

STANDARDS FOR THE ANALYTICAL PRECISION OF SUGAR AND MOLASSES ANALYSES

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Abstract

The Sugar Milling Research Institute, South African Sugar Terminal and Huletts Research and Development laboratories carried out a programme of analyses on raw sugar and final molasses to establish analytical standards for both inter- and intra-laboratory quality control. The precision obtained both within and between the laboratories is also discussed.

Introduction

During 1981, the Sugar Milling Research Institute (SMRI), SA Sugar Terminal (SAST), and Huletts Research and Development (R & D) laboratories carried out a programme of analyses to investigate a system of quality control for raw sugar and final molasses analyses.

Two quality control parameters, i.e. reproducibility and repeatability were investigated. These quantities may be defined as follows:

Repeatability of an analytical method is the value below which the absolute difference between two analytical results obtained from the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and short interval of time) may be expected to lie with a specified probability (95%).

Reproducibility of an analytical method is the value below which the absolute difference between two single test results on identical material obtained by operators in different laboratories, using the standardised test method, may be expected to lie with a specified probability (95%).

Procedure

1. Sugar analyses

- (a) Five large (ca 50 kg) samples of VHP sugar were collected from a bulk storage silo at SAST and care was taken to select samples with wide variation in appearance of colour, grain size, etc. Each sample was subsequently mixed well and reduced in size by riffing to a quantity of ca 15 kg. These samples were coded 1, 2, 3, 4 and 5 respectively.
- (b) About 100 g of each of the above prepared samples were sub-sampled into plastic sachets which were then heat sealed. In this way 16 sub-samples from each code were obtained and these were equally and randomly distributed between the SMRI and SAST laboratories for duplicate analysis of each parameter. Sachets containing 100 g were prepared in order to facilitate the duplicate analysis of each parameter thus minimising errors due to moisture changes which may have occurred with repeated opening of larger containers. These samples were analysed for reducing sugars, starch, gums, colour, phosphate, sulphated ash, conductivity ash, filterability and grain size.
- (c) Three samples of VHP sugar coated with HTM and one sample of VHP sugar were selected and prepared as described under (b) above for duplicate pol and

moisture analyses, each sample being analysed five times. The reason for using coated sugars in addition to VHP sugar was to obtain a reasonable spread of pol values i.e. from ca 97,7 to 99,4°, which would not have been possible if only VHP sugars were used.

- (d) The SMRI laboratory employed three different analysts to analyse for each parameter while the SAST laboratory employed four. The frequency of analysis was kept constant amongst the analysts.
- (e) Methods of analysis employed were those described in The Laboratory Manual for South African Sugar Factories.¹

2. Final molasses analyses

- (a) One hundred and eleven samples of cane final molasses collected from twelve South African sugar factories were analysed by the R & D and SMRI laboratories. These samples were produced over the whole of the 1980/81 season and prior to analysis they were thoroughly mixed and sub-sampled to provide each laboratory with enough sample for analysis. Analyses were performed by both laboratories within one week of production to exclude any differences in analyses which may have originated from deterioration on standing.
- (b) Methods of analysis were those described in The Laboratory Manual for South African Sugar Factories¹ and samples were analysed for Karl Fischer dry solids, pol, refractometer brix, Lane and Eynon reducing sugars, sucrose and sulphated ash.
- (c) Each laboratory employed two analysts to perform the analyses.

3. Statistical analyses

(a) Raw sugars

The variation in the analytical results was investigated by using two way analyses of variance.² This technique results in the following breakdown of the variations:—

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F-Value
Between Lab	$k-1$	SS_B	MS_B	F_B
Between sample	$n-1$	SS_S	MS_S	
Interaction	$(k-1)(n-1)$	SS_I	MS_I	
Error	$N-k-n+1-(k-1)(n-1)$	SS_E	MS_E	
Total	$N-1$			

where N is the total number of observations.
 k is the number of laboratories.
 n is the number of samples.

Then F_B is used to test for significant differences between the laboratories.

Let the number of replicates per cell be R_C .

Let the total number of observations per laboratory be T .

Let the analytical error variance = σ_E^2

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Then $MS_E = \sigma_E^2$ (1)

Let the interaction variance = σ_I^2

Then $MS_I = \sigma_E^2 + R_C \cdot \sigma_I^2$ (2)

Let the between laboratory variance = σ_B^2

Then $MS_B = \sigma_E^2 R_C \cdot \sigma_I^2 + T \cdot \sigma_B^2$ (3)

Equations (1), (2) and (3) may now be solved for σ_E^2 , σ_I^2 and σ_B^2 :-

From (1) : $\sigma_E^2 = MS_E$

(2) : $\sigma_I^2 = \frac{MS_I - MS_E}{R_C}$

(3) : $\sigma_B^2 = \frac{MS_B - MS_E - \left(\frac{MS_I - MS_E}{R_C}\right)R_C}{T}$

Then repeatability variance = $2 \cdot \sigma_E^2$

and repeatability, $r = tn; \alpha/2 \cdot \sqrt{\text{Repeatability Variance}}$

where $n = \text{degrees of freedom error.}$

Reproducibility variance = $2(\sigma_E^2 + \sigma_I^2 + \sigma_B^2)$

and reproducibility, $R = t \cdot \sqrt{\text{Reproducibility Variance}}$

where t may be approximated by $t \approx 2$.

