

EXHAUSTION PERFORMANCE YARDSTICKS IN THE SOUTH AFRICAN SUGAR INDUSTRY

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Abstract

Various exhaustion performance yardsticks used in the SA sugar industry over the past decade are reviewed. The most recent formula, based upon the highly specific gas-liquid chromatographic (GLC) analytical technique for sucrose, glucose and fructose, is shown to be superior to the previous yardsticks. This is largely attributable to the improved analytical accuracy of the GLC technique.

Introduction

In almost every field of human or scientific endeavour, it is not possible to assess the excellence of one's performance without having some realistic standards against which to make critical comparisons. The production of such standards for molasses exhaustion has received considerable attention from many eminent sugar technologists over the years. A number of formulae have been developed in other countries such as Australia,¹ Hawaii,² India,³ Mauritius,⁴ Puerto Rico⁵ and Taiwan⁶ and some of these are discussed in greater detail in recent reviews by Watson⁷ and Moritsugu.⁸ However it is evident from the literature that, at present, there is no single complete and all-embracing exhaustion formula, which is applicable anywhere at any time.

Local Exhaustion Formulae

Most investigators have attempted to correlate the final equilibrium purity of molasses with its composition, as expressed by various individual constituents or groups of constituents.

This concept for measuring boiling house performance was introduced to the SA sugar industry in 1949 by Douwes-Dekker, who proposed the formula⁹:-

$$\text{Target Purity} = 35,886 - 0,08088X_1 + 0,26047X_2 \quad (1)$$

where Target Purity = expected equilibrium purity (calculated)

X_1 = reducing sugars % non-sucrose

X_2 = sulphated ash % non-sucrose

In common with most other formulae, the above equation reflects the opposing influences which reducing sugars and ash, respectively, have on sucrose solubility in molasses. This formula found fairly wide application in South Africa for nearly twenty years. However as factory exhaustion performances improved, it became evident that, as a yardstick, the Douwes-Dekker equation tended to favour the high reducing sugars or low ash factory.

Investigations at the Sugar Milling Research Institute (SMRI) culminated in 1972 with the development of the formula¹⁰:-

$$\text{LEP} = 51,02 - 10,89 (\text{RS/A}) \quad (r = -0,842) \quad (2)$$

where LEP = predicted target purity for molasses based upon chemical sucrose (by Lane & Eynon)

RS = reducing sugars % molasses (by Lane & Eynon)

A = sulphated ash % molasses

This equation was based upon the results from laboratory boiling down tests on 28 final molasses samples, which were allowed to equilibrate for 24 hours at 40°C and a viscosity

of approximately 100 Pa.s (1000 poise). Full details of the experimental procedure and the analytical methods used in the boiling down tests are contained in the original paper.¹⁰

Subsequent work indicated that for reducing sugar/ash ratios (RS/A) above approximately 1,35 this linear relationship predicted target purities which deviated progressively from what could actually be achieved (i.e. it prejudiced the high RS/A factory).

A further 6 boiling down tests were performed on specially prepared molasses samples having RS/A ratios between 1,38 and 2,29. This resulted in a modified logarithmic formula,¹¹ similar to that used by the Australian industry.

$$\text{LEP} = 39,94 - 19,6 \log (\text{RS/A}) \quad (r = -0,851) \quad (3)$$

This logarithmic equation has, in turn, also been criticised in that it still displays some bias in favour of the factory with a low RS/A ratio.¹²

Experience has shown that the difference between true purity and the calculated target purity serves as a good measure of the degree of exhaustion obtained for a particular molasses. Such comparisons of exhaustion performance between all factories in Southern Africa are undertaken routinely by the SMRI.

However it is often preferable for a factory to assess its own exhaustion performance. The sulphated ash and dry solids determinations, which are required, amongst others, in the calculation of both true purity and target purity, are not performed as a matter of routine in most sugar factories. It was suggested that these parameters should be replaced by others which were more readily available in a mill laboratory.

This led to the development of correlations¹³ from which:-

(a) molasses true purity could be calculated from refractometer gravity purity

$$\text{True Purity} = 0,932 + 1,013 \text{RGP} \quad (r = 0,98) \quad (4)$$

where RGP = refractometer gravity purity

(b) molasses target purity could be calculated using conductance measurements:-

$$\text{Target Purity} = 39,94 - 19,6 \log (\text{RS/Y}) \quad (5)$$

where $Y = 8,4 \times 10^{-3}C + 0,8$

and C = specific conductance of molasses under standard conditions.

