

# COMPOSITION OF SOUTH AFRICAN FINAL MOLASSES

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## Abstract

A survey has been carried out on the composition of final molasses from South African sugar factories. Regional and seasonal trends in various parameters have been noted, and the degree of exhaustion of the molasses has been commented upon. Included in the survey are data on the non-sucrose constituents of molasses, and the inorganic ash components. Comparisons are made with a similar survey conducted in 1955/1956.

## Introduction

A detailed survey of the composition of South African final molasses was carried out 15 years ago<sup>3</sup>. Since then three new factories have been opened in order to serve newly developed areas, the combined crushing rate of the mills has more than doubled and the average crushing rate has increased by 70%. Purity of mixed juice has dropped by about two points and the varietal scene has altered significantly (Co.331 and N.Co.310 varieties represented 80% of the cane crushed during 1955/56 season compared to 20% during the 1969/70 season). The methods of clarification have also changed. In 1955, defecation was practised by eight out of 17 factories. There was one carbonatation factory and the remaining mills used sulphitation. Profound changes, which could have influenced the composition of final molasses, have therefore taken place in the industry in the intervening years and it was felt that a new survey of the final molasses was highly desirable.

In order to assess the seasonal influences on the molasses composition, it was intended to collect four samples of final molasses from each factory, i.e. at the beginning of July, September, November and January. Ten mills supplied all four samples. Three samples were received from seven factories, either because they stopped crushing before January or for some other reason. RN sent two and PG one sample. ME, which produced high test molasses, was omitted from this survey.

Except for EN, where sulphitation is used, all other factories clarified their juice by either normal defecation or vacuum flotation (SZ, UK). However, ML, GH, SZ and PG are factories-cum-refineries. The first three use carbonatation with polishing sulphitation in their refining process and PG uses melt carbonatation only.

The analytical results obtained in the survey are presented in this paper and seasonal and regional influences on molasses and ash composition are discussed. Target purities are calculated by using the Douwes Dekker, Queensland and Mauritian formulae and are compared with the final molasses purities actually achieved.

## Experimental

The molasses samples which were analysed were composite samples from each factory for the first week of July, September, November and January respectively. The analyses for sucrose, reducing sugars, ash, dry solids, colour and viscosity were done as soon as possible after receipt of the samples to avoid any effects of deterioration. Analyses of the ash constituents and the organic non-sugars were completed at the end of the season when all the samples were available.

The methods of analysis were as follows:

### (a) Dry Solids

The method is detailed in the Laboratory Manual for South African Sugar Factories (1962) pages 67-8.

### (b) Refractometer Solids

The solids were determined on undiluted molasses at 20°C using an Atago Refractometer.

### (c) Sucrose

This determination was by Lane and Eynon titration after acid hydrolysis<sup>7</sup>.

### (d) Reducing Sugars

By Lane and Eynon titration<sup>7</sup>.

### (e) Sulphated Ash

As described in the Laboratory Manual for South African Sugar Factories (1962), page 56.

### (f) Colour

An approximately 50 Brix refined sugar solution was decolourised with 1% (on solids) of active carbon. The solution was filtered over kieselguhr (0.7% on solids) on a Buchner funnel, and the pH was adjusted to  $7.0 \pm 0.1$  with dilute HCl or NaOH. The Brix was then adjusted to  $50.0 \pm 0.1$ . One gramme of molasses and 99.0 g of the sugar solution were mixed to obtain a homogeneous solution. The colour was then determined by ICUMSA Method II<sup>6</sup> as is used for raw sugars. The colour attenuation was corrected for dry solids by multiply-

ing the result by  $\frac{100}{\text{dry solids}}$ , in order to eliminate the

effects of the varying water contents of the molasses.

### (g) Viscosity

The samples were adjusted to 80.0% dry solids by adding the calculated weight of water to a known weight of molasses and viscosity was determined with a Höppler Falling Ball Viscometer, at 25° and 50°C.

**(h) Filterability**

Two per cent by weight of molasses was added to a 60° Brix refined sugar solution, and the filterabilities were determined by the Nicholson and Horsley method<sup>8</sup>. The filterabilities obtained were then expressed as a percentage of the figure obtained for the refined sugar solution, which was determined as a blank.

**(i) Starch, Wax and Gums**

These were determined as described by Douwes Dekker<sup>3</sup>.

