USE OF STATISTICAL QUALITY CONTROL AT THE DURBAN SUGAR TERMINAL

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Abstract

The system of quality control used at the S.A. Sugar Terminals to assess and control the reliability of the different analyses carried out on sugar is described.

The values obtained for standard deviations which will form the basis for future control and further improvement, are given.

Introduction

The system of having the same analyst carrying out analyses in duplicate in order to obtain confidence in the result is far from satisfactory as errors arising from defective instruments and reagents can affect both determinations to the same extent. As a result, good precision without accuracy can still be obtained. On the other hand, if the unknown sample is analysed alongside a standard sample with known analytical value, any errors in the analysis will affect both the unknown and the standard to the same extent. The deviation of the value for the standard sample from its true or accepted value can be used as a means of assessing the reliability of the analysis on a statistical basis.

Briefly, the statistical control is based on the following: If the values of a sufficiently large number of replicate analyses on a sample are tabulated in ascending order and the frequency of these values plotted against their value, a Gaussian curve similar to that shown in Fig. 1 is obtained. The mean of all the values calculated from

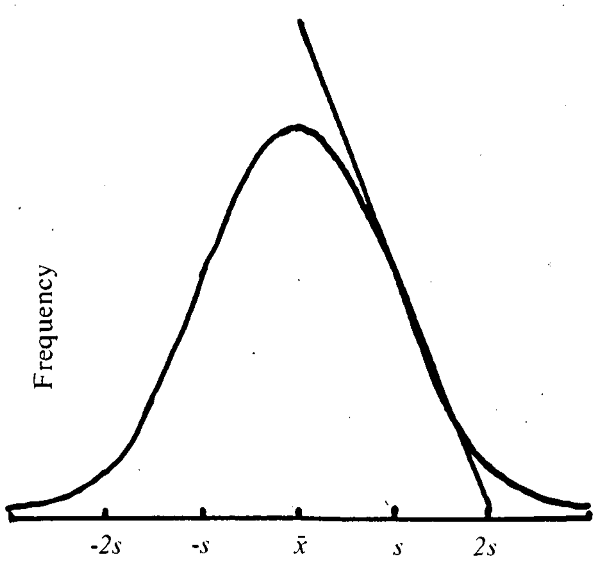

FIG. 1

The Gaussian curve

$$\bar{x} = \frac{1}{n} \sum x_i \qquad \text{Eqn. 1}$$

where $\bar{x}$ = mean value
x_i = individual values
n = number of determinations

can be proved mathematically to be a very efficient estimate of the true value. This mean value will coincide with the centre of the curve. If this mean value is now assigned a zero value, the points of inflection of the left-hand and the right-hand portions of the curve will have equal values but with opposite signs. This value, known as the standard deviation, can be calculated from the equation

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n}} \qquad \text{Eqn. 2}$$

where s = standard deviation
x = any single value
$\bar{x}$ = mean value
n = number of determinations (n is large)

where n is small, equation (2) becomes

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \qquad \text{Eqn. 3}$$

The standard deviation is used as a measure of reproducibility; the smaller the value, the more are the results accumulated around the mean value and the more precise they are.

The practical significance of the Gaussian curve is that, by its use, it is possible to determine whether or not a certain magnitude of error will be exceeded when a single determination is carried out. Statistically it can be shown that if we obtain an individual value equal to the mean value ± 2s, then there is a 95 per cent possibility that the value obtained will be a true one with only a 5 per cent possibility of the result being incorrect. In other words, the result would be correct in 95 out of every 100 such predictions. Normally, a maximum possibility of an error in only 1 out of every 20 determinations is accepted as a reasonable risk.

In practice, a standard sample is obtained in one of the following ways:

(i) from a Standard Samples Bureau. This is supplied with a certificate of analysis usually based on the results from several laboratories using a variety of acceptable methods

(ii) from a carefully ground mixture of the individual pure components

(iii) from an actual sample of the material which has been analysed a number of times, preferably not less than 20 and by more than one analyst.

Neither of the first two are applicable to the analysis of sugar, leaving only the third procedure as a basis to investigate the feasibility of using statistical methods for the control of the quality of the analysis.