Unfortunately equations 4 and 5 have not found wide application at sugar mills and considerable reliance is still placed on the regular comparisons, which are now undertaken on a weekly basis by the SMRI.

It has long been recognised that viscosity is one of the most important parameters influencing molasses exhaustion. Experience has also shown, from laboratory tests, that the final purity attained is highly dependent upon molasses viscosity, which cannot be controlled precisely at 100 Pa.s during the boiling down procedure. This led to the development of new boiling down equipment and procedures to facilitate operation at higher viscosities.¹⁴ With this equipment it has been found^{15, 16} that the final boiled down purity is almost independent of molasses viscosity, when this is above 400 Pa.s (4000 poise) at 40°C. However at these higher viscosities, the time required to reach equilibrium is longer and hence it was recommended that a new procedure be adopted in which the

boiled down molasses is equilibrated for 48 hours at 40°C and a viscosity > 400 Pa. s.

Independent studies have shown¹⁷ that this new procedure gives rise to non-sucrose/water (NS/W) ratios in molasses in the region of 5,0. The same authors have also shown that the final equilibrium purities obtained with this modified boiling down procedure are consistently lower than those predicted by the SMRI logarithmic formula (equation 3).

During 1978 and 1979, a systematic study of molasses exhaustion was undertaken using this modified procedure.¹⁶ Molasses analyses for sucrose and for reducing sugars (or fructose and glucose) were performed by both the conventional chemical methods (Lane & Eynon) and the new GLC technique. The results from 133 samples, analysed by both methods, were used to derive regression equations for purity as a function of reducing sugars/ash ratio as follows:—

$$LEP = 37,7 - 17,6 \log (RS/A) \quad (r = -0,85) \quad (6)$$

$$GCP = 33,9 - 13,4 \log (F + G)/A \quad (r = -0,84) \quad (7)$$

where LEP = target purity based on chemical sucrose (Lane & Eynon)

GCP = target purity based on GLC sucrose

RS = reducing sugars % molasses (Lane & Eynon)

(F + G) = (fructose + glucose) % molasses (by GLC)

The shape of these regression lines is very similar to that of the earlier SMRI logarithmic formula (equation 3), as can be seen in Figure 1.

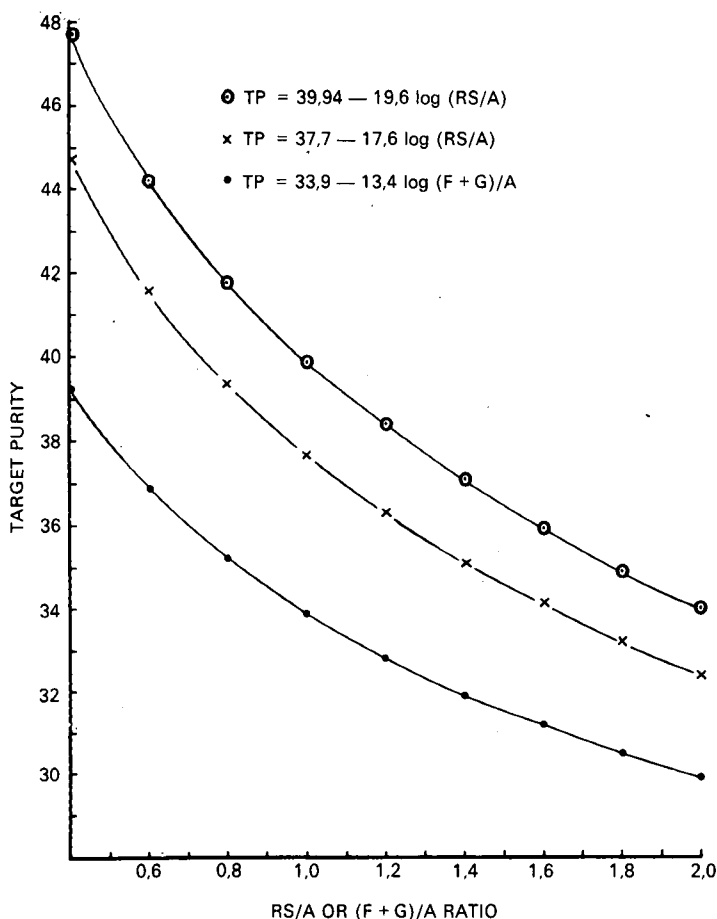


FIGURE 1 Comparison of recent target purity formulae.