**(j) Aconitic Acid**

Thirty-five grammes of molasses were dissolved in 250 ml water, and 50 ml of neutral lead acetate were added. The precipitate was washed free of wax and fats, and dried. Decarboxylation was carried out by boiling the precipitate with glacial acetic acid in the presence of potassium acetate. The CO<sub>2</sub> given off was collected and the amount determined, from which the aconitic acid was calculated.

**(k) CaO, MgO and K<sub>2</sub>O**

These were determined as described by Douwes spectroscopy<sup>10</sup>.

**(l) Chloride**

This was determined by automatic potentiometric titration as described by Comrie<sup>2</sup>.

**(m) Sulphate**

This was determined gravimetrically by precipitation with BaCl<sub>2</sub>.

**(n) Protein**

Nitrogen was determined by the micro-Kjeldahl method.

**(o) Silica**

As described by Vogel<sup>11</sup>.

### Results and Discussion

The analytical data are presented in Tables I, II and IV.

#### Dry Solids and Refractometer Solids

Refractometer solids in Table I have been determined on undiluted molasses samples. It was felt that the error which is obtained by this method is of a similar order to that when samples are diluted and filtered prior to reading. The average difference between refractometer solids and dry solids found for these samples was 2.78%, with a standard deviation between results of 0.82. A limited number of determinations carried out at the S.M.R.I. on various dilutions of molasses give differences ranging from 3 to 6.

The dry solids of the samples analysed varied between 76.89 and 84.79 with an average figure of 81.53. This is 2.18% higher than the average found in the previous survey<sup>3</sup> of Natal final molasses. This may be due either to the improvement which has been made in centrifugal performance in the last 15 years or to lower viscosities of final molasses. Unfortunately no comparative figures are available.

#### Pol and Sucrose

A number of the samples analysed were found to have a pol value lower than the chemically determined sucrose. In all but one of these cases the samples were taken during November, when the reducing sugars were generally low. Conversely the greatest differences between sucrose and pol were found in samples having a high reducing sugars content. The effect of this phenomenon on the apparent and gravity purities is obvious and some of the anomalous results which have been found in the past by the factories may have been due to this discrepancy.

#### Colour

It has been noted in the past that low pol sugars produced at certain factories were very much higher in colour than at others. As this was largely due to the colour of the final molasses coating, it was thought to be of some interest to present comparative data for molasses colours. It is apparent from Figure 1 that the molasses colours were at a minimum during September, when mixed juice purities were highest. During November and January colours were substantially higher. One exception to this was JB, where no seasonal influence was observed. Disregarding EM and DL, both of whom produced very highly-coloured molasses, there appeared to be a regional influence, as molasses produced on the South Coast and in the Midlands were higher in colour than those from Zululand and the North Coast.

Surprisingly, there appears to be no correlation between the nitrogen content of molasses and the colour.

#### Viscosity

It has been observed by a number of workers<sup>1,5,9</sup> that the limiting factor in molasses exhaustion is viscosity. In order to determine any seasonal or regional influences on the viscosities of Natal final molasses, the viscosities were determined at a fixed dry solids content of 80%. In most cases the viscosity of molasses from any one mill tended to reach a maximum during November. A very wide spread in viscosities between factories was observed, with figures ranging from 14 to 128 poises at 50°C and 93 to 855 poises at 25°C.

#### Filterability

It was felt that an indication of the suspended matter in molasses could be obtained from a filterability measurement. A method was devised which approximated to the conditions of the Nicholson and Horsley filterability test<sup>8</sup>, and comparative figures were obtained for the September and January samples. A marked seasonal influence was observed, with a drop in filterability occurring towards the end of the season. This is in agreement with the trend found in the results of filterability tests of unaffinated low pol raw sugars in South Africa.

#### Exhaustion of Final Molasses

As was mentioned earlier, the main limiting factor in molasses exhaustion is the viscosity. This has been borne out by this survey, in which it was found