In addition to the use of standardised samples, the two values obtained from duplicate analyses can be used to obtain a value for the standard deviation of the mean value. When only a small number of determinations, $n = 1$ to 10, are carried out on m different samples of the same material (daily mill composites for each mill), the standard deviation of the mean, $s_{\bar{x}}$, is calculated from[1]

$$s_{\bar{x}} = \sqrt{\frac{1}{mn(n-1)} \Sigma (x_j - x_{ij})^2} \qquad \text{Eqn. 4}$$

This value of $s_{\bar{x}}$ can be more conveniently calculated from

$$s_{\bar{x}} = \frac{kn}{\sqrt{n}} \bar{R} \qquad \text{Eqn. 5}$$

where R = average of the ranges between the lowest and highest values (for duplicates this is the arithmetic difference)

kn = constant dependent upon the value of n. For $n = 2$, $k_n = 0{,}8862$

Application

1. Pol and moisture

Samples were collected from consecutive deliveries from several mills. Composite samples were prepared for each of the mills by thoroughly mixing. This was then divided by a riffle type sample splitter and stored in 5 litre bakelite screw-capped polythene jars. As required, 200 ml quantities were removed from the jars. These were analysed in the normal way as a member of a coded batch and the results recorded. After approximately 20 analyses had been completed, the mean value and the standard deviation were calculated by equations (1) and (3) respectively. Thereafter, the individual value, x_i, obtained during a batch analysis for the standard sample was compared with the mean value, $\bar{x}$. If the deviation $(\bar{x} - x_i)$ was greater than twice the standard deviation, s, the whole batch of samples was rejected and, after investigating possible reasons for the error, repeated.

The results obtained for pol and moisture on the standard samples are shown in Table 1.

TABLE I

Mean and standard deviation values for pol standard samples

Sample	Date of analysis	Pol			Moisture		
		n	$\bar{x}$	s	n	$\bar{x}$	s
DL	28.8.70—24.9.70	31	99,63	0,065	24	0,046	0,009
	8.10.70—12.11.70	27	99,61	0,048	24	0,047	0,013
	13.11.70—2.12.70	18	99,63	0,054	18	0,046	0,015
		76	99,63	0,058	66	0,046	0,012
TS (A)	27.5.71—17.6.71	34	99,26	0,037	34	0,114	0,016
	22,6,71—15.9.71	25	99,28	0,038	27	0,127	0,015
	15.9.71—30.9.71	23	99,25	0,048	25	0,137	0,012
		82	99,27	0,042	86	0,125	0,017
JB	15.6.71—7.7.71	32	99,70	0,028	32	0,040	0,008
	8.7.71—25.7.71	34	99,70	0,029	34	0,045	0,010
	26.7.71—13.9.71	41	99,70	0,049	42	0,047	0,011
		107	99,70	0,037	108	0,045	0,010
DK	10.8.71—27.8.71	25	99,66	0,071	23	0,066	0,009
	1.9.71—10.11.71	34	99,63	0,039	30	0,073	0,009
	11.11.71—30.11.71	28	99,64	0,022	28	0,074	0,011
	1.12.71—13.12.71	22	99,64	0,027	22	0,080	0,013
		109	99,64	0,044	103	0,073	0,011
MV	14.9.71—11.10.71	25	99,67	0,044	21	0,064	0,015
	12.10.71—30.12.71	42	99,65	0,048	40	0,070	0,015
		67	99,66	0,048	61	0,068	0,015
EN	21.12.71—13.1.72	26	99,55	0,046	26	0,063	0,011
	14.1.72—2.3.72	24	99,51	0,048	24	0,075	0,016
		50	99,53	0,051	50	0,069	0,015
TS (B)	28.1.72—19.2.72	26	99,46	0,028	26	0,086	0,010
	21.2.72—7.3.72	11	99,43	0,020	10	0,097	0,010
		37	99,45	0,028	36	0,089	0,011

The mean values of the pols remained constant over the period of test (2—4 months) with standard deviations of, with two exceptions, 0,05 or less. The moisture values appeared to increase with time, but this was small and well within the range of ± 2*s* limits. The standard deviation values for moisture were 0,015 or less. The values were considered to be satisfactory at this stage although we hope to achieve improvements in the future.

In addition, as daily composite mill samples had been analysed in duplicate under code for pol, these values were used to calculate the standard deviations by use of equation 5 for all sugar sent to the Sugar Terminals for the 1971—72 season. These are given in Table II.

