STUDIES
ON
MAPLE SYRUP
AND
MAPLE SUGAR

STUDIES ON MAPLE SYRUP AND MAPLE SUGAR

by

L. V. Skazin

Presented to the Faculty of Graduate Studies
and Research, McGill University in partial
fulfilment of the requirements for the degree
of Master of Science

May 1930

Contents

Contents (Continued)

STUDIES ON MAPLE SYRUP AND MAPLE SUGAR

Introduction

The work presented in this thesis covers many branches of the Maple Products problem. The main purpose is to identify the flavoring principle in maple syrup. The work confirms the findings of Nelson (10) and makes clear to a certain extent the formation of maple flavor during the concentration of sap. The research work concerning decolorization of dark colored syrups, preparation of non-hardening and non-mottling sugar, as well as analytical studies of maple products for the detection of adulterants produced more definite results. Several methods for the improvement of maple products are described, and a simplified analytical method is proposed.

I. Attempts to devise color standards more permanent than caramel solutions

The color standards of Bryan (6) for maple syrup color determination are the only type utilized extensively to date. These color standards are made by dissolving caramel in glycerol. Unfortunately the exact color of the standard caramel preparation varies with the sugars used. Taking caramel made from highly purified sucrose as a standard, it is found that caramels from samples of commercial granulated sugar are more colored, as much as 300 per cent (2). It was thought that solutions of inorganic compounds might give more satisfactory color standards. Sodium cobaltinitrite and several iron salts were tested, but basic ferric sulphate (Monsel's Salt) gave the best results. Its color, as far as could be judged by simple comparison, was the nearest to that of maple syrup. The whole range of Bryan's scale can be prepared from Monsel's salt.

Method of preparation of color standards from Monsel's Salt.

To 300 grams of Monsel's salt (J. T. Baker Chemical Company) placed in an 800 cubic centimeter beaker, 350 cubic centimeters of hot distilled water are added. The salt is dissolved by constant stirring on a water-bath. The milky liquid is filtered. The filtrate is then concentrated over a low flame to 66° Be´ (108° Centigrade boiling point). This concentrated solution is No.20 in Bryan's scale. The other numbers are prepared by adding water and dilute sulphuric acid to the solution as indicated in Table I. The acid is prepared as follows: Five cubic centimeters of concentrated sulphuric acid, specific gravity 1.84, are made up to 250 cubic centimeters with distilled water.

These color standards were sent to the United States Department of Agriculture for spectrophotometric color analysis. It was found that in numbers 19 and 20 precipitation occurred. In numbers 2, 3 and 4 the stoppers of the vials became corroded, with possibly some accompanying change in the concentration and color of the sample. Figures I and II represent the spectrophotometric curves for the color grades numbers 4, 6, 8, 10, 12, 14 and 16 of Monsel's salt solution in one case, and a caramel-water solution in the other. It is to be noted that while the curves for the caramel solutions bear a systematic symmetrical relation to each other, the curves for the Monsel's salt solutions are distorted in the form of a hump which increases progressively with lower concentrations. Balch (2) found that the transmission curves of maple syrups agreed well with those of caramel solutions. Therefore it will be advisable to retain caramel solution for the maple color standards until some more suitable material, such as colored glass, is available.

Table I

Monsel's salt Color Standards for Maple Syrup

No.	Monsel solution 66° Bé	Water	Dilute Sulphuric acid. 10 cc., sp. gr. 1.84, to 500 cc.
20	25 cc.	-	-
19	175 cc. of No.20	25 cc.	-
18	175 cc. of No.19	25 cc.	-
17	175 cc. of No.18	25 cc.	-
16	175 cc. of No.17	20 cc.	5 cc.
15	175 cc. of No.16	20 cc.	5 cc.
14	175 cc. of No.15	10 cc.	15 cc.
13	175 cc. of No.14	-	25 cc.
12	175 cc. of No.13	-	25 cc.
11	175 cc. of No.12	-	25 cc.
10	175 cc. of No.11	-	25 cc.
9	175 cc. of No.10	-	25 cc.
8	175 cc. of No.9	-	25 cc.
7	175 cc. of No.8	-	25 cc.
6	75 cc. of No.7	-	25 cc.
5	75 cc. of No.6	-	25 cc.
4	75 cc. of No.5	-	25 cc.
3	50 cc. of No.4	-	50 cc.
2	25 cc. of No.3	-	25 cc.
1	-	25 cc.	-

Figure I

COLOR ANALYSIS

Caramel /in water/ of color equal to Monsel's salt color standards.

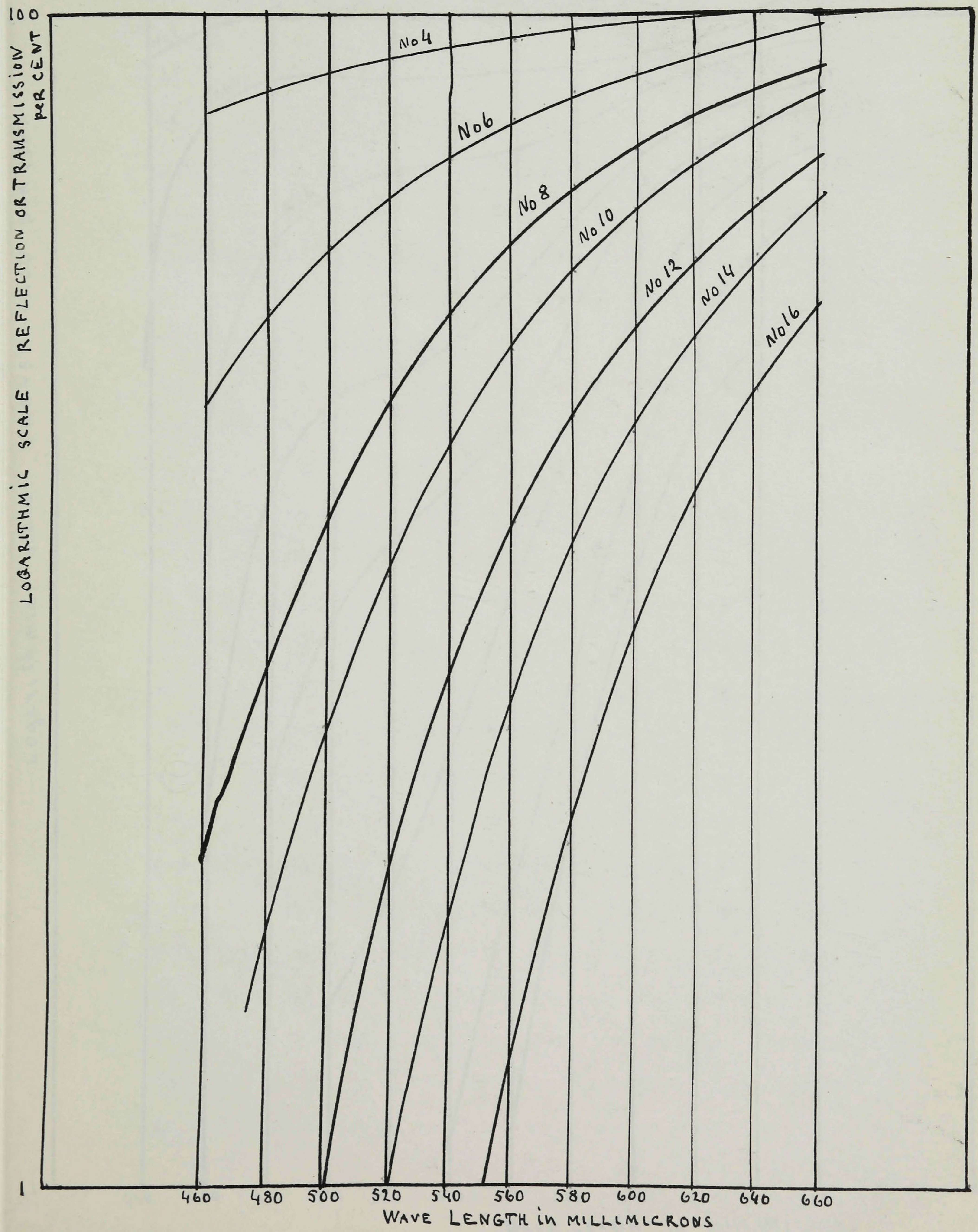
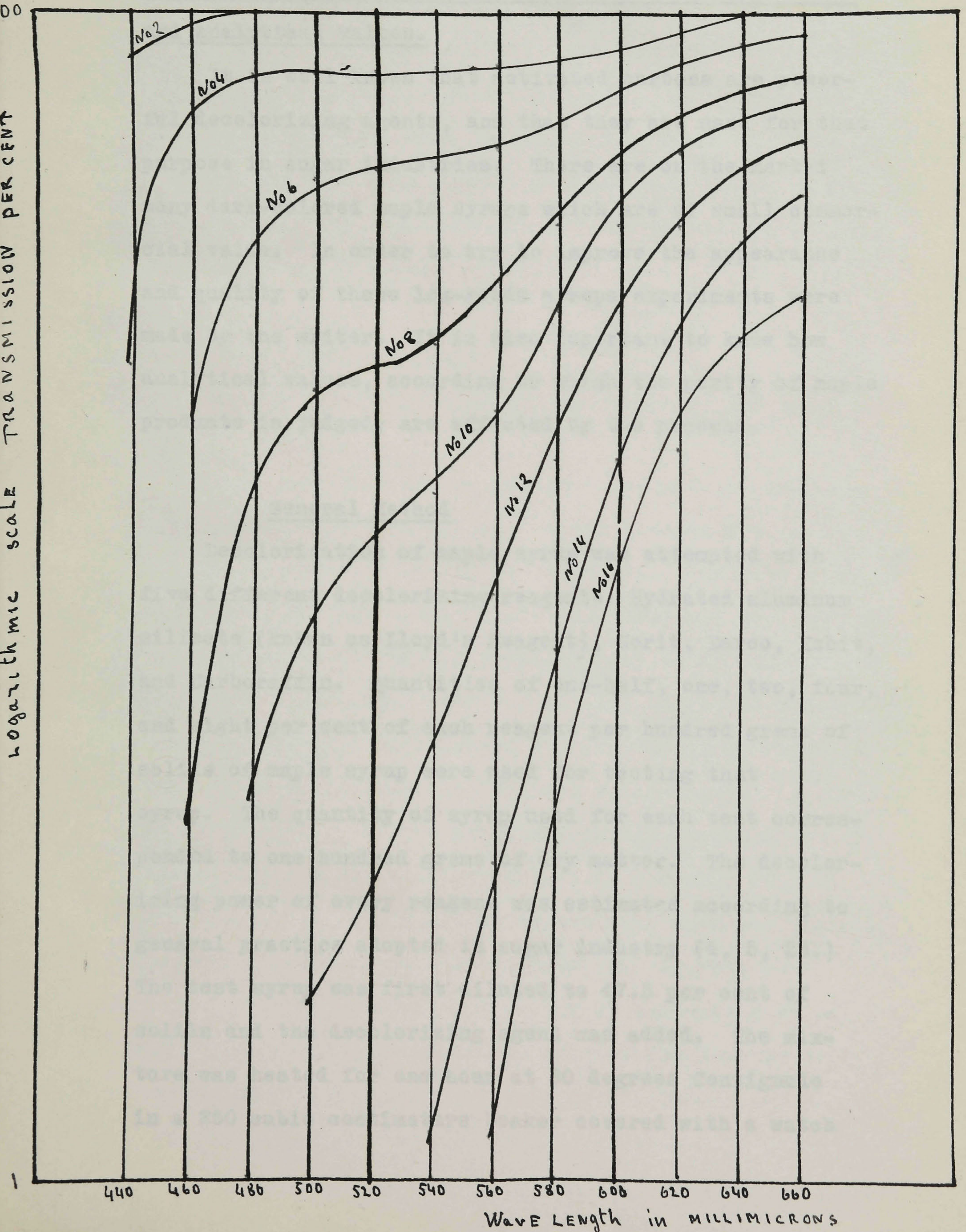


Figure II

Color analysis
Monsel's Salt Solutions



II Experiments on the decolorization of dark syrup by different reagents and their influence on color, flavor and analytical values.