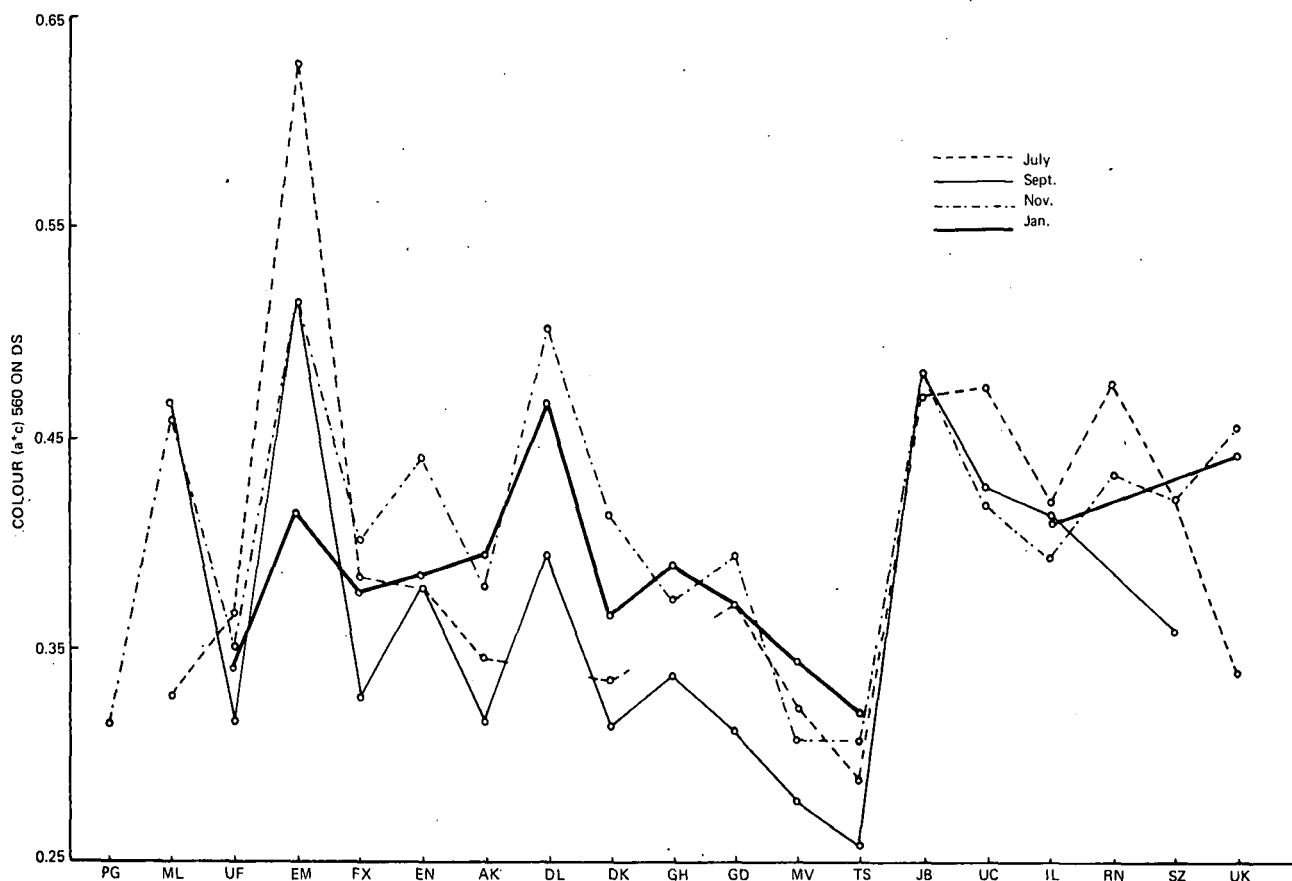


FIGURE 1: Seasonal variation of molasses colour.

that in most cases the highest molasses purities occurred in November, when the highest viscosities were recorded.

A number of formulae for the exhaustibility of final molasses are based on the ratio of reducing sugars to ash. Of the molasses samples analysed in this survey, almost all had the lowest reducing sugars/ash ratio in November, and a definite correlation is apparent with the degree of exhaustion. The data produced in this survey were applied to three different molasses exhaustion formulae, viz. the Douwes Dekker formula<sup>4</sup>:  $P = 35.886 - 0.08088 R + 0.26047A$ ; the Queensland formula<sup>1</sup>:  $P = 40.67 - 17.80 \log X$ ; and the Mauritian formula<sup>9</sup>:  $P = 44.60 - 4X$ , where  $P$  = target purity,  $R$  = RS% non-sucrose,  $A$  = ash % non-sucrose, and  $X$  = RS/ash.

In general the best agreement between the actual true purity and the target purity was obtained with the Douwes Dekker formula. However, in cases where particularly low reducing sugar/ash ratios were found, such as at EN and the South Coast mills, the Queensland formula provided better agreement. The formula originally derived from experimental data in Mauritius was as indicated above. However, it was found that a number of factories were consistently improving on the target, and hence it was decided to arbitrarily reduce the constant factor by three. Despite the fact that the equation was used in its original form when applying it to the results of this survey, the differences between true and target purities were greater in most cases than with the

other two formulae. This would seem to indicate that by Mauritian standards Natal final molasses is poorly exhausted, but as yet no direct comparison between viscosities have been made.

