

USE OF CONDUCTIVITY ASH FOR CALCULATING TARGET PURITY DIFFERENCE (TPD)

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Abstract

The analysis of final molasses for determination of target purity difference (TPD) involves a tedious ashing method (sulphated ash) which requires the use of sulphuric acid, a corrosive and environmentally hazardous chemical. An investigation was undertaken to determine whether the ash % measured via a conductivity method (conductivity ash) could replace sulphated ash in the TPD calculation. A comparison of the weekly molasses (1997-1998 season) sulphated and conductivity ash results showed that the mean absolute difference in ash % for all the mills studied was 0,45%. The ash differences did not affect the TPD results to the same extent, and the mean absolute difference in TPD based on sulphated and conductivity ash respectively was 0,19.

Introduction

As part of the continuing effort to eliminate the use of sulphuric acid, a respiratory irritant (Hill, 1992) and environmentally hazardous chemical that contributes to air pollution, conductivity methods for determining the ash % in molasses were evaluated for the South African industry. ICUMSA studies have shown that good agreement exists between the electrometric (ICUMSA conductivity ash) and gravimetric (ICUMSA sulphated ash) measurement of ash in molasses (De Villiers, 1982).

The aim of this investigation was two-fold:

- to determine the correlation between the ICUMSA (Anon, 1994) or SMRI (Anon, 1985) conductivity ash and the SMRI sulphated ash methods of measuring the ash % molasses
- to investigate how the use of an ash % molasses determined via a conductivity, as opposed to a gravimetric measurement, affected the TPD results.

Procedure

Part 1: A comparison of the ICUMSA [GS1/3/4/7/8-13] and SMRI [TM010] conductivity ash methods with the SMRI [TM057] sulphated ash method

In an initial study ca. 21 weekly molasses samples from five mills, representing the geographical regions of South Africa for the last six months of the 1996-97 season, were analysed according to the ICUMSA and SMRI conductivity ash methods. The samples were stored in a cold room and

analysed at three monthly intervals. The ash % molasses obtained from the respective conductivity ash methods were then compared with the results of the weekly sulphated ash analyses.

- *SMRI sulphated ash method for molasses* [TM057] (Anon, 1996): The molasses sample ($4 \pm 0,2$ g) is weighed into a crucible and placed on a water bath (ca. 5 minutes) prior to the addition of 2-3 ml concentrated sulphuric acid. After the sample has been carbonised on a Bunsen burner it is incinerated at $650 \pm 25^\circ\text{C}$ for one hour, cooled and a few drops of sulphuric acid added. The sample is heated on a Bunsen burner until no fumes are visible and incinerated at $650 \pm 25^\circ\text{C}$ for a further two hours. The sulphated ash % molasses is determined gravimetrically.
- *SMRI conductivity ash method for molasses* [TM010] (Anon, 1996): A solution is prepared by dissolving the molasses sample ($2 \pm 0,2$ g) in a 200 ml volumetric flask using deionised water. The conductivity of the sample is recorded at 20°C and converted to a conductivity ash result, which closely corresponds to the sulphated ash result, according to the equation developed by Matthesius and Mellet (1976):

$$\text{Conductivity ash \% molasses} = 8,4 \times 10^{-3} \times C + 0,8$$

where:

C = the specific conductance (μS) of the sample, i.e. $C_{\text{sample}} - C_{\text{water}}$.

- *ICUMSA conductivity ash method for molasses, raw sugar, juice and syrup* [GS1/3/4/7/8-13] (Anon, 1994): A solution is prepared by dissolving the molasses sample (0,25 g) in a 100 ml volumetric flask using deionised water. The conductivity of the sample is recorded at $20 \pm 0,2^\circ\text{C}$ and converted to conductivity ash, using the equation developed by ICUMSA (De Villiers, 1982). This equation was derived using the results obtained from a study in which 14 laboratories analysed four beet and two cane molasses samples.

$$\text{Conductivity ash \%} = (16,2 + 0,36D) \times 10^{-4} \times C \times f$$

where:

D = dry substance concentration of the solution tested in g/100 ml, e.g. for 0,25 g/100 ml and dry substance content of 80 g/100 g; $D = 0,8 \times 0,25 = 0,20$ g/100 ml

