

THE PRESENCE AND SIGNIFICANCE OF CRYSTALLINE ACONITATE SALTS IN MASSECUITES AND MOLASSES

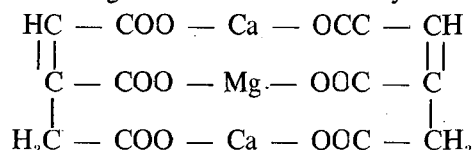
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Abstract

The occurrence of relatively large concentrations of crystalline calcium magnesium aconitate in South African molasses and massecuites is noted. The effect of this impurity on the viscosity of molasses is measured at varying concentrations.

Introduction

Aconitic acid was first shown to be a constituent of cane molasses as early as 1877⁷, and in 1911 Yoder³⁰ showed that it was the major organic acid present in cane juice. McCalip and Siebert²⁰ noted the presence of crystalline impurities in A and B molasses, which they identified as calcium aconitate. They suggested that it might be commercially feasible to extract aconitic acid from molasses. Balch *et al*⁶, in 1945, analysed factory products from crusher juice to C-molasses, finding up to 4.4% of aconitate on solids in the latter. In view of the increased demand for plastics and synthetic rubber during the war these authors outlined a possible method for recovering aconitates from B-molasses. Ambler *et al*⁴ studied the naturally occurring salt in more detail, and showed it to be a complex salt, diacalcium magnesium aconitate hexahydrate.



The ratio of calcium to magnesium varied from 2:1 to 2.75:0.25, but the pure salts of calcium or magnesium aconitate were not isolated.

In 1946 Ventre *et al*²⁷ published a method for the extraction of calcium aconitate from sorgo syrup, and in the course of the next few years a large number of patents were taken out for extraction procedures. These could be divided into two categories, those precipitating the calcium salt through the addition of lime or calcium chloride^{28,11,26,5,23}, and those involving anion exchange^{18,24}. In 1955 a detailed review of the successful operation of an extraction plant at Godchaux's Raceland factory was published¹⁵, in which it was stated that molasses should contain at least 3% of aconitate to make recovery economically feasible.

In many countries the concentration of aconitic acid is well below the 3% level. Thus in Puerto Rico figures of from 0.5% to 3.0% have been reported⁸, in Taiwan 1.2 to 2.25%¹⁰, in India 2.0 to 2.9%¹⁴, British West Indies 0.5 to 3.5%¹² and South Africa 1.3 to 2.3%²¹. In Louisiana figures of up to 6.3% have been given¹³, in Brazil 6.1% has been found²⁵ while in Egypt 6.5% was reported¹⁷.

The occurrence of calcium magnesium aconitate in South African molasses

Data on the presence of aconitates in South African final molasses published for 1969²¹ showed the average level to be about 1.8%. During the 1970/71 crop large quantities of very small crystals ($\pm 10\mu$) were observed in various massecuite and molasses samples. These crystals, which polarised light, had the appearance of false grain, but could not be washed out of a massecuite with water. (See Figures 1 and 2.)

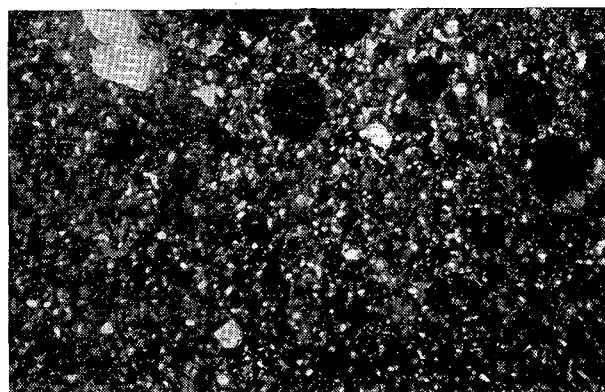


FIGURE 1: GD final molasses under polarized light (mag. x 100).

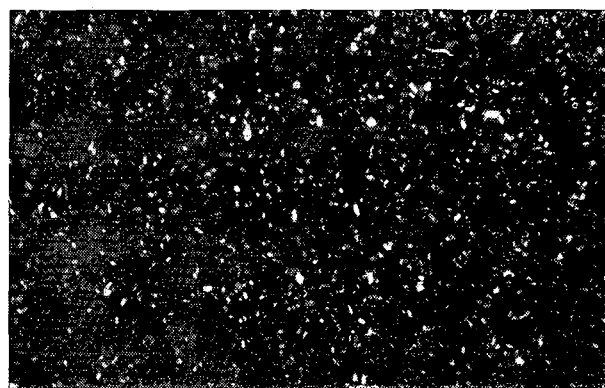


FIGURE 2: GD final molasses diluted 1:1 under polarized light (mag. x 100).