It has previously been shown that the conventional Lane & Eynon methods over-estimate both sucrose and reducing sugars in molasses^{18, 19}. Hence, the formula based upon the

more accurate GLC sugars analyses yields target purity values which are some 1-2 units lower than for the corresponding Lane & Eynon method.

In addition, the move to higher viscosities has resulted in target purities about 2 units lower than previously (cf. equations 3 and 6). Both these trends are clearly illustrated in Figure 1.

In 1981, the GLC based target purity formula (equation 7) was accepted by the Factory Control Advisory Committee as the official yardstick for the estimation of final molasses exhaustion in the SA sugar industry.

Comparison of Old and New Formulae

During the 1981/82 season, the actual exhaustion performance for all factories was compared using both the old and the new industrial yardsticks (as represented by equations 3 and 7). Throughout the season, weekly composite samples of final molasses from each factory were analysed. In view of the high analytical load which this entailed, the programme was divided, on a collaborative basis, between three laboratories, as follows:—

- (a) Huletts R & D: sucrose and reducing sugars (by Lane & Eynon).
- (b) Central Board: sucrose, glucose and fructose (by GLC).
- (c) SMRI: dry solids (by Karl Fischer) and sulphated ash.

It is customary to express the level of molasses exhaustion in terms of the difference between the measured purity and the calculated target purity for that sample, and is usually called the Target Purity Difference. However in the present study we are dealing with two separate target purity differences, which will be labelled ΔP_1 and ΔP_2 as defined by the following equations:—

$$\Delta P_1 = 100 \frac{LES}{DS} - 39,94 + 19,6 \log \frac{RS}{A} \quad (8)$$

$$\Delta P_2 = 100 \frac{GCS}{DS} - 33,9 + 13,4 \log \frac{(F + G)}{A} \quad (9)$$

where LES = chemical sucrose % molasses (Lane & Eynon)

GCS = GLC sucrose % molasses

DS = dry solids % molasses

Weekly figures for both ΔP_1 and ΔP_2 were published throughout the season for each factory. Direct comparisons between these two purity differences have been done by regressing the weekly data for each mill according to the equation:—

$$\Delta P_2 = a + b.\Delta P_1 \quad (10)$$

Details of these individual correlations for each mill, over the period May-November 1981 inclusive, are given in Table 1.

In each case the correlations are highly significant beyond the 99% level which indicates that both values follow the same trend, but not necessarily that the difference between them is constant. The monthly industrial average values for both ΔP_1 and ΔP_2 are listed in Table 2 and are depicted graphically in Figure 2.

It is readily apparent that the difference between ΔP_1 and ΔP_2 is not constant and that there is a distinct seasonal trend in the ΔP_1 values which is hardly evident for ΔP_2 .

Since both the purity difference formulae are designed to cancel out the effects of reducing sugars and of ash, there should be no residual effect of either on ΔP_1 or ΔP_2 . This was checked by regressing ΔP_1 vs RS/A and ΔP_2 vs (F + G)/A. No correlation was observed.

TABLE 1
Individual correlations for each mill using weekly data
for May–November, 1981

Mills	Value of "a"	Value of "b"	Corr. Coeff.	No. of Pairs
ML	2,70	0,41	0,78	31
PG	2,78	0,66	0,79	31
UF	2,91	0,94	0,80	27
EN	3,73	0,79	0,80	27
EM	3,36	0,82	0,80	31
FX	2,88	0,47	0,77	27
AK	2,92	0,70	0,74	31
DL	3,02	0,72	0,78	28
GD	4,06	0,40	0,62	29
GH	2,72	0,95	0,76	28
TS	4,24	0,29	0,54	29
ME	2,90	0,71	0,88	25
NB	2,08	0,83	0,82	25
UC	4,16	0,61	0,71	28
IL	3,47	0,73	0,89	23
SZ	2,96	0,77	0,83	30
UK	2,78	0,85	0,83	31
Ind. Ave.	3,33	0,52	0,88	7*

* Monthly data.

