalent of acids)	25.95 %	26.70 %	28.93 %
Basic lead	38.62 %	38.53 %	35.44 %
Neutral lead not accounted for by acids.	8.07 %	5.30 %	3.21 %

The composition of two theoretical forms of basic lead malate is as follows:-



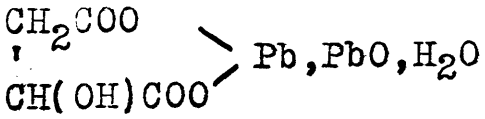
$$\begin{array}{l} CH_2COOPbOH \\ | \\ CH(OH)COOPbOH \end{array}$$

or



$$\left.\begin{array}{l} CH_2COO \\ | \\ CH(OH)COO \end{array}\right\rangle Pb,Pb(OH)_2$$

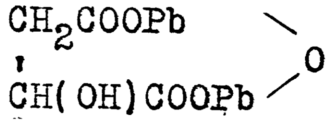
or



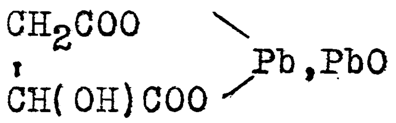
$$\left.\begin{array}{l} CH_2COO \\ | \\ CH(OH)COO \end{array}\right\rangle Pb,PbO,H_2O$$

Molr.Wt. 580; Pb, 71.38%; C, 8.82%; H, 1.03% and O, 18.87%

and



or



Molr. Wt. 562; Pb, 73.66%; C, 8.54%; H, 0.71% and O, 17.08%

It is seen that, in both of these compounds, the ratio of neutral to basic lead is 1, while in the precipitate itself, much more basic lead than neutral lead was found. The lead compound must be more basic than either of the compounds represented. This is in agreement with the results in determining the solubility of the precipitate. An insoluble residue was left, having a percentage of lead higher than that corresponding to either of the above basic lead malates.

All the basic lead malates may be looked on as being composed of normal lead malate, lead monoxide, and sometimes water. The amount of basic lead present in the precipitate is equivalent to the amount of lead oxide.

Approximately 97% of the neutral lead in the precipitate is in the form of lead malate. The remaining percentage is made up of sulphuric and perhaps other acids. They are all calculated as sulphuric.

Table XXVI Composition of the Lead-Maple Precipitate.

	Syrup 36	Syrup 41	Syrup 40
Lead Oxide (PbO)	41.61 %	41.51%	38.19 %
Lead Malate (Normal)	41.23	42.30	45.99
Other Lead Salts (as Sulphates)	1.14	1.17	1.27
Not accounted for	16.02	15.02	14.55

The proportions of the elements in the undetermined portions are given in Table XXVII in percentages of the total precipitate.

Table XXVII Composition of the Undetermined Portion of ppt.

	Syrup 36	Syrup 41	Syrup 40
Lead	8.07	5.30	3.21
Carbon	5.29	5.72	5.72
Hydrogen (approx.)	0.95	0.73	0.60
Oxygen (approx.)	2.05	3.58	5.44

Almost half of the total carbon is found to be in this undetermined portion. There is nothing to show what the compounds present in this portion are, or to show in what way the lead is held. Undoubtedly, we have here the flavouring principle of the syrup, and the colouring matter, and caramel, which is usually present in maple syrups and which is known to be held in the precipitate. The presence of caramel might account for the high percentage of carbon in this portion.

There seems to be some relation between the composition of the lead-maple precipitate and the total weight of the precipitate or the Canadian Lead Number.

By comparing the values, as found in the analysis of the precipitates from the three syrups, it is seen that the precipitates from syrup 36, which has a low Canadian lead number, are high in total lead, basic lead, and hydrogen, and low in carbon, oxygen, total acids and neutral lead. The precipitates from syrup 40 show high analytical values where low ones are found on those from syrup 36, and vice-versa, while those from syrup 41 show intermediate results on every value, which is in keeping with its intermediate Canadian lead number.

The Lead maple precipitates, from each of the three syrups examined, are of quite different composition. The results indicate a gradual change in the composition of the precipitate from syrup to syrup, corresponding to a change in the Canadian lead number itself. A large number of determinations would have to be made, however, before this could be definitely established.

SUMMARY OF EXPERIMENTAL WORK.

1. A study was made of the conditions under which the lead-maple compound is precipitated in the Canadian lead number determination. It was found that:

(a) The time, which the precipitate is allowed to stand in contact with the solution before filtering, made no difference in the results as far as could be detected by this method.

(b) The precipitates, formed in maple syrup solutions at a temperature of 60° C. or higher, were found to be much smaller than those formed at 20° C., while those formed at 40° C. were intermediate in value. This indicates that either a part or the whole of the precipitate is much more soluble in hot solution than in cold or that entirely different substances are precipitated at the higher temperatures.

(c) The volume of lead subacetate solution required to produce maximum precipitation in 20 c.c. of syrup solution containing 5 g. of dry matter was from 1 to 2 c.c., the actual amount varying with different samples. The results, when larger and smaller quantities of the reagent were used, indicated that the precipitate was somewhat soluble in excess of lead subacetate and in sucrose.

2. Experiments were carried out to comfirm the assumption that the lead-maple precipitate is soluble both in excess of lead subacetate, and in sucrose soltuions, with positive results.

3. The method prescribed for washing the precipitate was studied. Irregularities were found, which could at least partly account for the error involved in making this determination.

4. A modification of the Canadian lead number determination was devised in which the washing was done by decantation and the irregularities in washing largely avoided. The delicacy and accuracy of the method were greatly increased by this modification.

By using the modified method it was found that;

(a) The weight of the precipitate gradually decreased as the volume of the hot wash water was increased.

(b) The weight of the precipitate increased as the time, which it was allowed to stand in contact with the solution before filtering, was increased.

The original method was not accurate enough to detect either of these irregularities.

5. Another modification of the Canadian lead method was devised in which cold wash water was used, and the precipitate was not allowed to crack in the crucible, thereby insuring even washing. The results were more delicate and slightly higher than those by the original method.

6. The solubility of the precipitate in hot water and the percentage of lead in the water soluble portion were determined. Thirtyfive or forty percent of the entire precipitate was dissolved when treated with 250 c.c. of hot water. The percentage solubility was found to increase

greatly as the lead number increased from syrup to syrup. The proportion of lead in the water soluble portion was from 9 to 18 percent less than in the original precipitate, thereby indicating a separation of the precipitate into two or more different compounds by their solubilities. The portion not dissolved, when again treated with hot water in the same way was found to be much less soluble than the original precipitate.

7. An attempt was made to determine the composition of the lead-maple precipitate.

Precipitates from three syrups, representing a wide range of lead numbers were examined as to total lead, carbon and hydrogen, basic lead, total acids and malic acid. Values for total oxygen and neutral lead were calculated.

The values for carbon, oxygen, total acids, malic acid, and neutral lead were found to increase as the lead numbers increased, in the syrups examined. The opposite results were found on the values for total and basic lead and hydrogen.

The ratio of basic to neutral lead in the precipitate was found to be considerably greater than 1.0, thereby showing that the material is more basic than was generally supposed, and than would be expected considering the composition of the reagent used.

The percentage of malic acid corresponded very closely to the malic acid equivalent of the total acids, showing that malic is practically the only acid present.

The composition of about fifteen per cent of the precipitate remained undetermined. This portion was very rich in carbon, and undoubtedly included the flavouring principle of the maple syrups

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