They were present throughout a boiling, in some cases even appearing in the syrup, but did not appear to grow at all during the boiling time. These crystals were at first thought to be either calcium phosphate or calcium potassium sulphate, but tests for these compounds were negative.

The crystals were only sparingly soluble in water, and after dilution of final molasses they could be separated by centrifugation. After washing with

water and acetone they appeared as a light grey sludge, which under the microscope could be seen to be almost entirely crystalline. (See Figures 3 and 4.)

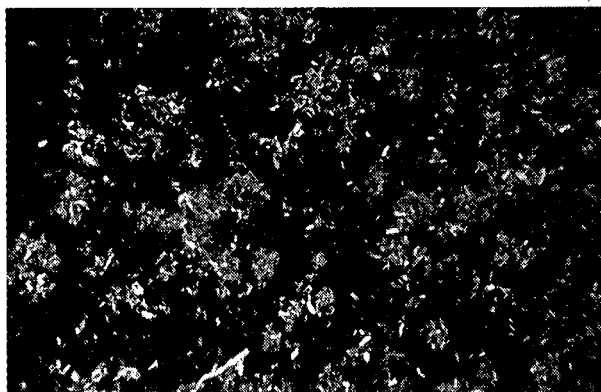


FIGURE 3: Crystalline sludge separated from DK final molasses (mag. x 100).

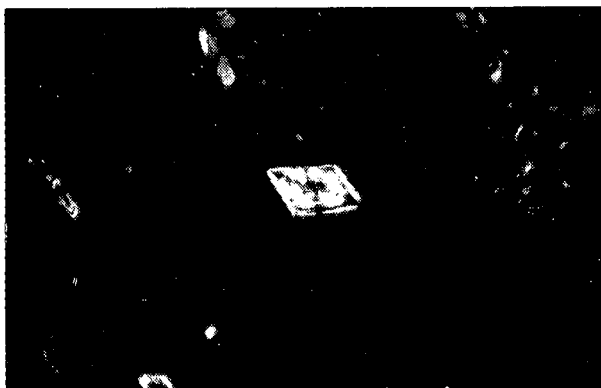


FIGURE 4: Typical shape of the crystals found in DK molasses (mag. x 450).

Analysis of these impure crystals is shown in Table I.

TABLE I
Composition of crystalline sludge separated from DK final molasses

Calcium, as CaO%	25,0
Magnesium, as MgO%	3,5
Aconitate%	34,75
Moisture%	5,77
Loss on ignition%	59,00

The dried calcium magnesium aconitate was dissolved in hot concentrated HCl, and, after filtering, crystals of free aconitic acid were separated. These could be further purified by re-crystallisation from glacial acetic acid.

The significance of calcium magnesium aconitate in molasses

It has been reported¹⁴ that aconitic acid definitely contributes to the viscosity of factory liquors. As far as massecuites are concerned it is well known that the crystal content is a major determining fac-

tor of the viscosity. It is therefore reasonable to assume that the presence of large amounts of crystalline impurities would lead to high viscosities in low grade massecuites, with a resultant decrease in the exhaustion efficiency. This was confirmed by adding varying amounts of the impure crystalline aconitate material extracted from molasses to a final molasses of known viscosity, and measuring the changes in viscosity after mixing for a fixed time under standard conditions. This precaution was taken in order to minimize the effect of air being beaten into the molasses. The actual increase in viscosity, measured with a Brookfield viscometer at 25°C is shown in Figure 5. The molasses used in this case contained naturally approximately 2,5% of crystalline aconitate.

A further test was carried out comparing the molasses used in the above experiment with a molasses which was virtually free of naturally occurring crystals. To both samples increasing amounts of aconitate were added; in addition varying amounts of crystalline calcium carbonate were added to a second portion of the crystal-free molasses. The results are shown in Figure 6.

It is quite apparent from these curves that apart from any effect dissolved aconitate may have, the presence of insoluble impurities has a very substantial influence on the viscosity of molasses, and presumably of massecuites. Figures 7 and 8 give an impression of the microscopic appearance, under polarised light, of C-molasses and C-massecuite taken completely at random at DK during January 1970. These samples contained about 3% of total aconitate.

