

# SOME EFFECTS OF BORAX ON THE POLARISATION OF SUGAR SOLUTIONS

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## Introduction

The influence of boric acid on the specific rotation of carbohydrates was studied by Böesecken<sup>1</sup> who used the phenomenon to determine the structure of hexoses.

Hernández<sup>4</sup> investigated the possibility of using borax to nullify the polarisation of common monosaccharides in sugar products in order to obtain a direct reading of sucrose content. Studies of the effect of borax on the polarisation of solutions of pure sugars and mixtures of pure sugars proved encouraging.

Hernández extended his investigations to impure sugar solutions, comparing results for direct pol, borax pol and Clerget sucrose. He concluded that the addition of 25 ml. of 2 per cent solution of disodium borate to 6.5 g. of a sugar product, diluted to 100 ml. resulted in a pol value very close to true sucrose.

Hernández's proposals were investigated by, *inter alia*, the Sugar Milling Research Institute<sup>2</sup>, who considered that no practical benefit could be gained by adopting the technique in South African sugar laboratories.

During investigations of the specific rotation of gums, Jennings<sup>6</sup> found that the addition of 20 ml. 5 per cent borax solution depressed the pol of pure sucrose by more than 2 per cent. Since other investigators had found similar discrepancies with the original experimental results of Hernández it was decided that the whole question of using borax to obtain close approximations of sucrose content by direct polarisation should be re-examined.

## Aspects Studied

At the outset the effect of borax on the rotation of solutions of pure sugars, and mixtures of pure sugars was investigated. Attention was paid to the effects on the rotation of (a) varying the concentration of borax added, (b) the pH of the solution and (c) the presence of impurities simulating the inorganic ash found in sugar products.

The effects of the addition of different concentrations of borax on the polarisation of impure sugar solutions was studied, special emphasis being given to devising a method for the rapid determination of the approximate sucrose content of invert syrups. The dependence of the final polarisation figure on the time interval between the addition of borax and polarisation was investigated.

## Methods Used

### (a) Pure Sugar Solutions

A. R. Dextrose having a specific rotation between 52.5° and 53.0°, and dried levulose having a specific

rotation not less than -81° and an ash content less than 0.5 per cent were used for all determinations involving pure monosaccharides. Highest quality sucrose, specially prepared, and polarising not less than 99.95° was used for all investigations with sucrose.

Aliquots of prepared solutions of pure sugars were transferred to 100 ml. flasks, the required quantity of borax added and the mixture made to volume, shaken, and allowed to stand for one hour before polarising in 200 mm. tubes in a standard saccharimeter. If the pH of the solution was to be adjusted the sodium hydroxide or carbonate was added before making to volume and pH determined after standing for one hour and polarising. A similar procedure was adopted during the investigations of the influence of inorganic matter.

### (b) Molasses

The method used for investigations on Refinery molasses was as follows:

32.5 g. molasses weighed into 250 ml. flask and made to volume.

50 ml. aliquots pipetted into 100 ml. flasks. Required amount of borax added before making to volume, clarifying with 2g. dry lead acetate and polarising, after leaving the filtrate to stand for one hour in a covered vessel, in 200 mm. tubes.

Sucrose on Refinery molasses was determined using the Jackson and Gillis Method IV, clarifying with 6 g. lead acetate and 2 g. potassium oxalate per 32.5 g. molasses and using the Walker method for inversion<sup>7</sup>.

The treatment of Mill molasses samples varied only in that 3 g. lead acetate were added to clarify borax polys and 10 g. lead acetate with 2 g. potassium oxalate per 32.5 g. molasses for sucrose determinations.

### (c) Invert Syrups

The following method was used to investigate the effect of standing time on the polarisation of invert syrups treated with borax.

6.5 g. syrup weighed into 100 ml. flask. Required amount of borax added and the flask immediately made to the mark and shaken. A 200 mm. tube was filled immediately and sealed to prevent evaporation, polarisations being recorded every 2 minutes from the time of the addition of the borax. No clarification was necessary with any of the invert syrups tested. A similar method, allowing a 60 minute interval before polarising was used for other tests with invert syrups.