#### Composition of Dry Solids

The composition of the molasses samples, on a dry solids basis, are shown in Table II.

There was a definite seasonal influence upon the reducing sugars content as a percentage of the solids (Figure 2). November samples were the lowest in every case, whilst in general the January samples were the highest. The opposite seemed to be the case with the sulphated ash percentage dry solids (Figure 3), where January was the lowest and November the highest.

On a regional basis the lower South Coast mills of RN, SZ and UK were low in reducing sugars, as was noted in the previous section. EN was also very low in reducing sugars. An explanation for this may possibly be found in the relatively high pH's which are used in the Rabe process at SZ and UK, and which are also found in the sulphitation process used at EN.

Three factories which were conspicuous for their low ash per cent dry solids figures were ML, JB and UC. All three of these mills service newly developed cane-growing areas, some distance inland. The low ash content is probably not due to the type of cane grown in these areas as there is a considerable difference between the varieties found in the Eastern Transvaal and in the Midlands.

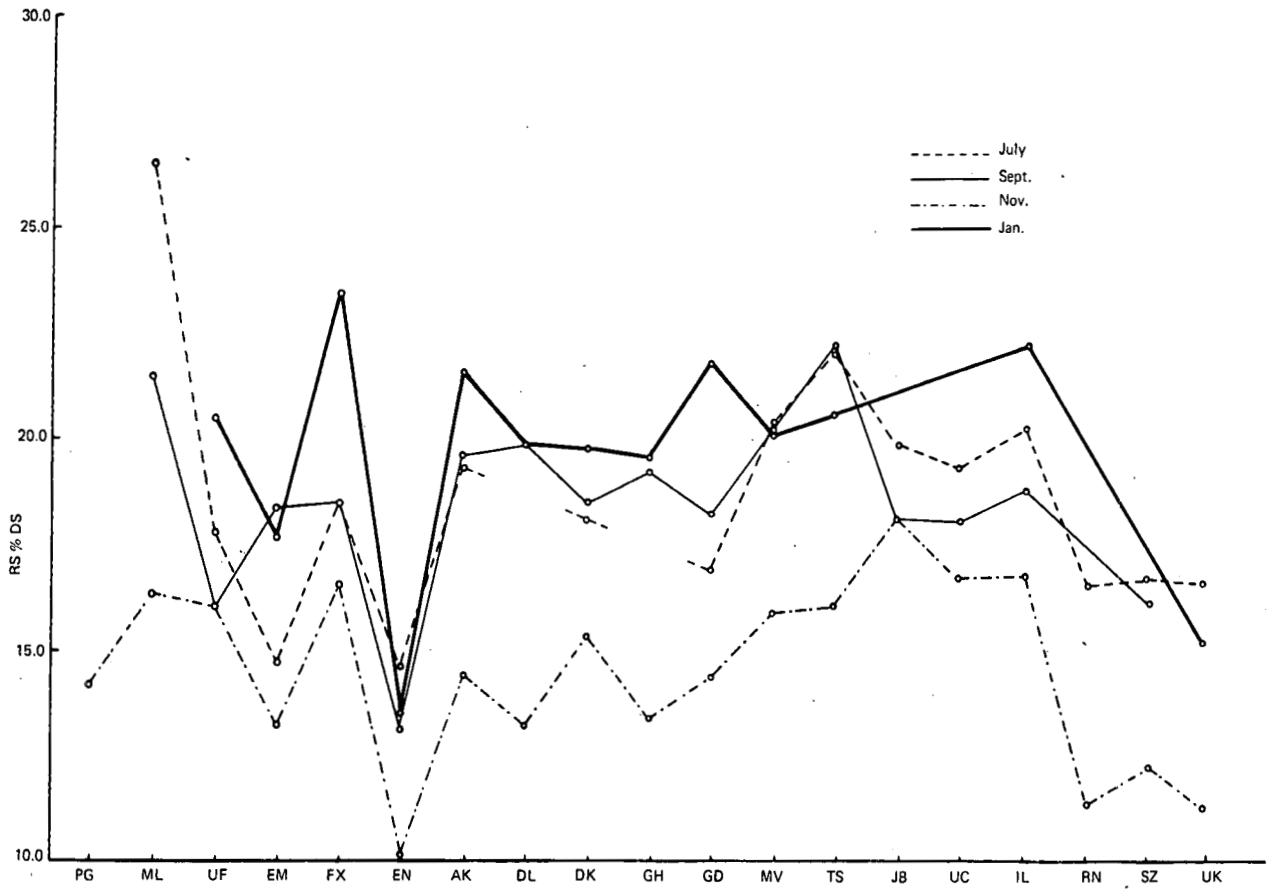


FIGURE 2: Seasonal variation of reducing sugar content of molasses.