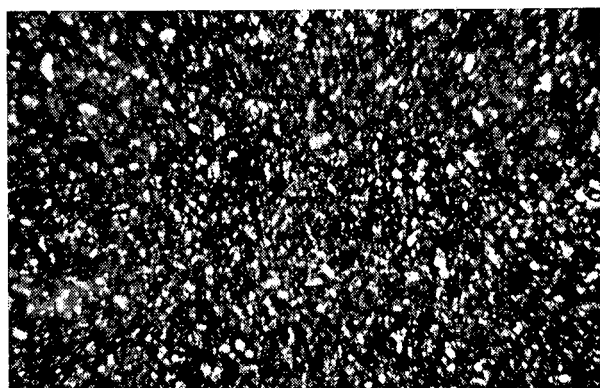


FIGURE 7: Final molasses under polarized light (mag. x 100).

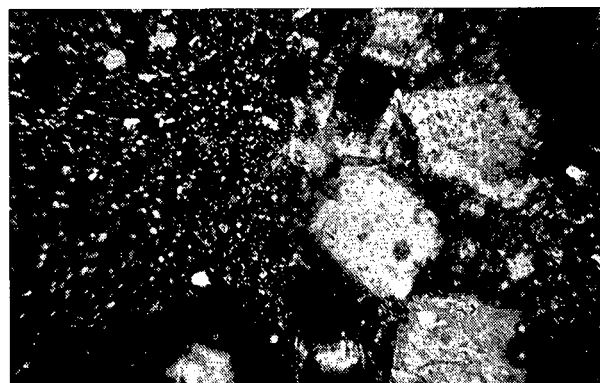


FIGURE 8: C-massecuite under polarized light (mag. x 100).