## Results

### A. The action of borax on solutions of pure sugars.

1. A re-examination of the investigations of Hernández.

Table I

Solution Concentration			Borax Concentration	Polarisation °s	
g. sugar in 100 ml.			ml. 2% Borax in 100 ml.	Hernández	Adam
Sucrose	Dextrose	Levulose			
—	0.5	—	—	1.9	1.8
—	0.5	—	25	0.1	0.75
—	—	0.5	—	-3.0	-2.7
—	—	0.5	25	0.0	-1.15
13.0	—	—	—	49.0	49.95
13.0	—	—	25	49.0	49.70
13.0	0.5	—	—	52.0	51.75
13.0	0.5	—	25	50.1	51.00
13.0	—	0.5	—	46.5	47.45
13.0	—	0.5	25	49.5	48.75
13.0	0.5	0.5	—	48.4	48.80
13.0	0.5	0.5	25	49.0	50.00

2. Variation of the concentration of Borax.

Table II

Concentration of Sugars (g. per 100 ml)			Polarisation (°s) of Sugar/Borax Sln.			
Dextrose	Levulose	Sucrose	Concentration of Borax per 100 ml.			
			0	25 ml. 2%	25 ml. 4%	50 ml. 4%
0.5	—	—	1.80	0.75	0.35	0.00
—	0.5	—	-2.70	-1.15	-0.90	-0.80
—	—	13.0	49.95	49.70	49.10	48.70
0.5	—	13.0	51.75	51.00	50.40	49.70
—	0.5	13.0	47.45	48.75	48.65	47.60
0.5	0.5	13.0	48.80	50.00	49.75	48.90
0.5	0.5	—	-0.45	-0.10	-0.30	-0.45
0.25	0.25	—	-0.25	-0.05	-0.25	—
0.25	0.25	13.0	49.70	49.80	49.45	48.85

3. Variation of the pH of the solution.

(a) Aliquots of a dextrose solution, each containing 2 g. of dextrose, treated with 50 ml. 4 per cent borax and N/1 Sodium Hydroxide to vary pH between 8.0 and 12.0.

Table III

pH	Polarisation
8.0	3.40
8.1	3.30
8.2	3.20
8.3	3.00
8.5	2.55
8.7	2.40
9.7	0.85
12.0	0.00

(b) 0.25 g. dextrose + 0.25 g. levulose + 25 ml. 2 per cent borax in 100 ml. pH adjusted using N/1 sodium hydroxide.

Table IV

pH	Polarisation
8.65	-0.15
8.95	-0.40
9.2	-0.50

4. The influence of inorganic impurities.

A solution was prepared containing salts in a ratio suggested by Deerr<sup>3</sup> to correspond closely to the inorganic content of sugar products. The aqueous solution contained the following salts, diluted to 500 ml.:

K <sub>2</sub> CO <sub>3</sub>	2.1 g.
NaCl	0.3 g.
CaCO <sub>4</sub>	2.1 g.
KCl	1.15 g.
Ca <sub>3</sub> PO <sub>4</sub>	0.4 g.
MgCO <sub>3</sub>	0.9 g.
K <sub>2</sub> SO <sub>4</sub>	1.76 g.
CaSO <sub>4</sub>	0.25 g.

Table V

	Concentration of Sugars (g. per 100 ml.)			Concentration of Salts (g. per 100 ml.)	Polarisation (°s) of Sugar/Borax Solution			
	Dextrose	Levulose	Sucrose		Concentration of Borax/100 ml.			
					0	25 ml. 2%	25 ml. 4%	50 ml. 4%
1	0.5	0.5	—	0.14	-1.20	+0.05	-0.15	-0.55
2	0.5	—	13.0	0.07	51.65	50.95	50.25	49.55
3	0.5	—	13.0	0.28	51.35	50.70	50.15	49.45
4	—	—	13.0	0.07	49.75	49.55	49.40	48.70

5. The effect of time upon the polarisation of sucrose/borax solutions. A. R. Sucrose from two different sources was used.

Table VI

Concentration of Sucrose g. per 100 ml.	ml. 5% Borax per 100 ml.	Pol at 5 mins.		Pol at 24 hrs.	
		A	B	A	B
26	0	99.95	99.90	99.95	99.90
26	20	98.30	98.20	98.40	98.30
26	40	96.90	97.00	97.10	97.00

B. The action of borax on impure sugar products.

2. Variation of the borax concentration.

(a) Imported raw sugars.