It is well known that activated carbons are powerful decolorizing agents, and that they are used for that purpose in sugar industries. There are on the market many dark-colored maple syrups which are of small commercial value. In order to try to improve the appearance and quality of these low-grade syrups experiments were made by the writer. It is also important to know how analytical values, according to which the purity of maple products is judged, are affected by the process.

General Method

Decolorization of maple syrup was attempted with five different decolorizing reagents: Hydrated aluminum silicate (known as Lloyd's Reagent), Norit, Darco, Esbit, and Carboraffin. Quantities of one-half, one, two, four, and eight per cent of each reagent per hundred grams of solids of maple syrup were used for testing that syrup. The quantity of syrup used for each test corresponded to one hundred grams of dry matter. The decolorizing power of every reagent was estimated according to general practice adopted in sugar industry (4, 5, 23.) The test syrup was first diluted to 47.5 per cent of solids and the decolorizing agent was added. The mixture was heated for one hour at 80 degrees Centigrade in a 250 cubic centimeters beaker covered with a watch glass, and stirred for one minute at 15 minute intervals. The hot mixture was then filtered through a Durieux gray filter paper and the clear filtrate concentrated by boiling to about 65-66 per cent of solids. On the decolorized syrup the following determinations were made: color, flavor, Canadian lead number, conductivity value, total ash, soluble and insoluble ash,and the alkalinity of soluble and insoluble ash.

Specific methods

a. Method for preparation of syrups of the same solid content.

As comparative determinations were made on decolorized and concentrated syrups, it was necessary to have all the syrups with nearly the same solid content. It was found that the usual method (11) does not give a uniform solids content in prepared samples of maple syrup for analytical work. Recent work (19) has shown that the solid content of prepared samples varies by about ten per cent, whereas the standard solid content is sixty-five per cent. This is explained partly by the difficulty of measuring the temperature in a beaker with a small amount of syrup and so determining when the standard temperature of one hundred and four degrees Centigrade has been reached, and partly by the ease with which maple syrup can be overheated. The method used in connection with the present work is as follows.

The syrup, after being diluted to forty-seven and one half per cent of solids, and heated to eighty degrees Centigrade with carbon added, and then filtered, was then concentrated in an eight hundred cubic centimeter beaker over a Bunsen burner. From time to time samples were withdrawn with a one cubic centimeter pipette. The pipette containing syrup was rapidly cooled in running water. Before a drop was put on an Abbe refractometer, it was necessary to allow a few drops to escape, as the syrup in the end of the pipette becomes diluted during cooling by the tap water. When the amount of total solids determined in this way reaches sixty-four and one half per cent it is necessary to remove the boiling syrup from the flame and to put it immediately into a well-stoppered bottle to prevent further concentration by evaporation. Taking out the sample with a pipette, cooling and reading on the refractometer requires less than two minutes, during which time the syrup which shows sixty-four and one half per cent of solids will be concentrated to the required density. The results obtained by this method showed that all the syrups had concentrations between sixty-five and sixty-six per cent, a variation of only one per cent, as compared with ten percent by the usual method.

b. Method for color determination

The determination of color required special color standards which were prepared in a way showing exactly the percentage of original color present in every vial. For preparation of these standards an amount of syrup corresponding to two hundred and fifty grams of solids was diluted with distilled water to forty-seven and one half per cent. The diluted syrup was then brought to boiling and filtered. The filtrate was concentrated to sixty-five per cent solids and cooled in a well-stoppered bottle. The color of the syrup so obtained was assigned the number 20 and the syrup was regarded as having one hundred per cent of color. The syrup is then mixed with pure glycerol so as to get number 19, 18, and so on down to number 1, the degree of color in them corresponding to ninety-five, ninety, down to five per cent. The whole set of color standards for that particular syrup will have twenty one numbers (0 to 20). By comparing decolorized syrups concentrated also to sixty-five per cent with the standards it is easy to estimate the color of syrup within one per cent of a color unit after short practice. These standards are used only for the particular syrup for which they were prepared, and others have to be used for each syrup tested. Table II shows how the color standards were prepared from the sixty-five per cent syrup under investigation.

Table II - Table of Color Standards for Decolorizing Experiments

Vial number	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Syrup, grams	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
Glycerol, grams	40	38	36	34	32	30	28	26	24	22	20	18	16	14	12	10	8	6	4	2	0
Percentage of color	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100

c. Method for flavor determination

There are no chemical methods for flavor testing so the only means of determining was by taste. To eliminate the subjective factor of an individual every sample was tasted by about seven different persons and the average value was taken as representing the real flavor value. To the natural syrup a flavor value of 5 was assigned and to the pure sucrose solution value 0. The decolorized syrups were judged in comparison with these two limiting values. The average value for every syrup was then multiplied by 20 and the result was taken as representing the percentage of flavor originally present in the syrup.

d. Canadian lead number, conductivity value, total ash, soluble and insoluble ash, alkalinity of soluble and insoluble ash determinations.

These were estimated according to the methods of analysis of the Association of Official Agricultural Chemists (11).

The results obtained are summarized in Tables III, IV, V, VI, VII, and VIII.

Figure III represents the decolorizing isotherms of reagents tested.

Table III - Test for Decolorizing Agent "Lloyd's Reagent"

No.	Per cent of carbon used	Solids in the final syrup	Color		Flavor		Canadian lead value	Conductivity value	Ash					Time of filtration min.
			left %	removed %	left %	removed %			total %	soluble		insoluble		
										%	alkal	%	alkal	
1	0.0	65.30	100	0.0	100	0.0	2.87	141.7	.88	.59	.69	.29	1.11	10
2	0.5	65.22	100	0.0	88.6	11.4	2.78	140.3	.86	.56	.67	.30	1.11	15
3	1.0	65.22	100	0.0	87.2	12.8	2.75	138.8	.87	.59	.63	.28	1.14	35
4	2.0	65.53	100	0.0	75.0	25.0	2.74	140.3	.84	.60	.56	.24	1.14	36
5	4.0	65.76	100	0.0	70.0	30.0	2.78	136.5	.85	.53	.53	.32	1.25	30
6	8.0	65.20	100	0.0	68.6	31.4	2.76	130.8	.81	.32	.42	.49	1.32	37

Table IV - Test for Decolorizing Agent "Special Grade Norit"

No.	Per cent of carbon used	Solids in the final syrup	Color		Flavor		Canadian lead value	Conductivity value	Ash					Time of filtration
			left	removed	left	removed			Total	Soluble		Insoluble		
			%	%	%	%			%	%	alkal	%	alkal	min.
1	0.0	65.25	100	0.0	100	0.0	2.88	142.5	.87	.56	.66	.31	1.11	13
2	0.5	66.0	61	39	66.5	33.5	2.84	143.2	.87	.57	.66	.31	1.13	45
3	1.0	65.51	52	48	47.0	53.0	2.89	144.7	.86	.52	.66	.35	1.12	10
4	2.0	65.49	45	55	54.7	45.3	2.95	149.0	.87	.56	.60	.31	1.16	9
5	4.0	65.52	39	61	41.1	58.9	2.99	150.3	.88	.58	.66	.31	1.17	9
6	8.0	65.55	36	64	33.7	66.3	3.10	152.9	.88	.51	.66	.37	1.23	8

Table V - Test for Decolorizing Agent "Darco"

No.	Per cent of Carbon used	Solids in the final syrup	Color		Flavor		Canadian lead value	Conductivity value	Ash					Time of filtration
			left	removed	left	removed			Total	Soluble		Insoluble		
			%	%	%	%			%	%	alkal	%	alkal	min.
1	0.0	65.11	100	0.0	100.0	0.0	3.19	141.0	.93	.57	.68	.36	1.12	
2	0.5	65.62	53	47	71.4	28.6	3.03	139.2	.83	.57	.68	.26	1.03	
3	1.0	65.65	28	72	55.7	44.3	3.07	141.0	.86	.58	.68	.29	1.01	
4	2.0	65.13	18	82	40.0	60.0	2.93	137.8	.86	.56	.66	.30	0.99	
5	4.0	65.11	11	89	27.1	72.9	2.99	139.3	.87	.60	.65	.27	1.11	
6	8.0	65.13	6	94	15.7	84.3	3.09	144.2	.87	.58	.55	.29	1.14	

Table VI - Test for Decolorizing Agent "Esbit"

No.	Per cent of carbon used	Solids in the final syrup	Color		Flavor		Canadian lead value	Conductivity value	Ash					Time of filtration min.
			left %	removed %	left %	removed %			Total %	Soluble		Insoluble		
										%	alkal	%	alkal	
1	0.0	65.52	100	0.0	100	0.0	2.97	142.5	.89	.54	.66	.35	1.05	9
2	0.5	65.55	47	53	77.5	22.5	2.78	140.3	.88	.52	.67	.36	1.10	21
3	1.0	65.76	26	74	65.0	35.0	2.73	141.7	.82	.50	.66	.33	1.08	17
4	2.0	65.25	13	87	49.4	50.6	2.73	142.5	.84	.50	.64	.34	1.07	23
5	4.0	65.50	7	93	38.8	61.2	2.71	143.2	.84	.52	.61	.32	1.06	11
6	8.0	65.00	3	97	28.6	71.4	2.71	144.7	.86	.52	.57	.34	1.03	16

