THE TESTING OF MOLASSES.

A Comparative Survey of the Methods of Analysis used in the Sugar Industry.

by

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Am. Chem. J.	American Chemical Journal.
A.H.S.T.	Association of Hawaiian Sugar Technologists' Methods.
Ann.	Annalen der Chemie (Liebig's).
A.O.A.C.	American Official Agricultural Chemists.
Archief.	Archief voor de Java Suiker Industrie.
Bull. U.S. Bureau.	Bulletin of the United States Bureau of Chemistry.
F. a. S.	Facts about Sugar. (N.York).

Author.	Title.
H.S.P.A.	Hawaiian Sugar Planters' Association Publication.
I. S. J.	International Sugar Journal.
J. Am. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. & Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J.S.C.I.	Journal of the Society of Chemical Industry.
Z. angew. Chem.	Zeitschrift fur Angewandte Chemie.
Z. ver Deut. Zuck.	Zeitschrift des vereins der Deutcher Zuckerindustrie.

NOTE: Throughout this work, please read A.H.S.T. (Association of Hawaiian Sugar Technologists) instead of H.S.P.A. (Hawaiian Sugar Planters' Association).

GLOSSARY.

Ash.	The residual mineral matter, after incinerating the sugar, molasses or syrup.
Brix.	The percentage of solids present in solutions of sugars, as found by using the Brix spindle. This spindle or hydrometer is calibrated in solutions of pure sucrose and in this case reads directly the percentage of sucrose when floated in the solution. The term "Brix." is used in the sugar industry for "per cent. solids".
Curing.	The separation of sugar crystals from the mother liquor by centrifuging.
D.S.	Dry substance. - the residue after drying.
Purity.	The relation between the sucrose and the total solids or D.S. present in impure sugar juices or syrups. $\frac{\text{Sucrose}}{\text{D.S.}} \times 100 = \text{Purity.}$
Purging.	Synonymous with Curing.
Reducing Sugars.	Mixtures of dextrose and levulose in any proportions: usually calculated, and referred to, as Invert Sugar.

Refractometer Brix.	Per cent. solids found by taking the refractive index of the sugar product and by reference to appropriate tables converting to per cent. sugar.

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INTRODUCTION

Molasses is a by-product of Sugar Factories and Refineries. In some sugar-producing countries where its disposal is a matter of great difficulty, it is literally a waste product. Where distilleries, however, are in close proximity to the factory, or where facilities for cheap transport to manufacturing centres are available, it is a material of considerable value. Molasses is the main source of industrial alcohol, and it is also used extensively in the preparation of cattle foods.

The weight of molasses obtained as a result of the manufacture of sugar from cane is about 24 per cent. of that of the sugar produced: in beet sugar manufacture, the corresponding quantity is about 20 per cent.

On the basis of a world production in 1934 of 16 million tons of cane sugar and about 9 million tons of beet sugar, the total quantity of molasses available for industrial purposes is in the region of 5½ million tons per annum.

The molasses represents a loss of sucrose sustained in concentrating the juice, whether it be cane or beet, to the finished crystalline product, and therefore it is essential in order to draw up the factory balance sheet, or "Sucrose Recovery and Loss Account", to know the exact amounts present of certain of its constituents. If the molasses is to be sold, or purchased, for manufacturing purposes at a price based on analytical tests, these tests become of paramount importance.

No standard methods for the analysis of molasses have been universally adopted as yet. The determination of the water content in particular, is a problem that remains unsolved.

At the 1933 Conference of the International Commission for Uniform Methods of Sugar Analysis, Molasses was one of the subjects under discussion, and the Testing of Molasses is to be on the Agenda as subject Number 10 at the next International Meeting to be held in London in August 1936.

The author has been interested in this question for some considerable time, and it is hoped that his investigations will assist the deliberations of the Commission, of whose British National Committee he is a member.

The term Molasses as used in this work refers to "Exhausted" or "Final" Molasses, which may be described in general terms as the effluent from the centrifugal machines during the purging of the lowest grade sugars produced in the factory.

In the cane sugar factory and in the refinery, it is the mother liquor of the final crystallization, from which no further quantity of sugar can be obtained by re-boiling. It is an extremely viscous material, almost black in colour, having a specific gravity of about 1.4.

Geerligs (Cane Sugar and its Manufacture, 1920) defines Cane Molasses as follows:- "Ideal cane molasses is a hydrated combination between sugar and salts, which cannot be broken up by dissociation when in a concentrated state, and therefore cannot yield sucrose in a crystallized form."

Van den Linden (Archief, 1916) considered the material from the phase rule aspect. He had observed that in the presence of invert sugar, less sucrose was dissolved by a definite quantity of water than was the case when no invert sugar was present. He concluded therefore that "ideal (cane) molasses is a saturated solution of sucrose in which the solubility of the sucrose is influenced by the presence of invert sugar and of certain non-sugars."

Helderman (Archief, 1921) confirms this view.

In "Cane Sugar Handbook, 1929" Spencer gives the following detailed analysis of a Louisiana cane molasses.

	Per Cent.		Per Cent.
Water	20.00		20.00
Ash	8.00	Silica, SiO_2	0.50
		Potash, K_2O	3.50
		Lime, CaO	1.50
		Magnesia, MgO	0.10
		Phosphoric Acid, P_2O_5	0.20
		Sulphuric Acid. SO_3	1.60
		Chlorine, Cl	0.40
		Soda, iron, etc., Na_2O, Fe_2O_3 etc	0.20
Sugars	62.00	Sucrose	32.00
		Dextrose	14.00
		Levulose	16.00
Nitrogenous bodies (Total N 0.5per cent)	3.00	Albuminoids	0.30
		Amids (as asparagin)	0.30
		Amido Acids (as aspartic)	1.70
		Nitric Acid	0.15
		Ammonia	0.02
		Xanthin bodies	0.30
		Other nitrogenous bodies	0.23
Soluble gums	2.00	(Xylan, Araban, Pectin. etc)	2.00
Free acids	2.00	Melassinic, Glutinic, Saccharinic acids, etc	5.00
Combined acids	3.00		
Total	100.00		100.00

Obviously an elaborate analysis such as the above would be beyond the scope of any industrial sugar laboratory, and from the point of view of both the manufacturer and the purchaser provides a great deal of information which might be of no practical value. Only the following items are of commercial interest:- Water, Sucrose, Polarization, Reducing Sugars and Ash. These constituents vary considerably, according to the locus of production and the method of clarification adopted in respect of the cane juice extracted by the milling plant.

Geerligs ("Cane Sugar") makes the following general statement as regards the composition of molasses:- "The total amount of sugars i.e. sucrose, dextrose and levulose is about 55 per cent., the relative proportions depending on the ratio of reducing sugars to ash; water is about 20 per cent. and ash about 9 per cent." The reducing sugars vary between such wide limits as 12 and 30 per cent.

The water content depends largely on the amount of water used in washing the crystals during "curing"; the reducing sugars depend on the original purity of the cane juice and of the amount of inversion taking place during the manufacturing operations, while the ash is derived from the clarifying agents and from saline materials which are originally present in the juice but which have not been removed during clarification because they form soluble salts as a result of the action of the clarifying agents.

Deerr (Cane Sugar,1920) gives these limits for the constituents of cane molasses.

	Per Cent.
Water	15-25
Sucrose	25-40
Reducing sugars	5-30
Ash	7-15
Gums	3- 5
Organic Non sugars	10-20.

Beet Molasses differs considerably from cane molasses both in its composition and in the fact that it is not "Exhausted" in respect of its content of crystallizable sucrose. Further crystals of sugar may still be obtained from it by chemical methods, or by dilution followed by dialysis and re-concentration. The sucrose content is high, generally about 50 per cent.; reducing sugars are present only in traces, while the saline contents are higher than in cane molasses. The absence of reducing sugars is significant, and this is one of the reasons why beet molasses presents a somewhat different analytical problem.

The following is a detailed analysis of a typical beet Molasses:- ("Sugar" Montgomery, 1927)

Sucrose	46.50
Reducing sugars	0.03
Water	20.34
Other organic matter	19.56
Mineral Ash	13.57
	100.00

SiO_2	0.074
$Fe_2O_3\ Al_2O_3$	0.080
$CaCO_3$	0.103
$CaSO_4$	0.141
$MgCO_3$	0.081
$MgSO_4$	0.116
Na_2CO_3	2.839
KCl	3.609
K_2PO_4	0.139
K_2SO_4	1.533
K_2SO_3	4.864
	13.579

A material of such complexity and such variability in composition as molasses, containing as it does substances which readily undergo decomposition, is bound to present serious difficulties in analysis. The necessity for standardizing the methods of testing has long been recognized and the various Sugar Technologists' Associations throughout the world have recommended certain methods which unfortunately have not yet been universally adopted.

In the cane sugar industry, the methods of analysis recommended by the Association of American Official Agricultural Chemists, the Hawaiian Sugar Planters' Association, the Cuban manufacturers and the Java Experimental Station are standard for their respective countries and they differ only slightly in detail. The chief methods in use are examined in this work and compared. The materials used were molasses from cane sugar factories in British West Indies, Cuba, Egypt, Hawaii, , Java, Natal, etc., and from beet sugar factories and refineries in this country.

The examination of molasses for commercial purposes is effected under these headings:-

1. Water, or conversely Total Dry Matter i.e.(100-water per cent.).
2. Sucrose
3. Reducing sugars, calculated as Invert.
4. Ash.

The methods of estimation of items 1, 3 and 4 are studied in this work. The determination of the sucrose content already has been exhaustively treated by a large number of workers in all parts of the world.

PART I.

PART I.

Estimation of Water.

The usual industrial methods are:-

1. Brix hydrometer, after dilution.
2. Drying on sand, or on pumice, in steam oven.
3. " " " " vacuum oven.
4. Distillation with immiscible liquids.
5. Refractometer.

No. 1 is a factory method, useful for routine work, but of doubtful value otherwise. Since the Brix spindle is graduated in degrees sugar, and is calibrated in solutions of pure sucrose, its accuracy depends on the absence of soluble constituents other than sucrose from the solution under examination. Impurities are present in considerable amounts in the molasses and as their specific gravities differ from that of sucrose, the error from this source is appreciable. Moreover, the high viscosity of molasses prevents the use of the spindle unless the molasses is suitably diluted. Contraction in volume resultant upon dilution causes a serious error which is multiplied, as shewn in the following table:-

Sample examined : Table Treacle.

Concentration	Degrees Brix	Degrees Brix calculated back to undiluted material
50 per cent.	43.2	86.4
25 " "	22.8	91.2
12.5" "	12.1	96.8
6.25" "	6.1	97.6

This method is at best an approximation, and while it is rapid and gives a speedy indication of water content sufficiently reliable for factory purposes, it is of little use from the analytical point of view.

Methods Nos. 2 and 3 are in general use. The samples are prepared in the same way for both steam and vacuum ovens. In order to present the largest possible drying surface, either broken pumice or fine sand is used. The former is seldom found in commercial sugar laboratories especially in tropical factories, and a pure sand which is generally readily obtainable provides a more suitable material, which is more easily manipulated.

The standard methods for drying on sand are given below:-

Drying on Quartz Sand.

A.O.A.C. Official Method for Molasses.

The sand should pass 40 mesh but be retained on 60 mesh. It is digested with H Cl, washed acid free, dried, ignited and stored in a stoppered bottle.

25-30 gms. of sand are placed in a dish about 40mm. in depth x 55mm. in diameter and dried in the steam bath, together with a short glass rod; after being cooled in a desiccator, the covered dish is weighed quickly. Then sufficient of the diluted sample * to yield 1 gm. dry matter is added and mixed thoroughly with the sand. The dish is heated on the sand bath for 15-20 minutes, the molasses being stirred at 2-minute intervals until it becomes too stiff.

It is then dried at 70°C under a vacuum of not less than 60 cm. Trial weighings are made at 2-hour-intervals towards the end of the drying period, until change in weight does not exceed 2 mgms.

For materials containing no levulose or other readily decomposible substance, the drying is done at the temperature of boiling water in 8-10 hours. The dish is covered in desiccator and weighed. The heating and weighing are repeated until the loss per hour does not exceed 2 mgms.

Loss of weight is reported as moisture.

* "The diluted material shall contain 20-30 per cent. solid matter".

H.S.P.A. Method. "Total solids are determined by drying, preferably in a vacuum oven at 100° C. If a vacuum oven is not available the samples may be dried in an air bath at 100° to 105° C.

Treat clean silica sand or coarsely ground pumice with hydrochloric acid, wash with distilled water and dry. Place 15 grams of sand or half this weight of pumice with a short piece of glass rod in a 7 c.m. covered aluminium drying dish. Dry at 150° C. and cool in a desiccator. Weigh the covered dish, add approximately 10 grams of juice or 2 to 3 grams of molasses, replace cover and weigh. Mix the sample thoroughly with the sand or pumice using 1 or 2 ml. of hot water if necessary. Dry until the mixture is in a friable condition, stir with the glass rod so that the maximum drying surface is exposed, dry for 5 hours, replace the cover, cool in a desiccator and weigh. Temperature and drying time have been specified rather than drying to constant weight because samples continue to lose weight on prolonged heating due to the destruction of organic matter at high temperatures."

Drying upon Quartz Sand. (Bull.107, U.S. Bureau of Chem.,p.64).

"In a flat-bottom dish place 6 to 7 gms. of pure quartz sand and a short stirring rod. Dry thoroughly, cool in a desiccator, and weigh. Then add 3 or 4 gms. of the molasses, mix with the sand, and dry at the temperature of boiling water for from 8 to 10 hours. Stir at intervals of an hour, then cool in a desiccator, and weigh. Stir, heat again in the water oven for an hour, cool, and weigh. Repeat heating and weighing until loss of water in one hour is not greater than 3 mgs.

"Before using, digest the pure quartz sand with strong hydrochloric acid, wash, dry, ignite, and keep in a stoppered bottle".

"In order to prevent the occlusion or retention of water in the dried residue, an hour of drying at 105° to 110°C. is advisable as under the determination of moisture in sugar."

All these methods are open to criticism.

In the A.O.A.C. method the end of the drying period is mentioned, yet this period is not defined. Additional 2-hour-intervals to this period, whatever it might be, might extend the duration of the estimation beyond the normal working day in any ordinary laboratory. The 8-10 hour period for the steam oven method plus hourly reheatings and re-weighings also is impracticable, and as will be seen later does not lead to the desired constancy of weight.

The H.S.P.A. at least fixes a time well within the limits of the usual "shift", but vacuum at 100° C and air bath at 100-105° C give totally different results. Weighing the molasses into the dish is not to be recommended. It should be added from the weighing bottle and the weight found by difference.

U. S. Bureau method. Mixing viscous molasses of 80-85° Bx. with sand is an extremely diff~~erent~~icult matter: even warming it does not make it sufficiently fluid for mixing. It must be diluted and as will be seen later this dilution does not prolong the duration of drying.

The same objection holds here as in the A.O.A.C. method as regards the duration of the drying.

The advice to stir at hourly intervals cannot be carried out as the molasses soon sets as solid as concrete.

The methods adopted by the author were as follows:-

Steam oven. The sand was prepared according to the foregoing directions; about 10 gms. were used each time and spread over the bottom of the dish of about 60mm. diam. The molasses sample was kept in a weighing bottle with ground stopper fitting on the outside. A small spoon for removing the desired quantity was kept within the bottle. The material being extremely hygroscopic, the weight of it taken for each estimation was found by difference after removal of the necessary amount from the weighing bottle. The drying dishes containing the 10 gms. of sand were weighed covered, together with a small glass rod, and after the sample had been added, 2-3 cc. water were used to dilute it to enable it to be thoroughly mixed with the sand. The dish was then placed in the steam bath and dried for stated periods.

When the vacuum oven method was used the sample was prepared in the same way. The oven was of the ordinary type, but a tiny hole was pierced in the door, so that a current of air could be drawn through during the drying. It was considered unnecessary to go to the elaborate precaution of drying this current of air as has been recommended by some sugar chemists. The vacuum was maintained by a dry air pump. The difficulty of keeping the temperature of the oven constant at 70° C was finally overcome by fixing an electric element to the bottom of the oven jacket, and controlling the temperature by means of a sliding resistance. When water was used in the jacket, this was a simple matter. During drying, it was imperative that the vacuum was kept a little below 45 cm. for the first hour, otherwise violent spurting occurred which ruined the experiment. After one hour's heating, the vacuum was increased to 60 cm. at which it was maintained for the remainder of the drying period.

It might be mentioned here that the choice of drying dishes was a somewhat difficult matter. After many tests a tin with a close fitting cover, in which a certain brand of tobacco is marketed, was eventually selected. This was cleaned up and tested by half filling with water, covering and shaking. If no drops of water were shaken out, the tin was accepted as tight. It was proved later, however, that this supposed tightness was insufficient. Actually moisture was absorbed by the extremely hygroscopic dried molasses in the covered tin while it was being weighed, and even while it was in the desiccator. Subsequently a squat glass weighing bottle with ground glass stopper was used. This will be referred to later.

Before the drying of the molasses was begun, it was considered expedient to obtain some definite information as to which of the sugars present in molasses was most liable to decomposition under the conditions employed. Tests were therefore made on solutions of pure sucrose, dextrose and levulose.

The solutions were made by weighing the sugar into a dropping bottle with ground teat-stopper, and by adding the water thereto. The solution was withdrawn by means of the teat dropper, and dropped on to the sand in the previously weighed dish. The weight of liquid thus taken was found from the difference in the weight of dropping bottle. The dish was dried for the specified times in the oven, covered and cooled in the desiccator for thirty minutes and weighed as rapidly as possible.

The results of these tests are as follows:-

Table No. I

Solution of Sucrose

Method. **Steam Oven** **19.99 per cent. Sucrose**

No. of hours heating.		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken =	3.2152	gms.	3.4933	gms.		
	Wt. of dish + sand	=59.5350	gms.	61.7548	gms.		
4.	: : : + D.S.	=60.1800	:	62.4569	:	20.06	20.09
5.	: : : :	=	:		:		
6.	: : : :	=60.1758	:	62.4520	:	19.93	19.96
7.	: : : :	=	:		:		
8.	: : : :	=60.1758	:	62.4520	:	19.93	19.96
9.	: : : :	=	:		:		
10.	: : : :	=	:		:	**Mean.**	**19.95**
11.	: : : :	=	:		:		
12.	: : : :	=	:		:		
13.	: : : :	=	:		:		
14.	: : : :	=	:		:		
15.	: : : :	=	:		:		

Drying complete in 6 hours.

Table No. **II**

Solution of Sucrose

Method. **Vacuum oven** **19.99 per cent. Sucrose**

No. of hours heating.	Wt. of **Solution** taken	I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken	= **3.8696**	gms.	**3.6892**	gms.		
	Wt. of dish + sand	=**57.4440**	gms.	**58.8209**	gms.		
4.	: : : + D.S.	=**58.2325**	:	**59.5735**	:	**20.40**	**20.40**
5.	: : : :	=	:		:		
6.	: : : :	=**58.2277**	:	**59.5680**	:	**20.25**	**20.25**
7.	: : : :	=	:		:		
8.	: : : :	=**58.2260**	:	**59.5678**	:	**20.21**	**20.22**
9.	: : : :	=	:		:		
10.	: : : :	=**58.2237**	:	**59.5655**	:	**20.15**	**20.18**
11.	: : : :	=	:		:		
12.	: : : :	=**58.2244**	:	**59.5657**	:	**20.15**	**20.18**
13.	: : : :	=	:		:		
14.	: : : :	=	:		:	**Mean**	**20.16**
15.	: : : :	=	:		:		

Drying complete in 10 hours.

Table No. III.

Solution of Dextrose.

Method. **Steam Oven.** **16.66 per cent. dextrose.**

No. of hours heating.	Wt. of **Solution** taken =	I. **4.9306** gms.	II. **4.5457** gms.	Percentage Dry Substance. I	II.
	Wt. of dish + sand =	**60.5495** gms.	**60.1774** gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	:	:		
6.	: : : : =	**61.3680** :	**60.9314** :	**16.60**	**16.59**
7.	: : : : =	:	:		
8.	: : : : =	**61.3668** :	**60.9332** :	**16.57**	**16.63**
9.	: : : : =	:	:		
10.	: : : : =	**61.3647** :	**60.9300** :	**16.53**	**16.56**
11.	: : : : =	:	:		
12.	: : : : =	**61.3650** :	**60.9315** :	**16.55**	**16.59**
13.	: : : : =	:	:		
14.	: : : : =	**61.3700** :	**60.9321** :	**16.64**	**16.60**
15.	: : : : =	:	:		
18.	: : : :	**61.3675** :	**60.9260** :	**16.59**	**16.47**

Drying complete in 6 hours.

Table No. IV.

Solution of Dextrose

Method. **Vacuum Oven.** **16.66 per cent. Dextrose.**

No. of hours heating.	Wt. of **Solution** taken	I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken	= 4.2220	gms.	3.8487	gms.		
	Wt. of dish + sand	=60.4522	gms.	60.1165	gms.		
4.	: : : + D.S.	=61.1525	:	60.7565	:	16.63	16.59
5.	: : : :	=	:		:		
6.	: : : :	= 61.1534	:	60.7528	:	16.53	16.61
7.	: : : :	=	:		:		
8.	: : : :	= 61.1530	:	60.7528	:	16.53	16.61
9.	: : : :	=	:		:		
10.	: : : :	=	:		:		
11.	: : : :	=	:		:		
12.	: : : :	=	:		:		
13.	: : : :	≠	:		:		
14.	: : : :	=	:		:		
15.	: : : :	=	:		:		

Drying complete in 4-6 hours.

Table No. V

Solution of Levulose.

Method. **Steam Oven.** **19.74 per Cent. Levulose.**

No. of hours heating.		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken =	3.4873	gms.	3.2747	gms.		
	Wt. of dish + sand	=60.4696	gms.	60.3949	gms.		
4.	: : : + D.S.	=61.1543	:	61.0318	:	19.63	19.45
5.	: : : :	=	:		:		
6.	: : : :	=61.1468	:	61.0286	:	19.42	19.35
7.	: : : :	=	:		:		
8.	: : : :	=61.1328	:	61.0132	:	19.02	18.88
9.	: : : :	=	:		:		
10.	: : : :	=61.1232	:	61.0098	:	18.74	18.78
11.	: : : :	=	:		:		
12.	: : : :	=61.1170	:	60.9977	:	18.56	18.41
13.	: : : :	∓	:		:		
14.	: : : :	=61.1080	:	60.9935	:	18.31	18.28
15.	: : : :	=	:		:		
17.	: : : :	-61.1061	:	60.9925	:	18.25	18.25
23.	: : : :	-61.0930	:	60.9794	:	17.88	17.84

Note progressive decomposition

Table No. **VI.**

Solution of Levulose

Method. **Vacuum Oven.** **19.74 per cent. Levulose.**

No. of hours heating.			I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken	=	3.0931	gms.	3.2083	gms.		
	Wt. of dish + sand	=	58.6827	gms.	61.3326	gms.		
4.	: : : + D.S.	=	59.2947	:	61.9658	:	19.78	19.73
5.	: : : :	=		:		:		
6.	: : : :	=	59.2947	:	61.9658	:	19.78	19.73
7.	: : : :	=		:		:		
8.	: : : :	=	59.2945	:	61.9658	:	19.78	19.73
9.	: : : :	=		:		:		
10.	: : : :	=		:		:		
11.	: : : :	=		:		:		
12.	: : : :	=		:		:		
13.	: : : :	=		:		:		
14.	: : : :	=		:		:		
15.	: : : :	=		:		:		

Constant weight attained in 4 hours; no decomposition on further heating.