TABLE II

Standard deviations obtained from duplicate pol analyses of daily mill samples

Mill / Date		UF	FX	EN	AK	DL	DK	GH	MV	TS	JB	UC	IL	SZ	UK
May 1971	*n*			6	21	13	38			14	5	12	23	17	12
	s			0,012	0,020	0,009	0,013			0,016	0,006	0,010	0,015	0,015	0,013
June	*n*	9		22	21	27	26		12	13	18	17	25	25	30
	s	0,015		0,012	0,022	0,017	0,015		0,016	0,016	0,017	0,017	0,015	0,016	0,016
July	*n*	25		15	28	30	26		20		27	24	27	26	31
	s	0,012		0,019	0,016	0,017	0,015		0,017		0,012	0,014	0,012	0,013	0,017
Aug	*n*	32		26	28	26	27		22		23	18	28	27	30
	s	0,018		0,020	0,018	0,021	0,017		0,016		0,018	0,020	0,013	0,019	0,018
Sept	*n*	25		34	27	31	26		23	19	25	22	29	29	27
	s	0,016		0,018	0,018	0,016	0,021		0,020	0,015	0,018	0,021	0,018	0,021	0,022
Oct	*n*	25		9	27	28	26		11	29	25	19	28	24	30
	s	0,015		0,013	0,016	0,015	0,016		0,017	0,013	0,018	0,015	0,020	0,017	0,015
Nov	*n*	24		26	25	28	27			30	25	21	30	24	30
	s	0,016		0,015	0,019	0,015	0,013			0,016	0,019	0,013	0,016	0,014	0,011
Dec	*n*	24	14	28	25	27	31	18	23	29	17	19	25	24	28
	s	0,014	0,012	0,015	0,017	0,014	0,014	0,015	0,016	0,014	0,015	0,011	0,016	0,012	0,018
Jan 1972	*n*	14		15	22	19		12	11	30			15	20	19
	s	0,012		0,012	0,013	0,013		0,017	0,027	0,012			0,023	0,012	0,015
Feb	*n*	23		28	15	9	20	20	5	30		12	29	20	30
	s	0,015		0,015	0,012	0,009	0,013	0,017	0,015	0,014		0,015	0,018	0,013	0,014

The arithmetic mean of these values was 0,015 and indicated that a difference, between any pair of duplicate results, of ± 2*s* should be less than 0,06. In practice, any duplicate results obtained with a difference greater than 0,06 are rejected.

2. Starch

Starch analyses were carried out in duplicate under code on weekly composite samples of VHP sugar and ships composite samples of coated sugar concurrently with standard samples. Mean values and standard deviations are shown in Table III.

From these results, the 2*s* confidence limits would be ± 20ppm.

As with pol and moisture samples, the duplicate values obtained on each sample were used to calculate the standard deviation from equation (5) with the values shown in Table IV.

The arithmetical mean obtained for these values was 4,8 and indicated that a difference, between any pair of duplicates, of ± 2*s* should be less than 20ppm.

TABLE III

Mean and standard deviation values for starch standard samples

Sample	Grade	Date of analysis	Starch *n*	$\bar{x}$	*s*
IL	VHP	3.5.71—28.5.71	18	171	10
		26.6.71—18.9.71	26	162	15
			44	166	14
TS	VHP	19.6.71—14.8.71	16	156	10
		2.10.71—1.1.72	28	150	12
		8.1.72—4.3.72	18	153	7
			62	152	11
Trefusis	LP	1.6.71—28.2.72	16	132	8
Trefusis	Affinated	1.6.71—28.2.72	18	95	8

3. Colour

Colour analyses were also carried out in the same way as starch analyses. The results are given in Tables IV and V.

These show that, for VHP and unaffinated LP sugar, an increase in colour occurs with time. This means that, although the standard samples can continue to be used over long periods, it is necessary to re-calculate mean values and standard deviations every 2 months. Acceptable standard deviations were 0,010 and 0,050 for measurements at 560nm and 420nm respectively. No increase in colour was noticeable with affinated sugar.

For duplicate analyses, the standard deviations were 0,005 and 0,025 for measurements at 560nm and 420nm respectively. These values indicated that differences between any pair of duplicate results of ± 2*s* should be less than 0,02 and 0,10 respectively, except for unaffinated LP sugar samples where it would appear that a higher value may have to be used for measurements at 420nm.

4. Reducing sugars

The only standard sample used for reducing sugars was an unaffinated LP sample (Trefusis). The mean value obtained from 20 analyses was 1,12 per cent with a standard deviation of 0,033. Values obtained for duplicate analyses are given in Table VI.

TABLE IV

Standard deviations obtained for duplicate starch and colour analyses

Sample	Grade	Starch		Colour			
				560 nm		420 nm	
		n	*s*	*n*	*s*	*n*	*s*
UF	VHP	36	6,2	36	0,005	36	0,022
EN		37	5,1	37	0,006	37	0,022
AK		44	5,5	44	0,007	40	0,022
DL		39	5,2	38	0,006	38	0,022
DK		39	4,1	39	0,004	39	0,022
GH		14	4,6	13	0,006	13	0,020
MV		30	5,6	29	0,007	29	0,030
TS		29	6,1	28	0,004	28	0,017
JB		32	4,8	32	0,004	31	0,016
UC		38	3,2	38	0,005	38	0,024
IL		42	4,8	42	0,005	42	0,022
SZ		40	4,6	39	0,005	40	0,022
UK		40	4,4	40	0,008	40	0,011
Ships	LP	25	4,2	25	0,006	24	0,034
	HP	15	4,0	15	0,007	15	0,023
	Affin-ated	—	—	40	0,005	40	0,009