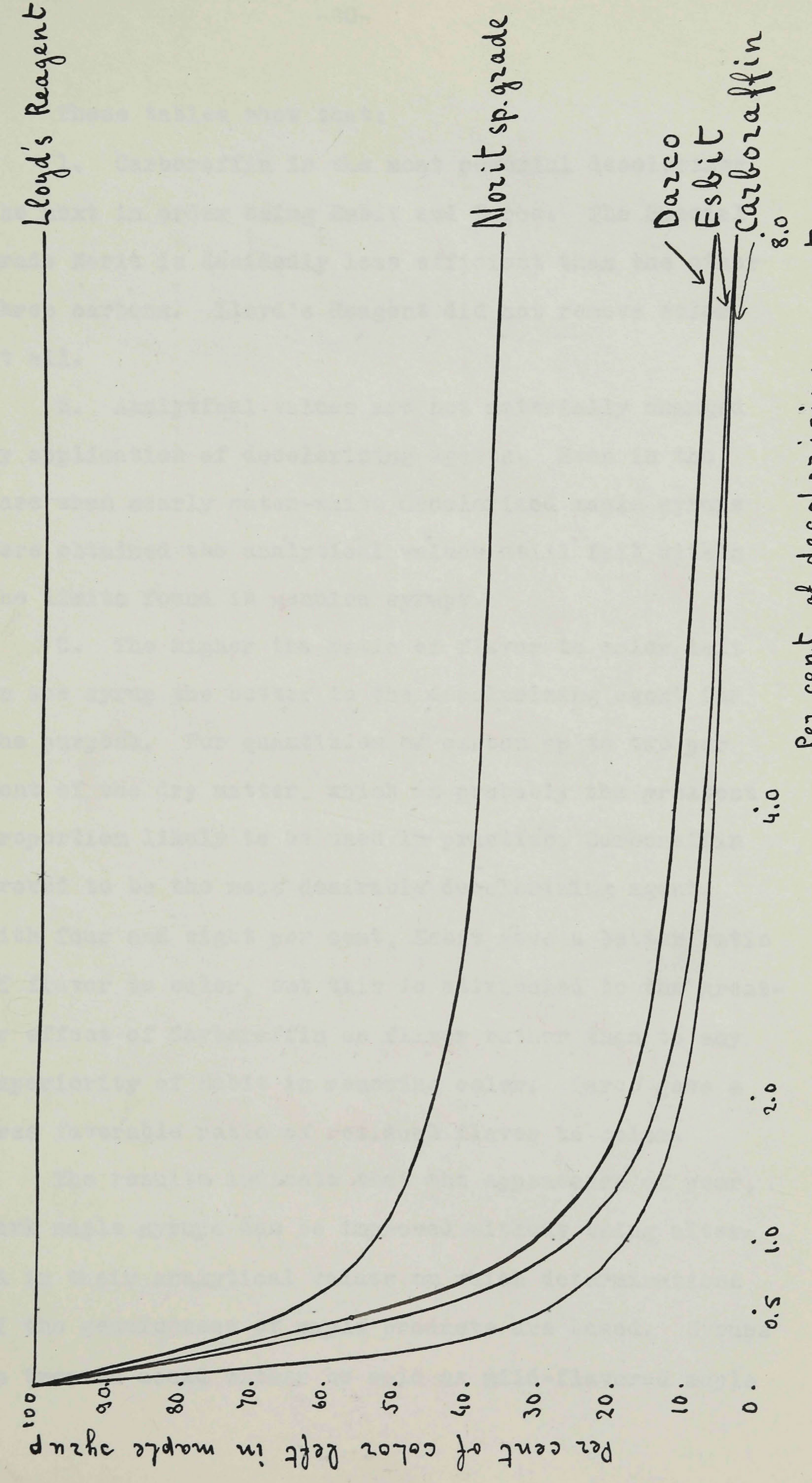
Table VII - Test for Decolorizing Agent "Carboraffin"

No.	Per cent of carbon used	Solids in the final syrup	Color		Flavor		Canadian lead value	Conductivity value	Ash					Time of filtration
			left	removed	left	removed			Total	Soluble		Insoluble		
			%	%	%	%			%	%	alkal	%	alkal	min.
1	0.0	65.60	100	0.0	100	0.0	2.92	141.7	.88	.56	.68	.32	1.10	10
2	0.5	65.25	29	71	72.3	27.7	2.90	143.2	.89	.55	.69	.34	1.11	21
3	1.0	65.61	18	82	52.8	47.2	2.82	141.7	.87	.59	.67	.28	1.10	14
4	2.0	65.65	10	90	39.0	61.0	2.87	144.0	.83	.50	.69	.34	1.06	11.5
5	4.0	65.62	6	94	28.2	71.8	2.90	145.9	.88	.59	.72	.30	1.05	11.0
6	8.0	65.64	3	97	12.8	87.2	2.93	153.1	.91	.65	.75	.27	1.01	11.0

Table VIII - Ratio $\frac{\text{Flavor}}{\text{Color}}$ left in syrups

% of Carbon	Carboraffin	Esbit	Darco	Norit	Lloyd's Reagent
0.0	1	1	1	1	1
0.5	2.5	1.6	1.3	1.1	0.9
1.0	2.9	2.6	2.0	0.9	0.9
2.0	3.9	3.8	2.2	1.2	0.8
4.0	4.7	5.6	2.5	1.1	0.7
8.0	4.3	9.5	2.8	0.9	0.7

Decolorizing isotherms.



These tables show that:

1. Carboraffin is the most powerful decolorizer, the next in order being Esbit and Darco. The Special Grade Norit is decidedly less efficient than the other three carbons. Lloyd's Reagent did not remove color at all.

2. Analytical values are not materially changed by application of decolorizing agents. Even in the case when nearly water-white decolorized maple syrups were obtained the analytical values still fall within the limits found in genuine syrups.

3. The higher the ratio of flavor to color left in the syrup the better is the decolorizing agent for the purpose. For quantities of carbon up to two per cent of the dry matter, which is probably the greatest proportion likely to be used in practice, Carboraffin proved to be the most desirable decolorizing agent. With four and eight per cent, Esbit gave a better ratio of flavor to color, but this is attributed to the greater effect of Carboraffin on flavor rather than to any superiority of Esbit in removing color. Darco gave a less favorable ratio of residual flavor to color.

The results indicate that the appearance of poor, dark maple syrups can be improved without being altered in their analytical values on which determinations of the genuineness of maple products are based. Syrups so treated could either be sold as mild-flavored maple syrups or blended with light colored syrups of good flavor to give products which would grade well as regards both color and flavor. By suitable blending, the factory product could be kept uniform in color and practically uniform in flavor throughout the season, and from season to season.

III Production of a non-mottling, non-hardening maple sugar.

By mottling is meant the presence of regions, spots or irregular patches of sugar lighter in color than the surrounding sugar. Van Zoeren (22),as well as Mitchell (9), found that mottled maple sugar in the light portions is higher in sucrose, and in the dark portions is higher in moisture, invert sugar, and soluble ash. No attempt was made to establish a process which will prevent the mottling. Mitchell (9) states that mottling will develop in maple sugar without regard to stirring, rate of cooling, or conditions of temperature and humidity during storage.

The primary purpose of this work was to devise a process which will completely prevent mottling of maple sugar. Whatever the phenomena of mottling were, one thing was clear, that the light and dark spots of maple sugar were due to migration of moisture and more soluble constituents from one place to another. It was thought that this phenomenon can be prevented by preparing sugar with less moisture content and by destroying the capillary structure between sugar crystals. This theory proved to be right as the writer succeeded in preparing absolutely non-mottling sugars. Another object of the work was to prevent hardening of maple sugar. It is impossible to reduce the hardness of sucrose crystals, but by preparing sugars in such a way that the crystals are loosely attached to each other it is possible to prepare sugars which remain friable. The process by which it is possible to produce non-mottling and non-hardening sugars has another advantage, in that the color of sugars so produced is much lighter, and that the appearance of the cake is much improved.

The following process has given very satisfactory results in the laboratory.

Boil maple syrup to a temperature of 119-120° Centigrade. Pour into a clean dry vessel, and either stir immediately, decreasing the rate of stirring as soon as the syrup becomes turbid due to crystallization, but continuing the stirring until the mixture is cooled to room temperature; or first cool to 45° Centigrade, then stir until crystallization takes place, and set aside for three or four minutes to allow crystallization to complete. The soft, solid mass obtained in either case is disintegrated by gentle rubbing and the particles passed through sieves to give any desired fineness. The granulated product so obtained can either be marketed as such for use on breakfast cereals, sliced bread, etc., or be gently pressed into moulds of any form to produce cakes which are much lighter in color than cast maple sugar and which remain unmottled during months of exposure to the air at room temperature, and remain easily friable.

It was interesting to make a determination of hardness of some sugars prepared by above-mentioned method and sugar made in the usual way. Cylinders of maple sugar, two inches in diameter, four and one half inches long, made in the way just described, and by casting the molten sugar, were allowed to stand on a high shelf in the laboratory for three months. Cylinders made by moulding after hot stirring averaged from 225 grams in weight; those made after cold stirring 265 grams; and the cast cylinders 311 grams. The pressed cylinders of both types lost about three to four per cent of their original weight during the three months storage and had a final moisture content from 0.5 to 0.8 per cent. The final moisture content was changeable from day to day according to the humidity of the air, up to 0.45 per cent. The loss in moisture of the cast cylinders was not determined. At the end of the three months determinations of crushing strength were made on three cylinders of each type. The results of the measurements are given in Table IX. Surprisingly, the cast cylinders showed less strength than the pressed. This is probably due to shrinkage in the interior of cast cylinders which leaves a weak, porous mass surrounded by a hard annular wall about 0.5 centimeter thick. The pressed cylinders, however, are much more easily broken down with the hands or teeth than the cast. The pressed cylinders are uniform in structure and color throughout, while the cast are dark in the mottled interior and much darker in the hard wall. The cast cylinders and cakes present a much less attractive appearance than those made by pressing the granulated product into the moulds.

It remains now to design the machinery for the carrying out of this process on a factory scale.