Table No. **VII.**

Solution of Levulose.

Method. **Vacuum Oven.** **59.13 per cent. Levulose.**

No. of hours heating.		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken =	3.0068	gms.	3.0240	gms.		
	Wt. of dish + sand =	61.6405	gms.	63.7392	gms.		
4.	: : : + D.S. =	63.4384	:	65.5500	:	59.79	59.88
5.	: : : : =		:		:		
6.	: : : : =	63.4302	:	65.5402	:	59.52	59.55
7.	: : : : =		:		:		
8.	: : : : =	63.4300	:	65.5389	:	59.50	59.51
9.	: : : : =		:		:		
10.	: : : : =		:		:		
11.	: : : : =		:		:		
12.	: : : : =		:		:		
13.	: : : : =		:		:		
14.	: : : : =		:		:		
15.	: : : : =		:		:		

6-8 hours necessary for complete drying at this concentration.

Table No. **VIII.**

Solution of Levulose.

Method. **Steam Oven.** **59.13 per cent. Levulose.**

No. of hours heating.		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Solution** taken =	**2.7774** gms.		**2.8282**	gms.		
	Wt. of dish + sand =	**60.4115** gms.		**63.0992**	gms.		
4. **3.**	: : : + D.S. =	**62.0472**	:	**64.7536**	:	**58.89**	**58.50**
5. **4¼.**	: : : : =	**62.0320**	:	**64.7337**	:	**58.35**	**57.80**
6. **6¼.**	: : : : =	**62.0090**	:	**64.7127**	:	**57.52**	**57.05**
7.	: : : : =		:		:		
8.	: : : : =		:		:		
9.	: : : : =		:		:		
10.	: : : : =		:		:		
11.	: : : : =		:		:		
12.	: : : : =		:		:		
13.	: : : : ǂ		:		:		
14.	: : : : =		:		:		
15.	: : : : =		:		:		

Decomposition evident even after 3 hours heating.

Table No. **IX.**

Mixture of Dextrose and Levulose in Aq.Solution.

Method. **Steam Oven** **19.91 per cent. dry substance.**

No. of hours heating.	Wt. of **Solution** taken =	I. 2.9869 gms.	II. 2.9994 gms.	Percentage Dry Substance. I	II.
	Wt. of dish + sand	=59.5570 gms.	60.1419 gms.		
4.	: : : + D.S.	=60.1395 :	60.7332 :	19.84	19.72
5.	: : : :	= :	:		
6.	: : : :	=60.1350 :	60.7310 :	19.35	19.64
7.	: : : :	= :	:		
8.	: : : :	=60.1316 :	60.7292 :	19.24	19.58
9.	: : : :	= :	:		
10.	: : : :	=60.1280 :	60.7243 :	19.08	19.42
11.	: : : :	= :	:		
12.	: : : :	=60.1211 :	60.7193 :	18.89	19.25
13.	: : : :	= :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Decomposition appears to take place in less than 4 hours heating.

Table No. **X.**

Mixture of Dextrose and Levulose in Aq.Solution.

Method. **Vacuum Oven.** **19.91 per cent dry substance**

No. of hours heating.		I.	II.	Percentage Dry Substance. I	Percentage Dry Substance. II.
	Wt. of **Solution** taken	= **3.0445** gms.	gms.		
	Wt. of dish + sand	= **42.9150** gms.	gms.		
4.	: : : + D.S.	= **43.5222** :	:	**19.94**	
5.	: : : :	= :	:		
6.	: : : :	= **43.5222** :	:	**19.94**	
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	= :	:		
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	∓ :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Constant attained weight in 4 hours.

From the foregoing tables it will be noted that with sucrose solutions constant weight is obtained in 6 hours in the steam oven and in 8-10 hours in vacuo. No decomposition on continued heating was observed. In the case of dextrose, drying by steam appears to be complete in 6-8 hours, but possibly some slight decomposition occurs on further heating. Irregularity in the weighings is noticeable and this is a common experience when moisture in solutions of dextrose is being estimated. In the vacuum oven, however, drying is complete in 4-6 hours. This confirms the view of Rice (J.I.E.C. 1933) that the water of crystallization of dextrose is driven off under vacuum at 70°C.

With regard to levulose in the steam oven, a result is obtained in 4 hours which might indicate that drying is complete within that period, but further heating produces decomposition which is progressive during the whole period of treatment. In the vacuum oven, constant weight is obtained in 4 hours, and no decomposition occurs on continued heating. Browne (Handbook, 1912) reports similarly on the drying of solutions of honey in vacuo.

The mixture of solutions of dextrose and levulose dried completely in vacuo in 4 hours.

It would appear from this, that the destruction of levulose is the cause of the high results for water when syrups containing it are dried by steam at ordinary pressure.

Spencer (Handbook, 1929) makes a definite statement to this effect.

The important fact emerging from these preliminary investigations is that vacuum drying is effective with the three sugars commonly found in molasses, and that the period necessary for complete dehydration is from 4 to 6 hours.

All the tests were made in duplicate so that for each material the conditions were the same. It may be mentioned that in commercial laboratories, duplicate analyses of these materials are not generally made. It requires considerable skill in manipulation and great attention to detail to get corroborative results, despite the apparent simplicity of the operation. (Reference is made later to "personal error"). When results were obtained that were not sufficiently close, the test was repeated in duplicate. All weighings of these preliminary tests are given in detail. It is important to observe the actual difference in the weight of the dish, which indicates better than the calculated percentage, the difficulty of obtaining constancy of weight even within the limits recommended in the standard methods.

Effect of diluting the Molasses on period necessary for drying.

To ascertain if the addition of dilution water to the samples of molasses in order to facilitate mixing with the sand affected the period of drying, tests were made with dry mixed and wet mixed samples as shewn below:-

Refinery Molasses. (Steam oven).

	"Dry" test.		"Wet" test.	
	I.	II.	I.	II.
gms. of molasses taken.	3.8226	5.6984	4.2198	5.1367
Per cent.D.S.after 5 hrs drying.	73.14	73.~~96~~ 69	73.59	73.95
" " " " 9 "	72.85	72.98	73.00	72.98
" " " " 12 "	72.52	72.35	72.77	72.73

Java Cane Molasses.

	"Dry"test.	"Wet" test.
gms. of molasses taken	2.0820	2.4139
Per cent. solids after 4½ hrs.	81.01	81.14
" " " 6 "	80.47	80.47
" " " 9 "	80.00	79.98

The above tests prove conclusively that no prolongation of the drying period is caused by the addition of 2-3 cc.water for the purpose of rendering the molasses more fluid.

The examination of typical samples of molasses was then undertaken. Refinery molasses, cane molasses, golden syrup and beet molasses were examined in detail. The golden syrup was selected as representing an almost pure mixture of sucrose and invert sugars, with a small percentage of ash (about 1 per cent.). The latter constituent was considered to be a factor of some importance. The beet molasses was selected as it contained a mere trace of invert sugar and an appreciable amount of ash. (9-10 per cent.).

Table No.

Golden Syrup.

Method. Steam Oven. Ref: Brix 82.1

No. of hours heating.		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Syrup** taken	= 2.2833	gms.	2.2269	gms.		
	Wt. of dish + sand	=72.6455	gms.	74.4732	gms.		
4.	: : : + D.S.	=	:		:		
5.	: : : :	=74.5435	:	76.3238	:	83.17	83.10
6.	: : : :	=74.5399	:	76.3216	:	82.98	83.00
7.	: : : :	=74.5391	:	76.3203	:	82.97	82.95
8.	: : : :	=74.5349	:	76.3163	:	82.75	82.77
9.	: : : :	=74.5305	:	76.3138	:	82.56	82.65
10.	: : : :	=74.5338	:	76.3142	:	82.70	82.67
11.	: : : :	=74.5298	:	76.3134	:	82.52	82.64
12.	: : : :	=74.5282	:	76.3113	:	82.46	82.54
13.	: : : :	=74.5264	:	76.3100	:	82.38	82.48
~~14.~~	: : : :	=	:		:		
~~15.~~	(After remaining in :desiccator overnight	=74.5329	:	76.3329)	:		
17.	: : : :	-74.5189	:	76.3003	:	82.05	82.05

Glass dishes with ground cover used, both of same size.

Table No.

Golden Syrup.

Method. **Vacuum Oven** Ref: **Brix 82.1**

No. of hours heating.	Wt. of **Syrup** taken	I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Syrup** taken	= **1.9288** gms.	**2.0152** gms.		
	Wt. of dish + sand	=**57.2048** gms.	**43.5528** gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	=**58.8333** :	**45.2662** :	**84.43**	**85.02**
6.	: : : :	=**58.8315** :	**45.2634** :	**84.34**	**84.88**
7.	: : : :	=**58.8296** :	**45.2602** :	**84.24**	**84.72**
8.	: : : :	=**58.8269** :	**45.2567** :	**84.10**	**84.55**
9.	: : : :	=**58.8268** :	**45.2555** :	**84.10**	**84.49**
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	‡ 58.8182 :	**45.2460** :	**83.66**	**84.02**
14.	: : : :	= :	:		
15.	: : : :	= :	:		

No.I Glass dish 60 mm diam. x 35 mm. depth.
" II " " 50 mm " x 30 mm. "

Difference between duplicate tests may be due in some measure to the difference in the size of the drying dishes.

Table No.

Beet Molasses.

Method. **Steam Oven.**

Ref. Brix.

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken =	3.3193gms.	3.1913 gms.		
	Wt. of dish + sand =	61.6356gms.	62.5131 gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	64.4238 :	65.1798 :	84.00	83.56
6.	: : : : =	64.4128 :	65.1723 :	83.69	83.33
7.	: : : : =	64.4027 :	65.1627 :	83.37	83.02
8.	: : : : =	64.3921 :	65.1561 :	83.05	82.81
9.	: : : : =	64.3865 :	65.1518 :	82.88	82.69
10.	: : : : =	64.3815 :	65.1484 :	82.72	82.58
11.	: : : : =	:	:		
12.	: : : : =	:	:		
13.	: : : : =	:	:		
14.	: : : : =	:	:		
15.	: : : : =	:	:		
116.	: : : : -	64.3652 :	65.1321 :	82.24	82.07

Table No.

Beet Molasses.

Method. **Vacuum Oven** **Ref. Brix.**

No. of hours heating.	Wt. of Molasses taken =	I. 3.9884	gms.	II. 4.0205	gms.	Percentage Dry Substance. I	II.
	Wt. of dish + sand	=61.2611	gms.	60.1832	gms.		
4.	: : : + D.S.	=64.7161	:	63.6607	:	86.62	86.49
5.	: : : :	=64.6868	:	63.6341	:	85.88	85.83
6.	: : : :	=64.6669	:	63.6134	:	85.38	85.31
7.	: : : :	=64.6539	:	63.6022	:	85.06	85.04
8.	: : : :	=64.6359	:	63.5867	:	84.87	84.65
9.	: : : :	=64.6346	:	63.5840	:	84.84	84.58
10.	: : : :	=64.6276	:	63.5790	:	84.66	84.46
11.	: : : :	=	:		:		
12.	: : : :	=	:		:		
13.	: : : :	∓	:		:		
14.	: : : :	=	:		:		
15.	: : : :	=64.6120	:	63.5631	:	84.01	84.06
20.	: : : :	-64.5998	:	63.5530	:	83.97	83.81
25.	: : : :	-64.5892	:	63.5419	:	83.69	83.54

Table No.

Beet Molasses I.

Method. **Steam Oven** Ref: **Brix 81.2**

No. of hours heating.	Wt. of **Molasses** taken =	I.		II.		Percentage Dry Substance. I	II.
		1.8697	gms.	**1.6311**	gms.		
	Wt. of dish + sand =	**48.9053**	gms.	**45.7840**	gms.		
4.	: : : + D.S. =		:		:		
5.	: : : : =	**50.4721**	:	**47.1501**	:	**83.80**	**83.75**
6.	: : : : =	**50.4717**	:	**47.1503**	:	**83.78**	**83.75**
7.	: : : : =	**50.4704**	:	**47.1496**	:	**83.71**	**83.72**
8.	: : : : =	**50.4696**	:	**47.1490**	:	**83.67**	**83.69**
9.	: : : : =	**50.4670**	:	**47.1475**	:	**83.53**	**83.59**
10.	: : : : =		:		:		
11.	: : : : =		:		:		
	(Overnight in desiccator	**50.4716**		**47.1509**			
12.	: : : : =		:		:		
13.	: : : : =		:		:		
14.	: : : : =	**50.4654**	:	**47.1450**	:	**83.44**	**83.44**
15.	: : : : =		:		:		

Table No.

Beet Molasses I.

Method. **Vacuum Oven** **Ref: Brix 81.2**

No. of hours heating.	Wt. of **Molasses** taken =	I. 1.3183 gms.	II. 1.7327 gms.	Percentage Dry Substance. I	II.
	Wt. of dish + sand =	48.4980 gms.	46.3706 gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	49.6196 :	47.8515 :	85.08	85.35
6.	: : : : =	49.6197 :	47.8496 :	85.08	85.24
7.	: : : : =	49.6175 :	47.8453 :	84.92	85.11
8.	: : : : =	49.6159 :	47.8434 :	84.80	85.00
9.	: : : : =	49.6145 :	47.8414 :	84.69	84.88
~~10.~~	: : : : =	:	:		
11.	: : : : =	:	:		
~~12.~~	: : : : =	:	:		
~~13.~~	(After remaining in desiccator : : overnight) : =	49.6197 :	47.8467 :		
~~14.~~ 12.	: : : : =	49.6138 :	47.8375 :	84.64	84.66
~~15.~~	: : : : =	:	:		
17.	: : : : -	49.6100 :	47.8326	84.35	84.38
22.	: : : : -	49.6094 :	47.8307 :	84.35	84.27
27.	: : : : -	49.6095 :	47.8300 :	84.35	84.23

Table No.

Java Molasses.

Method. **Steam Oven**

Ref: Brix 83.1

No. of hours heating.		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken	= 2.9366	gms.	2.7903	gms.		
	Wt. of dish + sand	=28.9266	gms.	29.1227	gms.		
4.	: : : + D.S.	=	:		:		
5.	: : : :	=31.3148	:	31.3892	:	81.32	81.23
6.	: : : :	=31.3021	:	31.3783	:	80.89	80.84
7.	: : : :	=31.2949	:	31.3746	:	80.65	80.70
8.	: : : :	=31.2885	:	31.3697	:	80.43	80.53
9.	: : : :	=31.2832	:	31.3648	:	80.25	80.35
10.	: : : :	=31.2797	:	31.3609	:	80.13	80.21
11.	: : : :	=31.2749	:	31.3578	:	79.97	80.10
12.	: : : :	=31.2744	:	31.3561	:	79.96	80.04
13.	: : : :	=31.2734	:	31.3561	:	79.91	80.04
14.	: : : :	=31.2688	:	31.3507	:	79.76	79.85
15.	: : : :	=31.2680	:	31.3459	:	79.73	79.68
20.	: : : :	31.2578	:	31.3409	:	79.38	79.49

Table No.

Java Molasses.

Method. **Vacuum Oven** **Ref: Brix 83.1**

No. of hours heating.	Wt. of **Molasses** taken		I.		II.		Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken	=	3.1282	gms.	4.1661	gms.		
	Wt. of dish + sand	=	61.3295	gms.	61.3173	gms.		
4.	: : : + D.S.	=	63.9835	:	64.8536	:	84.84	84.88
5.	: : : :	=	63.9670	:	64.8245	:	84.31	84.19
6.	: : : :	=	63.9563	:	64.8057	:	83.97	83.73
7.	: : : :	=	63.9460	:	64.7888	:	83.64	83.33
8.	: : : :	=	63.9342	:	64.7813	:	83.27	83.15
9.	: : : :	=	63.9271	:	64.7742	:	83.03	82.89
10.	: : : :	=	63.9208	:	64.7672	:	82.83	82.81
11.	: : : :	=		:		:		
12.	: : : :	=		:		:		
13.	: : : :	≠		:		:		
14.	: : : :	=		:		:		
15.	: : : :	=	63.9043	:	64.7485	:	82.31	82.36
20.	: : : :		63.8960	:	64.7351	:	82.04	82.04
25.	: : : :		63.8917	:	64.7271	:	81.91	81.85
30.	: : : :		63.8848	:	64.7191	:	81.68	81.65

Table No.

Beet Molasses II.

Method. **Steam Oven.**

Ref: Brix 82.3

No. of hours heating.	Wt. of **Molasses** taken	I.		II.		Percentage Dry Substance. I	II.
	=	**1.8426**	gms.	**1.6617**	gms.		
	Wt. of dish + sand =	**75.4648**	gms.	**58.4101**	gms.		
4.	: : : + D.S. =		:		:		
5.	: : : : =	**77.0286**	:	**59.8206**	:	**84.87**	**84.88**
6.	: : : : =		:		:		
7.	: : : : =		:		:		
8.	: : : : =		:		:		
9.	: : : : =	**77.0249**	:	**59.8170**	:	**84.67**	**84.61**
10.	: : : : =		:		:		
11.	: : : : =		:		:		
12.	: : : : =		:		:		
13.	: : : : =		:		:		
14.	: : : : =		:		:		
15.	: : : : =		:		:		

Table No.

Beet Molasses II.

Method. **Vacuum Oven**

Ref: Brix 82.3

No. of hours heating.	Wt. of **Molasses** taken =	I. **1.6946** gms.	II. **1.7645** gms.	Percentage Dry Substance. I	 II.
	Wt. of dish + sand =	**29.1859** gms.	**29.9889** gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	**30.6552** :	**31.5110** :	**86.75**	**86.26**
6.	: : : : =	:	:		
7.	: : : : =	:	:		
8.	: : : : =	:	:		
9.	: : : : =	**30.6392** :	**31.4963** :	**85.76**	**85.43**
10.	: : : : =	:	:		
11.	: : : : =	:	:		
12.	: : : : =	:	:		
13.	: : : : ≠	:	:		
14.	: : : : =	:	:		
15.	: : : : =	:	:		

Aluminium dishes used.

Table No.

Method. **Steam Oven**

Refinery Molasses.I.

Ref: Brix 76.7

No. of hours heating.	Wt. of **Molasses** taken =	I.	II.	Percentage Dry Substance. I	II.
		4.2198 gms.	**5.1367** gms.		
	Wt. of dish + sand	=**76.6733** gms.	**95.4895** gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	= **79.7787** :	**99.2895** :	**73.59**	**73.98**
6.	: : : :	= :	:		
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	=**79.7541** :	**99.2385** :	**73.00**	**72.98**
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	=**79.7440** :	**99.2255** :	**72.77**	**72.75**
13.	: : : :	= :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Table No.

Refinery Molasses. I.

Method. **Vacuum Oven** Ref: **Brix 76.7**

No. of hours heating.		I.		II.		Percentage Dry Substance. I	Percentage Dry Substance. II.
	Wt. of **Molasses** taken	= 3.0975	gms.	3.2107	gms.		
	Wt. of dish + sand	=60.2230	gms.	61.1176	gms.		
4.	: : : + D.S.	=	:		:		
5.	: : : :	=62.5837	:	63.5873	:	76.21	76.91
6.	: : : :	=62.5774	:	63.5778	:	76.00	76.60
7.	: : : :	=	:		:		
8.	: : : :	=62.5637	:	63.5498	:	75.24	75.75
9.	: : : :	=	:		:		
10.	: : : :	=	:		:		
11.	: : : :	=	:		:		
12.	: : : :	=	:		:		
13.	: : : :	=	:		:		
14.	: : : :	=	:		:		
15.	: : : :	=	:		:		

Table No.

Refinery Molasses II.

Method. **Steam Oven**

Ref: Brix 77.6

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken	= 1.6558 gms.	1.5826 gms.		
	Wt. of dish + sand	=73.1296 gms.	57.8259 gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	=74.4061 :	59.0437 :	77.09	76.95
6.	: : : :	= :	:		
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	=74.4006 :	59.0387 :	76.76	76.63
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	= :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Refinery Molasses II.

Method. **Vacuum Oven**

Ref: Brix 77.6

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken	= 1.6108 gms.	1.6555 gms.		
	Wt. of dish + sand	=55.4241 gms.	48.3555 gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	=56.6890 :	49.6595 :	78.53	78.77
6.	: : : :	= :	:		
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	=56.6821 :	49.6516 :	78.10	78.29
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	≠ :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Table No.

Natal Molasses.

Method. **Steam Oven.** **Ref: Brix 78.2**

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken =	1.6889 gms.	1.7220 gms.		
	Wt. of dish + sand =	56.9090 gms.	49.7816 gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	58.1788 :	51.0762 :	75.19	75.24
6.	: : : : =	:	:		
7.	: : : : =	:	:		
8.	: : : : =	:	:		
9.	: : : : =	58.1732 :	51.0700 :	74.84	74.82
10.	: : : : =	:	:		
11.	: : : : =	:	:		
12.	: : : : =	:	:		
13.	: : : : ≠	:	:		
14.	: : : : =	:	:		
15.	: : : : =	:	:		

Natal Molasses.

Method. **Vacuum Oven.** **Ref: Brix 78.2**

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken =	**1.6840** gms.	gms.		
	Wt. of dish + sand =	**62.7984** gms.	gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	**64.0988** :	:	**77.22**	
6.	: : : : =	:	:		
7.	: : : : =	:	:		
8.	: : : : =	:	:		
9.	: : : : =	**64.0882** :	:	**76.59**	
10.	: : : : =	:	:		
11.	: : : : =	:	:		
12.	: : : : =	:	:		
13.	: : : : =	:	:		
14.	: : : : =	:	:		
15.	: : : : =	:	:		

Beet Molasses No. 3.

Method. **Steam Oven** **Ref: Brix. 79.8**

No. of hours heating.	Wt. of **Molasses** taken	I.	II.	Percentage Dry Substance. I	Percentage Dry Substance. II.
		= **1.9641** gms.	gms.		
	Wt. of dish + sand	=**57.6082** gms.	gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	=**59.2040** :	:	**81.25**	
6.	: : : :	= :	:		
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	=**59.2004** :	:	**81.06**	
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	= :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Beet Molasses No. 3.

Method. **Vacuum Oven**   Ref: **Brix 79.8**

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken	= **1.9420** gms.	gms.		
	Wt. of dish + sand	=**57.9642** gms.	gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	=**59.5768** :	:	**83.04**	
6.	: : : :	= :	:		
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	=**59.5635** :	:	**82.35**	
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	= :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

Table No.

Beet Molasses No. 4.

Method. **Steam Oven** **Ref: Brix 79.3**

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken =	1.4818 gms.	gms.		
	Wt. of dish + sand =	62.8662 gms.	gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	64.0444 :	:	79.51	
6.	: : : : =	:	:		
7.	: : : : =	:	:		
8.	: : : : =	:	:		
9.	: : : : =	64.0444 :	:	79.51	
10.	: : : : =	:	:		
11.	: : : : =	:	:		
12.	: : : : =	:	:		
13.	: : : : =	64.0425 :	:	79.38	
14.	: : : : =	:	:		
15.	: : : : =	:	:		

This is the only case during the whole series of tests in which such agreement was observed.