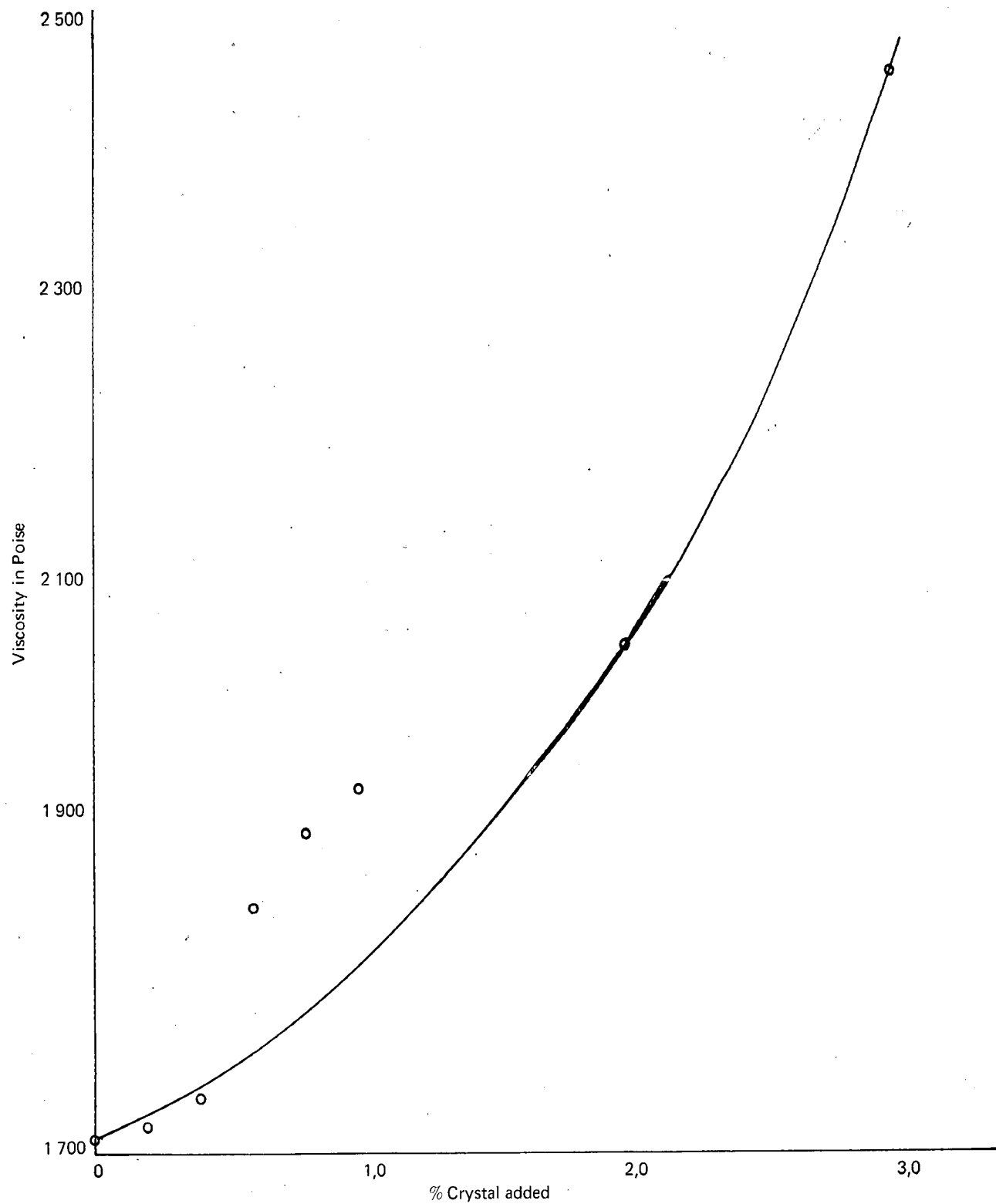


FIGURE 5: The change in viscosity with the addition of calcium magnesium aconitate crystals.