Table IX - Crushing Strengths of Cylinders of Maple Sugar

Method of Preparation	No.	Weight	Length	Crushing Strength
		Grams	Inches	Pounds
I. Casting	1	311.5	4.78	700
	2	312.9	4.73	532
	3	311.4	4.74	677
Average		311.9	4.75	636
II. Pressing after Hot Stirring	1	205.2	4.42	780
	2	238.9	4.62	2080
	3	202.8	4.52	821
Average		215.6	4.52	1227
III. Pressing after Cold Stirring	1	254.9	4.71	1230
	2	270.0	4.72	2837
	3	264.7	4.70	2490
Average		263.2	4.71	2186

IV Studies of analytical values concerning maple products for detection of adulteration

Fowler and Snell (8) published a paper on the study and modification of the Canadian lead method. In this paper they proposed a modification of the Canadian lead method in which the washing of the lead precipitate is done by cold water instead of hot.

At the same time Snell (8) has proposed further study of the cold water method, particularly on the advisability of using 1.0 cc. or 1.5 cc. of lead subacetate reagent instead of 2.0 cc. as suggested by Fowler (8) for the modified Canadian lead method. It is also known that the most important method for detection of adulteration of maple products beside the lead method is the conductivity value (15, 16, 17, 18).

The solutions of maple sugar require 25 grams of solids in 100 cc. of water for the Canadian lead method and 22 grams of solids in 100 cc. of water for conductivity value determinations.

The present study, therefore, was planned so as to answer the following:

1. What amount of lead subacetate reagent should be used, whether 2.0 cc., 1.5 cc., or 1.0 cc., and

2. If the same solution could be used for both analytical determinations.

Research work regarding these considerations was carried out on twenty different samples of syrup, the description of which is given in Table X.

The samples were diluted for analysis to 25 per cent and 22 per cent of solids respectively, and the following analytical values were determined:

1. Electrical conductivity value.
2. Canadian lead number, hot washing, 2.0 cc. basic lead acetate.
3. Canadian lead number, cold washing, 2.0 cc. basic lead acetate.
4. Canadian lead number, cold washing, 1.5 cc. basic lead acetate.
5. Canadian lead number, cold washing, 1.0 cc. basic lead acetate.
6. Total ash, soluble and insoluble ash, alkalinity of soluble and insoluble ash, ratio, on thirteen syrups.

The results of these determinations are summarized in Tables XI, XII, XIII, XIV, and the following conclusions can be made:

1. Conductivity values are by far the least variable of the values studied.

2. Lead values are higher when the precipitate is washed with cold water than with hot.

3. All three cold water washing modifications vary in their lead values. The syrups which have the lowest standard Canadian lead values give with smaller amounts

of reagent higher results, but with syrups of higher Canadian lead values this difference gradually disappears and finally the highest values are obtained with two cubic centimeters of lead reagent.

4. The mean variation between duplicates is smaller when the precipitate is washed with cold water. The smallest mean variation is obtained when one cubic centimeter of lead reagent is used.

5. The smallest range between maximum and minimum is obtained with one cubic centimeter of the reagent.

6. The ratio $\frac{\text{Max-min}}{\text{Min}}$ (see Table XIII) is the smallest for conductivity value and for one cubic centimeter of lead reagent modification.

7. Slightly higher lead values are obtained when the syrup is diluted to twenty-two per cent of solids.

8. There is no substantial difference in conductivity values if the reading is taken from the syrups diluted to twenty-two or twenty-five per cent of solids; they are somewhat higher in the twenty-five per cent solutions.

Table X - Description of Maple Syrups.

No.	County	Soil	Trees	Run	Color Bryan scale
1	Compton	Rolling, slatey	Hard maple	Early	6
2	"	" "	" "	Middle	6
3	"	" "	" "	Late	8
4	Huntingdon	Very low land, loam & gravel	65% soft maple	First	10
5	"	Gravel	Hard maple, young.	"	7
6	"	Gravel & loam	A few soft maple.	"	9
7	"	Gravel	Hard maple, young.	Middle	8
8	"	Gravel & loam	A few soft maple.	"	12
9	"	Gravel	Hard maple, young	Late	10
10	"	Very low land, loam & gravel	65% soft maple.	"	11
11	"	Gravel & loam	A few soft maple.	"	11
12	Beauce(St. Philibert)	Stony	--	"	13
13	"	"	--	Middle	8
14	"	"	--	First	7
15	Beauce (St.Martin)	Black	--	"	9
16	"	"	--	Middle	11
17	"	"	--	Late	13
18.	Vaudreuil		Hard maple	"	13
19	Beauce	Rocky & mountainous	--	Early	10
20	"	" "	--	Late	14

Table XI

25 gm. of solids in 100 cc. of solution

No.	No. of syrup	Conductivity value	Canadian Lead No. Hot washing, 2.0 cc.				Canadian Lead No. Cold washing, 2.0cc.				Canadian Lead No. Cold washing, 1.5cc.				Canadian Lead No. Cold washing, 1.0cc.			
			I det.	II det.	mean	var.	I det.	II det.	mean	var.	I det.	II det.	mean	var.	I det.	II det.	mean	var.
1	4	121.7	2.33	2.55	2.44	0.22	2.63	2.73	2.68	0.10	2.83	2.85	2.84	0.02	3.03	3.06	3.05	0.03
2	6	131.8	2.59	2.66	2.63	0.07	2.80	2.87	2.84	0.07	3.05	3.06	3.06	0.01	3.16	3.21	3.19	0.05
3	1	117.6	2.59	2.66	2.63	0.07	2.82	2.81	2.82	0.01	3.08	3.09	3.09	0.01	3.22	3.23	3.23	0.01
4	15	145.2	2.64	2.66	2.65	0.02	2.88	2.95	2.92	0.07	3.14	3.16	3.15	0.02	3.35	3.33	3.34	0.02
5	18	192.4	2.89	3.02	2.95	0.13	3.27	3.25	3.26	0.02	3.29	3.32	3.31	0.03	3.40	3.40	3.40	0.00
6	10	128.2	2.98	2.98	2.98	0.00	3.37	3.42	3.40	0.05	3.52	3.51	3.52	0.01	3.50	3.51	3.51	0.01
7	7	142.3	3.06	3.09	3.08	0.03	3.38	3.38	3.38	0.00	3.54	3.58	3.56	0.04	3.70	3.75	3.73	0.05
8	8	135.5	3.14	3.19	3.17	0.05	3.40	3.40	3.40	0.00	3.61	3.50	3.56	0.11	3.68	3.63	3.66	0.05
9	2	124.3	3.21	3.12	3.17	0.09	3.41	3.46	3.44	0.05	3.64	3.59	3.62	0.05	3.75	3.77	3.76	0.02
10	16	161.7	3.24	3.16	3.20	0.08	3.55	3.60	3.58	0.05	3.66	3.69	3.68	0.03	3.72	3.66	3.69	0.06
11	5	143.2	3.27	3.27	3.27	0.00	3.50	3.53	3.52	0.03	3.71	3.78	3.75	0.07	3.80	3.84	3.82	0.04
12	19	167.4	3.46	3.49	3.48	0.03	3.78	3.78	3.78	0.00	3.84	3.89	3.87	0.05	3.86	3.90	3.88	0.04
13	11	141.6	3.56	3.70	3.63	0.14	3.81	3.87	3.84	0.06	3.93	3.96	3.95	0.03	3.98	3.97	3.98	0.01
14	14	161.7	3.65	3.73	3.69	0.08	3.87	3.89	3.88	0.02	4.03	4.04	4.04	0.01	4.03	4.05	4.04	0.02
15	9	151.4	3.67	3.63	3.65	0.04	4.06	4.05	4.06	0.01	4.14	4.07	4.11	0.07	4.15	4.16	4.16	0.01
16	13	167.4	3.88	3.88	3.88	0.00	4.14	4.17	4.16	0.03	4.24	4.26	4.25	0.02	4.28	4.29	4.29	0.01
17	3	138.2	3.94	3.97	3.96	0.03	4.22	4.29	4.26	0.07	4.41	4.41	4.41	0.00	4.47	4.51	4.49	0.04
18	17	181.9	4.11	4.01	4.06	0.10	4.48	4.43	4.46	0.05	4.43	4.47	4.45	0.04	4.31	4.29	4.30	0.02
19	20	175.7	4.87	4.88	4.88	0.01	5.40	5.39	5.40	0.01	5.18	5.15	5.17	0.03	4.70	4.73	4.72	0.03
20	12	197.6	5.82	5.82	5.82	0.00	6.24	6.20	6.22	0.04	6.06	6.02	6.04	0.04	5.46	5.48	5.47	0.02
Mean variation between duplicates						0.058				0.037				0.035				0.027
Difference Max and Min					3.38				3.54				3.20				2.42	

Table XII

22 gm. of solids in 100 cc. of solution

No.	No. of syrup	Conductivity value	Canadian Lead No. Hot washing, 2.0 cc.				Canadian Lead No. Cold washing, 2.0cc.				Canadian Lead No. Cold washing, 1.5cc.				Canadian Lead No. Cold washing, 1.0cc.			
			I det.	II det.	mean	var.	I det.	II det.	mean	var.	I det.	II det.	mean	var.	I det.	II det.	mean	var.
1	4	119.6	2.53	2.67	2.60	0.14	2.77	2.89	2.83	0.12	2.88	2.88	2.88	0.00	3.12	3.18	3.15	0.06
2	6	132.4	2.72	2.95	2.84	0.22	3.02	3.13	3.08	0.11	3.07	3.22	3.15	0.15	3.41	3.42	3.42	0.01
3	1	111.2	2.82	3.03	2.94	0.19	3.18	3.21	3.19	0.03	3.31	3.44	3.38	0.13	3.51	3.67	3.59	0.16
4	15	140.9	2.98	3.04	3.01	0.06	3.19	3.23	3.21	0.04	3.38	3.41	3.40	0.03	3.50	3.49	3.50	0.01
5	18	187.2	3.05	3.09	3.07	0.04	3.42	3.52	3.47	0.10	3.53	3.61	3.57	0.08	3.69	3.80	3.75	0.11
6	10	127.1	3.06	3.02	3.04	0.04	3.68	3.69	3.69	0.01	3.64	3.69	3.67	0.05	3.90	3.98	3.94	0.08
7	7	135.4	3.25	3.43	3.34	0.18	3.68	3.56	3.62	0.12	3.69	3.62	3.66	0.07	3.97	3.99	3.98	0.02
8	8	135.6	3.15	3.17	3.16	0.02	3.46	3.44	3.45	0.02	3.61	3.55	3.58	0.06	3.62	3.59	3.61	0.03
9	2	118.1	3.20	3.46	3.33	0.26	3.58	3.36	3.47	0.22	3.70	3.59	3.65	0.11	3.97	4.07	4.02	0.10
10	16	149.8	3.43	3.58	3.51	0.15	3.65	3.60	3.63	0.05	3.78	3.85	3.82	0.07	3.99	3.99	3.99	0.00
11	5	140.9	3.48	3.31	3.40	0.17	3.65	3.74	3.70	0.09	3.89	3.92	3.91	0.03	4.02	3.95	3.99	0.07
12	19	163.6	3.57	3.43	3.50	0.14	3.83	3.87	3.85	0.04	3.90	4.02	3.96	0.12	4.13	4.19	4.16	0.06
13	11	140.9	3.65	3.51	3.58	0.14	4.08	4.10	4.09	0.02	4.18	4.36	4.27	0.18	4.20	4.23	4.22	0.03
14	14	158.1	3.65	3.89	3.77	0.24	4.19	4.32	4.26	0.13	4.25	4.26	4.26	0.01	4.12	4.11	4.12	0.01
15	9	154.7	3.86	3.58	3.72	0.28	4.19	4.17	4.18	0.02	4.32	4.42	4.37	0.10	4.34	4.34	4.34	0.00
16	13	161.7	4.16	4.25	4.21	0.09	4.51	4.49	4.50	0.02	4.31	4.34	4.33	0.03	4.57	4.51	4.54	0.06
17	3	137.5	4.01	4.01	4.01	0.00	4.57	4.50	4.54	0.07	4.54	4.65	4.60	0.11	4.65	4.53	4.59	0.12
18	17	175.7	4.10	4.29	4.20	0.19	4.37	4.39	4.38	0.02	4.63	4.67	4.65	0.04	4.64	4.59	4.62	0.05
19	20	174.6	5.17	5.28	5.23	0.11	5.36	5.29	5.33	0.07	5.48	5.49	5.49	0.01	4.89	4.94	4.92	0.05
20	12	192.3	5.89	5.92	5.91	0.03	6.53	6.52	6.53	0.01	6.22	6.25	6.24	0.03	5.65	5.53	5.59	0.12
Mean variation between duplicates						0.135				0.065				0.075				0.057
Difference Max and Min					3.31				3.70				3.36				2.44	