Table No.

Beet Molasses No. 4.

Method. **Vacuum Oven** — **Ref: Brix 79.3**

No. of hours heating.	Wt. of **Molasses** taken =	I.	II.	Percentage Dry Substance. I	II.
		1.7546 gms.	gms.		
	Wt. of dish + sand =	74.0708 gms.	gms.		
4.	: : : + D.S. =	:	:		
5.	: : : : =	75.4865 :	:	80.68	
6.	: : : : =	:	:		
7.	: : : : =	:	:		
8.	: : : : =	:	:		
9.	: : : : =	75.4780 :	:	80.20	
10.	: : : : =	:	:		
11.	: : : : =	:	:		
12.	: : : : =	:	:		
13.	: : : : ≠	:	:		
14.	: : : : =	:	:		
15.	: : : : =	:	:		

Beet Molasses No. 5.

Method. **Steam Oven.** **Ref. Brix 79.3**

No. of hours heating.		I.	II.		Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken =	1.7769 gms.	1.9772	gms.		
	Wt. of dish + sand	=69.4575 gms.	57.8570	gms.		
4.	: : : + D.S.	=	:	:		
5.	: : : :	=70.8960	: 59.4535	:	80.95	80.75
6.	: : : :	=	:	:		
7.	: : : :	=	:	:		
8.	: : : :	=	:	:		
9.	: : : :	=70.8920	: 59.4475	:	80.73	80.44
10.	: : : :	=	:	:		
11.	: : : :	=	:	:		
12.	: : : :	=	:	:		
13.	: : : :	=	:	:		
14.	: : : :	=	:	:		
15.	: : : :	=	:	:		

Beet Molasses No. 5.

Method. **Vacuum Oven.** **Ref: Brix. 79.3**

No. of hours heating.		I.	II.	Percentage Dry Substance. I	II.
	Wt. of **Molasses** taken	= **1.7970** gms.	gms.		
	Wt. of dish + sand	= **69.7910** gms.	gms.		
4.	: : : + D.S.	= :	:		
5.	: : : :	= **71.2766** :	:	**82.67**	
6.	: : : :	= :	:		
7.	: : : :	= :	:		
8.	: : : :	= :	:		
9.	: : : :	= **71.2665** :	:	**82.11**	
10.	: : : :	= :	:		
11.	: : : :	= :	:		
12.	: : : :	= :	:		
13.	: : : :	≠ :	:		
14.	: : : :	= :	:		
15.	: : : :	= :	:		

An examination of the weighings tabulated on pp. 32 - 53 shews that constant weight was obtained only in two cases, namely with beet molasses after 20 hours drying in vacuo and with Java molasses in the same time at 100°C at ordinary pressure. In neither case did the duplicate tests made at the same time afford corroboration.

These were the only two out of some 60 tests carried out by the author but not all reported here, in which constant weight was obtained after prolonged drying, and consequently it cannot be accepted that the attainment of a constant weight under the foregoing conditions is a practicable possibility.

A gradual but progressive decomposition is evident in all the tests reported in both the steam and vacuum ovens, but to a greater extent at the temperature of the former.

This is somewhat remarkable in the case of beet molasses. It contained no levulose, which the preliminary drying tests shewed to be decomposed at 100°C. though stable at 70° in vacuo, and consequently it would appear that the unstability of beet molasses at these temperatures is due to the decomposition of certain salts present and not to the destruction of sugar.

Spencer (Handbook) and others state definitely that the destruction of levulose is the cause of high results for water at 100°C.

With refinery molasses and cane molasses in which the reducing sugars are present to a considerable extent, decomposition would be expected at 100° but not at 70° C. In these cases also, the decomposition cannot be ascribed solely to the levulose, otherwise the drying in vacuo at 70° C. would have given constant results.

Similarly with Golden Syrup, failure to obtain constant weight at 70° C. in vacuo lends further support to the argument that levulose is not the cause of the progressive decomposition, but it will be noticed in this case that the rate of the loss in weight is less than in the others, especially when compared with Java molasses. The ash from the Syrup was about 1 per cent. as against 8-10 per cent. from the molasses, and this would indicate that the mineral matter content exerts a most important influence.

It must again be emphasized that solutions of sucrose and mixtures of solutions of dextrose and levulose dried out completely in the vacuum oven method. Golden syrup is a mixture of these three sugars together with certain salts which give about 1 per cent. of ash on incineration, and it must be inferred from this either that the salts themselves decompose on heating at 70° C. in vacuo or that their action on the reducing sugars at this temperature causes the decomposition.

Beet molasses, giving as it does about 10 per cent. of ash, shews similar decomposition, and appears to provide further proof that this is due not to the sugars but to the salts.

Comparing the results obtained for any one of the samples by the two methods, it will be observed that there is a considerable difference between them. At 70° C. in vacuo, less water, or more correctly, more residual "dry substance" is obtained than with drying at ordinary pressure at 100° C.

The difference also is less marked with Golden syrup and beet molasses than with cane molasses.

To find out which method gives a result more closely approximating the actual water content of molasses is a problem of some difficulty. Attempts to make up an "Artificial" molasses in which the amount of water present was known, were not very successful. The sugars did not present the greatest of the difficulties, although to prepare a solution of them at 70-80° Brix without applying heat, which might cause decomposition, is not an easy matter. Most of the salts mentioned on pg. 4 are only sparingly soluble, so that it is impossible to obtain a mixture which could be considered analogous to the complex natural product.

In the case of Golden Syrup, according to de Whalley (I.S.J., 1935) the dry substance can be calculated from the Refractometer Brix reading and a correction applied for the invert sugar content. This correction is given as 0.02 for every 1 per cent. of invert sugar present. In the case reviewed, the Ref. Brix was 82.1. Since the invert sugar present was found to be 47.76 per cent., the dry substance is 83.15. This agrees with the figure found for drying at 100° C.

for 5 hours, and points to the fact that vacuum drying at 70° C. does not remove all the water originally present, some being retained by the salts at this temperature.

In the case of cane molasses the difference between the two drying methods is greater, but it is not possible to use the knowledge of the Refractive Brix to get at a possibly true water content as in the former example. This is further considered on pg. 134.

Notes on the use of glass and metal dishes for drying.

During the early investigations in this work it was observed that, when tinplate dishes were used for the drying tests, the weight of the tightly covered dish with the dried molasses increased to a slight but still appreciable extent during the actual period of weighing. Further, when these dishes were left overnight in a desiccator over calcium chloride or sulphuric acid, an increase in weight was found on re-weighing them; before continuing the test.

Accordingly, glass weighing bottles, squat shaped, sizes 50 mm. diam. x 30 mm. deep, and 60 mm. x 35 mm. were procured, with ground glass covers fitting outside so as to ensure absolute airtightness. Weighings were made on an air-damped balance, on which the weights under 1 gm. could be applied by riders controlled from the outside of the balance case. This ensured rapid weighings and a minimum of disturbance during the operation.

Despite these precautions, an increase in weight was observed after a finished sample had been left for a period over Silica gel in an evacuated desiccator. and then re-weighed.

There was no possibility of a leak in the dish or in the desiccator, and attention was therefore directed to the behaviour of glass, tinplate, aluminium and nickel on being heated and cooled.

The tests were made on empty dishes, and the results are recorded below. The sequence of operations will be followed from the weighings, which are reported in chronological order.

Glass dishes. (1) 50 x 30 mm. and (II) 60 x 35 mm.

	(1) Gms.	(II) Gms.
Wt, after heating for 2 hours at 100°C and cooling for 30 minutes in desiccator	29.0403	59.2557
" " leaving overnight in desicc.	29.0433	59.2613
" " heating for 30 mins. and cooling for 30 mins. in desiccr.	29.0396	59.2560
" " returning to desiccator for further 60 mins.	29.0419	59.2608
" " returning to desiccr. for further 60 mins.	29.0424	59.2608

These separate tests were carried out at different times of the same day.

Similar results were obtained with the various metal dishes. The increases in weight could be due only to changes in atmospheric conditions in the balance room. The importance of keeping strictly to standard times for cooling etc. and not delaying the weighing of the finished sample cannot be over-emphasized. One dish (empty) was weighed quickly after being cooled in a desiccator for thirty minutes, and was allowed to remain on the pan of the balce for a similar period. An ihcrease of 1 mgm. was observed, after which the weight remained constant.

After completing a drying test on molasses in a tightly covered aluminium dish, the latter was left on the pan of the balance and the change in weight at thirty minute intervals was noted.

		gms.
Wt. of dish and dried molasses		31.5058
" " " " " "	after 30 mins.	31.5072
" " " " " "	" 1 hour	31.5076
" " " " " "	" 1½ "	31.5086
" " " " " "	" 2 "	31.5093
" " " " " "	" 4½ "	31.5123
" " " " " "	" 6½ "	31.5154

The above weighings shew the gradual but considerable increases, most of which can be due only to the extraordinary avidity for water displayed by dried molasses. After the test, the lid of the dish could be removed only with some difficulty. Although not actually airtight, this dish was the most closely fitting of all those used in the whole series of drying experiments. When glass weighing dishes were used, no such increases were observed.

The foregoing tests clearly demonstrate the fact that strict adherence to standard conditions is necessary, and that a standard type of drying dish must be used if results are to be obtained which are strictly comparative.

Personal error in estimating moisture by drying.

Reference has been made earlier in this section of the work, to the need for careful manipulation in the apparently simple operation of drying a weighed sample of the material under examination.

It is recorded in the I.S.J., 1913, that samples of molasses were sent to a number of eminent sugar technologists in Hawaii for determination of water content.

Considerable variation in results was obtained. The maximum difference by the steam oven method was over 3 per cent. and by the vacuum oven method, over 1.6 per cent. The variations must be regarded more as an indication of the effect of slightly different conditions during the estimation, than as a reflection on the skill of the analysts. To demonstrate this personal effect, and to shew how difficult it is to get "check" results from different observers, a sample of molasses was tested by the author and was then given to four other sugar chemists, who used exactly the same procedure, the same vessel and the same oven. Their results are given below:-

Steam Oven Method.	D.L.	A.	B.	C.	D.
wt. of molasses taken.	1.8426	1.8588	1.8319	1.7974	1.5983
D.S. after 5 hours.	84.87	84.98	85.35	85.18	84.72
" " 9 "	84.67	84.73	84.72	84.89	84.41

Vacuum Oven Method.	D.L.	A.	B.	C.	D.
wt. of molasses taken.	1.7296	2.7299	1.5193	1.6564	2.0639
D.S. after 5 hours.	86.50	87.89	86.42	86.04	87.34
" " 9 "	85.60	86.73	86.04	-	86.40

It will be observed that the variations are more pronounced in the vacuum oven method. The differences in weights of sample taken do not account altogether for the irregularities.

In all the drying tests done in the vacuum oven the agreement between the duplicate was not so close as was the case with those dried in the steam oven. It is possible that the position of the dishes in the vacuum oven may have been the cause of the difference, which was quite marked.

In view of the above observations, it gives one seriously to consider if the complete standardization of a method subject to such fluctuations is at all practicable.

Method No. 4. The estimation of water in molasses by distillation appears to have been suggested originally by Hoffman (Z.angew. Chem.,1902). His proposal was to distil the sample to be tested with an organic immiscible liquid and to collect the distillate in a calibrated receiver attached to a condenser in such a way that the condensed liquid was returned to the distillation flask, while the volume of water collected could be read off directly and calculated to percentage of water present in the original material. Xylol was the liquid proposed, but as its B.P. is about 140° C. it caused charring of the residue.

Clacher, (I.S.J.,1914) suggested the use of ordinary kerosene as the distilling liquid, but the B.P. of the mixture under treatment was about 170° C. and the risks of decomposition of the sugar product were considerable.

Van der Linden (Archief, 1917) stated that although the problem of water estimation in cane molasses was as then unsolved, a likely method appeared to be distillation with such liquids as benzene, toluene, xylene and paraffin oil. Of all these he recommended xylol as giving the best results.

Little further was heard of such proposals until Dean and Stark published their method of estimating water in certain substances including oil, coal and molasses, by means of distillation with toluene.

In 1925, Bidwell and Sterling (Ind. and Eng. Chem.) gave a detailed account of a modification of Dean and Stark's method.

Using a special receiver, differing only in detail from the original, with toluene as the liquid, they obtained (from a number of substances including molasses and similar syrups) results which they stated closely agreed with the oven method of drying on sand.

The apparatus is shewn on page 67, and has been slightly modified by the author for the ensuing investigations. The procedure also has been slightly altered and is as follows:-

Between 10 and 15 gm. of molasses are quickly weighed into the conical flask, a fairly rough balance sensitive to 0.005 gm. being quite suitable, 75cc. of toluene are added and the flask connected to the receiver. A further 15cc. of toluene are added via the condenser in order to fill the receiver, and the flask is then heated in an oil bath in which the temperature can be controlled.

On completion of the distillation, the condenser tube is washed down with a few cc. of toluene and then brushed down with a camel hair brush dipped in the same liquid, any tiny droplets of water adhering to the receiving tube being dislodged with a copper wire.

Bidwell and Sterling claim completion generally within one hour "and at any rate within four hours". The present author's experience is that while in the first hour about 90 per cent. of the water present may be collected in the receiver, it takes several hours more to obtain the remainder, as will be seen from the tabulated results. One great disadvantage of this method is that, since toluene is much lighter than molasses, it floats on the surface of the latter, which, as a result, is liable to bake on the bottom of the flask. The use of the oil bath prevents this to some extent, but charring of the residue cannot wholly be avoided.

Rice(Ind. and Eng. Chem., 1929) reports his difficulty with this charring, and he finally resorted to adding 2-10 gms. of sodium oxalate per 15 gm. of molasses before distilling. His object at first was to precipitate any calcium chloride which was present on the molasses and which was thought to be the cause of the charring.

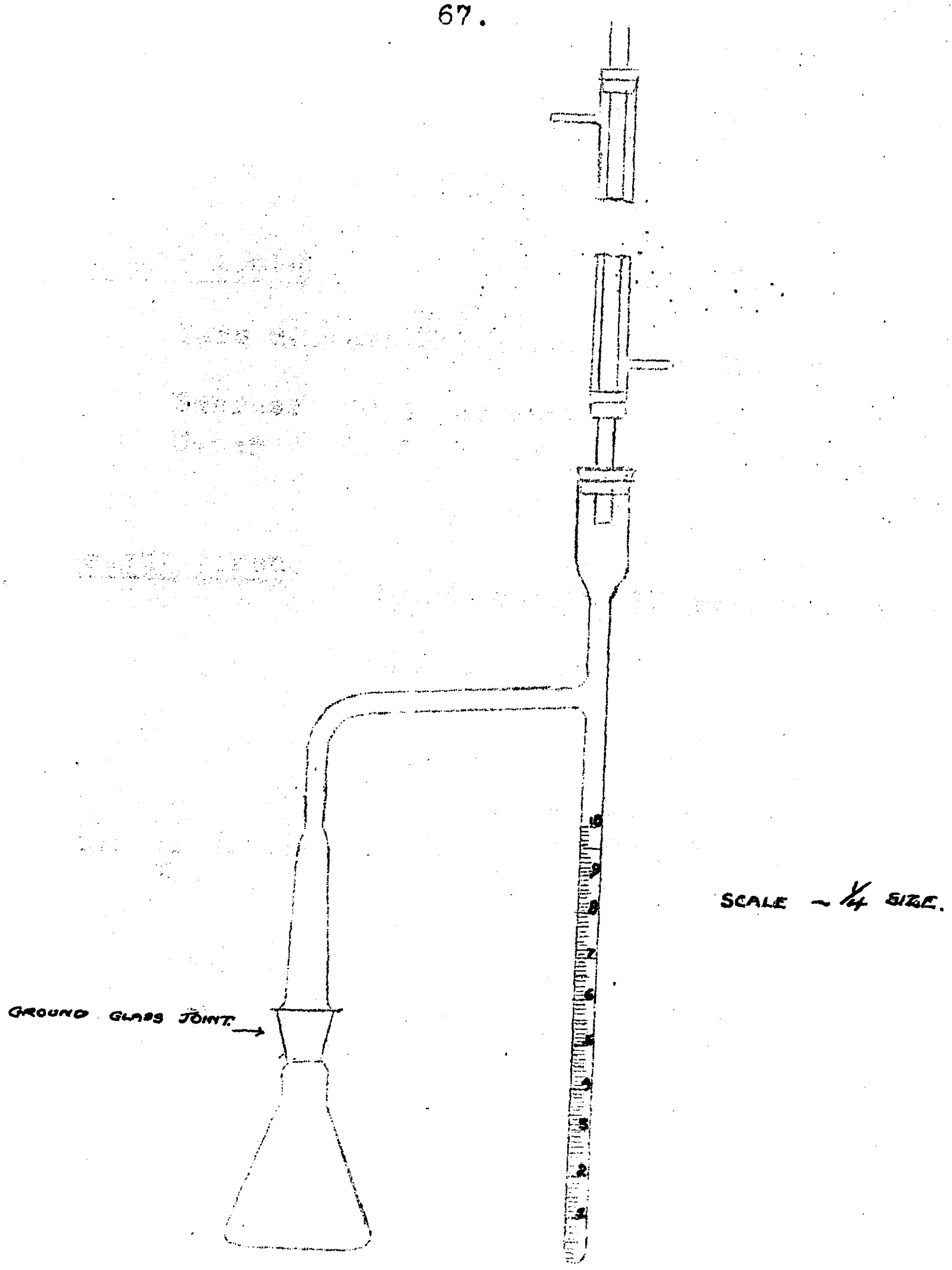
The action of the sodium oxalate, however, must be mainly physical. Only a small quantity of it would be necessary to remove what calcium chloride might be present in molasses. Rice further discovered that kieselguhr had the same effect, namely the prevention of charring.

During the following experiments with toluene distillation, it was found that not only was the addition of kieselguhr desirable but indeed absolutely essential. An attempt to estimate the water content of a pure sucrose solution was unsuccessful until a quantity of this material was added. This fact seems to prove that the action of the axalate used by Rice was purely physical, and confirmation is given by the results obtained on solutions of sucrose containing calcium chloride and potassium acetate to which were added kieselguhr, sodium oxalate and magnesium oxide as shewn on pp. 72 to 76 The accelerating action of the kieselguhr is evident, as is also its property of preventing decomposition of the solution. The fact that it is inert eliminates any possibility of chemical effect.

The temperature of the oil bath is important. This is indicated in the following tests which were made in the first place with solutions of known water content before the method was tried on various types of molasses. The toluene used for the distillation was the purest obtainable, and before use was tested thoroughly for acidity. In addition, a quantity of it was boiled under a reflux condenser with distilled water, and the water was afterwards tested for pH. No change was observed. This is extremely significant in view of the low pH. of the distillate in the case of the aqueous solution of pure sucrose. The acidity of the water collected in this and similar experiments was somewhat surprising.

In the following tests, the readings were not regarded as constant until three successive hourly readings shewed no change.

When serious charring took place the experiment was discomtinued.



Bidwell and Sterling's Moisture Apparatus.

slightly modified.

Sample tested:

Pure Sucrose Solution.

Sucrose 60.4 per cent.
Water 39.6 " "

Distilling liquid:

Toluene.

Temp. of oil bath 130°C.

Weight taken: (I) 10.25 gms. + **10 gms. Na. Oxalate**
(II) 10.00 "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	35.61	27.83
2.	38.06	31.74
3.	40.03	33.21
4.	40.49	33.50
5.	40.49	34.18
6.	40.49	34.66
7.	40.49	34.76
8.		35.05
9.		35.16
10.		35.45
11.		35.45
12.		35.45

Residues slightly charred.

Sample tested:	Distilling liquid:
Sucrose solution.	Toluene.
Water 39.6 per cent.	Temp. of oil bath 140°C.

Weight taken:
(I) 9.95 gms + 10 gms. kieselguhr.
(II) 10.03 " + 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	38.09	37.80
2	38.99	39.20
3.	39.41	39.50
4.	39.70	39.60
5.	39.70	39.80
6.	39.90	39.80
7.	39.90	39.80
8.	39.90	
9.		
10.		
11.		
12.		

Residues un-charred.

pH of distillates 2.8

Sample tested:	Distilling liquid:
Sucrose solution. Sucrose 60.6 per cent. Water 39.4 " "	Toluene. Temp. of oil bath 130°C.
Weight taken: (I) 11.59 gms. (II) 10.01 "	+ 10 gms. kieselguhr.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	19.85	38.47
2.	31.93	38.47
3.	32.78	39.47
4.	33.66	39.47
5.	34.51	39.47
6.	34.51	
7.	34.51	
8.	34.51	
9.	34.51	
10.		
11.		
12.		

The effect of the kieselguhr is clearly shewn here.

Sample tested:	Distilling liquid:
Sucrose Solution. Sucrose 60.6 per cent. Water 39.4 " "	Toluene. Temp. of oilbath 130°C.
Weight taken: (I) 10.41 gms. (II) 11.40 "	+ 5 gms. Na. Oxalate + 5 " MgO.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	31.23	30.70
2.	31.71	36.84
3.	35.55	38.60
4.	37.47	38.60
5.	38.43	38.60
6.	39.40	38.60
7.	39.40	38.60
8.	39.40	
9.		
10.		
11.		
12.		

pH of distillates about 4.0

Sample tested:

Solution containing:

Sucrose 54.38 per cent.
K. Acetate 9.06 " "
Water 36.56

Weight taken:
(I) 11.67 gms.
(II) 10.61 " +1 gm. MgO.

Distilling liquid:

Toluene.

Temp. of oil bath 160°C.

Time of distilling. Hours.	Per cent. water in sample.	
	(I)	(II)
1.	31.27	34.80
2.	33.42	36.26
3.	33.42	37.70
4.	34.28	37.70
5.	35.90	38.60
6.	38.90	38.60
7.	38.90	
8.	38.90	
9.		
10.		
11.		
12.		

Decomposition evident.
Test continued overleaf.

Sample tested:	Distilling liquid:
Solution as on previous page.	Toluene. Temp. of oil bath 160°.
Weight taken: (I) 11.59 gms.	+ 1 gm. Na. Oxalate.
(II)11.07 "	+ 10 " Kieselguhr

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	35.85	34.34
2.	37.11	35.25
3.	37.97	35.25
4.	38.40	36.15
5.	38.84	36.15
6.	39.26	36.15
7.	39.70	36.60
8.	39.70	36.60
9.	39.70	36.60
10.		
11.		
12.		

In these four tests, only the one in which kieselguhr was used gave the actual result for water.

Sample tested:

Solution containing

Sucrose	54.59	per cent.
$CaCl_2$ (pure)	9.30	
Water	36.11	" "

Weight taken:

(I) 12.81 gms.

(II) 10.05 "

Distilling liquid:

Toluene.

Temp. of oil bath 130°

+ 1.gm. Na. Oxalate

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	11.70	14.93
2.	16.40	20.89
3.	18.58	28.86
4.	23.46	29.95
5.	30.86	31.84
6.	33.57	37.77
7.	37.47	39.81
8.	38.25	39.81
9.		
10.		
11.		
12.		