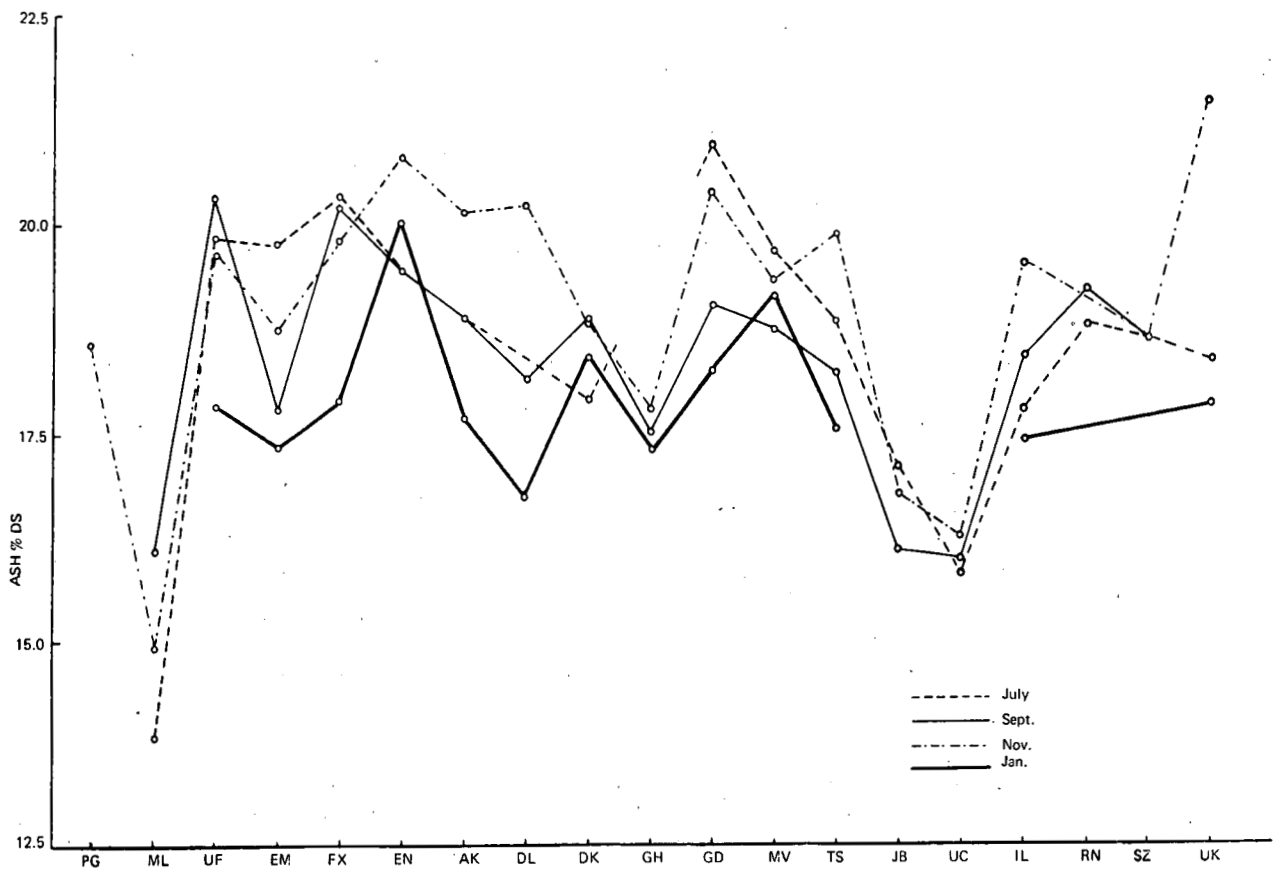


FIGURE 3: Seasonal distribution of ash content of molasses.