Table XIII

Comparison of Analytical Values Obtained on 25 g. and 22 g. in 100 cc. of solution

No.	No. of syrup	Conductivity Values		Canadian Lead No., Hot Washing Method		Modified Canadian Lead No., Cold Washing Methods					
				2.0 cc.		2.0 cc.		1.5 cc.		1.0 cc.	
		25 g.	22 g.	25 g.	22 g.	25 g.	22 g.	25 g.	22 g.	25 g.	22 g.
1	4	121.7	119.6	2.44	2.60	2.68	2.83	2.84	2.88	3.05	3.15
2	6	131.8	132.4	2.63	2.84	2.84	3.08	3.06	3.15	3.19	3.42
3	1	117.6	111.2	2.63	2.94	2.82	3.19	3.09	3.38	3.23	3.59
4	15	145.2	140.9	2.65	3.01	2.92	3.21	3.15	3.40	3.34	3.50
5	18	192.4	187.2	2.95	3.07	3.26	3.47	3.31	3.57	3.40	3.75
6	10	128.2	127.1	2.98	3.04	3.40	3.69	3.52	3.67	3.51	3.94
7	7	142.3	135.4	3.08	3.34	3.38	3.62	3.56	3.66	3.73	3.98
8	8	135.5	135.6	3.17	3.16	3.40	3.45	3.56	3.58	3.66	3.61
9	2	124.3	118.1	3.17	3.33	3.44	3.47	3.62	3.65	3.76	4.02
10	16	161.7	149.8	3.20	3.51	3.58	3.63	3.68	3.82	3.69	3.99
11	5	143.2	140.9	3.27	3.40	3.52	3.70	3.75	3.91	3.82	3.99
12	19	167.4	163.6	3.48	3.50	3.78	3.85	3.87	3.96	3.88	4.16
13	11	141.6	140.9	3.63	3.58	3.84	4.09	3.95	4.27	3.98	4.22
14	14	161.7	158.1	3.69	3.77	3.88	4.26	4.04	4.26	4.04	4.12
15	9	151.4	154.7	3.65	3.72	4.06	4.18	4.11	4.37	4.16	4.34
16	13	167.4	161.7	3.88	4.21	4.16	4.50	4.25	4.33	4.29	4.54
17	3	138.2	137.5	3.96	4.01	4.26	4.54	4.41	4.60	4.49	4.59
18	17	181.9	175.7	4.06	4.20	4.46	4.38	4.45	4.65	4.30	4.62
19	20	175.7	174.6	4.88	5.23	5.40	5.33	5.17	5.49	4.72	4.92
20	12	197.6	192.3	5.82	5.91	6.22	6.53	6.04	6.24	5.47	5.59
Difference Max-Min		75.9	72.7	3.38	3.31	3.54	3.70	3.20	3.36	2.42	2.44
Ratio $\frac{\text{Max-Min}}{\text{Min}}$		.62	.61	1.39	1.30	1.32	1.31	1.13	1.17	0.79	0.77

Table XIV

Ash Values and Conductivity Values

No.	No. of syrup	Conductivity Values		Ash										Alkalinity of ash						
		22 g. in 100cc	25 g. in 100cc	Total			Soluble			Insoluble			Ratio	Soluble			Insoluble			Ratio
				I det.	II det.	mean	I det.	II det.	mean	I det.	II det.	mean	sol./insol	I det.	II det.	mean	I det.	II det.	mean	sol./insol
1	1	111.2	117.6	0.86	0.87	0.87	0.45	0.43	0.44	0.40	0.44	0.42	1.05	0.58	0.58	0.58	1.20	1.26	1.23	0.46
2	4	119.6	121.7	0.79	0.79	0.79	0.51	0.52	0.52	0.27	0.28	0.28	1.88	0.62	0.62	0.62	0.78	0.78	0.78	0.82
3	10	127.1	128.2	0.91	0.92	0.92	0.48	0.47	0.48	0.43	0.45	0.44	1.09	0.63	0.63	0.63	0.96	0.98	0.97	0.66
4	8	136.6	135.5	0.95	0.95	0.95	0.46	0.45	0.46	0.49	0.51	0.50	0.92	0.58	0.60	0.59	1.09	1.09	1.09	0.54
5	3	137.5	138.2	0.99	0.94	0.97	0.52	0.50	0.51	0.46	0.44	0.45	1.12	0.66	0.69	0.68	1.30	1.30	1.30	0.57
6	15	140.9	145.2	0.85	0.84	0.85	0.58	0.60	0.59	0.25	0.27	0.26	2.31	0.73	0.74	0.74	0.66	0.66	0.66	1.14
7	16	149.8	161.7	0.89	0.90	0.90	0.57	0.59	0.58	0.32	0.31	0.32	1.81	0.78	0.78	0.78	0.77	0.74	0.76	1.03
8	9	154.7	151.4	1.08	1.06	1.07	0.51	0.52	0.52	0.57	0.55	0.56	0.93	0.75	0.77	0.76	1.20	1.23	1.22	0.64
9	19	163.6	167.4	0.97	0.99	0.98	0.66	0.66	0.66	0.31	0.33	0.32	2.06	0.71	0.71	0.71	0.90	0.94	0.92	0.77
10	13	161.7	167.4	1.13	1.15	1.14	0.80	0.82	0.81	0.33	0.34	0.34	2.43	0.80	0.82	0.81	0.69	0.71	0.70	1.20
11	20	174.6	175.7	1.19	1.17	1.18	0.78	0.79	0.79	0.41	0.38	0.40	2.00	0.85	0.85	0.85	1.20	1.18	1.19	0.72
12	18	187.2	192.4	1.08	1.06	1.07	0.77	0.77	0.77	0.42	0.41	0.42	1.87	0.86	0.84	0.85	1.10	1.12	1.11	0.78
13	12	192.3	197.6	1.34	1.36	1.35	0.81	0.81	0.81	0.52	0.54	0.53	1.52	1.02	1.02	1.02	1.48	1.51	1.50	0.68

The results justify a proposal of the following modification for the Canadian lead number and Conductivity value determination, which will simplyfy both methods and bring the values of the Canadian lead method into a narrower range:

1. The solution of maple syrup for both methods should be made to twenty-five per cent of solids. Before making the lead number determination, the same solution can be used for finding the conductivity value.

2. The Canadian lead number method should be modified, one cubic centimeter of lead reagent should be used instead of two cubic centimeters, and cold instead of hot water washing employed.

V Studies on maple flavor, its development, isolation and identification

1. Historical

The flavoring principles in maple products were studied in maple sugar by Robison (13), and in maple syrup by Nelson (10). It has also been said that a Canadian chemist at one time found the chemical nature of the material, but did not publish the results.

The first attempt to isolate the flavoring matter was by Sy (20). He based his experiment on the well-known fact that the flavoring substances are partly volatile at temperatures reached during the evaporation of sap, for there is always an aromatic odor in the vicinity of a sugar camp in operation. He boiled pure, fresh maple sap in a large glass flask, connected by a glass condenser with another flask. This second flask had a reflux condenser, the latter being connected at the top with another vertical condenser, the bottom of which reached into a small flask containing water. After six litres of sap had evaporated to a syrupy state, the second flask contained so little flavor, that it was impossible to compare it with anything. Into the third flask no odor of any kind came over. This shows that the flavoring substances are very little volatile and could not be isolated in this way.

Robison (13),working on the maple flavoring principle, after some consideration, decided that the best method of isolating the "flavoring matter" would be by the extraction of the maple sugar with a solvent which would remove the "flavoring matter" without interfering with the sugar or any other constituent of the maple product. In order to eliminate the formation of caramel in the conversion of the syrup into sugar, the maple syrup was placed in a twelve litre pyrex flask and heated under reduced pressure. He applied a water-bath and with a water pump produced such a vacuum in the flask that the syrup could be boiled at 67°C. He also collected the distillate for examination. He tried to produce large sugar crystals, because he considered that the larger the crystals are, the smaller is the total exterior crystal area, which causes a higher concentration of the flavoring matter over a unit of the exterior crystal area. After having prepared in this way the maple sugar from syrup, Robison tried different solvents by using Soxhlet's extraction apparatus and concluded that benzene gave the best results. The material brought down with the solvent was resinous matter together with a non-resinous material, which resembled an oil. The amount of the latter was very small in comparison with the former, while both were extracted in such small amounts that it was impossible to apply any method of analysis.

Robison tried also a method of removing the sugar from maple syrup as saccharate in order to get a concentrated solution of maple flavor. The mass was then extracted with alcohol and the extract was evaporated with the result that the same bitter material was recovered, which smelled faintly of maple.