Residues charred.

Tests continued overleaf.

Sample tested:	Distilling liquid:
Solution as on previous page.	Toluene.
	Temp. of oil bath 130°C.
Water 36.11 per cent.	
Weight taken:	
(I) 10.37 gms.	+ 5 gms. Na. Oxalate.
(II)10.20 "	+ 1 gm. MgO.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	28.93	34.82
2.	30.86	43.75
3.	33.80	44.85
4.	35.70	
5.	36.66	
6.	38.59	
7.	40.51	
8.	40.51	
9.		
10.		
11.		
12.		

Residues charred.

Tests continued overleaf.

Sample tested:		Distilling liquid:
Solution as on previous page. Water 36.11 per cent.		Toluene. Temp. of oil bath 130°C.
Weight taken:	(I) 14.22 gms.	+ 10 gms. Kieselguhr
	(II) 11.22 "	+ 20 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	36.57	35.66
2.	36.93	37.87
3.	37.62	37.87
4.	37.97	37.87
5.	37.97	37.87
6.	38.32	
7.	38.32	
8.	38.32	
9.	38.32	
10.		
11.		
12.		

Although the amount of water recovered is greater than that originally present, decomposition of the Sucrose is shewn to be lessened by the presence of Kieselguhr.

Sample tested:	Distilling liquid:
Solution of Dextrose:	Toluene.
Water 56.15 per cent. Dextrose 43.85 " "	Temp. of oil bath 140°C
Weight taken: (I) 10.02 gms.	+ 5 gms. Kieselguhr.
(II) 10.01 "	+ 10 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	55.40	55.05
2.	55.70	55.46
3.	56.00	55.55
4.	56.10	55.85
5.	56.19	55.95
6.	56.19	56.35
7.	56.19	56.35
8.	56.19	56.35
9.		
10.		
11.		
12.		

Residues un-charred.

pH of distillates 2.8

Sample tested:	Distilling liquid:
Solution of Dextrose:	Toluene.
Water 56.15 per cent.	Temp. of oil bath 140°C
Weight taken: (I) 10.23 gms.	
(II) "	

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	40.38	
2.	45.07	
3.	46.44	
4.	48.78	
5.	48.89	
6.	49.18	
7.	49.48	
8.	49.85	
9.	50.16	
10.	50.43	Residue slightly charred.
11.	51.53	
12.	51.62	

By comparing these results with those on the previous page, the influence of the kieselguhr will be easily seen.

Sample tested:	Distilling liquid:
Solution of Levulose.	Toluene.
Water 40.01 per cent. Levulose 59.99 " "	Temp. of oil bath 140°C
Weight taken: (I) 9.36 gms.	+ 10 gms. Kieselguhr.
(II) 9.68 "	+ 10 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	40.05	40.07
2.	41.02	40.75
3.	42.52	41.42
4.	42.84	41.94
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		

The residues were not badly charred, but decomposition is indicated by the quantity of water collected.

Sample tested:	Distilling liquid:
Solution of Levulose	Toluene.
Water 40.01 per cent.	Temp. of oil bath 140°.
Weight taken: (I) 9.54 gms.	+ 5 gms. kieselguhr and + 5 " Na. Oxalate.
(II) 11.91 "	+ 10 gms. Na. Oxalate only

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	38.90	32.32
2.	40.36	37.53
3.	41.52	40.54
4.	42.36	40.55
5.	42.67	41.31
6.	42.98	41.65
7.		
8.		
9.		
10.		
11.		
12.		

Residues were slightly charred.

Progressive decomposition apparent.

An examination of the results set out in the Tables on pp. 68-80 reveals some interesting information.

The accelerating action of the kieselguhr is clearly demonstrated, and the pH. of the water distilled over is shewn to be extremely low. This is significant in view of subsequent work.

From the estimations with sucrose and dextrose solutions it will be seen that the method is successful and gives results in close agreement with each other, but with levulose, progressive decomposition occurs, which is only to be expected at the temperature of the boiling mixtures.

The tests were continued with Golden Syrup (a mixture of the three sugars treated above), beet molasses (a strongly alkaline material) and refinery and cane molasses, which are acidic in character.

Sample tested:	Distilling liquid:
Golden Syrup.	Toluene . Temp. of oil bath 140°.
Weight taken: (I) 11.45 gms.	+ 10 gms. Kieselguhr.
(II) 10.20 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	15.54	14.02
2.	16.60	16.47
3.	17.21	16.66
4.	17.47	17.16
5.	17.48	17.56
6.	18.17	17.65
7.	18.43	17.74
8.	18.51	17.74
9.	18.69	18.44
10.	18.87	18.63
	15 hrs.	18.82
11.	17 "	19.12
	19 "	19.32
12.		

Residues slightly charred.

Per cent. water present, by de Whalley method, = 16.85. (See page 137)

Sample tested: Golden Syrup. as on previous page.	Distilling liquid: Toluene. Temp. of oil bath 130°C.
Weight taken: (I) 12.57gms.	+ 10 gms. Kieselguhr
(II) 12.17 "	+ 10 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	14.23	14.96
2.	16.21	16.44
3.	16.60	16.89
4.	17.00	17.26
5.	18.18	17.66
6.	18.18	17.84
7.	18.18	18.08
8.	18.18	18.08
9.		18.08
10.		
11.		
12.		

pH of distillates 4.2

Note effect of temp. of oil bath. c/f previous page.

Sample tested:	Distilling liquid:
Beet Molasses I.	Toluene. Temp. of oil bath 140°C.
Weight taken: (I) 13.36 gms.	+ 10 gms. Kieselguhr.
(II) 13.59 "	+ 10 " "

Time of distilling. Hours.	Per cent, water in sample. (I)	(II)
1.	13.48	14.06
2.	15.42	15.09
3.	15.80	15.60
4.	16.25	15.97
5.	16.39	16.12
6.	16.39	16.19
7.	16.62	16.27
8.	16.62	16.41
9.		16.41
10.		16.41
11.		
12.		

Sample tested:	Distilling liquid:
Beet Molasses I. as on previous page.	Toluene. Temp. of oil bath 140°.
Weight taken: (I) 25.55 gms +	10 gms. Kieselguhr.
(II) 16.42 " +	10 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	13.82	15.46
2.	15.23	16.57
3.	15.77	16.64
4.	16.24	16.64
5.	16.55	16.64
6.	16.55	16.64
7.	16.55	16.64
8.		
9.		
10.		
11.		
12.	Test continued overleaf.	

Sample tested:	Distilling liquid:
Beet Molasses I.	Toluene.
	Temp. of oil bath 140°C.
Weight taken: (I) 18.62 gms. +	10 gms. Kieselguhr.
(II) 22.18 " +	10 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	14.77	15.55
2.	15.73	16.24
3.	16.12	16.46
4.	16.12	16.46
5.	16.12	16.46
6.		
7.		
8.		
9.		
10.		
11.		
12.		

Mean of 6 determinations

16.43%

This result agrees with that obtained by steam drying for 9 hours, i.e. 16.44%.

Sample tested:	Distilling liquid:
Beet Molasses II.	Toluene . Temp. of oil bath 140°C.

Weight taken:
(I) 11.66 gms. + 5 gms. Kieselguhr.
(II) 14.69 " + 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	11.83	12.32
2.	13.20	13.33
3.	13.72	14.43
4.	14.40	14.63
5.	14.67	14.77
6.	15.09	15.04
7.	15.26	15.45
8.	15.44	15.59
9.	15.44	15.59
10.	15.44	15.59
11.		
12.		

No charring of residues.

pH of distillates 5.0

Sample tested:	Distilling liquid:
Beet Molasses II.	Toluene.
	Temp. of oil bath 140°.
Weight taken: (I) 10.37 gms. (II) "	+ 10 gms. Kieselguhr.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	13.98	
2.	14.28	
3.	14.28	
4.	14.86	
5.	15.15	
6.	15.43	No charring of residue.
7.	15.43	
8.	15.43	pH of distillate 4.6
9.		
10.	Mean of 3 results 15.49	
11.	Per cent. water found by drying in steam oven for 9 hours 15.36	
12.		

Sample tested: Refinery Molasses.	Distilling liquid: Toluene. Temp. of oil bath 140°
Weight taken: (I) 10.47 gms. (II) "	

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	21.67	
2.	22.67	
3.	23.00	
4.	23.33	
5.	23.67	
6.	23.93	
7.	24.00	
8.		
9.		
10.		
11.		
12.		

Residue badly charred.

pH of distillate 2.8

Sample tested:	Distilling liquid:
Beet Molasses No.3	**Toluene.** **Temp. of oil bath 140° C.**
Weight taken: (I) **10.80** gms. (II) **10.76** "	+ **5 gms. Kieselguhr** + **5 " "**

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	15.55	15.61
2.	17.22	18.58
3.	18.52	19.23
4.	18.71	19.42
5.	19.17	19.42
6.	19.17	19.42
7.	19.17	19.42
8.		
9.		
10.		
11.		
12.		

No charring occurred.

pH. of distillates 4.7

Sample tested:	Distilling liquid:
Beet Molasses No. 4	Toluene. Temp. of oil bath 140 C.
Weight taken: (I) 10.26 gms. (II) 10.48 "	 + 5 gms. Kieselguhr. + 5 " "

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	17.56	18.12
2.	18.81	18.60
3.		20.80
4.	20.18	20.98
5.	20.27	21.08
6.	21.24	21.08
7.	21.24	21.08
8.	21.24	
9.		
10.	No charring occurred.	
11.	pH. of distillate 5.2	
12.		

Sample tested:	Distilling liquid:
Beet Molasses No. 5	**Toluene.**
	Temp. of oil bath 140 C.
Weight taken: (I) 10.76 gms.	**+ 5 gms. Kieselguhr.**
(II) 10.28 "	**+ 5 " "**

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	**15.62**	**15.66**
2.	**16.63**	**16.73**
3.	**17.84**	**18.09**
4.		
5.	**18.59**	**18.98**
6.	**18.87**	**19.17**
7.	**19.24**	**19.36**
8.	**19.24**	**19.36**
9.	**19.24**	**19.36**
10.	**19.24**	**19.36**
11.		
12.		

No charring.

pH. of distillates 5.4

Sample tested:	Distilling liquid:
Java Molasses.	Toluene. Temp. of oil bath 140°
Weight taken: (I) 15.70 gms.	+ 5 gms. Kieselguhr.
(II) 17.21 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.		17.21
2.	18.15	18.26
3.	18.47	18.89
4.	19.11	19.17
5.	19.30	19.45
6.	19.94	19.80
7.	20.06	20.16
8.	20.19	20.44
9.	20.38	20.58
10.		
11.		
12.		

Residues badly charred.
pH of distillates below 3.6

Sample tested:	**Distilling liquid:**
Java Molasses.	Toluene.
	Temp. of oil bath 130°C.
Weight taken: (I) 14.55 gms.	+ 10 gms. Na. Oxalate.
(II) "	

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	18.21	
2.	18.55	
3.	19.24	
4.	19.93	
5.	20.62	
6.	20.96	
7.	21.30	
8.	21.30	
9.	21.30	
10.		No charring took place.
11.		
12.		

Sample tested:	Distilling liquid:
Java Molasses.	Toluene. Temp. of oil bath 1. 160°C. II. 140°C.
Weight taken: (I) 14.75 gms.	+ 10 gms. Na. Oxalate.
(II) 14.65 "	+ 10 " " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	20.67	15.70
2.	22.38	17.68
3.	23.05	19.04
4.	23.59	19.24
5.	23.93	19.59
6.	24.06	19.86
7.	24.61	20.13
8.	24.75	20.54
9.	25.01	20.67
10.	25.28	20.95
11.	25.42	21.02
12.		21.36
13		21.50
14		21.64
15		22.05
16		22.05
17		22.05

No appreciable charring.

Note the effect of temp. of oil bath.

Sample tested:	Distilling liquid:
Natal Molasses.	**Toluene.**
	Temp. of oil bath 140 C
Weight taken: (I)10.52 gms.	+ **5 gms. Kieselguhr**
(II)11.41 "	+ **10 " Na. Oxalate.**

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.		**19.89**
2.	**22,80**	**22.00**
3.	**24.04**	**23.05**
4.	**24.42**	**24.45**
5.	**24.61**	**25.07**
6.	**24.71**	**25.33**
7.	**24.79**	**25.58**
8.	**25.00**	**25.85**
9.		**26.03**
10.		**26.11**
11.		**26.11**
12.		**26.20**
13.		**26.46**

Complete charring of residues.

Sample tested:	Distilling liquid:
Hawaii Molasses.	**Toluene.** **Temp. of oil bath 140 C.**
Weight taken: (I) 10.78 gms.	+ **5 gms. Kieselguhr.**
(II) 10.67 "	+ **5 " "**

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	**21.98**	**21.36**
2.	**23.06**	**22.30**
3.	**23.46**	**23.15**
4.	**23.88**	**23.33**
5.	**24.02**	**23.43**
6.	**24.02**	**23.53**
7.	**24.12**	**23.61**
8.		
9.		
10.		
11.		
12.		

Complete charring in both tests.

pH. of distillates about 3.0

The results tabulated on pages 82 to 97 shew that when treating cane molasses constant readings were obtained in only one case, i.e., Java molasses, and that was when 10 gm. sodium oxalate were added instead of kieselguhr. The water content does not, however, agree with the figure found by either of the drying methods. To investigate further the action of the oxalate, another cane molasses were distilled under similar conditions. In the case of Natal molasses, as reported on pg.96 a constant reading was not attained.

The low pH. of the water distilled over in each case is noteworthy: even in the case of beet molasses, which is usually strongly alkaline, the pH. of the water distilled over indicates acidity.

With beet molasses the results of the distillation are remarkably consistent, and it would appear that the estimation of water can be completed in six hours.

Constant results could not be obtained with Golden Syrup, refinery or cane molasses except in the instance cited above.

It should be noted that a constant reading was obtained in each of the different tests with sucrose solutions, and these figures did not agree with each other. It would appear that a constant reading is not necessarily a correct one.

Many other distillations were made with refinery and cane molasses, including samples from Cuba, Egypt, Hawaii, Java and

West Indies, but in all cases decomposition, due no doubt to the effect of the high temperature on the reducing sugars, was apparent.

It can therefore be definitely stated that the toluene distillation method is not suitable for other than beet molasses.

It may be mentioned here that altogether more than eighty of these tests were carried out, and on two occasions the apparatus cracked, happily without serious results. In the absence of proper supervision the dangers attendant upon the use of such an inflammable liquid as toluene are considerable and this would preclude its use in most sugar laboratories.

Another disadvantage is that the temperature of the oil bath must be kept constant. A thermostat control is necessary for this purpose.

Developments of the distillation methods have recently taken place in connection with beet molasses and various non-inflammable heavy hydrocarbon derivatives have been proposed[*] for use as the immiscible liquids. These liquids and mixtures of liquids have a density of about 1.5 so that they "float" the molasses. This removes the possibility of decomposition of the molasses by its being "baked" in the flask and also obviates the danger due to the use of such an inflammable substance as toluene. A special type of apparatus is necessary to permit of the refluxing and return of the heavy distilling liquid and the collection of the water as the top layer in the receiver. The drawing on the following page (102) shews one of several types made up of simple parts by the author, and used by him for the preliminary experiments until an apparatus specially designed for the purpose was procured. This special type is also shewn on pg.103. This will be referred to as the "Q" type and the former as the D.L. apparatus.

<u>Calibration of Apparatus.</u> The burette forming the receiver of the D.L. apparatus was calibrated before it was made up, but in view of the peculiar non-wetting effect of the chloro derivatives on glass it was considered advisable to calibrate the whole apparatus as used in the estimations.

This was done by adding 1 c.c. of water at a time to the flask containing the distilling liquid and then distilling over the water.

[*] Thielepape & Fulde (Z. ver deut. Zuck.ind, 1931-2).

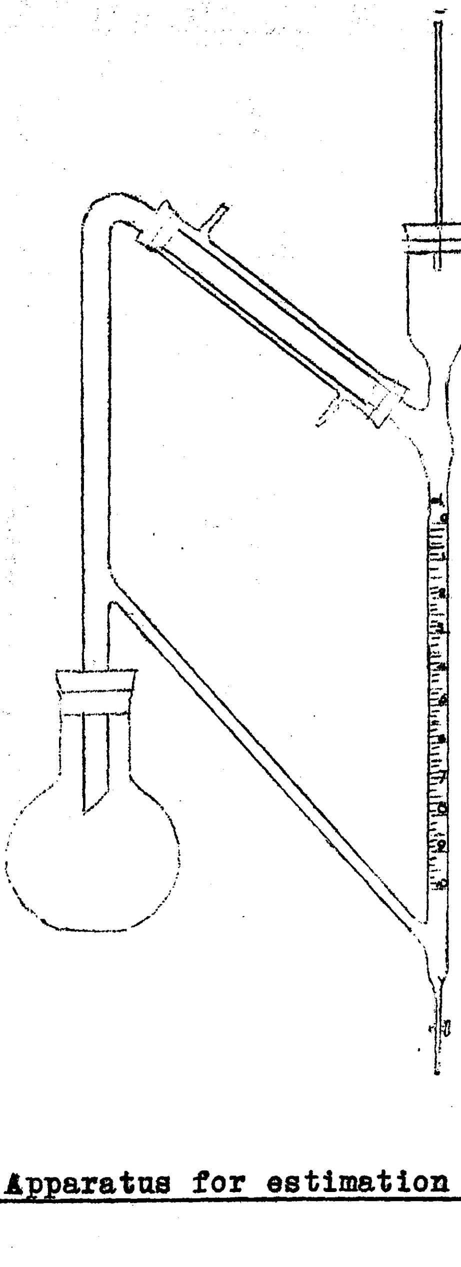
It was found that the only correction necessary was 0.02 for the first c.c. collected, and that no correction was needed when 2-3 c.c. was the amount collected during a test.

With the Q. apparatus, the presence of a coil condenser was responsible for a small amount of water being retained in the worm, the correction as found by the same method as in the previous case being 0.10 for 2-3 c.c. of water collected.

It may be mentioned here that the D.L. apparatus, despite its seeming crudity and the fact that it was graduated in tenths of a c.c. could be read easily to .01 c.c. and gave results equally as satisfactory as those obtained with the Q type whose receiver is graduated in .002 c.c. and whose cost is about ten times that of the simpler form.

The liquids suggested for these distillations include Tetrachloroethane and Trichloroethylene mixed in certain proportions to give a definite boiling point at which the molasses will not be decomposed, and Tetrachloro-ethylene. (B.P.116°C.).

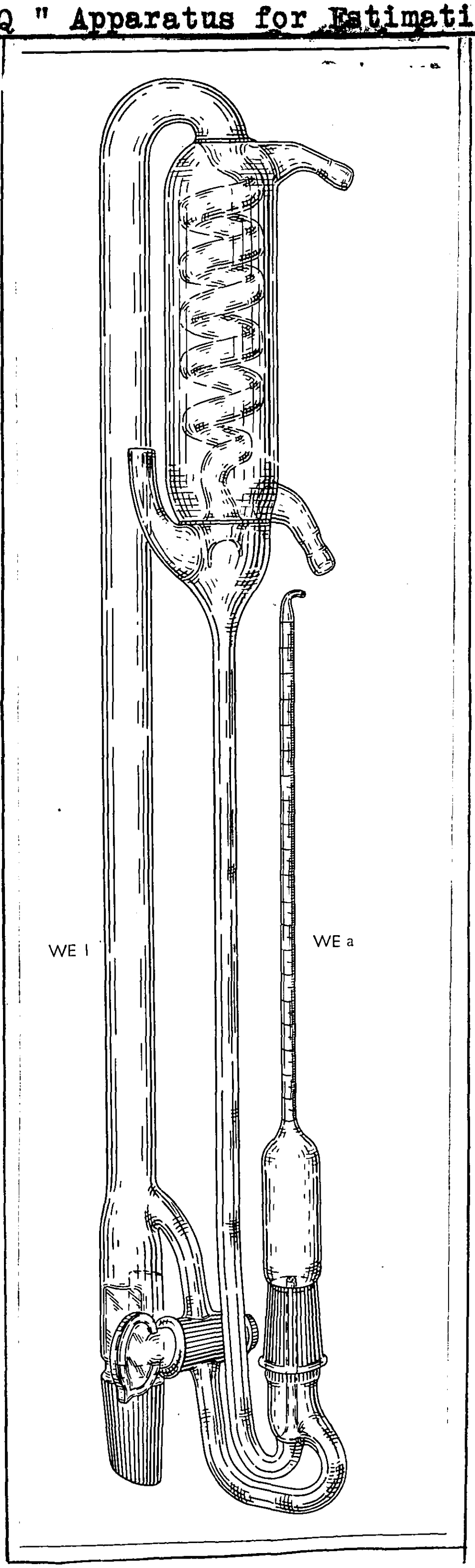
The toxic properties of the mixture have been adversely reported on in the technical press, but the last-named liquid is considered to be much safer in this respect. The author found that certain proportions of tetrachloro-ethylene and carbon tetrachloride gave mixtures which could be varied because of their definite boiling points, to suit required conditions.



Scale - 1/4 size.

The D.L. Apparatus for estimation of Water Content.

The " Q " Apparatus for Estimating Water Content.



The still head fits into a flask with ground glass neck.

Distilling Mixtures

9	parts	Tetrachloroethylene	and	1	part carbon	Tetrachloride	B.P. 114°C.
9	"	"	"	3	"s	"	" 106°C.
9	"	"	"	6	"	"	" 98°C.

The chemicals used were B.D.H. products, labelled Technical. None guaranteed absolutely pure could be obtained except the Carbon Tetrachloride. This is significant in view of certain difficulties encountered later.

During preliminary tests on beet molasses, when different types of apparatus were being tried out, some small variations in results were observed. These were attributed to defects in the apparatus. Some forty distillations were made in this preliminary work but no apparent decomposition of the distilling liquids was observed. After an interval of some weeks, however, the presence of phosgene was observed in some of the liquid that had been used repeatedly and left standing. Resumption of the work was made with new supplies of tetrachloroethylene, and Java (cane) molasses was used instead of beet. The boiling points of the liquid and of the carbon tetrachloride used for mixing with it were tested and found to be the same as of the original supplied. Beet molasses, cane molasses and golden syrup were examined as shewn later.

On distilling a sample of Java molasses, however, considerable charring of the material in the flask soon became evident, and some abnormal decomposition took place as will be seen from the table of results given below. (pg. 106). It was considered advisable at this point to investigate the action of these chloro derivatives on solutions of pure sucrose under the same conditions as before. Various distilling mixtures were made up having boiling points ranging from 97° C. to 116° C.

In every test, charring of the sugar commenced within the first half-hour's heating, and continued until the mass was completely carbonized. This was effected in about two hours. The pH. of the distillates were below 2.8.

The details of the tests are shewn in Tables on pages 106 to 129, and the cause of the decomposition is further discussed on page 130.

Sample tested:

Java Molasses.

Weight taken:
(I) 10.88 gms.
(II) "

Distilling liquid:

Tetrachlorethane and Trichlorethylene Mixt.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	17.92	
2.	19.30	
3.	19.76	
4.	20.45	
5.	20.68	
6.	21.14	
7.	21.37	
8.	22.06	
9.	22.20	
10.		
11.	Complete charring.	
12.		