Table VIII

Source of Sugar	Brazil	Santa Domingo	Mauritius
Pol of 26 g. sugar in 100 ml.	98.45	97.30	98.30
Pol of 26 g. sugar + 5 ml. 2% borax in 100 ml.	98.59	97.35	98.45
Pol of 26 g. + 10 ml. 2% borax in 100 ml.	98.25	97.30	98.22
Pol of 26 g. sugar + 25 ml. 2% borax in 100 ml.	98.00	96.95	97.95
Reducing sugars %	0.68	0.90	0.25
Clerget Sucrose	98.55	97.54	98.44

(b) Refinery Molasses.

Table IX

Sample	Pol using borax (ml. per 100 ml.)				Sucrose %	Direct Pol °s	Reducing Sugar %
	25 ml. 2%	25 ml. 4%	50 ml. 4%	50 ml. 5%			
1	41.40	40.60	38.80	38.70	38.90	39.20	7.65
2	38.80	38.20	36.40	36.10	36.21	36.20	8.09
3	42.00	41.60	40.40	40.00	40.64	38.40	13.27
4	40.80	41.20	39.80	39.50	39.49	36.40	21.21

(c) Mill Molasses

Table X

Sample	Pol using borax (ml. per 100 ml.)				Sucrose %	Direct Pol °s.
	25 ml. 2%	25 ml. 4%	50 ml. 4%	50 ml. 5%		
1	34.2	34.8	35.2	34.9	34.94	30.40
2	36.4	36.8	35.6	35.3	35.26	33.40
3	38.2	38.4	36.6	36.3	36.13	35.40
4	37.8	39.0	37.8	37.4	37.49	34.80
5	40.4	40.8	39.4	39.1	38.94	36.80
6	41.2	41.0	39.8	39.5	39.62	39.20

1. The Hernández technique applied to Refinery Products.

Table VII

Product	No. of Tests	Average Direct Pol	Average True Sucrose	Average Hernández Pol
Carbonation Supply	3	65.20	65.61	64.20
Affination Syrup	4	62.25	62.94	61.73
1st Recovery				
Massecuite	3	80.03	80.48	79.80
2nd Recovery				
Massecuite	4	76.95	77.07	76.70
3rd Recovery				
Massecuite	4	68.55	67.93	68.55
1st Crop Syrup	3	58.93	58.88	58.67
2nd Crop Syrup	4	53.35	52.61	52.85
Double Curing				
Syrup	3	57.97	57.29	57.36
1st Jet Syrup	4	68.68	68.82	67.67
2nd Jet Syrup	4	62.00	61.74	62.00
3rd Jet Syrup	4	68.32	67.82	67.87
Returned Syrup	5	60.96	60.29	62.20
Treacle Sugar	1	88.00	87.88	87.20
3rd Crop Sugar	1	92.20	92.14	91.40
Remelt Liquor	3	54.63	54.90	53.73
Refinery Treacle	38	42.63	41.23	43.49

(d) Invert Syrups.

Table XI

Sample	Pol using borax (ml. per 100 ml.)			Direct Pol°	Clerget Suc. %	Red. Sug. %
	25 ml. 2%	25 ml. 4%	50 ml. 4%			
1	34.75	38.85	38.80	26.20	38.74	44.69
2	33.60	37.40	37.60	25.25	37.68	44.69
3	29.60	34.80	35.00	21.20	35.14	47.62
4	29.90	34.60	34.80	20.95	34.81	48.51
5	30.00	34.13	34.60	20.55	34.61	47.91
6	28.00	33.20	33.60	19.10	33.51	47.91
7	28.40	32.60	33.00	19.40	32.77	49.34
8	26.80	31.40	31.80	18.20	31.76	52.34
9	25.20	30.15	30.40	16.60	30.44	50.95
10	24.60	29.40	30.60	16.20	30.34	54.64
11	21.80	27.40	27.80	13.10	27.86	53.00
12	—	-0.80	4.40	-18.80	4.30	78.31

3. The effect of time.

(a) Table XII illustrates progressive pol readings at two minute intervals for solutions containing 6.5 g.

invert syrup, with 25 ml. 4 per cent borax in 100 ml. (solution 1) and 50 ml. 4 per cent borax in 100 ml. (solution 2).