He also made an attempt to absorb the flavoring material by the use of charcoal. Both animal and vegetable charcoal were used. The extraction of the adsorbed flavor in the charcoal was accomplished by treating the latter with four or five applications of 90% alcohol. The filtrate was evaporated to dryness and the same bitter principle was obtained, which gave off a maple odor.

Having accomplished the preliminary tests, Robison decided to use benzene for extraction of the flavor. He started to extract larger amounts of sugar to obtain more maple flavor extract. The method decided upon was to allow the benzene to stand in contact with the sugar for some time, shaking at intervals.

Robison then applied different tests and reactions to the maple benzene extract in solution.

It may be said that bases tend to precipitate the unknown material in the maple extract, while acids tend to give color reactions. According to this, Robison suggested two methods for detecting adulteration in maple syrup:

1. Precipitate the unknown material from the ex-

tract by the use of calcium hydroxide, filter and weigh.

2. Add an acid (nitric or sulphuric) to the chloroform extract and compare color developed with a standard color solution.

Nelson's (10) investigation on the flavor of maple syrup was published in the middle of 1928. Nelson's first attempt to isolate the flavoring material was by the barium process devised by Sale and Wilson (14). Five litres of Vermont syrup were treated. The product was thoroughly extracted with ether. The ether solution was shaken out with dilute ammonia 1:10 and then the ammonia solution was acidified and extracted with ether. After the ether had been carefully evaporated the residue was stirred with 10 cc. of water and 25 cc. of ten per cent lead acetate solution and filtered, and the filtrate was extracted with ether. On evaporation of the ether, a reddish oil remained which did not crystallize. It had a sharp, acid odor. It was, therefore, dissolved in dilute sodium carbonate and extracted with ether. The other residue had a peculiar (phenolic) odor and with ferric chloride gave a green colour reaction.

The ether solution left after extraction with dilute ammonia was evaporated, the residue was dissolved in water, lead acetate solution was added and the mixture was filtered. The filtrate was extracted with ether and the ether was evaporated. The residue became partly crystalline. The crystals were separated on a porous plate and recrystallized from ethyl acetate. White, spindle-shaped crystals, which turned brown in the air, were obtained. The substance melted exactly at 212°C. but darkened at a lower temperature. It was insoluble in water, but dissolved in sodium hydroxide solution and when shaken, this solution became red. The substance reduced copper acetate and silver nitrate solutions and on boiling with ferric chloride a pungent chlorine-like odor was evolved and a crystalline substance condensed in the upper part of the tube. These reactions indicated a quinone derivative. Hydro-phlorone, which melts also at 212°C., was prepared and compared crystallographically with the unknown material, but the two were found to be different.

The oil absorbed by the porous plate was recovered. Most of it was soluble in water to a clear, yellow solution. Ferric chloride turned it red and caused turbidity. Nothing definite was obtained from it.

Nelson's next attempt to isolate the flavoring material was by direct extraction of 1 gallon of syrup with ether. The ether extract was washed with water, concentrated and finally evaporated in a vacuum desiccator. The residue was small and had an intense odor of maple. When it was dissolved in dilute sodium hydroxide, the maple odor disappeared and acidifying the solution did not restore the maple odor. This shows that the flavoring material is very sensitive to caustic alkalies.

The third attempt made by Nelson to isolate the flavoring material was by removing it with norite. One litre of syrup diluted with 1 litre of water was stirred 20 minutes with 50 grams of norite and filtered. The norite was washed with three 100 cc. portions of water, drained on a Büchner funnel and exhausted with ether in a Soxhlet extractor. On evaporating the ether, a red oil remained in which the maple flavor was indistinct. The syrup filtered from the norite, however, had lost its maple odor. Evidently the flavor, although absorbed by the norite, had either not been recovered from it or had become changed and lost its identity.

After completing these preliminary experiments, Nelson decided that a direct ether extraction is perhaps the best method of isolating the flavoring material, which is a very unstable substance, and therefore the use of fixed caustic alkalies and absorbents was avoided by him in the further study of the problem. Nelson extracted by ether 38 litres of Vermont and 38 litres of Michigan maple syrups. These extracts were shaken with a strong solution of sodium bisulphite and kept in an ice box with occasional shaking for 24 hours. The bisulphite solutions were separated and acidified with dilute sulphuric acid, and a stream of carbon dioxide was allowed to bubble through for some time to remove the sulphur dioxide. They were then extracted with ether and the ether was carefully evaporated. The residues were boiled out several times with petroleum ether and after the petroleum ether was evaporated, the residues had a distinct vanillin-like odor. The substance obtained from Vermont syrup showed a tendency to crystallize, but was not sufficiently pure for examination, though it gave a blue color reaction with ferric chloride.

The substance from the Michigan syrup was obtained in crystalline form. The entire quantity of material was only 127 milligrans, of which half was dissolved by petroleum ether. The substance gave a blue color reaction with ferric chloride and responded to resorcinol and phloroglucin tests for vanillin. It crystallized from petroleum ether in plates instead of in needles of vanillin. Crystallographic examination showed that it was neither vanillin nor the homologue of vanillin. It melted at 74-76°C. The odor was intense and very much like that of vanillin. On boiling with dilute ferric chloride and cooling, a crystalline precipitate corresponding to dihydrodivanillin was obtained, but it was found to be different from dehydrodivanillin in optical properties.

The residues left after boiling with petroleum ether were not crystalline and had an odor like maple. The residue insoluble in petroleum ether from the Michigan syrup had a particularly agreeable odor, somewhat like heliotrope (piperonal).

After extracting with sodium bisulphite the ether solutions were shaken twice with ammonium hydroxide 1:10, 50 cc. being used for each extraction. The dilute ammonia solutions were separated, poured into dilute sulphuric acid and shaken with ether. On careful evaporation of the ether, reddish-yellow residues which were very resinous and had an intense odor of maple remained. The residue of Vermont syrup weighed 0.4 gr. and of Michigan syrup 0.5 gr.

All efforts to induce crystallization failed. Methylation and acetylization also failed to afford crystalline derivatives. A hydro-alcoholic solution, treated with a few drops of dilute ferric chloride, was colored red which changed to greenish yellow. The substance changes easily to a darker colored resin, at the same time losing its characteristic maple odor. This change seems to take place to some extent on evaporating its ethereal solutions, but whether it is owing to polymerization or oxidation is undetermined. Boiling with ferric chloride failed to give a volatile quinone-like substance such as was observed in the crystalline substance isolated from the products of the experiment in which the Sale-Wilson process was used.

The ether solutions remaining after treatment with sodium bisulphite and dilute ammonia were evaporated. The residue was very small and did not have a maple odor. It was reddish and melted at 210-212°.

Nelson thinks that the maple flavor appears to depend to a great extent on an unstable, phenolic substance, or substances, the exact nature of which remains undetermined. He thinks that this substance may be related to the vanillin-like material associated with it, and possibly, also, to the phlorone-like substance which gave a volatile, pungent crystalline derivative on boiling with ferric chloride.

2. Experimental

This work consisted essentially of two series of experiments: (1) with original sap from the maple trees, and (2) with finished products. In the first series of experiments, the writer tried to find out if different methods of concentrating sap to the syrupy state affects or changes the flavor, and in the second series of experiments, to isolate and identify the maple flavor.

3. Maple flavor in syrups obtained from sap by different methods

The sap running period extended, during 1928, from March 21 to April 20. It was of some interest to know the pH value of this sap. On March 24, 1928, the reading was taken directly in the maple bush by Dr. McKibbin and the writer. The readings are given in Table XV.

Table XV. pH value of maple sap

Tree Number	First bucket	Second bucket
1	6.4	6.4
2	6.4	6.4
3	6.6	6.7
4	6.3	6.5
5	6.4	6.5
6	6.7	6.8
7	6.4	6.4
8	6.6	6.6
9	6.6	6.6

The sap was concentrated by three different methods.

a. Ordinary atmospheric pressure boiling in an open pan.

b. Reduced-pressure boiling in pyrex flasks.

c. By freezing out the water.

a. <u>Ordinary atmospheric pressure boiling in an open pan.</u>

The pan was 2½ feet x 5 feet, and was placed on a hot gas plate. Great care is necessary during the concentration of the sap as burning occurs very easily. The sap was put into the pan as a thin layer about 8-10 cm. deep and was concentrated to about 35-40 per cent of solids, as further concentration was dangerous. The bottom of the pan was not level and the liquid did not cover, after evaporation of a certain amount, the whole surface. This half-concentrated syrup was removed and put into big porcelain evaporating dishes where it was concentrated until the boiling temperature reached 219.5°F. and was then preserved in well stoppered bottles.

b. Reduced pressure boiling in pyrex flasks

The vacuum method has necessitated some complicated arrangements. It was necessary to avoid local overheating and for this purpose the best way to heat the flasks was not over a flame but in a water-bath.

Two big twenty two litre pyrex flasks were put into a water-bath into which compressed steam was allowed to bubble. The temperature of the water-bath was usually between 75° and 85°C. and never exceeded 90°C. The pyrex flask was closed with a specially adjusted thick rubber stopper to withstand tremendous pressure. This rubber stopper was triple-perforated, one hole for a long thermometer which reached to the bottom of the flask, for temperature readings of the boiling sap, the second for a special funnel through which maple sap could be introduced into the flask, and the third hole served for a glass tube which was connected with a condenser, and the latter with a big receiving flask for distillate and water pump, which produced the necessary vacuum. The vacuum was measured by means of a mercury manometer which was connected with the whole system by a thick rubber tubing. All this arrangement allowed very close control of the boiling point of the liquid. In Table XVI are summarized the conditions under which the sap was allowed to boil.

Table XVI

Conditions under which sap was concentrated in vacuum

Date		Barometer Reading mm.	Vacuum mm.	Difference mm.	Temperature of boiling sap °C	Temperature of water-bath °C
March	26	753	705	48	39	79
"	27	738.9	707	31.9	34	81
"	27	738.9	687	51.9	43	82
"	28	754.2	713	41.2	41	85
"	28	754.2	677	77.2	49	76
April	2	763.3	704	59.3	49	81
"	2	763.3	711	52.3	44	83
"	3	762.8	717	45.8	40	75
"	11	760.4	690	70.4	51	87
"	11	760.4	713	47.4	42.5	79
"	20	763	692	71	52	87

This table shows that sap was boiled at very low temperatures, when no caramelization took place. This is very important as all syrups boiled this way showed a lighter color in comparison with the same sap boiled under ordinary conditions.

c. Freezing Method

The third method of concentrating the sap, namely, by freezing, did not give very satisfactory results as the ice-and-salt ice cream machine, in which the freezing was done, was of very small capacity. The method consisted of freezing the sap in the cylinder of the ice cream machine. The ice was formed on the walls of the cylinder and inside the liquid was left richer in total solids, which did not freeze in a given amount of time.