S = mass of sample (g) in 100 ml

f = dilution factor of the solution relative to 5 g/100 ml, i.e. $f = 5/S$

C = the specific conductance (μS) of the sample, i.e. $C_{\text{sample}} - C_{\text{water}}$

Part 2: A comparison of the ash results obtained via the ICUMSA conductivity [GS1/3/4/7/8-13] and SMRI sulphated [TM057] ash methods

Based on the results obtained in the initial investigation (Part 1) the ash % molasses, determined via the SMRI sulphated and ICUMSA conductivity ash methods, were compared for the entire 1997-98 season (April to December/January). To evaluate how a change from the conventional SMRI sulphated ash to ICUMSA conductivity ash analysis would affect the South African sugar industry, all the mills were included in this study. The sulphated ash analyses were completed on the weekly molasses samples within the week of arrival. All these samples were subsequently stored, under varying conditions, and the ICUMSA conductivity ash analyses completed during the off-crop (February to March).

Results and discussion

Part 1: A comparison of the ICUMSA [GS1/3/4/7/8-13] and SMRI conductivity [TM010] ash methods with the SMRI sulphated [TM057] ash method

The results show that the conductivity ash and the sulphated ash results correlate well for the molasses samples analysed (Table 1). The mean difference between the results obtained using the conductivity and sulphated ash methods is presented in Figure 1, for each of the mills studied. It is evident that the mean difference in the ash results (comparing the conductivity and sulphated ash methods) is reduced significantly when the ICUMSA, as opposed to the SMRI, conductivity ash method is used (Figure 1 and Table 1). In all the instances, however, the average conductivity – sulphated ash difference is negative irrespective of the method used for the determination of the conductivity ash.

A regression analysis of the respective sets of data showed that good agreement exists between the SMRI sulphated and ICUMSA conductivity as well as the SMRI sulphated and

SMRI conductivity ash methods, with correlation coefficients of 0,92 and 0,94 (n=106), respectively. The correlation coefficient of each mill is listed in Table 1. The mean absolute difference between the SMRI sulphated and conductivity ash is $-1,0 \pm 0,3$, compared with a mean absolute difference of $-0,4 \pm 0,4$ between the SMRI sulphated ash and ICUMSA conductivity ash methods for the five mills studied (Table 1). The better agreement between the ash results in the latter instance prompted the use of the ICUMSA conductivity ash method in all further investigations.

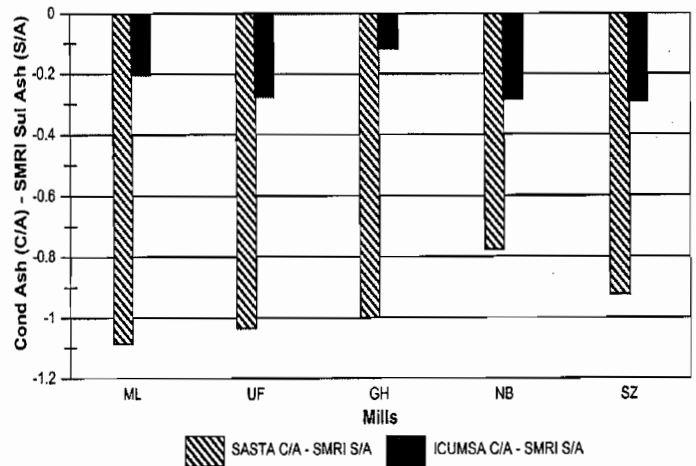


Figure 1. Mean ash differences for molasses from five regional mills.

The results obtained suggest that the poor agreement between the sulphated (SMRI) and conductivity (SMRI) ash methods reported previously for mixed juice (Dunsmore and Bax, 1983), might be attributed to the large discrepancies in ash %, relative to sulphated ash, when the SMRI conductivity ash method is used (Figure 1 and Table 1).

Table 1. ICUMSA and SMRI conductivity ash versus SMRI sulphated ash data.