It should be noted that r and R are only indications of repeatability and reproducibility, since more than one analyst was used.

(b) Final molasses

Since each sample was not analysed at least in duplicate, it is not possible to carry out the calculations described for the raw sugars. It is possible however to calculate an approximate value for the repeatability of each analysis, again using analysis of variance.

Discussion

The results obtained for raw sugar and final molasses are given in Tables 1 and 2 respectively.

1. Sugar

(a) RAW SUGAR

Repeatabilities for raw sugar analyses were investigated by Radford.² His results for starch, reducing substances, ash, gums, phosphate and pol are similar to the present ones. In the case of moisture however, Radford's result is better with a repeatability of 0,015 against the present value of 0,04.

The present results also show that for a number of analyses the means are statistically different between the two laboratories. It should be noted however that a significant difference may have no practical importance if the value of the difference between the two means is too small to have a practical meaning. A significant difference does however indicate a consistent bias and would require further investigations.

Table 1 also includes the standard deviations for each analysis, in each laboratory. These indicate the precision achieved in each laboratory and show that in general the SAST laboratory is more precise than the SMRI laboratory.

The reproducibility (R) column in Table 1 indicates the analytical tolerances which could be allowed between two laboratories for analysis of the various components. In practice these figures fit the anticipated and applied tolerances used by both laboratories fairly well. In fact better agreement between the two laboratories than that indicated in Table 1 is often the case, e.g. if colour at 560 nm differs by more than 0,04 or gums by more than 100 ppm or

TABLE 2

Statistical Analyses of the SMRI/Hulett's R & D Analytical Data

Analysis	Mean		Repeatability (r)
	SMRI	R & D	
Dry Solids	76,00	75,92	0,5
Brix	80,8	80,4	0,9
Chem Suc	32,21	31,98	0,8
Pol	30,00	30,06	0,4
Red sugars	14,25	14,41	0,4
Sulph Ash	13,98	14,04	0,3

TABLE 1

Statistical Analyses of the SMRI/SAST Analytical Data

Analysis	Anova	Mean		Std. Dev.		Repeatability (r)			Reproducibility (R)
		SMRI	SAST	SMRI	SAST	SMRI	SAST	Both Labs	
Gums	Labs. sig. diff. (1%)	1 210	1 240	56	67	171	196	180	200
Starch	Labs. sig. diff. (1%)	140	150	9	4	28	11	21	32
Filterability	Labs. sig. diff. (1%)	26	24	1,6	0,8	4,4	2,2	3	6
Inorg. P ₂ O ₅	Labs. sig. diff. (1%)	55	52	2,2	2,3	7	7	7	9
Total P ₂ O ₅	Labs. sig. diff. (1%)	77	70	3,2	4,1	9,6	11,4	11	13
Sulph. Ash	Labs. sig. diff. (1%)	0,18	0,18	0,01	0,01	0,04	0,02	0,03	0,04
Red. Sugars	Labs. sig. diff. (1%)	0,15	0,18	0,02	0,01	0,05	0,02	0,03	0,06
Cond. Ash	Labs. not sig. diff. (1%)	0,17	0,17	0,01	0,01	0,02	0,02	0,02	0,02
Pol	Labs. not sig. diff. (1%)	98,58	98,58	0,02	0,02	0,07	0,05	0,06	0,06
Moisture	Labs. not sig. diff. (1%)	0,29	0,29	0,02	0,01	0,04	0,03	0,04	0,08
Moist. + Pol	Labs. sig. diff. (5%)	98,57	98,55	0,03	0,02	0,10	0,08	0,09	0,10
Grain Size CV	Labs. not sig. diff. (1%)	28	27	1,2	0,5	3,8	2,1	3	3
Grain Size % Fines	Labs. not sig. diff. (1%)	16,1	16,0	2,2	1,6	6,8	5,6	6,2	6,2
Grain Size SGS	Labs. not sig. diff. (1%)	0,74	0,74	0,02	0,01	0,07	0,05	0,06	0,06
Colour 560 nm	Labs. sig. diff. (1%)	0,31	0,28	0,01	0,01	0,02	0,04	0,03	0,07
Colour 420 nm	Labs. sig. diff. (1%)	1,53	1,45	0,04	0,09	0,13	0,25	0,20	0,24

starch by more than 15 ppm, the analyses will be repeated by both laboratories to achieve closer agreement.

(b) FINAL MOLASSES

The results show that brix and chemical sucrose are the least precise of the analyses and pol/dry solids purity would be more precise than the traditional pol/brix purity.

As is the case with the sugar analyses, it is often found that in practice closer agreement between laboratories is achieved than indicated in Table 2. The reason for this is that repeat analyses by both laboratories are performed whenever any doubt exists about the accuracy of an analysis.

Conclusions

The investigation confirmed that the existing agreement between the SMRI and SAST laboratories in sugar analysis

falls within the anticipated values and also agrees well with figures previously established. Statistically derived figures for tolerances of molasses analyses between laboratories have also been established and the figures obtained can be used in future as a guideline for inter-laboratory analyses.

Acknowledgements

The authors would like to thank the staff in the different laboratories for their participation in this investigation.

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