Final concentration of solids by freezing from a 1.75 per cent sap was 24.00 per cent. The total amount was about 200 cc. and to get it, it was necessary to do about 30 freezings.

4. Discussion of the results

The total quantity of sap brought to the college, 8 times in 20 gallon lots, was 160 gallons. The sap was concentrated in the three different ways already described. The vacuum syrup was partially reboiled. This reboiling was done in an Erlenmeyer flask, over flame, with a reflux water condenser for one hour, so that the syrup was boiled at the same temperature as in the atmospheric pressure evaporation. The resulting syrups could be characterized for flavor as shown in Table XVII.

Table XVII. Flavor values of syrups

	Date		Sap	Flavor Values*											
No.	Day	Month	% of solids	Snell			McKibbin			Skazin			Average		
				A	V	R	A	V	R	A	V	R	A	V	R
1	21	March	4.0	2	4	4	2	3	4	2	4	4	2	3.7	4
2	26	"	3.7	1	3	1	1	2	1	1	4	2	1	3	1.3
3	27	"	1.7	1	3	1	2	4	2	1	4	1	1.3	3.7	1.3
4	2	April	3.5	1	3	3	1	4	4	1	4	3	1	3.7	3.3
5	2	"	4.0	1	4	3	1	4	2	1	4	2	1	4	2.3
6	11	"	2.5	1	3	3	1	2	2	1	3	2	1	2.6	2.3
7	15	"	1.75	by freezing: Water melon taste.											
8	20	"	1.75	3	3	4	2	3	2	2	3	2	2.3	3	2.6
Total													1.37	3.39	2.45

Key -- 1 = Strong flavor 2 = Medium flavor 3 = Weak flavor 4 = No flavor

A = Atmospheric V = Vacuum R = Reboiling

From Table XVII we can see that there is a big difference between the two methods of preparing maple syrup. The seven syrups prepared in the ordinary way under atmospheric pressure showed an average flavor value of 1.37. Syrups boiled from the same saps but under vacuum have much lower flavor values and the average is only 3.39, which is between no flavor and weak flavor. From these two values we can see that maple flavor is developed when the sap is evaporated under atmospheric pressure. Vacuum-evaporated, reboiled syrup shows a very interesting phenomenon. The flavor value is higher than vacuum-boiled syrup and is near to the ordinary boiled syrup. This leads us to the conclusion that maple flavor is present in maple sap, but does not develop until the syrup is heated to a certain temperature. Dr. Snell thinks that this is due to the probability that the constituents of flavor are in some chemical compounds (glucosides?) which are changed on heating and the flavoring substances are liberated.

The freezing method was not very successful. This freezing was done on an ordinary hand working ice-cream machine, and as a freezing mixture, ice, snow, and salt were used. The thirty freezings which were done required very careful attention and in spite of this, in some cases the salt from the freezing mixture entered inside and could be recognized very distinctly by salty taste.

But in spite of all these difficultues the resulting syrup did not have the usual maple flavor, but one somewhat like that of water-melon. A whole can of maple sap was also put in a cold storage room of a butcher's shop. The freezing was very slow and required about 2 weeks. During this time a considerable amount of microorganisms had a chance to develop and the final product was worthless for flavor investigation.

5. Analysis of Maple Flavor

One hundred and sixty gallons of maple sap, which were brought to the laboratory, gave in all only about three and one-half gallons of syrup. The work of Nelson (10) has shown that it is necessary to use large quantities of maple syrup for flavor investigation as the flavoring material is present in very small quantities. Unfortunately, in the season of 1928 no syrup of the highest quality was available. The ten gallons of syrup which were used for flavor investigation came from The Maple Sugar Producers of Quebec", without any definite information as to the origin and methods of manufacture. The quantities of material available for the experiment were too small to enable me to carry the work to a definite conclusion.

6. Method of extraction of Maple Flavor

Having the experience in isolation of flavoring principle from maple syrup of Nelson (10), and after trying to extract maple flavor from maple sugar in a special large extracting apparatus by means of ether, with little success, it was decided to adopt the method of isolating the flavoring substance directly from syrup, and then, if possible, to carry out quantitative analysis and determinations.

The syrup which was used for flavor determination had 67.5 per cent of solids, was light in color (No.7.) and of good flavor.

As it was necessary to use some solvent to extract the flavor from maple syrup, it was decided to try various solvents and to determine the quantities of dissolved and extracted materials, which the solvents would remove from maple syrup. It was found that the best concentration of maple syrup for extraction was about 35 per cent of solids. This concentration permits more rapid separation of two layers and is not very dilute as to enlarge considerably the total quantities which would undergo the extraction.

Six different solvents were used: carbon tetrachloride, carbon disulphide, petroleum ether, benzene, ether and chloroform. For every extraction, 50 cc. of syrup were taken. This quantity was mixed with 50 cc. of water, and as the total solids of original syrup were 67.5 per cent, the percentage of solids in the mixtures was 33.75 per cent. Table XVIII shows different solvents and the solubility of maple flavor in them expressed as per cent of the undiluted syrup.

Table XVIII

Comparison of Extracts Made with Various Solvents

No.	Solvent	Parts per million	Color	Maple odor
1	CCl_4	14	pale yellow	No
2	Petroleum ether	17	pale yellow	No
3	CS_2	18	reddish yellow	Approx.
4	C_6H_6	33	yellow	Approx.
5	Et_2O	38	yellow	Yes
6	$CHCl_3$	57	reddish brown	Yes

All residues uncrystalline.

All residues soluble in chloroform.

From Table XVIII it is evident that chloroform extracted the largest quantity from the same amount of syrup of any of the solvents, and as the odor of the extract was very characteristic of maple flavor, and as all other extracts were soluble in chloroform, it was decided to make the extraction of maple flavor from the whole quantity of syrup by means of chloroform as a solvent.

7. Chloroform extraction of maple flavor

To extract such a large amount of syrup, a butter churn,in which a big, glass, 4-gallon bottle with a glass stopper was fitted,was used. At one time only one gallon of syrup, which was diluted with one gallon of distilled water, could be shaken. The amount of chloroform for each extraction was 1 litre. Every portion was extracted twice with the same quantity of solvent, as the amount of flavor left in the solution after the second extraction was very small.

Table XIX. Amount of material extracted from one gallon of syrup by three successive portions of chloroform.

Amount of syrup	Solvent	Extraction	Residue	In %
One gallon of maple syrup diluted with one gallon of water	Three one-litre portions of chloroform	first	0.3100 gm.	87.79
		second	0.0428 "	12.03
		third	0.0032 "	0.18
Total			0.3560 gm.	100.00
or			60 p.p.m. of syrup	

Table XIX shows that practically all (99.82%) the chloroform soluble material was isolated by the first two extractions.

Every individual portion was shaken in the churn for six hours. The churn was turned slowly by means of an electric motor and thus the contentsof the bottle were well mixed. After six hours the bottle with the mixture of chloroform and diluted maple syrup was put aside for a few hours to allow the liquid to separate. The chloroform layer was then syphoned out and finally separated from diluted maple syrup and washed with distilled water in separating funnels. The diluted maple syrup, after being concentrated to the original concentration, had no maple flavor and tasted just sweet. That was another evidence that the flavor had gone to the chloroform layer. The chloroform solution was concentrated by distillation in a Soxhlet extraction apparatus.

The color of concentrated chloroform extract was reddish-brown (caramel is insoluble in chloroform). The chloroform extract was covered with water and kept in a well-stoppered bottle to prevent oxidation. The water which covered the extract was colored after a few days slightly yellow. Amount of solids in chloroform solution was 0.65 grams per hundred cubic centimeters.

8. The analysis of chloroform extract

The analysis of chloroform extract was performed in the following way. One hundred and fifty cubic centimeters, containing 0.975 gram of solids, of chloroform extract were shaken for twenty minutes with 200 cc. half-saturated solution of sodium bisulphite (3). After standing for a while the bisulphite layer was separated and the chloroform was shaken again with a new 100 cc. portion of half-saturated sodium bisulphite solution.

During shaking, the chloroform layer lost most of its color, but at the same time a brown precipitate, which was insoluble in both chloroform and in sodium bisulphite solution, was produced. This precipitate, which was obtained in very small amounts, dispersed readily in distilled water and gave a milky, colloid-like colorless solution. On acidification with concentrated sulphuric acid, the liquid became clear and brownish-red.

Sodium bisulphite solution was washed several times with pure chloroform, and then decomposed with warm, dilute sulphuric acid (3 volumes sulphuric acid + 5 volumes of water; for every 100 cc. bisulphite solution, 150 cc. of dilute sulphuric acid were taken), and a stream of carbon dioxide was bubbled through the liquid for about three hours to remove sulphur dioxide.

The acidified sodium bisulphite solution was then shaken five times with 100 cc. portions of chloroform. After carefully evaporating the chloroform the total weight of residue was 0.0485 grams. The residue was not crystalline but had a strong odor of vanillin. It was boiled out several times with petroleum ether. The petroleum ether extract, after careful evaporation, was in a crystalline state with vanillin odor. The crystals, under the microscope, appeared to be in needles with some yellow drops in them. The weight of these crystals was 0.0133 gm.

As these crystals had an odor of vanillin, the color reactions for vanillin (1) were tried on the obtained substance with the following results:

Tests	Vanillin-like substance	Vanillin
1. Phloroglucinol and HCl	Red	Red
2. Resorcinol and HCl	Violet-gray-reddish	Violet-reddish
3. Ferric chloride	Bluish	Bluish

The melting point of the crystals was determined under a microscope by means of a hot stage (7). It consisted of a glass box, such as is commonly employed for the spectroscopic examination of liquids, the open end of which was provided with a cork plate with three holes, two for circulating hot water and one for inserting a thermometer. By regulating the rate of flow of hot water very gradual rises of temperature were obtained. The melting point of Vanillin-like substance so observed was 77-79°C., (Vanillin 81°C.). The melting point of **the** crystals was somewhat lower than for vanillin, which may be due to the impurities. On heating, the crystals darkened until they became almost black.