TABLE 2
Monthly industrial average target purity difference
figures for 1981

Month	May	June	July	Aug	Sept	Oct	Nov	Dec
ΔP_1	2,3	1,3	1,0	0,6	1,1	1,2	1,6	2,0
ΔP_2	4,5	4,1	3,6	3,7	4,1	3,8	4,2	4,2
$\Delta P_2 - \Delta P_1$	2,2	2,8	2,6	3,1	3,0	2,6	2,6	2,2

Discussion

From Figure 2 it appears that there is a distinct seasonal trend in the industrial average purity differences obtained from the old SMRI logarithmic formula (ΔP_1). Individual graphs of ΔP_1 for each mill were plotted using weekly data and in most cases a similar trend was evident. There are a number of possible explanations for this seasonal trend, which will be considered in turn.

Factory Non-Sucrose Loading

It could be argued that non-sucrose loadings in the factory are usually highest early and/or late in the season, when juice purities are low and that these increased loadings on the factory backend are responsible, in part, for a poorer exhaustion performance. However, if this hypothesis is correct, one would expect to see a similar seasonal trend with the GLC based data, which is not evident in the values for ΔP_2 . Hence it is unlikely that less efficient factory work (apart from at start-up and final boil-off) is a major cause for the seasonal variation of ΔP_1 .

Analytical Bias

It is well known that the Lane & Eynon method for sucrose determination over-estimates true sucrose in molasses^{18, 19}. This has been attributed in part to the presence of oligosaccharides, such as kestose, which also hydrolyse, thereby inflating the sucrose figure. It has also been shown¹⁸ that the kestose concentration in final molasses from a number of SA mills varies from month to month and tends to be substantially higher towards the end of the season. This would lead to the determination of inflated molasses purities late in the season.

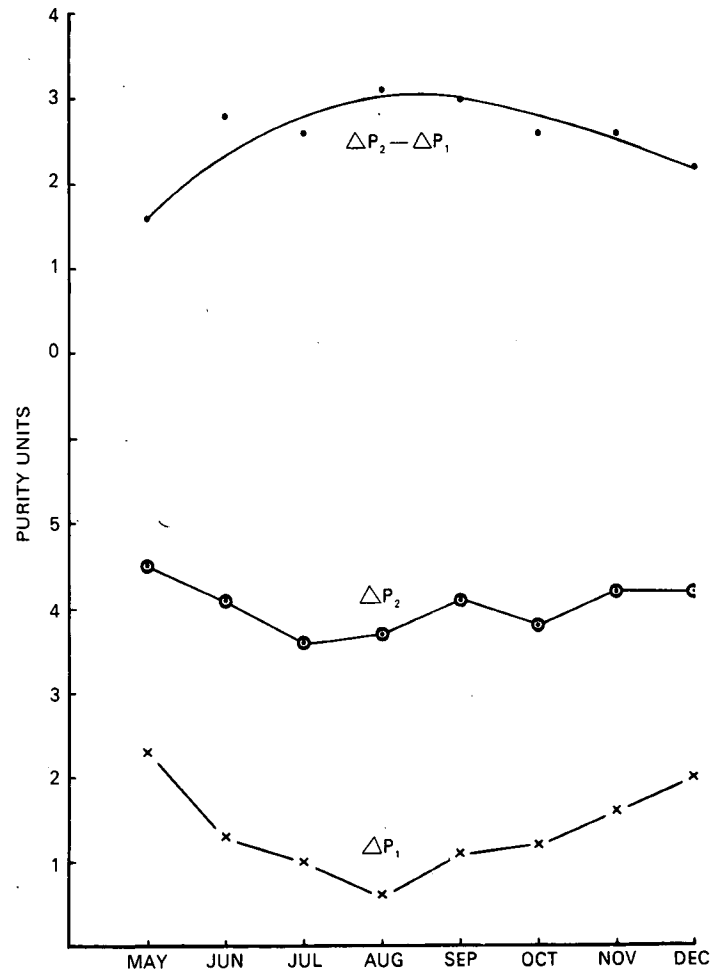


FIGURE 2 Comparison of target purity difference figures for 1981.