Q. apparatus used.

Sample tested:	Distilling liquid:
Sucrose solution. 39.60 per cent. water. 60.40 " " sucrose.	Tetrachlorethane and Carbon tetrachloride. B.P. 103.5°C
Weight taken: (I) 10.15 gms. (II) "	

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	33.51	
2.	35.47	
3.	37.94	
4.	39.42	
5.	40.40	
6.	43.36	
7.	45.33	
8.		
9.	Complete charring rapidly took place.	
10.		
11.		
12.		

Sample tested:	Distilling liquid:
Sucrose solution. Water 39.60 per cent. Sucrose 60.40 " " Weight taken: (I) 10.67 gms. (II) 10.62 "	Tetrachloroethylene.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	36.55	36.72
2	43.58	43.32
3.	47.79	46.85
4.		
5.		
6.		
7.	D.L. apparatus.	Q. apparatus.
8.		
9.	Complete charring ocuurred in both tests.	
10.		
11.		
12.		

Sample tested:	Distilling liquid:
Sucrose solution.	Tetrachloroethylene and carbon tetrachloride.
Water 39.60 per cent. Sucrose 60.40 " "	B.P. of mixture 103°C.
Weight taken: (I) 10.15 gms. (II) 10.15 "	

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	32.53	31.53
2.	38.92	40.40
3.	41.38	41.88
4.	45.82	47.30
5.		
6.		
7.	D.L. apparatus.	Q. apparatus.
8.		
9.		
10.		
11.		
12.		

Complete charring occurred in both cases.

Refer to page 130.

Sample tested:	Distilling liquid:
Sucrose solution. Water 39.60 per cent. Sucrose 60.40 " " Weight taken: (I) 10.17 gms. (II) 10.11 "	Tetrachloroethylene and carbom tetrachloride. B.P. of mixture 97°C.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	23.60	19.31
2.	32.45	30.94
3.	34.91	34.41
4.	36.87	36.14
5.	38.84	37.38
6.	39.93	38.37
7.	40.86	39.36
8.		40.34
9.	D.L. apparatus.	Q. apparatus.
10.		
11.	Rapid and complete charring took place.	
12.		

Sample tested:	Distilling liquid:
Sucrose solution. Water 39.60 per cent. Sucrose 60.40 " " Weight taken: (I) 10.20 gms. (II) 10.20 "	Trichlorethylene and tetrachlorethane mixt.

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	35.30	31.86
2.	41.67	37.01
3.	45.10	41.42
4.	47.25	44.61
5.	48.04	46.33
6.		
7.		
8.		
9.	D.L. apparatus.	Q. apparatus.
10.		
11.		
12.	Complete charring occurred.	

Sample tested:	Distilling liquid:
Beet Molasses No.1	Tetrachloroethylene Mixt. B.P. 106°C.
Weight taken: (I) 10.58 gms.	+ 5 gms. Kieselguhr.
(II) 11.21 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	12.77	10.92
2.	14.98	14.05
3.	14.98	
4.	15.60	15.38
5.	15.70	15.61
6.	16.06	15.83
7.	16.06	16.06
8.	16.06	16.06
9.		16.06
10.		
11.		
12.		

No charring.
pH of distillates about 4.6

Q. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 1	Tetrachlorethylene Mixt. B.P. 106°C.
Weight taken: (I) 10.48 gms. (II) "	

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	12.17	
2.	13.60	
3.	14.32	
4.	14.55	
5.	14.96	
6.	15.27	
7.	15.31	
8.	15.75	
9.	15.75	
10.	15.75	
11.		
12.		

Constant reading obtained, but the result differs from those reported on the previous page. No kieselguhr was used in this test.

Sample tested:	Distilling liquid:
Beet Molasses No. 1	Tetrachloroethylene.
Weight taken: (I) 11.17 gms. (II) 10.85 "	+ 5 gms. Kieselguhr

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	14.87	15.48
2.	16.15	16.13
3.	16.15	16.59
4.	16.65	16.77
5.	17.02	17.05
6.	17.02	17.05
7.	17.02	17.05
8.		
9.		
10.	No charring.	
11.	pH. about 5.0	
12.		

Sample tested:	Distilling liquid:
Beet Molasses No. 1 (continued)	**Tetrachloroethylene.**
Weight taken: (I) (III) 10.89 gms. (II) "	**+ 5gms. of Kieselguhr.**

Time of distilling. Hours.	Per cent. water in sample. (III)	(~~II~~)
1.	**15.61**	
2.	**16.53**	
3.	**16.80**	
4.	**16.98**	
5.	**16.98**	
6.	**16.98**	
7.		
8.		
9.	**No charring.**	
10.	**pH. of distillate 5.0**	
11.		
12.		

Sample tested: Beet Molasses No. 2	**Distilling liquid:** Tetrachloroethylene.
Weight taken: (I) 12.79 gms. (II) 10.22 "	 + 5 gms. Kieselguhr. + 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	15.05	14.92
2.	15.63	15.41
3.	16.03	
4.	16.03	16.14
5.	16.03	16.14
6.	16.03	16.14
7.		
8.		
9.		
10.		
11.		
12.		

No charring of residues.

pH of distillates 1.2

Q. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 2	Tetrachloroethylene.
Weight taken: (III) 15.04 gms.	+ 5 gms. Kieselguhr.
(IV) 12.55"	+ 10 " "

Time of distilling. Hours.	Per cent, water in sample. (III)	(IV)
1.	13.63	14.94
2.	14.63	15.34
3.	14.96	15.53
4.	15.21	15.74
5.	15.40	16.03
6.	15.40	16.03
7.	15.40	16.03
8.		
9.		
10.		
11.		
12.		

Note. Test No. (III) does not give same result as the others.

No charring. pH. of distillates about 1.2

Q. apparatus used.

Sample tested: Beet Molasses No. 2	Distilling liquid: Tetrachloroethylene.
Weight taken: (V), 10.21 gms.	+ 10 gms. Kieselguhr.
(VI) 10.37 "	+ 10 " "

Time of distilling. Hours.	Per cent. water in sample. (V)	(VI)
1.	15.02	14.37
2.		14.95
3.	16.01	15.72
4.	16.0 1	15.72
5.	16.01	15.72
6.		
7.		
8.		
9.		
10.		
11.		
12.		

No charring.

D.L. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 3	Tetrachloroethylene.
Weight taken: (I) 13.26 gms.	+ 5.gms. Kieselguhr.
(II) 12.12 "	+ 5 " "

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.		17.91
2.	18.56	18.51
3.	18.77	
4.	18.86	19.05
5.	19.01	19.14
6.	19.08	19.14
7.	19.08	19.14
8.	19.08	
9.		
10.		
11.		
12.		

No charring occurred.

pH. of distillates 3.8-4.0

D.L. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 3	**Tetrachloroethylene.**
Weight taken: (III) 10.37gms. (II) "	**+ 5 gms. Kieselguhr.**

Time of distilling. Hours.	Per cent water in sample. (I)	(III)	(II)
1.		**17.36**	
2		**18.32**	
3.		**18.80**	
4.		**19.17**	
5.		**19.29**	
6.		**19.29**	
7.		**19.29**	
8.			
9.			
10.			
11.			
12.			

pH. of distillate 3.8

Q. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No.4	Tetrachloroethylene.
Weight taken: (I) 10.52 gms.	+ 5gms. Kieselguhr
(II) 10.76 "	+ 5 " "

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	19.67	19.05
2.	20.43	19.98
3.		
4.	20.90	20.91
5.	20.90	20.91
6.	20.90	20.91
7.		
8.		
9.		
10.		
11.		
12.		

No charring.

pH. of distillates 5.1

D.L. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 4	Tetrachloroethylene.
Weight taken: (I) 10.36 gms.	+ 5 gms. Kieselguhr.
(II) 10.24 "	+ 5 " "

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	20.64	19.05
2.	21.00	20.03
3.	21.23	20.51
4.	21.23	20.89
5.	21.23	20.89
6.	21.23	20.89
7.		
8.		
9.		
10.		
11.		
12.		

No charring occurred.

pH. of distillates 5.1

Q. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 5	Tetrachloroethylene.
Weight taken: (I) 10.45 gms.	+ 5 gms. Kieselguhr.
(II) 10.34 "	+ 5 " "

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	17.13	19.34
2.	18.19	19.34
3.	18.86	19.44
4.	19.23	19.44
5.	19.23	19.44
6.	19.23	
7.		
8.		
9.		
10.		
11.		
12.		

No charring.

pH. of distillates 5.4

D.L. apparatus used.

Sample tested:	Distilling liquid:
Beet Molasses No. 5	Tetrachloroethylene.
Weight taken: (I) 10.55 gms.	+ 5 gms. kieselguhr
(II) 11.08 "	+ 5 " "

Time of distilling. Hours.	Per cent water in sample. (I)	(II)
1.	17.66	18.51
2.	18.65	18.86
3.		
4.	19.39	19.41
5.	19.39	19.41
6.	19.39	19.41
7.		
8.		
9.		
10.		
11.		
12.		

No charring.

pH. of distillates 5.4

Q. apparatus used.

Sample tested:	Distilling liquid:
Natal Molasses.	Tetrachloroethylene.
Weight taken: (I) 10.53 gms.	+ 5 gms. Kieselguhr.
(II) 10.60 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	25.40	25.48
2.		25.94
3.	26.60	26.29
4.	26.83	26.75
5.	27.31	26.88
6.	27.54	27.13
7.	27.77	27.59
8.	28.02	
9.		
10.		
11.	Complete charring took place.	
12.		

Sample tested:	Distilling liquid:
Natal Molasses.	Tetrachloroethylene.
Weight taken: (I) 12.53 gms.	+ 5 gms. Kieselguhr.
(II) 13.27 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	24.98	
2.	25.70	25.56
3.	26.10	
4.	26.34	26.54
5.	26.58	26.83
6.	26.91	26.99
7.	27.15	27.29
8.	27.46	
9.		27.82
10.		27.97
11.		28.27
12.	Complete charring of residues. pH. below 2.8	

D.L. apparatus used.

Sample tested: Hawaii Molasses.	Distilling liquid: Tetrachloroethylene.
Weight taken: (I) 10.47 gms.	+ 5 gms. Kieselguhr.
(II) 11.83 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	22.61	22.62
2.	23.21	22.53
3.	23.59	23.97
4.	23.97	24.15
5.	24.16	
6.	24.35	24.60
7.	24.55	24.96
8.		25.05
9.		25.49
10.		25.76
11.		25.85
12.		

Residues completely charred after about two hours' heating.

D.L. apparatus.

Sample tested: Refinery Molasses.	Distilling liquid: Tetrachloroethylene.
Weight taken: (I) 10.39 gms.	+ 5 gms. Kieselguhr.
(II)10.46 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	22.14	21.17
2.	22.62	23.18
3.	23.59	23.18
4.	23.88	23.90
5.	24.16	24.14
6.	24.55	24.62
7.	25.03	
8.	25.23	
9.	25.51	
10.	25.80	
11.	25.90	
12.		
	D.L. apparatus	Q. apparatus.

Complete charring occurred.

pH. of distillates 2.8

Sample tested:	Distilling liquid:
Refinery Molasses.	Tetrachloroethylene and carbon tetrachloride mixt. B.P.106 V.
Weight taken: (I) 10.56 gms.	+ 5 gms. Kieselguhr.
(II) 10.91 "	+ 5 " "

Time of distilling. Hours.	Per cent. water in sample. (I)	(II)
1.	20.65	20.63
2.	21.78	22.55
3.		22.64
4.	22.73	22.74
5.	23.20	23.10
6.	23.20	23.28
7.	23.20	
8.		
9.		
10.		
11.		
12.		24.11

Residues charred.
pH. below 2.8

Referring to Table pg.110 the sucrose solution should not have charred at a temperature of 97°C. In order to eliminate any possibility of the sugar solution itself being responsible for this peculiar behaviour, some of it was boiled under a reflux condenser for a considerable time, the boiling point being about 103°C. Not the slightest trace of decomposition or discoloration was observed. This confirmed the findings of Noel Deerr (H.S.P.A.) that sucrose solutions are stable even at a somewhat higher temperature than 103°C.

Obviously the caramelization and carbonization of the pure sucrose solution in the case cited above could have resulted only from inversion due to the combined effects of acid and temperature. The aqueous distillate when tested was found to be acidic and chloride was present. The pH. was below 3.0.

Some of the tetrachloroethylene was next boiled under a reflux for an hour with some distilled water which was afterwards separated and tested. The presence of HCl was confirmed.

At this point the special "Q" apparatus for use in the estimation of water in molasses, by using a mixture of tetrachlorethane and trichloroethylene, was received, and an attempt was immediately made to reproduce results obtained by the patentee, using Java (cane) molasses. In this case also, rapid charring took place. The experiment was repeated with beet molasses and consistent results were obtained, as was also the case when beet molasses was distilled with the same mixture which caused the trouble with the cane molasses.

It was thus made evident that the chloro derivatives of the heavy hydro carbons are unstable when heated. The fact that the beet molasses was not affected was no doubt due to its alkalinity which neutralized the acids produced by the distilling mixture.

Tucker and Burke (Analyst, 1935) mention that in distilling cereals with tetrachlorethane for the determination of moisture, consistent results may be obtained under standard conditions. They give a list of other materials in which the water content may be determined by this method, but they state that cane sugar syrups cannot be so estimated. They do not, however, suggest any reason for this.

An examination of the various chloro compounds was next undertaken. A definite quantity was boiled up with distilled water under a reflux condenser and the acidity determined in the water so treated, by titration with N/10 NaOH. The figures given below shew conclusively the unstability of these compounds under the conditions recommended by continental sugar technologists for the estimation of moisture in beet molasses.

Examination of Chloro-Derivatives.

In each case 100 cc. of the chloro-compound and 20 cc. of distilled water were boiled in a flask under a reflux condenser for two hours. The water was then separated by means of a separating funnel, tested for the presence of Chloride radicle, its pH. ascertained by the comparator, and 10 cc. of it were titrated against N/10 NaOH.

pH. of Distilled water - 4.8

	pH. of Water.	No. of cc N/10 NaOH required.	Cl'.
Carbon tetrachloride	4.8	-	Absent.
Trichlorethylene	1.2	30.8	present.
Trichlorethane	3.0	2.12	"
Tetrachloroethylene	1.2	7.36	"

The behaviour of the saturated compound is somewhat unexpected.

Before coming to any final decision as to the unsuitability of the method when applied to cane molasses, a communication was sent to the makers of the chemicals who were asked if they could supply these chloro compounds of guaranteed purity. They replied that they were unable to do so, and that the tests they themselves applied corroborated the findings of the author. They also stated that they quite expected that the chloro derivatives would decompose under the conditions of the distillation.

It may be concluded, therefore, that the estimation of water in cane molasses cannot be effected by means of these chloro solvents, and that the continued use in the case of beet molasses is attended with considerable risk unless the distilling liquid or mixture is fresh. Constant use even with alkaline beet molasses is bound to lead to decomposition of the distilling liquid as well as of the molasses under treatment, and to give results which may be highly inaccurate and not immediately apparent.

Method No. 5. Brix by Refractometer.

In 1906, Tolman and Smith (J.Am.Chem.Soc.) shewed that the index of refraction of solutions of pure sucrose varies directly with the concentration. They and other workers including Main and Geerligs demonstrated the utility of its application in the chemical control of the refinery and also of the raw sugar factory. Tables of reference, first published by Tolman and Smith (loc.cit.), by Main (I.S.J.,1907), and also by Geerligs and Van West (Archief.1909) are now extensively used for converting the reading of the refractive index of the solution to per cent. sucrose, or alternatively to per cent. water in the solution of sucrose.

The form of instrument in general use for the purpose of determining the refractive index of sugar solutions is a development of the Abbé type, and the per cent. solids so determined is referred to as the Refractometer Brix, or ref.brix.

The ref. brix of sugar syrups, etc. may be rapidly determined by merely placing a drop of the liquid between the prisms of the instrument and reading the scale through the ocular. The scale is graduated either in per cent. sugar or in refractive indexes. In the latter case by reference to the appropriate tables the index is read off as per cent. sugar; (100 - ref.brix) will represent the per cent. water.

The prisms are kept at a constant temperature of 20 C. at which the scale is graduated, but tables of corrections are available in order to bring the reading at any other temperature to this standard.

When this method is employed, it is assumed that the refractive indexes of the salts in solution under examination have the same values as sucrose. This, of course, is not the case, and with impure juices, molasses, etc. the difference may be considerable. Despite this fact, the use of the value "ref. brix" throughout the factory chemical control has been advocated by many sugar technologists, but in this work we are only concerned with its relation to the solid content of molasses as found by other methods.

In each of the tests on molasses and syrups reported in part I, the ref.brix is stated. For purposes of comparison, the solid matter as found by the various methods are tabulated on pg. 136 so that any relation can be readily observed.

An examination of Table 136 does not reveal any definite relation between the brix obtained by the refractometer and the dry substance found by any other method.

De Whalley (I.S.J., 1935) states that for golden syrups, the addition to the ref. brix of 0.022 for every 1 part of invert sugar found to be present, will give the per cent.

	D.S.		D.S.		Ref.Brix.	Invert Sugar
	Vacuum Oven.		Steam Oven			Per cent.
	5 hrs.	9 hrs.	5 hrs.	9 hrs.		
Refinery Molasses I.	76.56	75.50	73.79	72.99	76.7	12.05
Beet Molasses I.	83.77	83.56	85.22	84.78	81.2	Trace
" " 2.	86.50	85.60	84.88	84.64	82.3	nil.
" " 3.	83.04	82.35	81.25	81.06	79.8	"
" " 4.	80.68	80.01	79.51	79.51	79.3	"
" " 5.	82.67	82.11	80.85	80.44	79.3	"
Golden Syrup.	84.72	84.30	83.13	82.60	82.1	47.76
Java Cane.	84.25	83.95	81.28	80.30	83.1	23.21
Natal Molasses.	77.22	76.59	75.21	74.83	78.2	14.46

solids actually in the syrup. He claims also, that the same correction is applicable to cane molasses, but he makes no mention of its utility in the case of beet molasses.

In the case of golden syrup reported on page 32 the invert sugar content was found to be 47.76 per cent. According to de Whalley the true solids are 82.1+(.022 x 47.76) i.e., 83.15 which figure agrees with that obtained by drying in the steam oven for 5 hours.

In the case of Natal molasses, in which the invert sugar was 14.46, the solids per cent. by this reasoning would be

78.2 +(.022 x 14.46) i.e. 78.5

This figure, 78.5 is very different from the results obtained by the oven methods, being higher than both.

Similarly with Java molasses.

83.1 + (.022 x 23.2) = 83.6

In this case the result is higher than the D.S. obtained by steam oven drying and lower than that obtained by drying in vacuo.

With the refinery molasses, where the invert sugar was found to be 12.05 per cent., the solids would be 76.7 + (0.022 x 12.05) i.e. 77.0. This figure is nearly 4 per cent. higher than that obtained by heating for 9 hours in the steam oven. Furthermore, it shews a considerable difference from the results obtained by drying in vacuo.

In the case of beet molasses, in samples No. 3, 4 and 5, the ref. brixes have practically the same value. In No. 4, this agrees with the percentage D.S. obtained by drying in the steam oven, but a considerable difference is observed in the other two samples.

It may, therefore, definitely be stated that there is no relation between the ref. brix and the per cent. dry substance in the case of cane molasses, refinery molasses and beet molasses.

The knowledge of the refractive brix may be of considerable value for control purposes in a factory dealing with these products but the assumption that it gives a figure representing the true solid contents is unfounded.

It is somewhat difficult to draw any definite conclusions from the work carried out in Part I. In the absence of any precise knowledge of the true water content of any of the materials dealt with, it is not possible to state which method gives the closest result. It is the general opinion of sugar chemists that the vacuum oven method gives results nearest the truth, but the work carried out here does not furnish much evidence in support of this view.

One can understand the difference between vacuum and steam oven results in the case of products containing levulose, which does decompose at 100° C., but there is also a difference, though not of the same magnitude, in the case of beet molasses containing no levulose.

It has been claimed that the distillation methods are accurate because the water is actually collected. Reference to Table No. 140 however, shews little to substantiate this claim. While results obtained by the two distillation methods may be said to agree with each other, they are nearer the figures found for drying at 100° C. for 9 hours than those at 70° C. in vacuo. This, of course, may be expected, as the B.P. of the distilling liquids is approximately 115° C.

Distillation using tetrachlorethylene might be a suitable method for beet molasses, if precautions were taken

Results of determination of Water Content in Beet Molasses by different Methods.

	Steam Oven		Vacuum Oven.		Toluene	Tetrachlorethylen
	5 hrs.	9 hrs.	5 hrs.	9 hrs.		
Beet Molasses 1.	16.23	16.44	14.78	15.21	16.43	17.02
" " 2.	15.13	15.36	13.50	14.40	15.49	15.89
" " 3.	18.75	18.94	16.96	17.65	19.30	19.07
" " 4.	20.49	20.49	19.32	19.99	21.16	20.98
" " 5.	19.15	19.42	17.33	17.89	19.30	19.39

to change the liquid frequently, but its only advantage appears to be that the estimation involves only one rapid weighing and requires the minimum of attention. As the apparatus must be thoroughly cleaned before use, however, the saving in labour is somewhat offset.

With regard to cane and refinery molasses, distillation methods are definitely inapplicable. The only solution of the problem appears to lie in the adoption of a standard method under specified conditions, so that results obtained by different workers may be strictly comparable.

If it were possible to dehydrate a sample of molasses without the application of heat some valuable information might be obtained which would settle the question as to whether the result obtained by drying at the temperature of the steam oven or that found by drying in vacuo at 70° C. is nearer to the true actual water content of the molasses.

This has been attempted, with doubtful success.

Rice, in a paper on the determination of moisture in sugar syrup (Ind. and Eng. Chem. 1929) refers to the fact that the A.O.A.C. (Methods, 1925) report the progressive decomposition during the drying of molasses at 70° C. in vacuo and that samples of the same syrup prepared in the same way reached constant weight when left in a Hempel desiccator over ~~with~~ sulphuric acid ~~in~~ for 48 hours at a pressure of 2.5 cm. and that no further loss of weight was found after 10 days.

Experiments were made by the present author who attempted to dry a sample of molasses in an evacuated desiccator over H_2SO_4 but after a week was unable to reach a figure within about 3 per cent. of that obtained by oven drying methods.

Conc. H_2SO_4 is not a pleasant substance to work with and a substitute was found in Silica Gel which during a long series of experiments was proved to be a very efficient drying agent, much more so in fact than any other used in the tests.

The silica gel is sold in perforated aluminium containers which are placed in the vessel to be dried. The silica gel can be revivified by heating the container in the oven and then storing in the special tin provided. The size of this desiccator is about 2" dia. x ½" deep. A "tell tale" paper disc treated with cobalt nitrate shews when the gel needs regenerating, by the change in its colour from blue (when dry) to pink.

Samples of molasses were made up as in the ordinary oven drying tests, placed in a glass bell-desiccator and three of the silica gel desiccators were inserted with a "tell tale". The change in colour of the small disc shewed that dehydration was taking place.