An attempt was made to determine the chemical constitution of this substance by means of Pregl's methods for organic microanalysis (12). Unfortunately the combustion determination was spoiled during the procedure but one analysis was carried out more or less successfully. As there was no substance left for duplicate determination, the result must be taken with reservation. The results are:

Vanillin-like substance			Nearest formula	Vanillin
Weights mgm.		%		
of material	2.145	100	$C_8H_6O_3$	$C_8H_8O_3$
of H_2O	0.803	H - 4.16	H - 4%	4.2%
of CO_2	5.039	C - 64.00	C - 64%	63.2%
Oxygen by difference		O - 31.84	O - 32%	31.6%

All the analytical results show that the crystals obtained from petroleum ether are very close to analytical date for Vanillin. Color tests are the same for both substances, melting point is somewhat lower, and combustion analysis, which should be repeated, is very close to that of Vanillin. Another evidence, which has some interest, is the fact that syrups from which the flavor was removed by extraction, after addition of a certain amount of artificial vanillin had very much the same taste as the original syrup.

Chloroform extract left after sodium bisulphite extraction was shaken three times with 25 cc. dilute ammonia. After separation, the ammonia extract was poured into 50 cc. dilute 0.36 N. sulphuric acid, and shaken with chloroform. The total quantity of this extract was 0.0622 gm. The residue was reddish-yellow, resinous and had an agreeable odor. No crystallization could be induced. A microchemical combustion was performed. The duplicates agreed well and showed: carbon 66.6 per cent, hydrogen 7.4 per cent, nitrogen 0.0 per cent, oxygen (by difference) 26.0 per cent. This corresponds to $C_{10}H_{14}O_3$ formula.

The chloroform extract left after extraction with sodium bisulphite and dilute ammonia was carefully evaporated and weighed. The amount of the substance was very large in comparison with the other protions and was 0.6598 gm. Nelson, in his analysis, obtained but little of this final residue. This residue was dark brown resin and had a very faint maple-like odor. It was **insoluble in** water, slightly soluble in ether and very easily in alcohol and chloroform. It readily dissolved in hot 10 per cent potassium hydroxide alcoholic solution to a brown liquid, which gave a yellow precipitate with dilute sulphuric and hydrochloric acids, calcium chloride and lead acetate. Microcombustion analysis showed the following results: H = 5.02 per cent, C = 47.48 per cent, O = 47.40 per cent, N = 0.1 per cent? (or $C_8H_{10}O_6$).

Various observers have applied to resins the methods which have been found so valuable in the examination of fatty and essential oils (1). The acid, saponification and ester numbers were obtained on this residue in the usual way. The results are: Saponification Number 433.5, Acid Number 58.7, Ester Number 347.8.

It appears that the saponification number is very high and must correspond to an acid with comparatively low molecular weight. These acids (or this acid) are for the most part in the form of esters, as acid number is only 58.7.

About 0.2 gm. of the resin was saponified with dilute potash and then acidified with dilute sulphuric acid. A colloidal voluminous precipitate resulted. This colloidal precipitate was collected on a filter, carefully washed with cold water and dried. The dry precipitate was then dissolved in absolute alcohol; a little undissolved material was left. The solution was filtered. The alcohol extract was evaporated to dryness and the residue was boiled out several times with benzene. About half was soluble in benzene. After the benzene was carefully evaporated, an amorphous brownish-yellow resinous mass appeared, which had no odor. The benzene solution of this precipitate, after being shaken with concentrated H_2SO_4, gave an orange-brownish color in the acid layer and light violet pink color in the benzane layer. Fehling's solution was not reduced by this resin. Microanalysis of this substance showed the following result: H = 8.34, C = 66.87, O = 24.79, N = trace: (or $C_{15}H_{22}O_4$).

Different constituents of the chloroform extract of maple syrup show the following proportions, as far as success was obtained in separating them.

1. Sodium bisulphite extract.		
a. Soluble in petroleum ether	0.0133 gm.	1.4%
b. Insoluble in petroleum ether	0.0353 "	3.6"
2. Ammonium extract	0.0622 "	6.4"
3. Resin	0.6598 "	67.7"
4. Unknown parts (by difference)	0.2044 "	20.9"
Total	0.9750 "	100.0%

General Summary

1. Sodium cobaltinitrite, ferric sulphate and basic ferric sulphate were tried in an effort to devise color standards more permanent than caramel solutions. Ferric sulphate and Monsel's salt,with and without sulphuric acid, gave the best results, covering the range of Bryan's numbers from 0 to 18. A spectrophotometric analysis of these solutions showed, however, that their colors corresponded less closely to that of maple syrup than did those of caramel solutions.

2. Experiments on the decolorization of dark colored syrup by different decolorizing agents and their influence on color, flavor, and analytical values were performed.

A method for preparation of syrups of the same solids content is described. By this method the variation between different syrups is only 1 per cent (65-66) as compared with the variation of solids up to 10 per cent in syrups prepared by the standard A.O.A.C. method. This method is based on the Abbe Refractometer.

Lloyd's Reagent, Norit, Darco, Esbit and Carboraffin were tested.

Carboraffin was found the most powerful decolorizer, the next most powerful being Esbit and Darco. Lloyd's Reagent was found not to remove the color at all.

The analytical values are not materially changed by applications of decolorizing agents.

Carboraffin and Esbit give the most favorable ratio flavor/color. In other words, color is more readily removed by these carbons than flavor.

The results show that poor, dark maple syrups can be decolorized without being altered in their analytical values on which are based the determinations of the genuineness of maple products. The decolorized maple syrup, mildly flavored, can be used as such, or, in admixture with strong flavored maple syrups which are too dark in color, and a product uniform in color and flavor could be obtained throughout the season and from season to season.

3. A process for the production of a non-hardening and non-mottling maple sugar, which gives satisfactory results on the laboratory scale, is described. Non-mottling and non-hardening sugar can be prepared by two modifications (hot stirring and cold stirring) of the same process. Sugar cakes prepared by these methods are much lighter in color, do not mottle at all, but harden to some extent after the first or second month, but still remain easily friable.

4. Analytical values concerning maple products for detection of adulteration were studied. The results obtained show that:

a. Lead values are higher when the precipitate is washed with cold water.

b. The three cold water modifications vary in their lead values. The syrups, which have the lowest standard Canadian lead values, with smaller amounts of reagent, give higher results, but the syrups with higher Canadian lead values show that this difference gradually disappears and finally the highest values are obtained with 2.0 cc. of lead reagent.

c. Mean variation between the duplicates is smaller when the precipitate is washed with cold water. The smallest mean variation is obtained when 1.0 cc. of lead reagent is used.

d. The smallest range between maximum and minimum is obtained with 1.0 cc. of the reagent.

e. Ratio $\frac{\text{Max-Min}}{\text{Min}}$ is the smallest with 1.0 cc. of lead reagent.

f. There is no material difference in conductivity values if the reading is taken from the syrups diluted to 22 per cent or 25 per cent solids, although they are somewhat higher in 25 per cent solutions.

The results justify the proposal of the following variations for Canadian lead number and conductivity value.

a. 25 per cent solution should be used for both methods.

b. 1.0 cc. of reagent and cold water washing should be used for Canadian lead number method.

5. Studies on maple flavor, its development, isolation and identification are described.

Maple syrups were prepared by three different methods.

1. Ordinary atmospheric pressure boiling in an open pan.
2. Reduced pressure boiling in pyrex flasks. The boiling point of syrup was below 52°C.
3. By freezing out the water.

The syrup obtained by freezing had not the true maple flavor, but one resembling that of watermelon.

The syrup obtained by vacuum evaporation had no flavor or a weak one, but when reboiled under ordinary pressure changed its flavor to one more closely resembling that of ordinary maple syrup.

Ether and chloroform were found to give the highest extract from maple syrup and that extract had an odor resembling that of maple.

Chloroform extract contained the same three fractions as were obtained in Nelson's work with ether.

First fraction was obtained by shaking the chloroform extract with sodium bisulphite solution, acidifying, and again extracting with chloroform. From this fraction crystalline substance resembling in properties vanillin was obtained. Second fraction was obtained by shaking remaining chloroform extract with dilute ammonia. Reddish-yellow, resinous non-crystalline substance was obtained. Fraction three, which was obtained by evaporating to dryness the chloroform extract after removing the first two fractions, was a dark brown resin, insoluble in water, easily soluble in hot 10 per cent aqueous KOH. It was found to have a saponification value of 433 and an ester value of 59. Elementary analysis was performed on all substances but none of the substances isolated were identified, and the flavor of maple syrup still remains a mystery.

In conclusion I wish to extent my hearty thanks to Dr. J. F. Snell for his helpful suggestions and to Dr. H. Hibbert and Dr. G. S. Whitby for permission to use their microanalytical equipments.

Bibliography

1. Allen, Alfred H., "Commercial Organic Analysis", pages 107-110, 1907.
2. Balch, R.T., Ind. Eng. Chem., 22, 255, 1930.
3. Beilstein, Dr.F., "Handbuch der Organischen Chemie", VIII Band, page 254, 1925.
4. Blowski, A.A., and Bon, G.H., Ind. Eng. Chem. 18, 1 pages 32-42, 1926.
5. Bradley, A.B., J. Soc. Chem. Ind., V. 38, 22, pages 396-98, 1919.
6. Bryan, A.H., Bur. Chem., U.S.Dept. Agr. Bull. 13, 1910.
7. Chamot, Emil M., "Elementary Chemical Microscopy", New York, 1915.
8. Fowler, D.E., and Snell, J.F., Ind. Eng. Chem., Anal. Edn., 1, 8, 1929.
9. Mitchell, C.R., Unpresented thesis, "The Mottling of Maple Sugar". Macdonald College, 1926-27.
10. Nelson, E.K., J. Am. Chem. Soc., 50, 2009-12, 1928.
11. Official and Tentative Methods of Analysis of the A.O.A.C., Second Edn., pages 202-205, 1924.
12. Pregl, F., "Quantitative Organic Microanalysis". Translated by Ernest Fyleman, 1924.
13. Robison, S.C., "The Isolation and Identification of the Flavoring Principle in Maple Syrup". M.Sc. Thesis, McGill University, 1923-24.

14. Sale and Wilson, U.S. Pat. 1,642.789, 1927.

15. Snell, J.F., Trans. Roy. Soc. Can., III, 165, 1913.

16. " " Jour. Ind. Eng. Chem., 8., 331, 1916.

17. " " and Van Zoeren, G.J., Ind. Eng. Chem. 8, 421, 1916.

18. " " Trans. Roy. Soc. Can. III, 225, 228-31, 1919.

19. " " Collaborative work of A.O.A.C., 1929.

20. Sy., Albert S., Ph.D., "History, Manufacture and Analysis of Maple Products, 1908.

21. Thorpe, J.F., and Whiteley, M.A., "A Student's Manual or Organic Chemical Analysis, 1925.

22. Van Zoeren, G.J., Unpublished work done at Macdonald College in 1916.

23. Vytopil, Ing Zd, Z. Zuckerind. Cechoslovak. Rep., pp. 511-514, 1926-27.