Table XII

Minutes after borax addition	2	4	6	8	10	12	14	16	18	20	22
Pol reading x 4—Soln. 1	16.2	18.4	20.8	21.6	22.8	24.0	24.8	25.2	25.6	26.0	26.2
Pol reading x 4—Soln. 2	20.8	21.6	22.2	23.0	23.8	24.6	25.2	25.8	26.2	26.6	26.8
Minutes after borax addition	24	26	28	30	32	34	36	38	40	50	60
Pol reading x 4—Soln. 1	26.4	26.6	26.8	26.8	27.0	27.2	27.2	27.4	27.4	27.4	27.4
Pol reading x 4—Soln. 2	27.0	27.2	27.4	27.6	27.6	27.8	27.8	27.8	27.8	27.8	27.8

(b) Aliquots containing 6.5 g. invert syrup adjusted to various pH values between 4.2 and 7.8, 50 ml. 4 per cent borax added to each aliquot.

Table XIII

pH of Solution	4.2	6.6	7.4	7.8
Initial Pol °s.	5.1	5.1	5.35	5.35
Pol after 5 min.	5.65	5.7	5.8	5.9
Pol after 10 min.	6.2	6.15	6.15	6.3
Pol after 20 min.	6.75	6.8	6.6	6.6
Time (min.) taken to reach final Pol (6.95°s)	28 min.	29 min.	38 min.	40 min.

Discussion and Conclusions

Tichlá and Friml<sup>9</sup> have concluded that three moles of borax are required to nullify the polarisation of one mole of dextrose, while 2 moles of borax reduce the pol of one mole of levulose to a minimum. However, Swann, McNabb and Hazel<sup>8</sup> suggest the formation of a 1 : 1 complex of borate with the enol form of levulose, while Böeseken<sup>1</sup> and Hernández<sup>4</sup> favour a combination in the ratio of 2 moles of the hexose to one mole of borate.

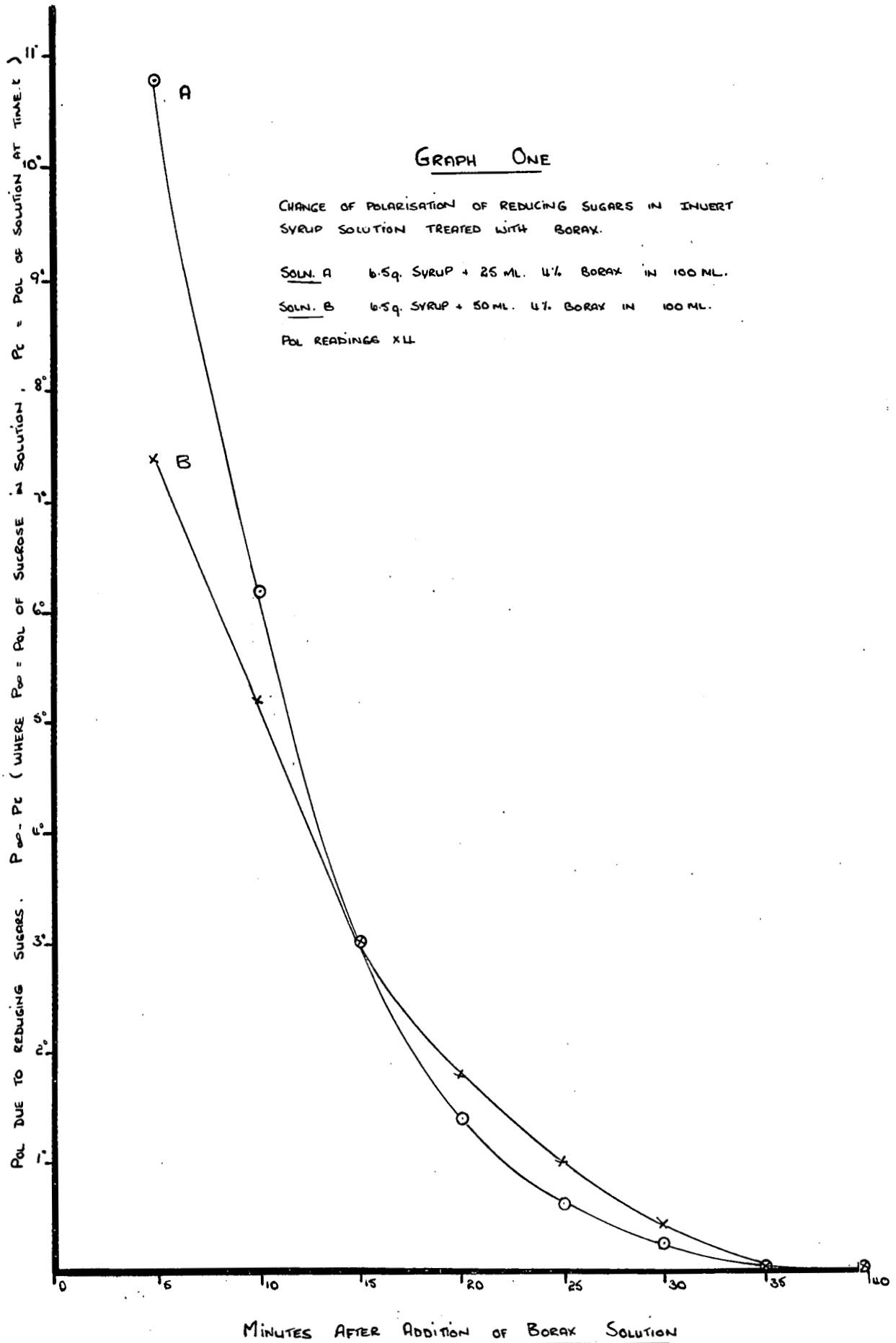
In the original experiments of Hernández the mole ratio of borax to both dextrose and levulose was 129 : 277. This ratio would appear to be too low to allow for complete nullification of the pol of the sugars.