TABLE V

Mean and standard deviation values for colour standard samples

Sample	Grade	Date of Analysis	Colour					
			560 nm			420 nm		
			n	$\bar{x}$	*s*	*n*	$\bar{x}$	*s*
IL	VHP	8.5.71—19.6.71	10	0,193	0,007	10	0,867	0,030
		26.6.71—25.9.71	25	0,193	0,009	25	0,882	0,042
			35	0,193	0,008	35	0,877	0,039
TS	VHP	19.6.71—28.8.71	20	0,216	0,019	20	1,062	0,062
		2.10.71—1.1.72	28	0,226	0,009	28	1,112	0,042
		8.1.72—4.3.72	18	0,235	0,012	18	1,161	0,058
			66	0,225	0,015	66	1,110	0,065
Trefusis	LP	2.9.71—9.11.71	10	0,380	0,008	10	1,900	0,041
		4.12.71—15.3.72	10	0,401	0,018	10	1,975	0,069
			20	0,391	0,017	20	1,938	0,067
Trefusis	Affinated	1.9.71—15.3.72	18	0,106	0,010	18	0,516	0,033

These indicate that the differences between any pair of duplicate results, of ± 2*s*, should be less than 0,04 per cent which is in agreement with the standard deviation of 0,033 obtained for the standard sample.

5. Ash

A standard sample has, so far, not been used to control ash analyses. Comparing duplicate analysis results for conductivity ash gave the values shown in Table VI.

The arithmetical average of the values for conductivity ash was 0,003. This indicates that differences between any pair of duplicates should be less than 0,01 per cent. For sulphated ash on coated sugar, the standard deviations for duplicates were 0,005 (n = 25) for low pol sugar and 0,010 (n = 15) for high pol sugar. Any difference between duplicate analyses should therefore be less than 0,02 per cent.

6. Filterability

Filterability tests have been controlled by the use of a standard sample of unaffinated sugar (Trefusis). Only single determinations are carried out, so no comparison can be made between duplicate values.

The mean value obtained from 12 tests was 37 with a standard deviation of 1,75. This high standard deviation, giving 2*s* confidence limits of

TABLE VI

Standard deviations obtained for duplicate reducing sugar and ash analyses

Sample	Grade	No. of Analyses	Reducing Sugar	Conductivity Ash
UF	VHP	9	0,003	0,003
EN		10	0,004	0,004
AK		10	0,002	0,006
DL		10	0,004	0,004
DK		9	0,001	0,003
GH		4	0,003	0,003
MV		9	0,006	0,004
TS		8	0,002	0,004
JB		8	0,004	0,003
UC		9	0,001	0,001
IL		10	0,004	0,003
SZ		10	0,006	0,004
UK		10	0,002	0,002
Ships	LP	25	0,008	0,002
	HP	15	0,011	0,003

±3,5 may be a true reflection on the inadequacy of the method, but more results will have to be obtained for standards of uncoated, coated and affinated sugar.

7. Gums

The only standard sample used for gums was an affinated sample (Trefusis). The mean value obtained from 18 analyses was 890ppm with a standard deviation of 65ppm. Values obtained from duplicate analyses of affinated sugar gave a standard deviation of 28 and indicated that differences should be less than 110 ppm.

8. Phosphate

The mean values obtained from 18 analyses of an affinated sample (Trefusis) were 21ppm for inorganic phosphate and 32ppm for total phosphate with standard deviations of 1,4 and 3,2 respectively.

Values for standard deviations obtained from duplicate analyses were 1,2ppm and 1,1ppm for inorganic and total phosphate respectively and indicate that differences should be less than 5ppm.

Discussion

The results quoted above must be considered as a preliminary to achieving something better. Plans have been made to extend the availability of standard samples to cover, wherever possible, all analyses carried out on sugar and high test molasses. As far as possible, analyses will be carried out in duplicate so that standard deviation values can be calculated for duplicate results as well as for standard samples. However, it is hoped that with further experience of control by means of standard samples, the advisability of carrying out all analyses in duplicate will fall away and that adequate control will be exercised through the standard samples with only occasional duplicate or feed-back samples. Where it is considered that the values for the standard deviations are high, these will be used as a basis for comparison in any investigations carried out into the possibility of improving the accuracy and precision of the method and its application.

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