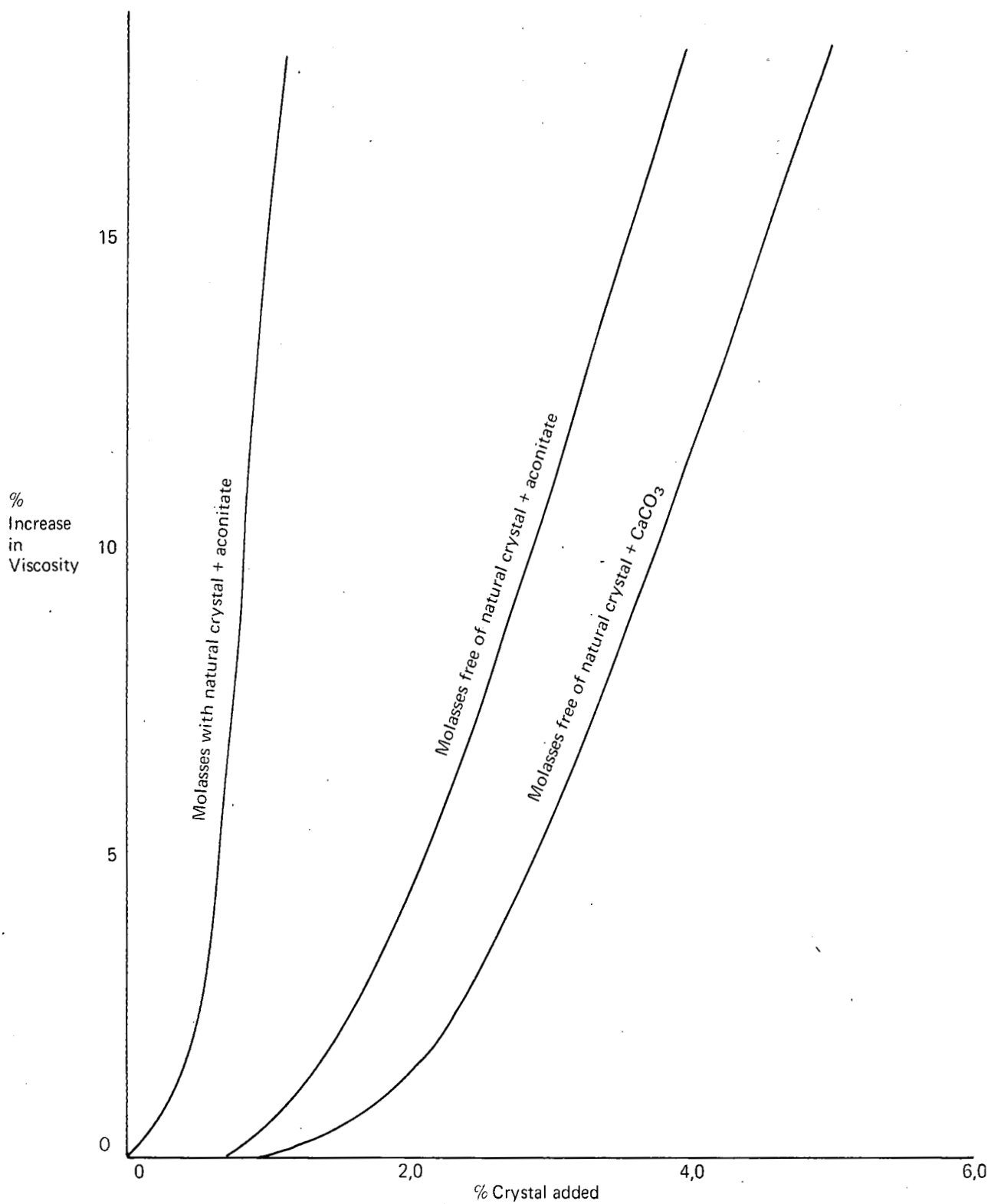


FIGURE 6: The change in viscosity in two different molasses samples with the addition of crystalline aconitate or CaCO₃.

Calcium aconitate may well have other effects on sugar processing. There have been numerous references to the presence of calcium aconitate in evaporator and pan scale^{6,20,28,22}. In 1955 Wolfrom *et al*²⁹ linked salts of aconitic acid with the formation of colour under simulated clarifier conditions. Löwry¹⁹ showed that the presence of aconitates had an inhibitory effect on colour removal by bone char.

One of the problems in an extended investigation into aconitic acid in sugar products is to get reproducible analytical data. Early workers extracted the acid with ether, or precipitated the lead salt, and determined it titrimetrically with standard alkali⁶, or potassium permanganate¹⁶. Ambler and Roberts^{1,2,3} developed a decarboxylation method which is widely used, but Gupta¹⁴, comparing this method with the polarographic method of Drake *et al*¹², found it to yield results which were low by as much as 60%. Bureau⁹ has recently published a polarographic method suitable for use with plant material, and it is hoped to use this method to trace the aconitic acid from the cane into the factory this coming season.

There is no doubt that the viscosities of low grade products were increased during the 1970/71 season at many Natal factories, due to the presence of crystalline calcium magnesium aconitate. Unfortunately we have no available data on whether this was something unique to last season, or whether these crystals are a normal occurrence. In addition we have very little data on comparative viscosities at various factories throughout the season. Nevertheless the fact that viscosity is affected by aconitates will have led to a poorer exhaustion of final molasses than should otherwise have been obtained, and the financial losses to milling companies may have been considerable. A great deal more work is required before we can evaluate the extent of these losses, but in the coming season the occurrence of aconitates at all factories will be carefully monitored.

Acknowledgements

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Discussion

Dr. Matic (in the chair): As these crystals have only recently been found in factory products we have no previous data for comparative purposes.

We do not know, for instance, whether the high viscosities experienced by some factories last year were due to these crystals or not.

This investigation will take some time to complete but it could be of considerable importance to the industry.

Mr. Francis: The refinery has had experience of crystals in molasses but unfortunately they were not identified.

Mr. MacGillivray: They are easily distinguished from sugar by dilution and inspection under a high-powered microscope. A polarising lens is required as the crystals are almost colourless.

Dr. Tilbury: Has the presence of aconitate been investigated in the cane itself?

Mr. MacGillivray: When our polarographic method is working properly we will investigate cane. According to the literature, immature cane is responsible for formation of aconitate.

The level of aconitic acid in final molasses at four different points in the season was fairly constant.

There is more aconitic acid in cane than any other acid.

Mr. du Toit: Quick-growing cane and cane tops are responsible for aconitic acid.

Mr. Alexander: In America five-month-old cane was milled in order to recover its aconitic acid content.

Mr. Smith: Will the fact that aconitic crystals are dextro-rotatory have any effect on sucrose determination?

Mr. MacGillivray: Quite a number of calcium salts are optically active in the crystalline form but there would be no effect on polarisation in a solution.

Mr. Lenferna: Because of the heavy rainfall in Mauritius cane is crushed at a younger age than in South Africa and they have been aware there of

aconitic acid.

Mr. Lamusse: I first saw aconitic crystals ten years ago when looking for false grain under polarised light in a microscope. Aconitate crystals are not all that common in Mauritius but do occur in high rainfall areas.

Mr. Jennings: We must be careful about confusing polarised light when referring to microscopy with the use of polarimetry for sugar analysis. The two cases are not the same thing at all.