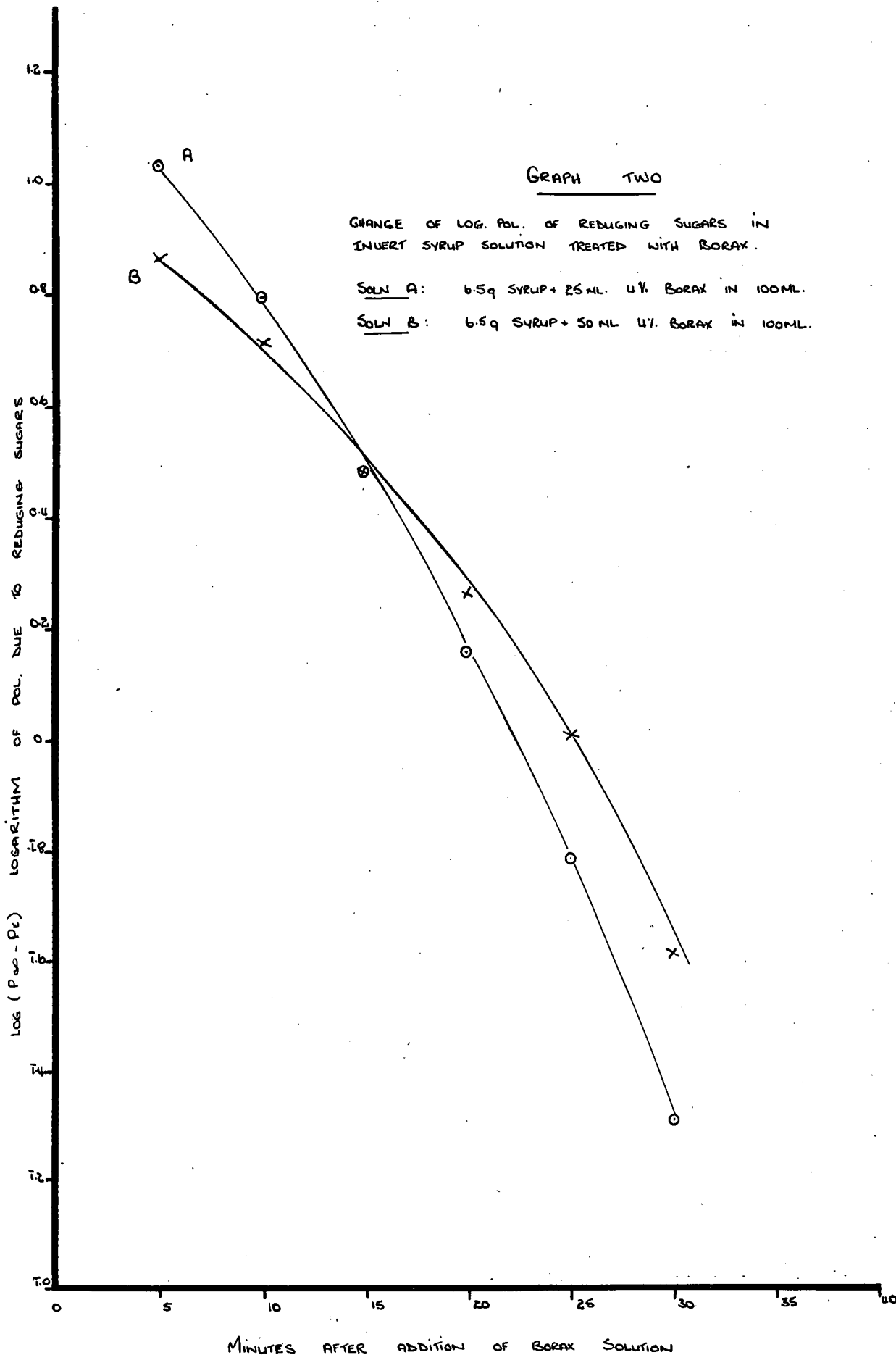
It can be seen from table II that if 50 ml. 4 per cent borax are added to 0.5 g. of dextrose the reduction of the polarisation of the monosaccharide is complete. The ratio in this case was 2 borax to 1 dextrose. However a 2 : 1 ratio of borax to levulose will not reduce the polarisation beyond -0.8°.