The gel dishes were changed at intervals varying from 6 hours at first to 24 hours latterly, and others that had just been revivified were then inserted.

The progress of the drying may be followed from the weighings tabulated below.

Sample Tested. Natal Molasses.

As this molasses was rather fluid, one weighed portion was mixed with the sand without the addition of water and two others were made up in exactly the same manner as for the tests by the drying ovens : 2 - 3 cc. water was used for facilitating mixing with the sand. Each dish was dried separately in a desiccator over silica gel.

"Dry" mixed test.

Weight of molasses taken.	1.5615 gms.
Per cent. of D.S. after 1 day.	84.22
" " " " " 2 days.	83.12
" " " " " 3 "	82.41
" " " " " 6 "	81.88
" " " " " 8 "	81.70
" " " " " 9 "	81.46
" " " " " 10 "	81.27
" " " " " 13 "	80.96
" " " " " 14 "	80.88
" " " " " 15 "	80.69
" " " " " 20 "	80.48

"Wet"mixed test.	I.	II.
Weight of molasses taken.	1.6391	1.7090
Per cent. of D.S. after 4 days.	86.68	83.96
" " " " " 7 "	83.27	83.15
" " " " " 9 "	82.71	82.53
" " " " " 11 "	82.15	82.14
" " " " " 14 "	81.95	81.88
" " " " " 17 "	81.49	81.55
" " " " " 22 "	80.93	80.11

After this period alight increases were recorded, so after a total period of twenty eight days the experiments were abandoned.

Five similar tests were carried out, some in evacuated desiccators but the lowest percentage of D.S. found was 80.11.

The information provided by these tests is not of much assistance in settling the question of what is the true water content of molasses. It does shew a remarkable consistency in the rate of drying in duplicate tests and is a striking proof of the efficiency of silica gel as a dehydrating agent.

The author also considered that it might be possible to heat the sample under examination in a special type of oven, and to collect and weigh the moisture and products of decomposition given off. The loss in weight of the sample treated should be equal to the weights of products collected.

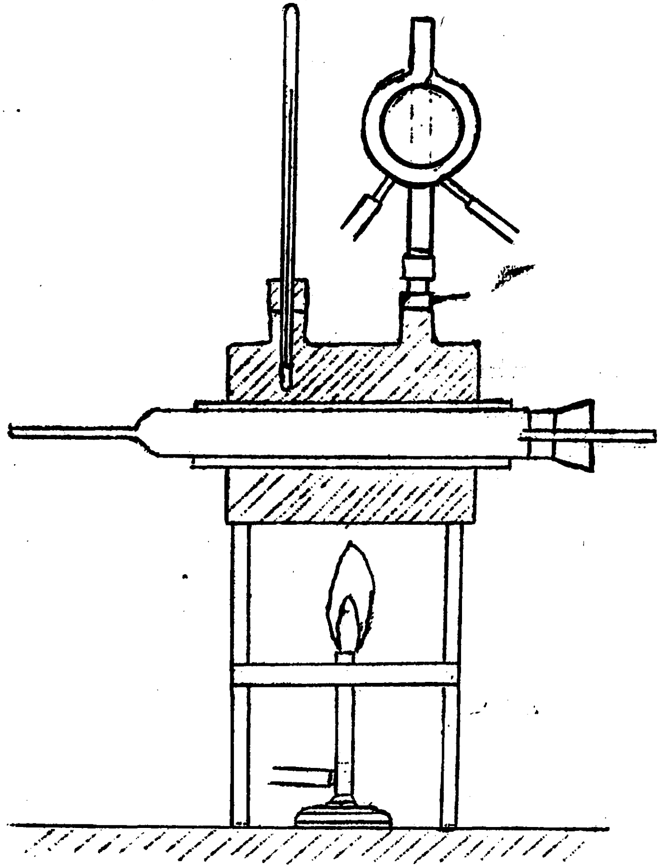
As it would be impossible to separate the different products of decomposition, it was decided to collect the moisture and any CO_2 driven off in a series of U tubes containing calcium chloride and soda lime respectively. The increase in the weights of the tubes so obtained should be equal to the weight lost by the sample of molasses.

Two special ovens were designed for this purpose by the author and are shewn on the sketch on page 146.

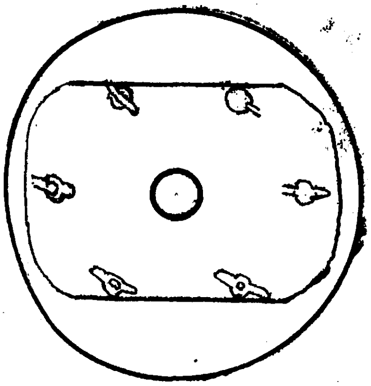
Oven "B" consists of a copper tube of rectangular cross section, which could contain the same size of dish as was used for the steam and vacuum oven tests. One end of this tube is "drawn out" and brazed to a $\frac{1}{4}$" copper tube. The whole is fixed in a copper jacket in which circulates a mixture of water and glycerine, which is heated in order to keep a constant temperature of 102°C. A suitable rubber insertion and a heavy brass door closes the other end of the tube, and through the door a tube passes through which a current of dried and purified air is drawn to sweep out the vapours produced on heating the molasses.

The water driven over is collected in the U tubes and bulbs.

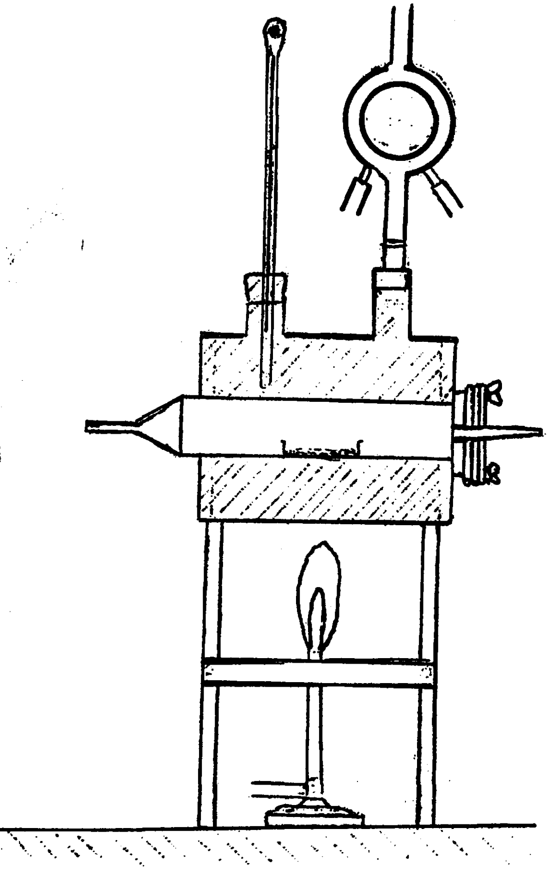
A series of blank experiments was carried out to see if the method was practicable. First, air from the compressed



A.



DETAILS OF DOOR.



B.

air supply was passed in after being thoroughly dried, first in H_2SO_4 bubblers and then in special towers containing fresh calcium chloride and soda lime. A Lanseidle bulb containing sulphuric acid was the first absorbing vessel, and the acid in this rapidly turned brown. It appeared that the compressed air was contaminated with oil from the compressor and the organic matter was trapped not in the drying towers but in the sulphuric acid, after it had passed through the heated oven.

Attempts to purify the air were unsuccessful. It was also observed that there was an increase in weight in the soda lime tubes. This was finally traced to the decomposition of the rubber insertion of the door. Tests made on this material shewed that progressive loss of weight took place on heating it at 100° C.

Attempts were then made to draw the current of air through by means of a dry air pump. Despite all the precautions taken, slight increases of weight in all the drying tubes as well as the soda lime tubes indicated leaks which could not be altogether prevented.

It was then decided to use a different type of oven. Sketch "A" indicates a glass tube drawn out at one end, passing through a cylindrical copper water-jacketed oven. A train of U tubes was attached to the narrow tube, and a very slow current of purified air was drawn through while the sample was being heated.

A number of blank tests were first made, but increases in the weights of the U tubes always resulted. Even the smallest leaks in the apparatus, which could not be located, seemed to have a considerable cumulative effect during the five hours of the run.

Before the attempts which had occupied a number of months were abandoned, a few experiments were completed.

Although the loss in weight suffered by the sample did not agree with the gain in weight found in the calcium chloride and soda lime tubes, there was a sufficient increase in the latter to indicate that decomposition of the molasses at the temperature of the oven, i.e. 100°C to 102°C. resulted in the production of an appreciable amount of CO_2 .

This field of investigation might profitably be explored by workers skilled in micro-technique, but in view of the difficulties encountered and the fact that the weights of the tubes composing the rather extended collecting train were out of all proportion to the small increases in weight which were being sought, the author decided to discontinue the attempt.

A few results are given to shew the order of the figures obtained.

Sample - Natal Molasses.

Per cent. loss in sample.	Per cent. gain in $CaCl_2$ tubes.	Per cent. gain in soda lime tubes.
23.08	22.31	0.14
21.45	22.52	0.18
26.28	26.64	0.21

PART II.

PART II.

Estimation of Reducing Sugars.

The determination of reducing sugars in cane molasses and refinery products is a problem which is still under investigation by the members of the International Commission for Uniform Methods of Sugar Analysis.

The methods in general use involve the precipitation of cuprous oxide from Soxhlet's alkaline copper tartrate solution (commonly referred to as Fehling's solution) as a result of the action of the reducing sugars. The precipitate is then estimated either gravimetrically after conversion to cupric oxide, or volumetrically after dissolving it in specified reagents. Tables shewing the relation between weights of copper oxide and various sugars have been produced by Allihn, Herzfeld, Meissl, Munson and Walker and others, and are used to find the percentage of reducing sugar present. This is usually reported as Invert Sugar.

The most interesting method, however, is the direct titration against Fehling's solution of the solution containing the sugar, methylene blue being used as an internal indicator. This method first published by Lane and Eynon (J.S.C.I., 1923) is rapidly gaining favour, and only the conservatism of the sugar industry has so far prevented its more extensive application.

The reducing action of sugars upon different salts of copper was originally observed by Trommer, 1841 (Ann.39, 360.), and his methods were improved by Barreswil in 1844. The details of the procedure as now employed were worked out by Fehling in 1848 (Ann. 72, 106.). Gravimetric methods are widely used on the Continent and in this country. The A.O.A.C. recommend the Munson and Walker procedure for the gravimetric determination of cupric oxide, which by reference to their special tables is read off as Invert Sugar. The Lane-Eynon method is given as a "tentative" one. The H.S.P.A. recommends both the Munson and Walker and the Lane-Eynon procedures in its Methods of Chemical Control for Cane Sugar Factories (1929).

Any comparison of the results obtained by the various methods does not appear to have been published by an independent worker. An attempt is made, therefore, in this section to shew the differences in results obtained by using different methods, and the variations obtained by different analysts.

The methods compared are the Lane-Eynon, Munson-Walker, Low's Iodide and the Permanganate.

The directions for making up the stock solutions and the details of the procedure in the methods examined are as follows.

Preparation of Fehling's Solution.

A. 69.28 gms. $CuSO_4.5H_2O$ per litre.

B. 346. " of Rochelle Salts, and 100 gms. NaOH per litre.

For analysis mix equal volumes of A and B just before using.

Lane-Eynon's Method.

"The Standard Method of titration is carried out as follows: 10 ml. or 25 ml. of Fehling's solution is measured, with a pipette accurately standardized for this purpose, into a hard glass flask of 300-400 ml. capacity, and of the ordinary round form with flattened base. A 50 ml. burette having a pinch-cock instead of a glass tap is filled with the solution to be titrated, and almost the whole volume required to reduce the Fehling's solution is run into the flask, so that only about 0.5 to 1 ml. (but not less than 0.5 ml.) is required later to complete the titration. The contents of the flask are well mixed in the cold by shaking round, and then heated to boiling on a tripod stand covered with plain wire gauze over a bunsen flame. The liquid is kept in moderate ebullition for 2 mins. and then 3-4 drops of the methylene blue* solution are added, preferably without touching the sides of the flask, and the titration is completed in 1 min. further, by addition of the sugar solution 2-3 drops at a time, at intervals of about 10 secs., until the colour of the indicator is completely discharged, and the boiling reaction liquid resumes the bright orange appearance (due to cuprous oxide), which it had before the indicator was added. The titration is thus completed in 3 mins. from the commencement of ebullition, and during the whole time the flask should remain on the wire gauze, the

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* 1 per cent. aq. solution.

continuous emission of steam from the neck being an effective safeguard against back-oxidation of the Fehling's solution or the indicator by air. During additions of sugar solution to the boiling liquid the burette is held in the hand; if the short outlet tube of the burette is bent to one side permanently the main burette tube can be kept out of the steam whilst the jet is brought over the mouth of the flask.

Duplicate titrations by this method should agree to within 0.1 ml. in the volume of sugar solution required. In the titration of Dextrose, laevulose, or invert sugar in absence of much sucrose, the results are not appreciably affected if the total period of boiling is reduced to 2 mins. or prolonged to 4 or 5 mins., but with lactose and maltose and with invert sugar in presence of a large excess of sucrose, it is advisable to adhere approximately to the total boiling period of 3 mins.

From the volume of sugar solution required the concentration of the solution is found by reference to the appropriate Table."

Munson and Walker Method.

"Transfer 25 cc. each of solutions A and B of the Soxhlet reagent to a 400-cc Jena or Non-sol beaker and add 50 cc. of reducing sugar solution, or if a smaller volume of sugar solution be used add water to make the final volume 100 cc. Heat the beaker upon an asbestos gauze over a bunsen burner, so regulate the flame that boiling begins in four minutes, and continue the boiling for exactly two minutes. Keep the beaker covered with a watch glass throughout the entire time of heating. Without diluting, filter the cuprous oxide at once on a Gooch crucible, using suction. Wash the cuprous oxide thoroughly with water at a temperature of about 60 C, then with 10 cc of alcohol and finally with 10 cc of ether. Dry for 3 0 minutes in a water oven at 100 C, cool in a desiccator, and weigh as cuprous oxide or determine the copper by one of the methods given on pages 86-90 Circular of the Bureau of Standards No. 44, 1918.

The analytical procedure for any one of these sugars may be verified by carrying out the operation upon the standard dextrose sample or upon the invert sugar solution.

A table by Munson and Walker has been computed for the determination of reducing sugar in the presence of sucrose under conditions where a large quantity of reducing substance is present and where a small quantity is present. If the composition of the mixture is known approximately, the weight of substance required can be judged without a previous assay. If less than 10 per cent of reducing sugar is present, a weight of 2 g. of total sugar should be taken in 50 cc. If more than 10 per cent 0.4 g. in 50 cc is the required amount. For unknown mixtures it is best to make an analysis with either one of the amounts of total sugar. This will serve either as a preliminary or final assay according to the amount present. The method allows great latitude of procedure."

Low's Volumetric Iodide Method. (J.Amer.Chem.Soc., 24, p.1082 and Bull.Bur.Chem., 107, p.241).

"(1) Standardization of the Thiosulphate Solution. - Prepare a solution of sodium thiosulphate containing about 19 g of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.2 g of pure copper foil and place in flask of about 250 cc capacity. Dissolve by warming with 5 cc of a mixture of equal volumes of strong mitric acid (sp.gr. 1.42) and water and then dilute to about 50 cc. Boil for a few minutes to expel partially the red fumes and then add 5 cc of strong bromine water and boil until the bromine is thoroughly expelled. The bromine is to insure the complete destruction or removal of the red fumes. Remove from the heat and add a slight excess of strong ammonia water. Ordinarily it suffices to add 7 cc. of ammonia water of 0.90 sp.gr. Again boil until the excess of ammonia is expelled, as shewn by a change of colour of the liquid and a partial precipitation of the copper as hydroxide or oxide. Now add strong acetic acid in slight excess, perhaps 3 or 4 cc of the 80 per cent acid in all and again boil for a moment if necessary to redissolve the copper precipitate. Cool to room temperature and add about 3 g of potassium iodide or 6 cc of a solution of the salt containing 50 g in 100 cc. Cuprous iodide will be precipitated and iodine liberated according to the reaction.

$$2\ Cu\ (C_2H_3O_2) + 4\ KI = Cu_2I_2 + 4\ (KC_2H_3O_2) + 2\ I$$

The free iodine colours the mixture brown. Titrate at once with the thiosulphate solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Continue the titration cautiously until the colour due to free iodine has entirely vanished. The blue colour changes toward the end to a faint lilac. If at this point the thiosulphate be added drop by drop and a little time be allowed for complete reaction after each addition, there is no difficulty in determining the end point within a single drop. One cubic centimeter of the thiosulphate solution will be found to correspond to about 0.005 g of copper. The reaction between the thiosulphate and the iodine is:

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

The starch liquor may be made by boiling about 0.5 g of starch with a little water and diluting with hot water to about 250 cc. The liquor should be homogenous and free from lumps. It should be used cold and must be prepared frequently.

(2) Analysis. - After washing the precipitated cuprous oxide, cover the Gooch crucible with a watch glass and dissolve the oxide by means of 5 cc of warm nitric acid (I : I) poured under the watch glass with a pipette. Catch the filtrate in a flask of 250 cc capacity and wash watch glass and Gooch crucible free of copper; 50 cc of water will be sufficient. Boil to expel red fumes, add 5 cc of bromine water, boil off the bromine and proceed as in the standardizing of the thiosulphate."

The Permanganate Method. The same procedure is followed as in Munson and Walker's method, but the precipitate of cuprous oxide together with the asbestos is transferred to a beaker, and mixed with 50 cc. of a concentrated solution of pure ferric sulphate in 20 per cent. sulphuric acid. The precipitate is dissolved with the aid of heat and then the whole contents of the beaker are transferred to a conical flask. After being cooled to between 60° and 70°C. the mixture is titrated with a solution of Potassium Permanganate containing 5 gms. per litre.

This solution had been previously standardized for copper value against thiosulphate solution as used in Low's method.

In all the estimations carried out by the Munson-Walker procedure, the crucible containing the precipitated cuprous oxide was heated for 1 hour in the muffle furnace and the cuprous oxide was thus converted to cupric oxide. By reference to the special table, the weight of sugar corresponding to the weight of oxide was obtained.

Before proceeding with the examination of samples of molasses, it was considered advisable to work with substances of known purity in order to form some idea of the relative accuracy of the methods and the need for special precautions in manipulation.

Pure anhydrous dextrose (A.R.) was selected for this purpose. Various test quantities and solutions were made up by a disinterested assistant and analysed by the author by different methods. Quantities were also given to other workers comprising experienced sugar analysts and students in training, who represent the various stages of proficiency to be encountered in commercial sugar laboratories. The results were compared with the weights of material given for the tests. pg. 159. The letters refer to the different analysts.

It will be seen from the study of Table R.S.1. that the accuracy of the Lane-Eynon method is clearly established.

The percentage differences obtained in all these methods appear to be somewhat high, but this is due to the fact that only a portion of the dextrose solution given, or made up, was used for the estimation, and any small error in the result was magnified considerably when the percentage on the basis of the original volume was calculated.

TABLE. R.S.1.

Method Lane and Eynon.

	A.	B.	C.	D.	E.	F.
Wt. given, gms.	1.5000	1.5480	1.3645	1.4035	1.5630	0.8620
" found, "	1.5064	1.5510	1.3739	1.3982	1.5586	0.8600
Difference per cent	+0.42	+0.19	+0.69	-0.38	-0.28	-0.23

Method. Munson & Walker.

	A.	B.	C.	D.	E.	F.
Wt. given, gms.	1.5000	1.5480	1.3645	1.4035	1.5630	1.8960
" found, "	1.4520	1.4795	1.3320	1.3820	1.5113	1.9340
Difference per cent.	-3.20	-4.43	-2.38	-1.53	-3.18	+2.00

Low's Method.

	A.	B.	C.	D.	E.	F.
Wt. given, gms.	1.5000	1.5480	1.3645	1.4035	1.5630	1.7717
" found, "	1.4570	1.6030	1.3300	1.3575	1.5398	1.7850
Difference per cent.	-2.87	+3.43	-2.53	-3.28	-1.49	+0.75

Permanganate Method.

	A.	B.	C.	D.	E.	F.
Wt. given, gms.	1.5000	1.5480	1.3645	1.4035	1.5630	1.5838
" found, "	1.4430	1.5920	1.3590	1.3475	1.5490	1.5930
Difference per cent.	-3.80	+2.84	-0.40	-3.99	-0.90	+0.58

The examination of samples of different types of molasses was next undertaken. Each sample was analysed by the four methods, the procedure in each case being exactly as described previously, and duplicate and sometimes quadruplicate tests were made simultaneously.

The concentration of the solution for the E-L tests was 1.04 per cent. and for others 0.8 per cent.

Clarification of the solution in the direct titration method was effected by means of normal lead acetate solution, the excess of lead being removed by the addition of potassium oxalate as described in the J.S.C.I., 1923, 42. In the other cases, after the solution of molasses had been made up to the required volume, 1 gm. of kieselguhr was added, and the liquid shaken up and filtered.

Table RS2. pg. 161 shews the results of these tests.

With certain varieties of molasses, notably Honolulu, Natal and some refinery samples, considerable difficulty was met with when filtering and washing the precipitate of cuprous oxide, due no doubt to the gummy nature of the original material.

The tedious procedure in all the methods except the first-named involves attention to detail and the display of manipulative skill that are seldom to be encountered in industrial practice.

In contrast with this, the simplicity of the Lane-Eynon

Table No. RS 2.

Sample.	Lane & Eynon Method.			Munson & Walker Method.					Permanganate Method.			Low's Thiosulphate Method			Mean of all Four Methods.
	I.	II.	Mean.	I.	II.	III.	IV.	Mean	I.	II.	Mean.	I.	II.	Mean.	
Antigua	25.28	25.23	25.26	24.84	24.60	24.82	24.62	24.72	24.94	24.94	24.94	24.38	24.39	24.39	24.88
Cuban	15.63	15.57	15.60	15.65	15.92			15.79	15.82	15.76	15.79	15.77	15.71	15.74	15.73
Egyptian	16.50	16.50	16.50	16.56	16.45	16.45	16.36	16.46	16.77	16.67	16.72	16.59	16.47	16.53	16.55
Hawaiian	17.28	17.28	17.28	17.39	17.52			17.46	17.85	17.79	17.82	17.19	17.30	17.25	17.45
Honolulu	13.32	13.32	13.32	13.95	14.01	13.80	13.78	13.64	14.01	13.80	13.91	13.48	13.42	13.45	13.58
Iloila	25.59	25.59	25.59	24.98	25.17	24.99	25.16	25.08	25.29	25.27	25.28	25.11	24.90	25.01	25.24
Java I.	23.40			22.93	22.93			22.93	23.70			22.80			23.21
Java II.	23.11	22.93	23.02	22.87	22.81	23.21	23.08	22.99	23.31	23.46	23.39	23.16	23.23	23.20	23.15
Manila	30.76	30.76	30.76	30.54	30.49	30.52	30.75	30.56	30.55	30.73	30.68	30.19	30.21	30.20	30.55
Natal	14.46	14.45	14.46	14.13	14.22	14.07	14.18	14.15	14.20	14.16	14.18	14.05	14.00	14.03	14.21
West Indian.	17.03	16.98	17.01	16.83	16.87	16.92	16.82	16.86	16.81	16.82	16.82	16.81	16.82	16.82	16.88
Golden Syrup.	47.79	47.73	47.76	47.71	47.85	47.79	47.65	47.75	47.96	48.08	48.02	47.93	47.86	47.90	47.83

method is acknowledged by all who have used it. Even in the hands of unskilled operators a high degree of accuracy can be obtained. In order to prove this, a test sample of molasses was procured from Messrs. Eynon and Lane, with a note of the invert sugar content as found by themselves. The molasses was analysed by three other workers as well as by the author, with the following results:

Sample: Hawaiian Molasses.