The hypothesis that the variations in the difference between ΔP_1 and ΔP_2 are due, in part, to the analytical differences between the two methods of sucrose determination was tested, using the monthly average data for all mills in the 1981 season. This produced a statistically significant correlation, as shown below:—

$$\Delta P_2 - \Delta P_1 = 4,24 - 1,18 (\text{LES} - \text{GCS}) \quad (11)$$

$$(n = 134, r = -0,69)$$

It has also been established that the Lane & Eynon analysis for reducing substances is consistently higher than can be accounted for by invert sugar alone.¹⁹ The magnitude of this difference is not constant and has been shown to be a function of the non-fermentable reducing substances content of molasses, which is typically high in the early part of the season. Both fructose and glucose suppress sucrose solubility, thereby assisting the attainment of lower molasses purities in the factory. If the other (non-fermentable) reducing substances present do not exert a similar influence, then their presence, as measured by the Lane & Eynon method, will depress the calculated target purity without producing a corresponding drop in the actual factory purities attained. This could partially explain the presence of high Lane & Eynon purity differences early in the season when non-fermentable reducing substances are also at high levels. The GLC purity difference (ΔP_2), which is based specifically on fructose and glucose, would not be expected to display a similar trend and this is illustrated in Figure 2.

Once again the hypothesis that the variations in the difference between ΔP_1 and ΔP_2 are due, in part, to the analytical differences between reducing substances (by Lane & Eynon)

and fructose + glucose (by GLC) was tested. This, too, produced a significant negative correlation:—

$$\Delta P_2 - \Delta P_1 = 4,72 - 0,558 (RS - F - G) \quad (12)$$

(n = 134, r = 0,47)

The combined effects of the analytical bias in the determination of both sucrose and reducing sugars produced the following multi-linear correlation:—

$$\Delta P_2 - \Delta P_1 = 6,77 - 1,29 (LES - GCS) - 0,66 (RS - F - G) \quad (13)$$

(n = 134, r = -0,88)

This indicates that the analytical bias introduced by the Lane & Eynon method for both sucrose and reducing substances, accounts for nearly 80% ($r^2 = 0,77$) of the variations between the two purity differences.

Finally there is also the fact that both the formulae (equations 3 and 7) are based upon the use of vacuum oven drying to determine the total solids in molasses, whilst the routine weekly figures give total solids by Karl Fischer titration. This latter method yields values which are often up to 1 unit lower than by vacuum drying; a factor which would tend to inflate the reported ΔP_1 and ΔP_2 figures. It is also probable that the difference between Karl Fischer and vacuum oven figures is not constant, but varies seasonally, depending upon molasses composition. This could introduce a slight seasonal bias into both ΔP_1 and ΔP_2 but it is likely that this would be smaller than the analytical reproducibility of the molasses purity determination.

Inherent Bias in the Formula

One would expect that a multi-linear correlation should account for some of the analytical bias mentioned in the previous section, unless the effects mentioned (i.e. high kestose and/or non-fermentable reducing substances) were not present to the same extent in the original set of samples on which the correlation was based.

The new GLC formula is based upon 133 samples from nine factories spread fairly evenly over two full seasons. However the original SMRI formula used only 28 samples from the 1971 season plus 6 samples in 1972 which were artificially spiked with invert sugar. Hence the latter data base is somewhat smaller and it is not clear whether these samples spanned an entire season or not. If they were drawn predominantly from only a portion of the season, then the correlation may not account for molasses qualities which fall outside those of the original data set.

Residual Problem Factors

It is evident from the correlation coefficients associated with both equations 3 and 7, that the independent variables, viz. reducing sugars and ash, only account for some 70% of the observed variation in equilibrium molasses purity. The situation may possibly be somewhat worse than is indicated, because there may be a measure of inherent, internal correlation between the various variables involved.¹⁰

Hence there are obviously additional factors, not included in the existing formulae, which influence either the equilibrium molasses purity or the rate at which that equilibrium is attained or both. One such factor which warrants further investigation is the amount of suspended matter present in molasses. The existing procedures do not distinguish between soluble and insoluble ash when determining either sulphated ash or total solids % molasses. This introduces possible errors in the calculation of both molasses true purity and target purity. In addition it is likely that suspended and dissolved matter exerts different influences on both sucrose solubility and crystallisation rate.

It would be of interest to perform a series of boiling down tests on pre-clarified molasses in order to assess the magnitude of these effects.