Seasonal influences in the gum content (Figure 4) are also apparent, with November again having the highest figures, and January the lowest. There seemed to be a slight increase in wax content from September to January while the protein content declined slightly over the same period. No seasonal differences could be detected in the aconitic acid contents.

Table III shows the comparison between the average non-sucrose constituents of the molasses produced in July/September 1955 and September/January 1969/70. The carbonated ash shown for 1969 has been calculated from the relationship:—

Carbonated ash = sulphated ash × 0.752. This is an approximation based on the figures presented by Douwes Dekker<sup>3</sup>.

**TABLE III**  
Average composition of the "Non-Sucrose" of Final Molasses

	1969/70	1955/6
Total non-sucrose % molasses	45.95	42.75
Reducing sugars % N-S	33.80	30.50
Carbonated ash % N-S	24.27	26.75
Starch % N-S	0.34	1.04
Gums % N-S	5.86	7.43
Wax % N-S	1.10	0.94
Crude protein % N-S	11.88	7.13
U.O.M. % N-S	22.75	27.30

It would seem from Table III that the reducing sugars are higher and the ash lower now than was the

case 15 years ago. This is reflected in the true purities of final molasses which were on the average 46.2 in 1955 and 44.7 in 1969/70 seasons.

As was to be expected, owing to the introduction of starch-removal processes, the starch and total gums are lower than in 1955. The sum of the protein and undetermined organic matter is very similar in both surveys and the difference in protein figures is not thought to be significant. Wax content is of very much the same order in both cases.

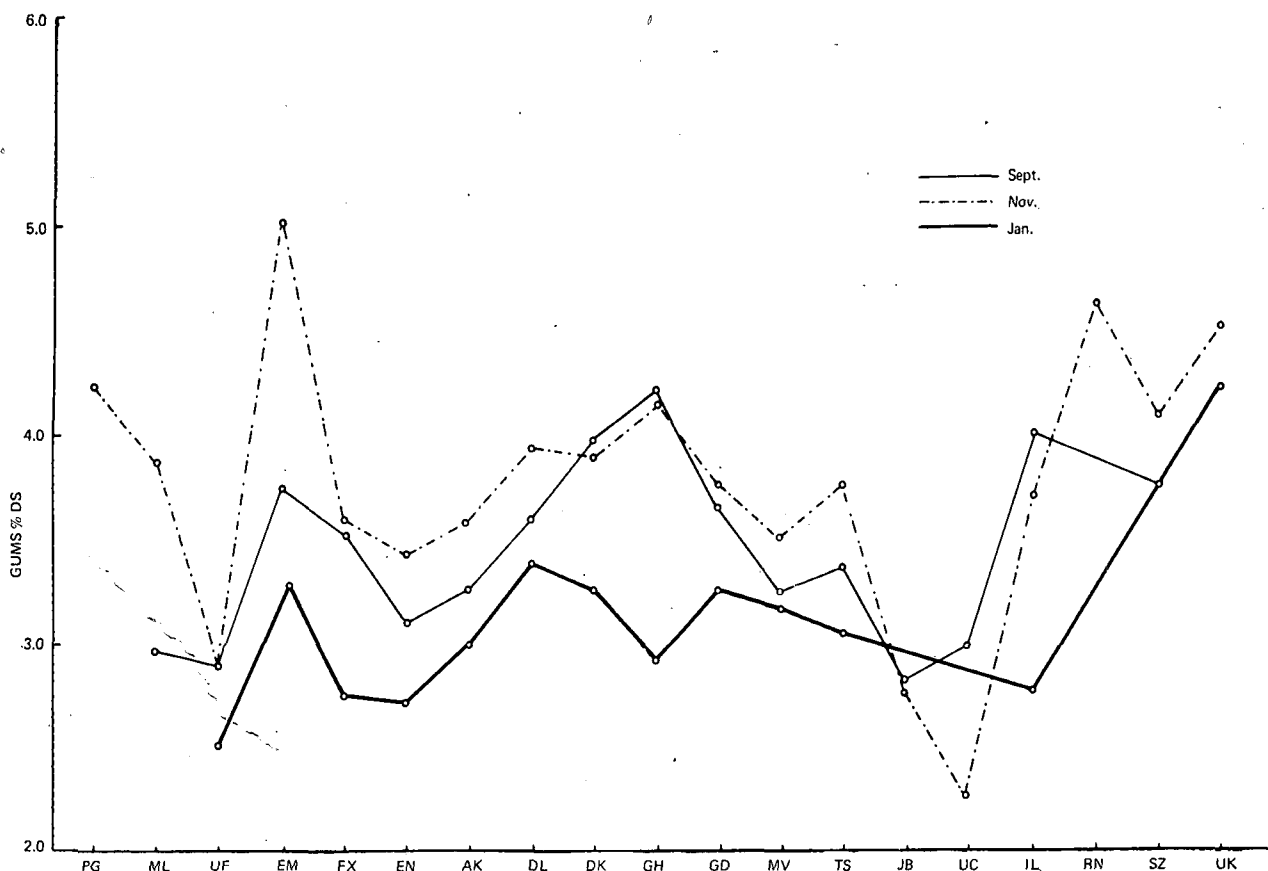
*Composition of the Inorganic Ash of Molasses*