	L.	A.	B.	C.	Eynon & Lane.
Invert Sugar found.	17.33	17.28	17.28	17.22	17.40

The rapidity with which the Lane-Eynon test can be carried out is in itself a sufficient recommendation. The determination of the reducing sugars in molasses can be completed by even the most leisurely worker in less than one hour (as against 1½ - 2 hours by the other methods). The fact that its accuracy is of such high order should encourage its wider application.

SUMMARY OF PART II .

After an extensive investigation into the four methods in general use in the Sugar Industry for the analysis of Reducing Sugars (Invert Sugar), the author recommends that

> "In view of the simplicity of the procedure in the Lane and Eynon method, and the accuracy of results attainable by its use, this method should be officially recommended for the determination of Invert Sugar in Cane molasses and Refinery Products."

PART III.

PART III.

The determination of ash is of considerable importance in the technical analysis of sugar factory products, and it is carried out by one of the following methods:

1. Incineration.
2. Electrometric means.

1. The ash produced by direct incineration is referred to in the sugar industry as "carbonate ash", but the general procedure is to add sulphuric acid prior to the incineration and from the resultant "sulphated ash" a deduction of 10 per cent. is made to convert the "sulphated ash" to what is termed "normal ash".

In this work the term sulphated ash will be used to indicate the weight of ash obtained by incineration after adding conc. sulphuric acid, less 10 per cent.

It should be mentioned here that the results obtained by the above two methods do not agree with each other. It was formerly considered that carbonate ash was the more reliable figure. Withrow and Jamison (Ind. and Eng. Chem. 1923) strongly supported the view that it was more accurate than that obtained by the sulphation method, but they recommend a deduction of 33 per cent. from acid treated ash in the case of Cuban raw sugar.

The H.S.P.A. deducts 25 per cent. when dealing with final molasses.

On the other hand, Browne and Gamble, (Facts about Sugar Dec. 1923), proved that the carbonate ash was subject to great variation owing to the volatility of the chlorine, sulphur and other constituents of the molasses, at the temperature at which ashing is conducted. Lunden (Z. ver deut. Zuckerind. 75, 1925) supported this view.

Strictly speaking, neither the carbonate nor the sulphated ash, after 10 per cent. deduction, gives a correct indication of the quantity of salts originally present in the substance under examination, but the latter figure is now generally recognized as the one capable of close reproduction in "check" tests.

As a result of many analyses, the present author formed the opinion that it is impossible to get corroborative results with molasses when direct incineration is employed. A difference of over 1 per cent. was frequently found in duplicate tests of the same samples owing to the irregular decomposition of certain of the salts at the temperature of the muffle furnace used. When, however, the sulphation was used, remarkably close agreement was always obtained. See Table pg. 168.

The A.O.A.C. permits the use of both ~~the~~ direct incineration and sulphation. The H.S.P.A. recommends the determination of carbonate ash if a muffle furnace is available, otherwise the sulphate ash should be determined using a direct flame for the heating.

The International Commission, 1933, recommended the use of the sulphation method for molasses, with 10 per cent. deduction. The electrometric method, which is of comparatively recent introduction, has not yet been discussed.

The procedure for carrying out the estimations is as follows:

Carbonate ash. 3-5 gms. of the sample are accurately weighed, preferably in a platinum basin of 80-100 cc. capacity, to which a gentle heat is applied. The mass swells up and carbonizes, and unless care is exercised it may overflow the basin. After all the sugar has been charred, the basin is heated in the muffle furnace at a dull red heat (about one hour's heating is sufficient), cooled in a desiccator, covered with a watch glass and weighed.

Sulphated ash. 3-5 gms. of the sample are accurately weighed out as above, and about 2 cc. of conc. sulphuric acid are poured over it. The dish is then gently heated until the sample is caramelized. The ashing is completed in the furnace as above. From the percentage of ash so obtained, a deduction of 10 per cent. is made, the balance being reported as "normal ash" or, as sometimes ~~named~~ termed, "Sulphated ash".

Both of these methods are officially recognized, but some modifications have been made. The American instructions (Bull. 107 U.S. Bur. of Chem.) state that a platinum basin should be used. The H.S.P.A. method recommends platinum but also permits the use of silica and "even porcelain" (sic.) dishes.

The author found that results obtained when using fused silica ware were always lower than those obtained in platinum and porcelain dishes. Investigation shewed that silica dishes progressively lost weight on being heated, and because of this gave erroneous results whenever they were used.

All the tests reported in this section were carried out in triplicate, two in platinum basins and one in a flat porcelain dish. In every case remarkably corroborative results were obtained, proving the suitability of porcelain for this purpose.

This confirms the findings of Withrow and Jamison (loc. cit.) in this connection.

The sulphated ash method has been modified by some workers who recommend double sulphation. After the first ashing, a few drops of conc. sulphuric acid are added to the residue, and a further ignition of the basin volatilizes the acid, after which the basin is cooled and weighed.

Spencer (Handbook) gives directions for the double addition of acid.

TABLE.

Carbonate Ash.

Sample	1.	2.	3.
Refinery molasses.	4.95	5.52	4.52
* Natal "	7.73	8.91	

Sulphated Ash. (Double sulphation less 10 per cent.)

	1.	2.	3.	
Refinery molasses.				7.96(mean of 5 tests)
* Natal	11.83	12.02	12.09	
West Indian	9.60	9.81	9.75	
Antigua	9.53	9.61	9.64	
Hawaii	14.49	14.75	14.64	
Philippine	6.20	6.31	6.28	
Cuba	8.97	8.99	8.99	
Egyptian	13.49	13.33	13.76	
Java	10.41	10.30	10.20	

Tests Nos. 1 and 2 were carried out in platinum basins, Nos. 3 in porcelain dishes.

The author investigated this point, since to his personal knowledge the customary method in industrial practice is to add the acid only to the sample before heating.

The weights of the ash obtained by single sulphation were noted, and then another 10 drops of acid were added. After a further ignition, the dish was cooled and weighed. In every case an increase in weight was observed.

The addition of acid to the ash, which was usually dark grey in colour, caused the odour of sulphuretted hydrogen to become distinctly perceptible. Some of the original sample was then incinerated without acid, and the resultant ash tested for sulphide radicle. In every case the test was negative. This indicated that it could only have been produced as a result of the first sulphation, by the action of the carbon on the sulphuric acid. The second sulphation converted the sulphide to sulphate.

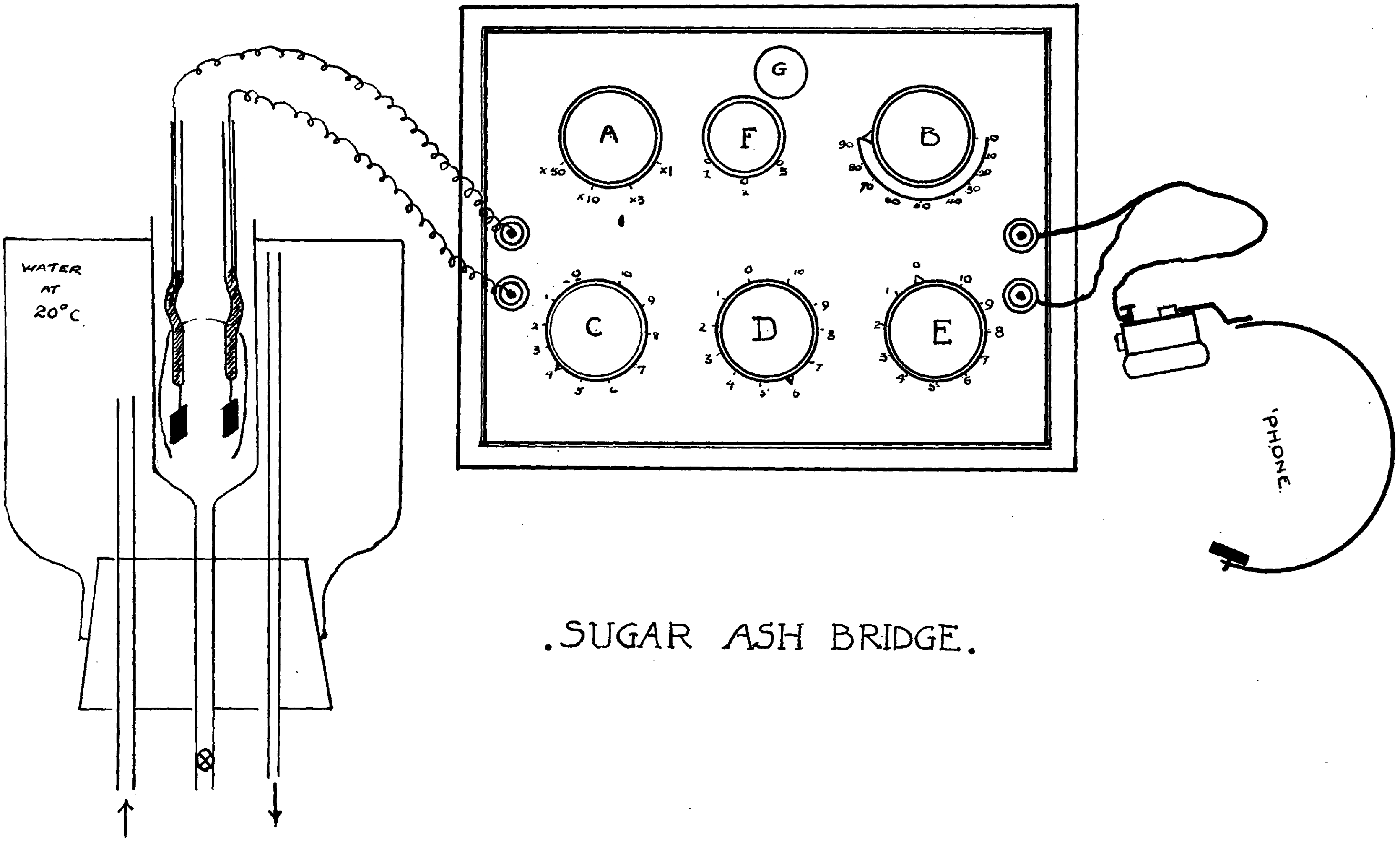
The increase in weight in all the cases as a result of the second application of acid appears to confirm this.

The quantity of sulphuric acid used by different authorities for the first sulphation varies between 0.5 and 3 cc. It was found that the quantity used initially was not so important; sulphide was always produced and had to be oxidized by the second addition of acid to the ash.

The necessity for double sulphation does not appear to be fully realized by those using the acid treatment, but the author is convinced of the impossibility of obtaining true results otherwise.

The object in carrying out the work in this part of the research, was to try to find a simple method of determining, by electrometric means, the ash contents of molasses, comparing the results so obtained with those for sulphated ash, which is the accepted standard at present.

The electrometric method as used in the sugar industry will therefore be discussed in detail.



.SUGAR ASH BRIDGE.

2. Electrometric methods.

About the year 1909 some Continental investigators studied the relation between the ash content of sugar products and their conductivity, but it was not until 1924 that attention was directed to the determination of ash by electrometric methods. In this field, the names of Lunden and Toedt are prominent in connection with their work on beet products (Z. ver deut. Zuck. 1925), and Zerban and Sattler have contributed valuable data in respect of cane products (Facts about Sugar 1926-27-28.).

It is stated by Spencer (Handbook) that the results of electrometric ash determinations are "comparable in accuracy with sulphated ash determinations made under the most exacting research conditions".

The electrometric estimation of the ash content of sugar products is based on the fact that distilled water and also solutions of pure sucrose in distilled water have only a very low electric conductivity. The presence, however, of impurities consisting of inorganic and also organic salts, causes ionic dissociation, and from a knowledge of the conductivity, it is possible to estimate the percentage of mineral matter or "ash" present.

The apparatus used for this purpose is shewn on page 171. It consists of a resistance bridge of special design and a cell having platinum electrodes. In view of the necessity of working at a constant temperature, this cell was placed in a water bath, which was formed by cutting a 2-litre bottle through the middle and using the neck portion inverted, for the water bath. Water at a constant temperature of 20°C. was passed in from a thermostatically controlled circulator. A microphone hummer is incorporated in the bridge box and sensitive headphones are used to detect the change in note.

Determination of the cell constant. The value of the cell constant which depends on the size of the electrodes and their distance apatt is determined by finding the resistance of a solution of known conductivity. For this purpose a N/100 solution of Potassium Chloride was made up by dissolving 0.746 gms. of pure KCl in distilled water and making it up to 1 litre. The conductivity of this solution is 0.001278 at 20°C.

The value of the cell constant is re-determined from time to time. In testing sugar solutions a correction is made for the conductivity of the distilled water used in making up the solution. No correction is considered necessary for the effect of the acidity of sugar products on the conductivity. The resistance of a solution is determined as follows:

The switch "A" is set at "x1" and the switches "B", "C", "D" and "E" at zero. Switch "E" is now rotated through 1, 2, 3, etc. to 10 until a point is reached where the note disappears, then at the next higher number reappears. If no such point is reached, the pointer of switch "E" is left at 10 and the procedure is repeated with switch "D", and if necessary with switch "C" leaving "D" at 10.

If when switches "C", "D" and "E" are all at 10, the note has not disappeared, switch "A" is turned to "x3", and starting with "C", "D" and "E" at 0 the operations described above are repeated.

With pure products it will be necessary to use the apparatus with switch "A" on "x10", and sometimes on "x50".

The right "multiplier" having been found, the first operation described above is repeated, but in a reverse direction, i.e. starting with switch "C" until the note of the hummer is at its minimum intensity.

Knob "B" is now rotated until a point is reached at which the diminution of the note no longer continues. The Compensation Range (switch "F") should be set at about the most convenient position to allow knob "B" to be used at about the middle of the calibration. In general, highly refined products call for Range 1, and low-grades for Range 3. The balancing operations of the switches "C", "D" and "E" are now repeated until the note of the hummer entirely disappears or reaches its minimum intensity.

The resistance of the solution is then read off from the dials "C", "D" and "E" and the multiplier "A"; e.g., if "C" is at 5; "D" at 9 and "E" at 7; and the multiplier "A" is at "x3", the Resistance in ohms will be :

$$597 \times 3 = 1791 \text{ ohms.}$$

If "A" had been at x10 the resistance would have been 5970 ohms; if at x50 it would have been 29850 and conversely if it had been at x1 it would have been 597 ohms. (In recording the Resistance, no notice is taken of the setting of the Compensator "B" or the Compensator Range (Switch "F") which is incorporated in the instrument solely in order to make the balance-point more accurate and easier to determine.

Calculation of the Ash Content.

The Specific Conductance of a solution is found by dividing the cell constant by the figure found for the resistance in ohms, thus:

$$\text{Specific Conductance (Sp.C.)} = \frac{\text{Cell Constant}}{\text{Resistance in Ohms.}}$$

Corrections must be made for the conductivity of the distilled water and also for the temperature, if other than 20° C. be used, but as all the electrometric determinations on molasses here reported were carried out at 20° C. no corrections for temperature were necessary.

In the case of raw sugars, for the ash content of which the electrometric determination is officially recommended, the following is the method of calculation, using a 5 per cent. solution:

$$\text{Ash per cent. in sample} = \frac{\text{Sp.C} \times \text{K} \times 100}{\text{Weight of sample in 100cc.Solution.}}$$

Where K is a special factor worked out for various types of raw sugars by Zerban and his co-workers as an expression of the relationship between the specific conductance and the (sulphated) ash of the sugar. This factor (for 5° Brix solution) varies between 78.6 for Natal sugars and 87.8 for Cuban raw sugars. The average figure taken by Zerban for cane sugars is 81.8.

The factors must be established by each investigator for every class of sugar dealt with, with solutions always at 5° Brix. e.g.

Trinidad Raw Sugar.

10 gms. made up to 200 cc. with distilled water.

Sp.C. of distilled water = 0.0000162 mhos.

Cell Constant. = 0.28

K. = 83.7

$$\text{Sp.C.} = \frac{0.28}{920} = 0.000304 \text{ mhos.}$$

Sp.C. due to ash. = 0.000304 - 0.0000162

= 0.000278

$$\text{Per cent. ash} = \frac{0.000278 \times 83.7 \times 100}{5}$$

= 0.465

When dealing with a raw sugar of unknown origin, some discrepancies occur when the "average" K is used, and in order to eliminate these, Zerban and Sattler (F. a. S. 1926) worked out a method dispensing with factors altogether, and calculated ash from the formula:-

$$\text{Ash per cent.} = 0.00001757 \times (9.13\,K + 1935 - K_1)$$

where $K =$ conductivity of sugar solution as described above, and $K_1 =$ conductivity of sugar solution in acid solution.

For the acid conductivity, 200 cc. of the original 5° Brix solution are carefully mixed with exactly 5 cc. N/4 HCl, and the conductivity is determined.

(In the above equation 1757 represents K for Cuban sugars $\times \frac{100}{5}$).

The application of similar methods to the determination of ash in molasses and refinery syrups is due mainly to Zerban and Sattler of the New York Sugar Trade Laboratory, whese work in this field is reported in F. a. S. 1926, 1928; Ind. and Eng. Chem. 1930, V.I. and II, 1931, V.III, 1932.

In a paper read before Am. Chem. Soc. (Division of Sugar Chemistry) 1930, they referred to the variations in the ratio $\frac{\text{Ash}}{\text{Conductance}}$, the (C-ratio) due to geographical difference in the sources of supply of the raw materials and reported the development of a formula as a result of statistical analysis by Lo~~d~~rge of Columbia University, of a number of conductivity determinations, from which

Per cent. ash = $0.0191369\ K_1 - 0.002249\ K_2 - 0.001210\ K_3 + 3.07$

where K_1 = Sp. conductance of the solution $\times 10^6$

K_2 = " " " " " to which 5cc.N/4 KoH has been added per 200 cc. solution.

K_3 = Sp. Conductance of the solution to which 5 cc. normal orthophosphoric acid has been added.

In 1932 (Ind. and Eng. Chem. pg.435) these workers put forward yet another equation.

$$\text{Ash per cent.} = 0.01556\ K - 0.001125\ K_1 - 0.000623\ K_2 - 0.000219\ K_3 + 3.083$$

where K = Sp. conductance of the solution $\times 10^6$

K_1 = " " " " " to which 5cc. N/4 HCl has been added per 200 cc. Solution.

K_2 = Sp. Conductance of the solution to which 5cc. N/4 KoH has been added per 200 cc. Solution.

K_3 = Sp. Conductance of the solution to which 5cc. normal orthophosphoric acid has been added per 200 cc. of Solution.

In the work carried out in this Part, the determination of ash in the case of each sample of molasses was made by the double sulphated ash method, and by conductometric means using this unwieldy formula of Zerban and Sattler, as given above.

One example is given here to shew the method:

Sample. Natal Molasses.

Cell constant 0.119 at 20°C.

Sp. Cond. of water used 4.0×10^{-6}

25 gms. of molasses were dissolved in hot conductivity water, filtered through silk (150 mesh) and made up to 250 cc. 50 cc. of this solution were diluted to 1 litre, thus giving a concentration of 0.5 gms. molasses per 100 cc.

Then

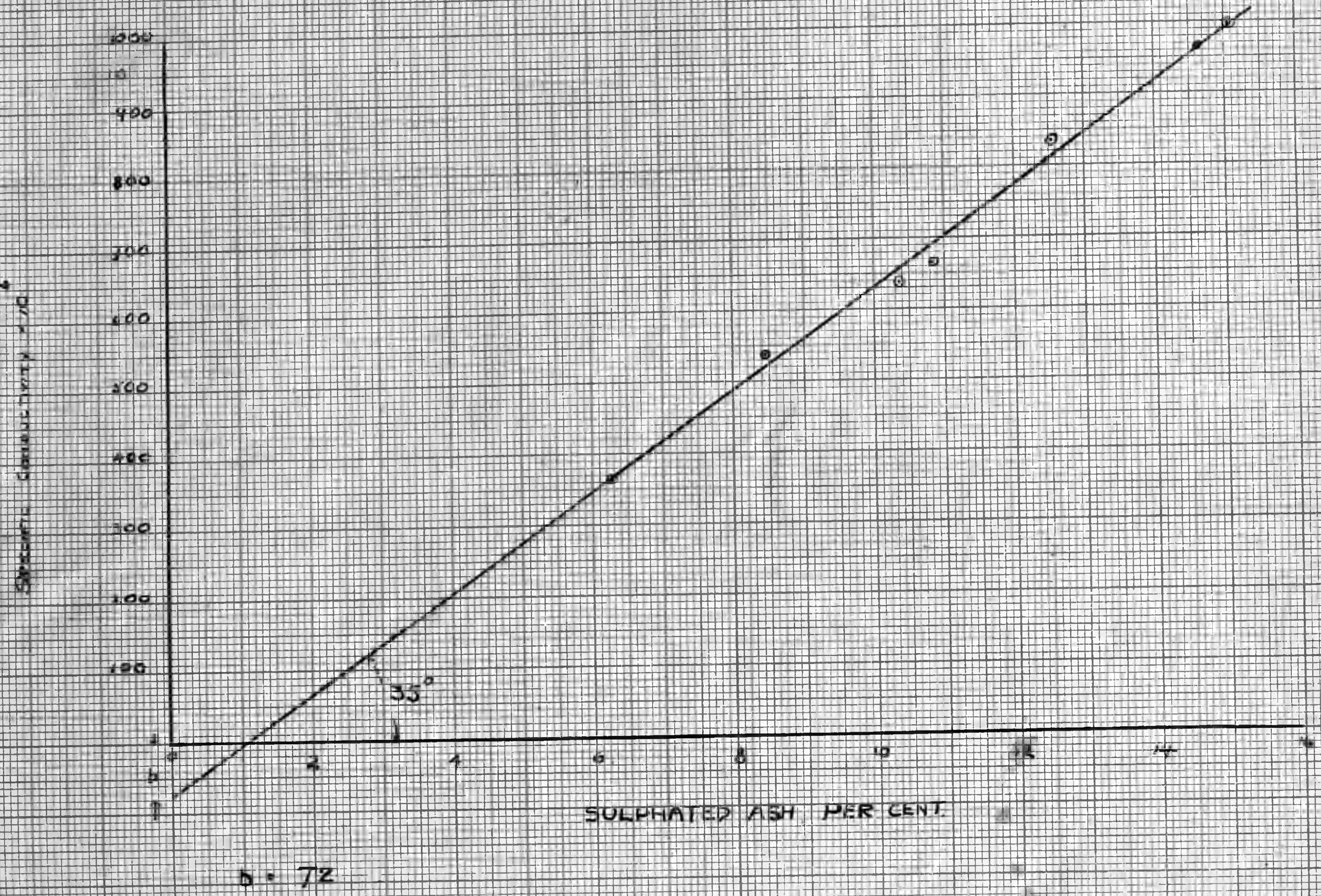
R = 151 ohms. for molasses solution
R_1 = 65 " " (200cc " " + 5cc. N/4 HCl)
R_2 = 76 " " " " " + 5cc. N/4 KoH
R_3 = 67 " " " " " + 5cc. N. H_3PO_4

K = 793
K_1 = 1927 where K = Sp. Conductivity $\times 10^{+6}$
K_2 = 1562
K_3 = 1772

$$\text{Per cent. ash} = 0.01556\,K - .001125\,K_1 - .000623\,K_2 - .000219\,K_3 + 3.083$$

$$= 0.01556 \times 793 - 0.001125 \times 1927 - 0.000623 \times 1562 - 0.000219 \times 1772 + 3.083$$

$$= 11.89$$


Specific Conductivity × 10^6
1000
900
800
700
600
500
400
300
200
100
0
b
0
2
4
6
8
10
12
14
16
35°
SULPHATED ASH PER CENT
b = 72

In view of the extremely tedious procedure and laborious calculations involved, an attempt was made by the author to simplify both the procedure and the calculation.