Without a knowledge of the respective rates of reaction of borax on levulose and/or dextrose it is not possible to calculate the expected polarisation of a mixture of the two hexoses when treated with borax in various concentrations. Clearly, however, the mechanics of the nullification of the polarisation of the hexoses by borax is complex.

A major discrepancy between the results obtained by Hernández and the findings expressed in this paper is the depression of the polarisation of sucrose (Tables I, II, VI). While Hernández mentions the depression of the sucrose pol in his text, and even goes so far as to offer an explanation for the phenomenon, his published results indicate no depression. One is left wondering whether a "sucrose" which yielded a polarisation of 49° in semi-normal solution (Table I) was a satisfactory starting material for his investigations.

Tichlá and Friml have noted that "if more than 0.5 g. of borax is added to 100 ml. of a 0.25-1.0 N solution, the sucrose polarisation will be reduced. From Table I it can be seen that even the addition of 0.5 g. of borax to semi-normal solution reduces the sucrose pol by 0.5 per cent. The results in Table VI indicate that the addition of larger amounts of borax can reduce the pol of the sucrose by almost 3 per cent. This phenomenon must always be taken into account when proposing techniques for direct sucrose determination using borax. Whether the pol of sucrose is reduced if reducing sugars are present in sufficient quantity to utilise all the existing borax is not clear. It seems certain however, that the addition of borax to sucrose/reducing sugar solutions in a ratio larger





than required to neutralise the reducing sugars will cause a depression of the sucrose pol (Table VIII).

Table III illustrates the effect of pH on the reduction of dextrose polarisation by borax. It is not clear however whether the reduction of the pol at higher pH values is due to enhancement of the effects of the borax on the dextrose, or to other factors.

The effect of inorganic impurities on the polarisation of sugar/borax solutions is shown in Table V. The changes in polarisation are probably due to the influence certain salts have on the pol of monosaccharides<sup>5</sup>, and not to any additive effect by the mineral salts on the nullifying action of the borax.

While the addition of borax in the ratios suggested by Hernández has proved of little value under South African conditions<sup>2</sup> (Table VII), the use of larger concentrations of borax has yielded encouraging results. With both refinery molasses and mill molasses (Tables IX and X) the addition of 50 ml. 4 per cent or 5 per cent borax yields a polarisation figure far closer to true sucrose than a direct polarisation. It would appear that a very reasonable approximation of sucrose in molasses can be made rapidly by using 50 ml. of 4 per cent borax.