The composition of the ash of the final molasses samples analysed is shown in Table IV.

Potassium represents roughly one-third of the ash in most cases. Magnesium is a major constituent, but in contrast to the figures reported in 1955, in no case was the magnesium content higher than that of the calcium. JB, and to a lesser extent UC, are low in magnesium while EN, JB and UK are rather higher than average in calcium.

An interesting feature of Figure 5, where average results for various constituents are plotted, is the relationship between potassium and chloride on the one hand and calcium and sulphate on the other. Very little regional or seasonal trend in inorganic constituents is apparent.

The molasses samples from EN were somewhat different from the rest of the factories in their ash composition, particularly with respect to potassium, chloride, calcium and sulphate. This was no doubt due to the sulphitation process still practised in this factory.



**FIGURE 4:** Seasonal distribution of gums content of molasses.

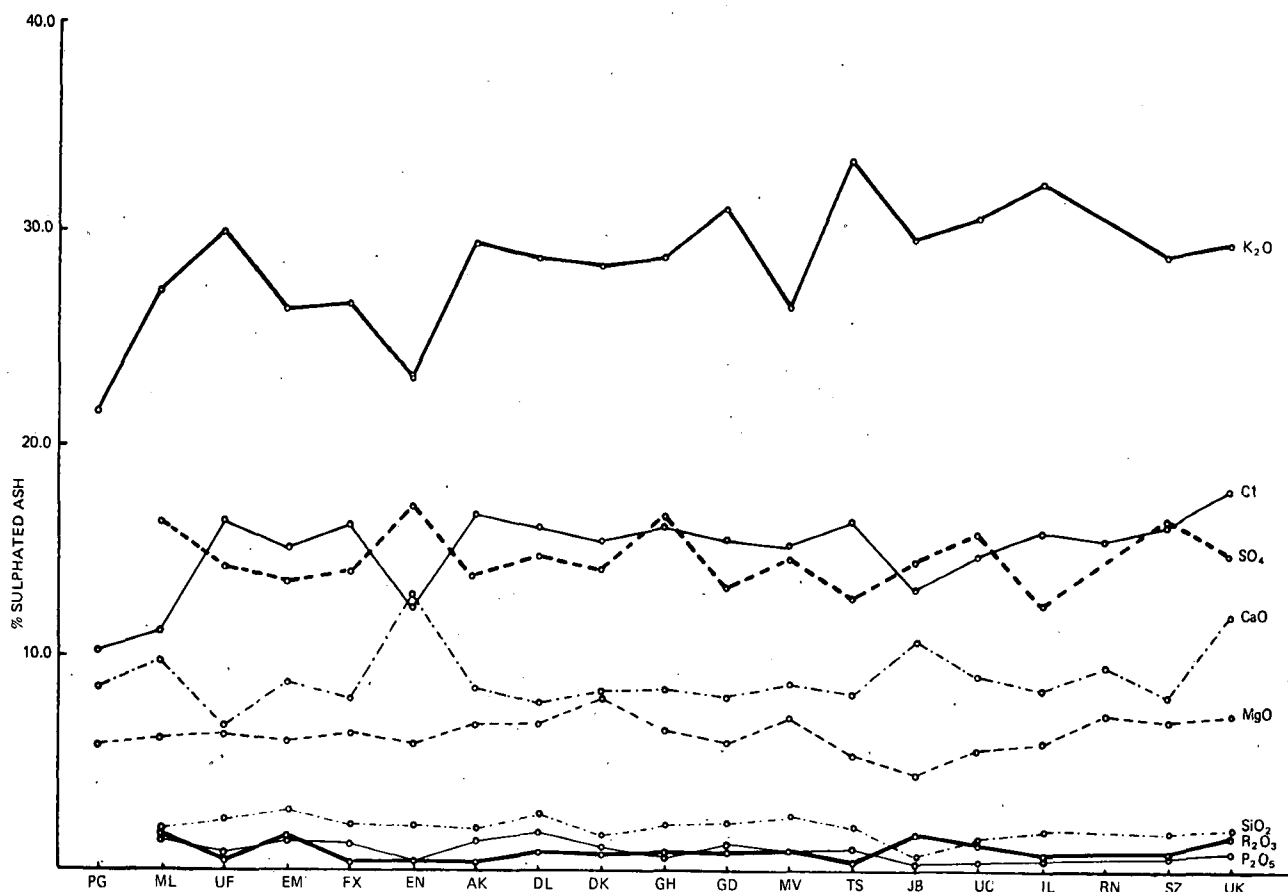


FIGURE 5: Distribution of ash constituents.

### Acknowledgements

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### Discussion

**Mr. Jennings:** When viscosity was measured, was any allowance made for air and the presence of grain?

I notice that reference No. 10 is to an unpublished report by the S.M.R.I. and I hope that this will soon be made available.

In Table IV we start with sulphated ash percentage solids in molasses and then there are a number of constituents which add up to about 75% of the ash. Where is the other 25%?

I would like to hear Mr. Hoekstra's opinion of the Douwes Dekker formula.

**Mr. MacGillivray:** When measuring viscosity, the samples were not re-aerated and grain was not taken into account.

De-aeration is very difficult to carry out successfully and I am not sure that the viscosities obtained on de-aerated samples are any more significant. At the time we did these tests we were particularly interested in how the molasses from different mills would handle at the Terminal, and in this context viscosity is a function of the degree of aeration to quite a marked degree. I think there is a valid point about grain.

We warmed the samples and added the applicable

amount of water to bring them to 80% solids and we hoped this would take care of grain.

Our atomic absorption data has not yet been published as we are not sure that our methods tie up with conventional methods of determination of calcium and magnesium.