After a number of determinations had been made, it was decided to construct a graph shewing the relation between Specific Conductivity and Sulphated Ash as found by incinerations.

With ash per cent as abscissa and specific conductivity as ordinate, the results for ~~ten~~ seven samples were plotted, and a straight line was found to pass remarkably close to all these points so plotted, making an angle of 35° with the abscissa.

It thus appeared that a simple relation existed between these values and this was worked out from the equation of the graph

$$Y = ax - b$$

from which $$x = \frac{y+b}{a} = \frac{y+b}{\tan 35^\circ} = \frac{y+b}{0.7002}$$

$$\text{Ash per cent.} = \frac{(\text{Sp.Conductivity} + .000072) \times 10^{+4}}{0.7002}$$

$$= (\text{Sp.Conductivity} + .000072) \times 14282$$

$$= (\text{Sp.Conductivity} \times 14282) + 1.028$$

All the samples available to the author were tested by the three methods, namely, double sulphation and incineration, electrometrically by Zerban and Sattler's method and also by using the formula developed as above for a concentration of 5 gms. of molasses in 1 litre of water.

The results are tabulated on page 183, and shew that for cane molasses the figures obtained by the new method, when compared with those for sulphated ash, are in as close agreement as those obtained by Zerban's method.

The differences between the two electrometric methods and the incineration method are set out in the table, from which it will be seen that neither equation is suitable for beet molasses, but for cane and refinery molasses the new formula gives very satisfactory results. In only one case, with Antigua molasses, was the difference at all appreciable.

It has the advantage over Zerban's method, of simplicity and rapidity. The determination can be completed in twenty minutes and requires neither special solutions nor skill in manipulation.

No.	Molasses.	Per Cent. Sulphated Ash x 0.9 a	Per cent. Electrometric ash (Zerban). b	Difference. (a-b)	Sp.Conductivity x 10^6 c	Per cent. Conductivity Ash.New Formula d	Difference (a-d)
1	Antigua	9.64	10.07	-0.43	649.7	10.30	-0.66
2	Cuba	8.99	8.86	+0.13	562.8	9.06	-0.07
3	Egyptian	13.41	13.10	+0.31	845.0	13.09	-0.32
4	Hawaiian I	14.64	14.55	+0.09	967.2	14.82	-0.18
5	" II	12.52	12.69	-0.17	833.5	12.91	-0.39
6	Honolulu	15.05	15.28	-0.23	997.7	15.27	-0.22
7	Java I	10.35	10.81	-0.46	639.3	10.16	+0.19
8	" II	10.86	11.14	-0.28	662.4	10.49	+0.37
9	Natal	11.98	11.89	+0.09	794.2	12.35	-0.37
10	Philippine	6.28	5.78	+0.50	364.5	6.23	+0.05
11	Refinery I	7.96	7.91	+0.05	515.9	8.39	-0.43
12	" II	8.42	8.88	-0.46	538.3	8.71	-0.29
13	" III	9.58	9.46	+0.12	600.7	9.61	-0.03
14	" IV	8.84	9.41	-0.57	563.7	9.08	-0.24
15	West Indies	9.75	9.35	+0.40	615.5	9.82	-0.07
16	Cupar Beet I	10.42	11.6	-1.18	680.3	10.75	-0.33
17	Cupar " II	9.70			667.9	10.57	-0.87
18	Ely Beet	7.48			587.4	9.41	-1.93
19	Peterborough	9.56			650.0	10.48	-0.92
20	Old Beet	9.50			614.3	9.80	-0.30

SUMMARY, PART III.

The author submits to the Sugar industry a new equation suitable for the rapid determination by electrometric means, of the ash contents of cane and refinery molasses:-

$$\text{Ash per cent.} = (\text{Specific conductivity} \times 14282) + 1.028$$

He believes that the simplicity of the procedure and of the calculation shew a considerable advance on former methods and he is confident that it will receive the careful attention of his colleagues in the Sugar industry.

Special acknowledgement is made of the collaboration, in this part of the work, of Mr. M. Mazumder, one of the author's students in the School of Sugar Manufacture.

Reprinted from the *International Sugar Journal*, 1936, **38**, pp. 303-304.

ADDENDUM TO PART III.

DETERMINATION OF ASH IN CANE MOLASSES.

A General Conductometric Formula.

BY

D. LEVER, B.Sc., A.R.T.C., F.I.C., and M. M. MAZUMDER, M.Sc.

School of Sugar Manufacture, the Royal Technical College, Glasgow.

Determination of Ash in Cane Molasses.

A General Conductometric Formula.

By D. LEVER, B.Sc., A.R.T.C., F.I.C., and M. M. MAZUMDER, M.Sc.,
School of Sugar Manufacture, The Royal Technical College, Glasgow.

The formula correlating ash with specific conductivity, reported in the June issue of this Journal,[1] was developed primarily with the object of expediting the examination of certain widely different samples of cane molasses then under investigation. But the authors believe that the method would be also of considerable value for routine estimations in cane producing countries, if the equation were stated in a form suitable for use under the temperature conditions usually encountered in the tropics.

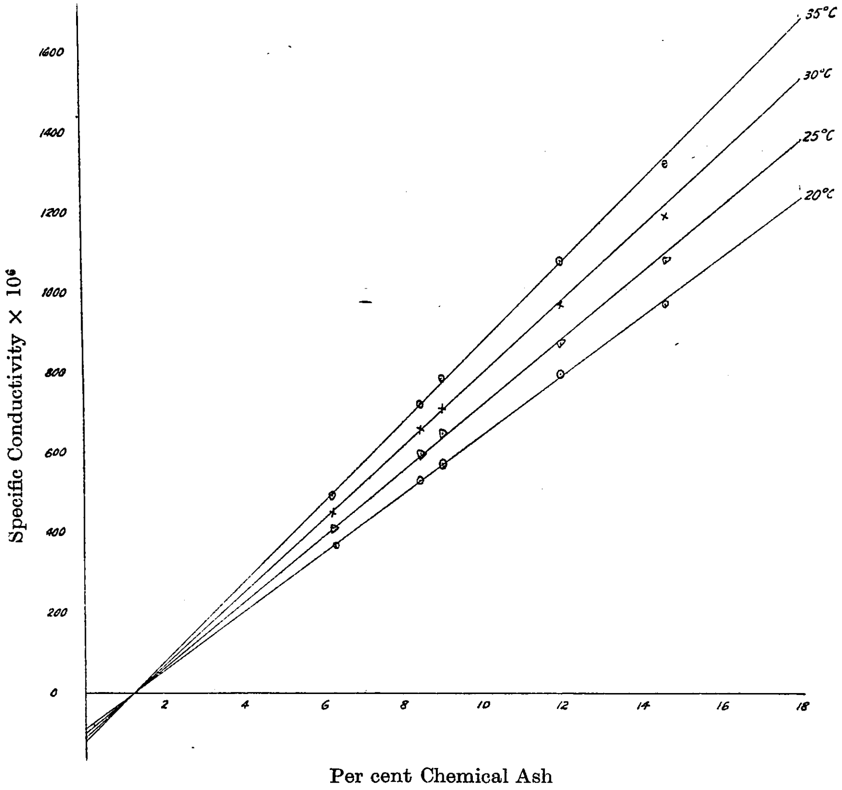


Fig. 1.

With this in view, the work on the samples previously examined was continued and the specific conductivities were determined at temperatures of 20, 25, 30 and 35°C. As before, the "Salometer" was used. The cell was immersed for these experiments in a water-bath controlled at the desired temperature by means of a sensitive electrical thermo-regulator.

Graphs of Ash-Conductivity were then plotted, as is shown in Fig. 1. For each temperature a straight line was obtained, and all the lines intersected at the point (1·25, 0). The equations for these lines are :—

For 20°C. Ash per cent. = Sp. conductivity $\times$ 13900 + 1·25

For 25°C. Ash per cent. = Sp. conductivity $\times$ 12580 + 1·25

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[1] Page 214.

For 30°C. Ash per cent. =

$$\text{Sp. conductivity} \times 11260 + 1{\cdot}25$$

For 35°C. Ash per cent. =

$$\text{Sp. conductivity} \times 10000 + 1{\cdot}25$$

It will be observed that the formula for 20°C. differs slightly from that previously reported, but the results obtained by their use agree closely with each other. The circumstance that the lines intersect at a point enables the following general equation to be obtained :—

$$\textbf{Ash per cent.} = \textbf{Specific conductivity} \times 13900\,[1 - 0{\cdot}019\,(t - 20)] + 1{\cdot}25,$$

where t is the temperature, and 0·019 is the temperature coefficient of conductivity.

This formula should be of considerable value as it can be used for any temperature in the range 20 to 35°C.

Table I showing the experimental results obtained by calculating with the general formula indicates the accuracy of the latter. To facilitate and expedite routine estimations and control, a simple table can be constructed which will show directly the percentage of ash for the different values of specific conductivity at a stated temperature.

TABLE I.

EXPERIMENTAL RESULTS USING THE GENERAL FORMULA.

Origin of Molasses	Per cent. Chemical Ash	Per cent. Conductometric Ash			
		at 20° C	at 25° C	at 30° C	at 35° C
Hawaii I	15·05	15·12	15·18	14·89	14·56
,, II	14·64	14·70	14·73	14·63	14·29
Natal	11·98	12·29	12·16	12·09	11·84
Java I	10·35	10·14	10·15	10·10	9·87
Philippine	6·28	6·31	6·37	6·28	6·12
Cuba I	8·99	9·07	9·42	9·27	9·04
Refinery I	7·96	8·42	—	—	—
Antigua	10·12	10·28	10·17	9·99	9·96
Hawaii III	12·52	12·83	13·06	12·93	12·79
Java II	10·86	10·46	10·39	10·35	10·12
Refinery II	8·42	8·73	8·74	8·65	8·40
,, III	9·58	9·60	8·88	8·97	8·75
,, IV	8·84	9·08	8·71	8·80	8·37
West Indies	9·75	9·80	9·66	9·68	9·46
Egypt	13·41	12·99	12·81	13·52	12·34
Mixed I	10·12	10·33	10·27	10·09	9·87
,, II	10·34	10·21	—	—	—
,, III	10·98	10·99	11·13	10·91	10·54
Hawaii IV	14·62	14·21	14·74	14·63	14·19
Cuba II	9·79	9·42	9·73	9·71	9·45
Unknown I	8·78	8·24	8·32	8·29	8·15
,, II	8·33	8·05	8·03	8·06	7·79
Barbados I	9·83	10·56	10·52	10·19	10·15
,, II	10·02	10·76	10·76	10·51	10·27

ADDENDUM TO PART I. OF THESIS

"THE TESTING OF MOLASSES"

by

DAVID LEVER.

All the gravimetric estimations reported in Part I. of the thesis were carried out by the author. When the distillation tests were being carried out, the dangerous nature of some of the liquids and the fact that readings had to be taken every hour over long periods made it necessary to have a relief worker. Assistance in this connection was given by a student in the author's laboratory.

The analysis of cane molasses, reproduced on page 4 of the thesis "The Testing of Molasses", is stated by Spencer to have been condensed from a large number of analyses made at the Louisiana Experimental Station. That the results have been "adjusted" is obvious from the fact that a total of 100.00 per cent. is shown, although none of the constituents is obtained by difference and there is no undetermined matter.

Spencer's statement of composition serves, however, to illustrate the complexity of the substance, but it does not indicate that it contains some components whose composition is quite unknown. Noel Deerr, one of the world's leading sugar technologists, states that he regards it as an "indefinite mixture".

A large number of organic non-sugars is found in molasses. Some of these originate in the cane or beet, and are expressed or diffused into the juice, but many of them are produced during the processes of clarification and crystallization of the sugar liquors.

The first step in the defecation of the raw juice is the addition of milk of lime, which has the effect of neutralizing the natural acidity of the juice, precipitating the phosphoric acid as the insoluble phosphate, and which forms calcium salts of the organic acids originally present. The subsequent boiling of the liquor frequently aids the decomposition of the glucose even at this stage into principally organic acids.

In the manufacture of white sugar at the plantation, a considerable excess of lime is used, and before the limed juice can be boiled this excess has to be removed. This is effected by passing in carbon dioxide, in the Carbonatation process, or sulphur dioxide, in the Sulphitation process. During the passage of the gas, the temperature must be controlled at about 60° C, in the case of cane juice, otherwise destruction of the organic matters by the combined action of the lime and heat takes place.In this event, humic acid, acetic acid, formic acid, carbonic acid and apoglucinic acid are formed.

The excess of lime employed results in the formation of saccharates and glucosates of calcium. The former are more stable than the latter which do not crystallize and which decompose readily at about 50° C. The effect of the gas is as follows:-

$$C_{12}H_{22}O_{11}\cdot CaO + \begin{matrix} CO_2 \\ \text{or} \\ SO_2 \end{matrix} = C_{12}H_{22}O_{11} + \begin{matrix} CaCO_3 \\ \text{or} \\ CaSO_3 \end{matrix}$$

$$C_6H_{12}O_6\cdot CaO + \begin{matrix} CO_2 \\ \text{or} \\ SO_2 \end{matrix} = C_6H_{12}O_6 + \begin{matrix} CaCO_3 \\ \text{or} \\ CaSO_3 \end{matrix}$$

After the application of the gas, the liquor is boiled. Decomposition of the sugars present cannot wholly be avoided. Some of the saccharates and glucosates are not broken up as shown above,and the heating causes complex decompositions to occur, while other compounds are formed in the juice consequent upon the addition of the acid gas.

The treated liquors are then settled or filtered, and are next concentrated in multiple effect evaporators under gradually diminishing pressure which varies from a slight pressure in the first vessel to about 27" of vacuum in the last vessel. During the passage of the juice through the evaporating system, many complex reactions occur. Certain substances which are soluble in the thin liquor in the first vessel are precipitated at the lower boiling temperatures existing in the succeeding vessels, while the concentrated syrup in the last body, wher the sucrose content is between 50 and 60 per cent., dissolves some of the precipitated matters which would be insoluble or only slightly soluble in water at that temperature.

In addition, the action of lime and heat on the nitrogenous substances originally present in the juice forms ammonia, and this gives rise to certain compounds which are included under the general heading of "amino compounds". Complex reactions, investigated by Browne in Louisiana, occur during the process of manufacture, between the amino compounds and the reducing sugars of the cane juice.

All the soluble substances other than the sugars which are found in the thick juice leaving the evaporators, together with some of the insoluble matters carried over with the liquor, pass through the remainder of the process, which has for its object the removal of the sucrose in a crystalline form, and they finally remain in the molasses.

The difficulty of analysing such a material as this final molasses will be readily appreciated. It cannot be synthesized in such a manner as to enable one to know its water content with sufficient accuracy to serve as a standard for judging the efficiency of the various methods employed for estimating water in molasses. Moreover, a simple mixture of sugars and salts cannot be considered to be similar in any way to the indefinite mixture of substances which are found in molasses, and which have undergone, in its formation, so many complex changes.

The remarkable difficulties encountered in the investigation of molasses are set out by Dr. C.A.Browne of the Bureau of Chemistry and Soils, Washington, U.S.A. in Ind. and Eng. Chem. 1929, pg. 601. He gives an account of the complex substances isolated, notably "glucic acid". This unstable substance was first examined by Peligot and named by Dumas. It is stated to decompose suddenly into carbon dioxide, formic, acetic, apoglucic and humic acids, as well as"other unrecognisable volatile substances of acrid odour". Browne, after reviewing the researches on this subject, says that the substances which were called "glucic acid" and examined by the various investigators, were for the most part variable mixtures of unidentified compounds, and that they varied greatly in properties and composition. Browne, (loc. cit.), states that on distilling in a current of steam some samples of molasses that had been stored for some time, small quantities of CO_2 were obtained, and from the distillates, which were acid, he isolated acetic and formic acids

Noel Deerr (Cane Sugar pg. 499), mentions CO_2 as being dissolved in molasses. The present author shows on page 149 of his thesis that CO_2 was obtained on heating molasses at 100° C., and on pages 89, 93 and 97 that the distillates obtained when distilling cane molasses with acid free toluene were acid.

It is his opinion,(an opinion now shared by most sugar chemists), that the complex constituents of molasses when heated even below 70° C., decompose and give off water as one of the products of decomposition; CO_2 is another.

The foregoing statements show why it is impossible to determine the true water content of molasses.

Van der Linden,(Archief. 1917), in suggesting possible methods for the estimation, stated that the problem at that time was still unsolved.

Noel Deerr(loc. cit.), says:- " the direct determination of water is made by the expulsion of the water as vapour at a temperature equal to, or above, the boiling point at the pressure at which the determination is made.. The accuracy of the determination depends on water being the only material expelled, and is vitiated by the presence of other volatile bodies such as acetic acid and even carbon dioxide which is often found to a considerable extent in molasses."

Spencer,(Handbook pg. 260), states:- "The determination of the total solids and moisture in sugar-house materials is one of the most unsatisfactory tests the Chemist is called upon to make. This is due to the ready decomposition of several of the constituents, and under some conditions to their tendency to occlude moisture."

Sugar Chemists have not yet reached a decision as to the definition of "water" in molasses. Because of this, the Association of Hawaiian Sugar Technologists recommends drying for a definite period and recording the "loss in weight of the sample". Dr. R.T.Balch, of the Bureau of Chemistry and Soils, U.S. Dept. of Agriculture, in a communication to the International Commission, considers that the sample should be regarded as made up of a "solid phase" and a "non-solid phase". The latter would include all volatile matter at the temperature of drying, and should be accounted for as "water".

The author, in his thesis, hesitated to dogmatize as to which method gave results nearer the "correct" one, since the "correct" one cannot be analytically ascertained. He regarded his experimental work more as evidence to be adduced for or against the various methods employed in the industry when discussions were to be held among International sugar chemists as to the adoption of one of these methods as standard. Had it been possible to prepare an "artificial" molasses of known water content, the problem would have presented little difficulty, but the preparation of an artificial molasses is precisely the question whose solution has so far evaded those professionally interested.

Basing his opinion on the experimental proofs that solutions of sucrose, dextrose and levulose can be dried completely and without decomposition at a temperature of 70° C in vacuo, but not at 100° C. under ordinary pressure, the author makes the following recommendation:-

" The drying of the sample of molasses for the determination of the water content should be carried out at 70° C. under a vacuum of 60 c.m., for a period of five hours. A current of dry air should be drawn through the oven during the whole period. The quantity of sample to be taken should be about 2 gms. weighed on to 10 gms. of the prepared sand, and diluted with 2 c.c. of water to ensure thorough mixing. Since the area of the surface of the sample exposed influences the results obtained, a standard size of airtight dish should be used, suitable dimensions being 65 mm. diam. x 35 mm. high.

The loss in weight should be regarded for industrial analytical purposes as " water".

P.T.O.

Investigation of pH. value of distillates obtained by the Toluene distillation method.

During the initial experiments on the determination of the water content of sugar solutions by distillation with toluene, the low pH of the distillates was a remarkable feature which was not investigated at the time, further than thoroughly testing the sample of toluene used. This was found to be absolutely acid free.

The question was taken up again at a later date, and had rather an interesting conclusion.

A 25 per cent. solution of pure sucrose in distilled water was prepared, and its pH, as determined by the calomel electrode, was found to be 5.8 .Some of this solution was boiled under a reflux condenser for three hours, after which period the pH was again tested and was observed to have dropped slightly to 5.4 . The solution was found to have been inverted to a small extent. 20 cc. of the original solution was next boiled under the same conditions with 100 cc. of pure toluene. The solution was separated off and its pH. tested. The same drop in value, viz. 0.4 was found. No perceptible discolouration of the solution took place.

10 cc. of the original sucrose solution was then distilled in Bidwell & Sterling's apparatus with 100 cc. toluene, the temperature of the oil bath being maintained at 140°C, as des-

-cribed on page 64 of the thesis. After a period of three hours the distillate was examined and its pH was found to be 3.2 . The residual sugar, however, was observed to be slightly discoloured. It was separated and dissolved in distilled water. This aqueous solution had a yellowish tint, and a pH. of 3.6 .

It appeared to be the case that the prolonged boiling of the sucrose solution, especially towards the end of the distillation, caused a slight caramelization of the sugar, and that the low pH. values were due to the acids produced by this decomposition.

"Caramel" is the term used to denote the indefinite residue of the decomposition of sucrose by moist heat. The substance is widely used in the foodstuffs and other industries as a colouring agent, but in sugar manufacture its presence is most undesirable. Although its composition is uncertain, it is known that at the onset of the "burning" of the sugar, formic, acetic, humic and other complex organic acids are produced, and CO_2 also is evolved. Caramelization for industrial purposes is carried out by "burning" the sugar(and other ingredients) to a certain stage, this stage being dependent on the desired depth of the colour which is obtained when the burnt mass is dissolved in water or alcohol.

To investigate the change in pH. of the residue due to the extent of the "burning", six quantities of table sugar, each weighing 0.4 gm., were gently heated in a platinam dish to different stages denoted by the depth of colour of the residues, which were afterwards dissolved in distilled water and made up to 100 cc. in each case. The colours of the six solutions varied from a yellowish tint, in No. I. to a pronounced brown in No. VI. The pH values were determined as follows:-

Distilled water used	pH	5.8
No. I solution	"	3.7
" II. "	"	4.0
" III. "	"	3.7
" IV. "	"	3.7
" V. "	"	3.7
" VI. "	"	3.6

From these observations it appears that the pH. of the caramel is not affected to any appreciable extent by the degree of caramelization to which the sugar has been subjected. Even a very slight burning is sufficient to cause the considerable drop in pH.

This is a point which appears to have escaped the notice of sugar manufacturers who use the pH. control for their process. The formation of caramel cannot wholly be avoided, and the effect of its presence , in view of the above, may be to cause a disturbance of the control.

In the case of distillations for water determination using toluene, the volatile organic acids produced by even the slight dedomposition of the sugar are collected in the aqueous distillates. In the example quoted above, the presence of traces of formic and acetic acids ~~were~~ was confirmed.This accounts for the low value for the pH.