With invert syrups, having very high reducing sugar contents, the agreement between Clerget sucrose and a direct pol; using 50 ml. 4 per cent borax is even more striking (Table XI). With the large quantities of reducing sugars present in the syrup it is difficult to reconcile this agreement with the theories of Tichlá and Friml, for the mole ratio in, for example, sample nine of Table XI is of the order of 5 borax to 18 reducing sugars. A further conclusion of these authors that "the nullpoint occurs when the weight of borax added equals that of the invert sugars" is also not borne out by this sample for which 2 g. of borax were added to nullify the polarisation of 3.3 g. reducing sugars.

It is obvious that the reaction between borax and the reducing sugars is most complex. Table XIII indicates that the polarisation of a sucrose/reducing sugar solution in the presence of borax is a function of time, while the rate of reaction is affected to some extent by the addition of alkali. Graph 1 has been constructed to illustrate the change in the polarisation of the reducing sugars with time, taking  $P_{\infty}$ , the final pol of the solution, as the pol due to sucrose alone. Graph 2 is a plot of time against the logarithm of the pol of the reducing sugars.

It is reasonable to expect that at least three separate reaction mechanisms combine in this complex chemical relationship: (1) The reaction between dextrose and borax, (2) the reaction between levulose and borax, (3) the mutarotation of the monosaccharides. To these can be added the possible reduction in the polarisation of sucrose though it can be seen from Table VI that the reduced pol of a sucrose/borax solution is unaffected by time.

While it would be foolhardy at this stage to attempt to decipher the mechanisms of the reactions which take

place when borax is added to an invert syrup solution it is not unreasonable to suggest a method for the rapid determination of sucrose in invert syrups. In all cases studied the pol of the solution had reached stability after 40 minutes. The suggested method for direct sucrose determination in invert syrups allows a 60 minute interval between the addition of borax and polarisation.

### Rapid determination of Sucrose in Invert Syrups

6.5 g. of the test syrup are weighed into a 100 ml. flask 50 ml. 4 per cent borax is added, the contents of the flask mixed by swirling and set aside for 60 minutes. After this time the solution is made to volume, mixed and polarised in a 200 mm. tube in a standard saccharimeter. If clarification of the solution is necessary a minimum of dry lead acetate should be added after the solution has been made to volume. The pol reading x 4 will give the percentage sucrose in the sample.

### Summary

Observations of the effects of borax on the polarisation of solutions of pure sugars have proved inconsistent with the findings of J. A. López Hernández (I.S.J., 65, 1963, 46-48, 72-73, 107-109). The use of borax in greater concentrations than recommended by Hernández, to determine the sucrose content of impure solutions, has proved promising. Following a brief study of the mechanism of the reaction between borax and the reducing sugars, a method is proposed for the rapid determination of sucrose in invert syrups.

### Acknowledgments

The authors wish to thank the directors of Hulett's South African Refineries, Limited, for permission to publish the results which appear in this paper.

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**Mr. Alexander** (in the chair): Although this paper was presented by two authors I would like especially to congratulate Mr. Dave Adam since he must have created a record by producing his first paper at the age of 65. Mr. Adam is a pensioner and has given up a large amount of his time to carry out this research.

**Dr. Matic:** I was about to congratulate the Refinery once again on producing a paper both of scientific merit and of practical significance to the industry as a whole. Now I find that the work was done by an individual researcher working in his spare time—an even more creditable effort!

**Mr. Alexander:** In reply to Dr. Matic I would like to mention that Mr. Adam has connections with

the Refinery—he in fact worked at Hulsar for 47 years!

While it is obvious from the paper that we at the Refinery do not understand the workings of the borax/reducing sugar reaction, we feel that the phenomenon has considerable practical possibilities and we appeal to other laboratories to test the method, especially as far as molasses is concerned. The advantages of a quick method for determining sucrose in molasses are obvious.

**Dr. Graham:** The S.M.R.I. conducted experiments using borax concentrations greater than those proposed by Hernandez but did not reach the high concentration levels used by Mr. Adam.