Regarding the balance of the ash, the fact that the constituents were determined independently of the sulphated ash will have caused the difference in the total. If the various constituents were shown as a percentage of carbonated ash they would total approximately 100%.

We were trying to show the difference in various ash levels between the samples and we also wished to show how the constituents fell in the samples from different mills.

The intention was not to do a total ash balance.

**Mr. Hoekstra:** We are endeavouring to make a mathematical model of a sugar factory, including the boiling house, and we thought the Douwes Dekker formula might assist in putting molasses exhaustion on a more scientific basis.

$$\text{Purity} = A_0 + A_1 \times \frac{\text{Reducing Sugar}}{\text{Total Non-Sucrose}} + A_2 \times \frac{\text{Sulphated Ash}}{\text{Total Non-Sucrose}}$$

where  $A_0$ ,  $A_1$  and  $A_2$  are constants

$$\text{But Purity} = \frac{\text{Sucrose}}{\text{Total Solids}} \times 100$$

and  $\text{Total Non-Sucrose} = \text{Total Solids} - \text{Sucrose}$

As sucrose is by implication on the left-hand side and the right-hand side of the equation we suspected

there might be a mathematical bias in the formula.

When a Douwes Dekker correlation was done by multiple linear regression analysis on the actual results of four Hulett factories, approximately 300 sets of data, we found a fair mathematical correlation — about .6.

We wondered what the correlation would be if, instead of actual factory data, random values of purities, reducing sugar/total non-sucrose, and sulphated ash/total non-sucrose were used. Yesterday, Mr. Young mentioned the Monte Carlo technique and we used this technique for generating these random values.

We determined from factory data what the means and the standard deviations were for these three variables. We got the computer to generate sets of random numbers corresponding to those particular means and standard deviations.

Doing a multiple linear regression analysis on these sets of data, we got a correlation co-efficient of approximately .5, as compared with the .6 for actual data.

Therefore, although there is an improvement of .1 when using actual data, most of the correlation is due to mathematical bias inherent in the formula.

We tried reducing sugar/ash, ash/reducing sugar, and also reducing sugar/reducing sugar plus ash.

We again got a correlation of approximately .5 with random numbers but we did not get as good a correlation when using actual factory data.

So, although we have not yet found a formula that does not have an inherent mathematical bias, our conclusion is that the Douwes Dekker formula is still slightly better than the others.