Conclusions

In the light of the foregoing discussion it can be concluded that:—

- (a) the old and the new target purity difference formulae are well correlated and follow similar trends at all factories;
- (b) the difference between ΔP_1 and ΔP_2 is not constant but shows a distinct seasonal trend; these variations have been shown to be largely as a result of analytical errors introduced through the use of the Lane & Eynon method in the old SMRI formula;
- (c) the new GLC based exhaustion formula is clearly a superior yardstick because:—
 - it is based on the more accurate GLC method for the determination of sugars
 - it is based upon a much larger and possibly more evenly time-distributed data base
 - it did not display any marked seasonal trend during the 1981/82 crop.

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Nomenclature

LEP	= target purity based upon sucrose and reducing sugars analysis by Lane & Eynon
GCP	= target purity based upon sucrose, glucose and fructose analysis by GLC
RGP	= refractometer gravity purity
RS	= reducing sugars % molasses
(F + G)	= (fructose + glucose) % molasses
A	= sulphated ash % molasses
RS/A	= reducing sugars/ash ratio
(F + G)/A	= (fructose + glucose)/ash ratio
NS/W	= non-sucrose/water ratio
LES	= sucrose % molasses by Lane & Eynon
GCS	= sucrose % molasses by GLC
DS	= dry solids % molasses by Karl Fischer
ΔP_1	= target purity difference for molasses based upon Lane & Eynon
ΔP_2	= target purity difference for molasses based upon GLC.

REFERENCES

1. Behne, E. R. (1947). Low grade massecuite treatment. *QSSCT Proc* 14, 149.
2. Moritsugu, T., Somera, B. J. and Sloane, G. E. (1974). A new exhaustibility relationship for Hawaiian final molasses. *ISSCT Proc*, 15, 1236-1245.
3. Gupta, S. C. and Ramaiah, N. A. (1968). On the formulae for the exhaustibility of final molasses. *ISSCT Proc* 13, 1822-1826.
4. de Saint Antoine, J. D. and Vignes, E. C. (1968). *Maur Sug Ind Res Inst Ann Rep* 16, 129.

5. Serbia, G. R. and Balsa, J. (1965). A simple and practical method to evaluate the exhaustibility of final molasses. *ISSCT Proc* 12, 1701-1705.
6. Chen, W., Hsu, T. H. and Wang, P. (1952). *Rep Taiwan Sug Exp Stn* 9, 212.
7. Watson, J. A. (1981). The recovery of sucrose from low grade refinery syrups. *Sug Tech Rev* 8, 117-122.
8. Moritsugu, T. (1974). Exhaustibility of cane molasses. *Sug Tech Rev* 2, 73-93.
9. Douwes-Dekker, K. (1949). Comments on the exhaustibility of final molasses. *SASJ* 33, 709-713.
10. Bruijn, J., Fitzgerald, J. R., Koenig, S. and MacGillivray, A. W. (1972). Exhaustion of South African final molasses. *SASTA Proc* 46, 103-109.
11. Fitzgerald, J. R. and MacGillivray, A. W. (1972). *SMRI Int Rep* 25/72.
12. Morgan, R. W. L. (1976). A statistical analysis of industry data with particular reference to the low grade end of factory operations. *SASTA Proc* 50, 198-205.
13. Matthesius, G. A. and Mellet, P. (1976). An exhaustion formula for South African molasses. *SASTA Proc* 50, 206-207.
14. Bruijn, J. (1977). Exhaustion of molasses - equipment to determine target purities. *SASTA Proc* 51, 123-124.
15. Bruijn, J., Koenig, S. and Wolff, M. (1980). Influence of gum on molasses exhaustion. *ISSCT Proc* 17, 2429-2441.
16. Rein, P. W. and Smith, I. A. (1981). Molasses exhaustibility studies based on sugars analysis by gas-liquid chromatography. *SASTA Proc* 55, 85-91.
17. Lionnet, G. R. E. and Rein, P. W. (1980). Pilot plant studies on the exhaustion of low grade massecuites. *ISSCT Proc* 17, 2328-2350.
18. Kort, M. J., Matic, M., Mellet, P. and Nurok, D. (1975). Analysis of final molasses for sucrose and pol. *SASTA Proc* 49, 99-102.
19. Morel du Boil, P. G. and Schäffler, K. J. (1978). Application of gas chromatography in a preliminary investigation into changes in some non-sucrose constituents during sugar-boiling. *SASTA Proc* 52, 96-105.