Mills	(n)	SMRI C/A versus SMRI S/A				ICUMSA C/A versus SMRI S/A			
		R ²	AVG _{diff} [#] (C/A-S/A)	SD (AVG _{diff})	AVG (ABS _{diff}) [*]	R ²	AVG _{diff} [#] (C/A-S/A)	SD (AVG _{diff})	AVG (ABS _{diff}) [*]
ML	21	0,96	-1,08	0,30	1,11	0,87	-0,20	0,58	0,50
UF	22	0,91	-1,03	0,25	1,02	0,91	-0,27	0,38	0,30
GH	22	0,97	-1,00	0,30	1,04	0,92	-0,11	0,29	0,26
NB	21	0,96	-0,77	0,22	0,76	0,96	-0,28	0,23	0,30
SZ	20	0,37	-0,92	0,63	0,99	0,34	-0,29	0,66	0,46
Overall:		0,94	-0,96	0,34	0,98	0,92	-0,23	0,43	0,36

AVG_{diff} = Average C/A-S/A difference

* AVG (ABS_{diff}) = Average absolute C/A-S/A difference

Part 2: A comparison of the ash results obtained via the ICUMSA conductivity [GS1/3/4/7/8-13] and SMRI sulphated [TM 057] ash methods

To demonstrate the differences that could be expected as a result of using conductivity rather than sulphated ash, the results from two mills were compared. Figure 2 represents a poor correlation between the ash methods illustrated by both the seasonal ash trends and the scatter plot, whereas Figure 3 depicts a good correlation between the ash methods. From the seasonal trends it is evident that the difference between the sulphated and conductivity ash is approximately constant throughout the season.

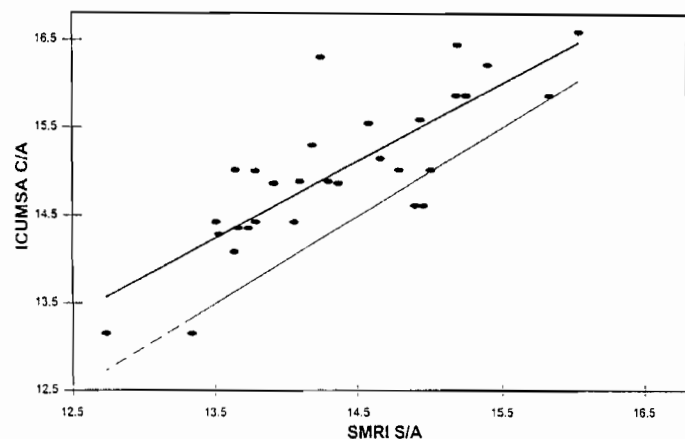
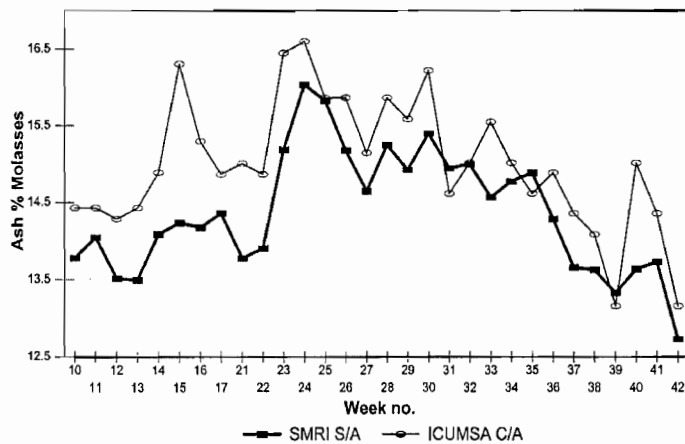


Figure 2. Poor correlation between sulphated and conductivity ash.

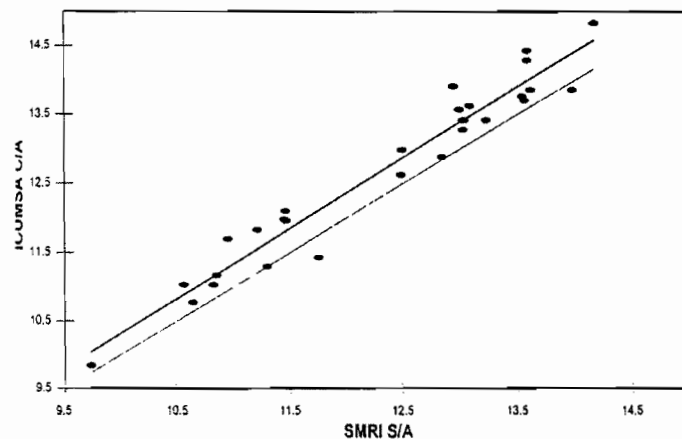
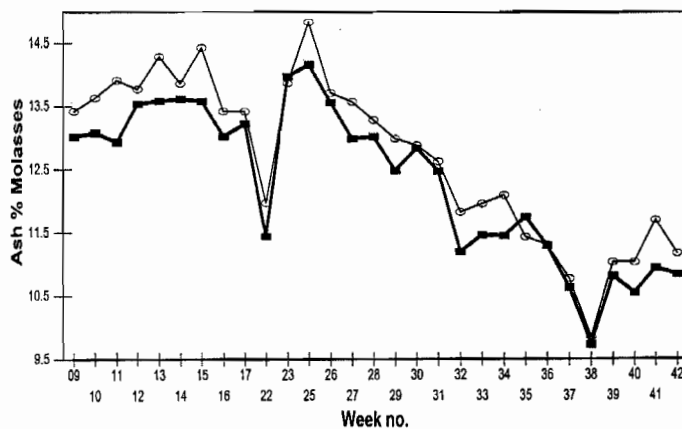


Figure 3. Good correlation between sulphated and conductivity ash.

The average conductivity (ICUMSA) – sulphated (SMRI) ash difference for each mill was calculated (Table 2) and is illustrated in Figure 4. Although there appears to be a slight geographical trend in the ash differences, which are lower in the southern region, the conductivity ash results appear to be consistently higher than the sulphated ash results for the South African industry, with the exception of two mills.

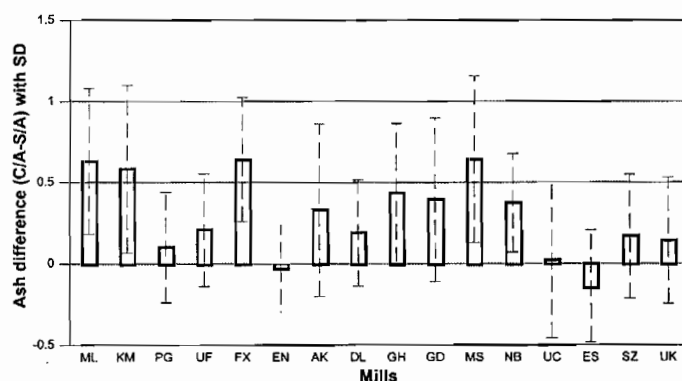


Figure 4. Mean ash differences of the South African mills for the 1997-98 season.

Table 2. ICUMSA C/A and SMRI S/A data and the effect on TPD.

Mills	n	ICUMSA C/A versus SMRI S/A				TPD _{C/A} versus TPD _{S/A}			
		R ²	AVG _{diff} [#] (C/A-S/A)	SD (AVG _{diff})	AVG (ABS _{diff}) [*]	R ²	AVG _{diff} [#] TPD _(C/A-S/A)	SD (AVG _{diff})	AVG (ABS _{diff}) [*]
AK	30	0,819	0,33	0,45	0,53	0,980	-0,12	0,17	0,20
DL	23	0,928	0,19	0,31	0,29	0,995	-0,07	0,12	0,11
ES	30	0,871	-0,14	0,34	0,28	0,993	0,07	0,17	0,14
EN	22	0,646	-0,02	0,38	0,30	0,992	0,01	0,18	0,14
FX	24	0,805	0,64	0,38	0,64	0,990	-0,28	0,16	0,28
GD	23	0,823	0,39	0,49	0,56	0,974	-0,17	0,21	0,24
GH	22	0,854	0,43	0,42	0,50	0,994	-0,19	0,18	0,21
KM	34	0,895	0,58	0,51	0,64	0,982	-0,22	0,19	0,24
ML	32	0,807	0,63	0,44	0,64	0,991	-0,25	0,17	0,25
MS	30	0,660	0,64	0,50	0,69	0,988	-0,27	0,21	0,30
NB	29	0,947	0,37	0,29	0,40	0,998	-0,19	0,14	0,20
PG	24	0,883	0,37	0,50	0,50	0,997	-0,15	0,21	0,21
SZ	29	0,733	0,17	0,37	0,34	0,976	-0,07	0,17	0,15
UC	27	0,811	0,02	0,47	0,36	0,993	-0,00	0,24	0,18
UF	23	0,906	0,21	0,37	0,34	0,989	-0,09	0,16	0,15
UK	30	0,806	0,14	0,39	0,33	0,983	-0,06	0,17	0,15
Overall:		0,930	0,30	0,48	0,45	0,993	-0,12	0,21	0,19

AVG_{diff} = Average difference between results (C/A - S/A) or (TPD_{C/A} - TPD_{S/A})

* AVG(ABS_{diff}) = Average absolute difference between the results

The difference between the sulphated and conductivity ash results is not unexpected (Ducattillon, 1990). The fact that the difference is constant throughout the season suggests that a conductivity measurement for determining ash in molasses could be used in preference to the sulphated ash analysis with its inherent disadvantages.

- The sulphated ash method involves the use of concentrated sulphuric acid. In addition to the corrosive nature of this acid, the pungent and corrosive SO₂ fumes generated during this analysis cause:
 - (a) atmospheric pollution
 - (b) respiratory problems (Hill, 1992), thereby placing the analysts' health at risk
 - (c) damage to the extraction fans in the fumehoods.
- The sulphated ash method is more labour intensive and lengthy than the conductivity ash method.

In view of a growing global concern for the safety and health of employees, accompanied by world-wide pressures to minimise the environmental impact of industrial operations, these factors deserve due consideration.

A regression analysis, including all the results obtained from this study, shows that a good correlation exists between the sulphated (SMRI) and conductivity (ICUMSA) ash methods (R²=0,93; n=432). The results from the t-test did, however, show that a statistically significant difference exists between the SMRI sulphated and ICUMSA conductivity ash results [t=12,76 > t_{crit}(two-tail) = 1,97]. Three different samples were analysed five times each to determine a repeatability of 0,07% for the ICUMSA conductivity ash method (Bissel, 1994). This result is in agreement with the repeatability of 0,08% reported previously (De Villiers, 1982). Based on the

SMRI control analyses for the 1996 and 1998 seasons, the repeatability for the SMRI sulphated ash method was found to be 0,06%. It should be noted that an earlier collaborative study between two of the South African testing laboratories found that the repeatability of the SMRI sulphated ash method was 0,3 (Mellet *et al.*, 1982). The repeatability of the ICUMSA conductivity ash method (0,07%) is approximately equivalent to that of the SMRI sulphated ash method (0,06%) and would therefore be equally precise.

The discrepancy between the average ash difference (ICUMSA conductivity - SMRI sulphated ash) for this study (AVG_{diff} = 0,30±0,48, Figure 4, Part 2) compared with the preliminary investigation (AVG_{diff} = -0,23±0,43, Figure 1, Part 1), is attributed to the fact that, in this study, the molasses samples for the entire season were stored under varying conditions. As a consequence, it is difficult to assess whether the larger differences between the ICUMSA conductivity and SMRI sulphated ash results in Part 2 of this investigation are merely reflecting changes in the samples as a result of deterioration, or whether these differences are a function of the method of analysis employed (Table 2). Currently under investigation are the effects of time and sample deterioration on the conductivity ash results. A comparison of the results in Figure 1 and Figure 4 suggests that the conductivity of the samples increases with time and results in an increase in conductivity ash, adversely affecting the ICUMSA conductivity - SMRI sulphated ash difference. This conclusion is supported by the fact that an earlier ICUMSA study (De Villiers, 1982) showed that the conductivity ash results were approximately 10% lower than the sulphated ash results. It would therefore be reasonable to conclude that the preliminary results (Part 1) gave a better

indication of the true correlation between the SMRI sulphated and ICUMSA conductivity ash.

The most important consideration when evaluating a new ash method is how the results impact on the target purity difference (TPD) (Ravnö and Lionnet, 1982). Despite the statistically significant difference between the SMRI sulphated and ICUMSA conductivity ash (mean absolute difference of 0,45; n=432) and resultant TPD figures (mean absolute difference of 0,19; n=432), the TPD results are not affected markedly (Table 2). The mean difference in TPD ($TPD_{cond} - TPD_{sul}$), when the conductivity rather than the sulphated ash result was used to calculate the TPD, for each mill is represented in Figure 5. The TPD results are all biased in the same direction, except for two of the mills; therefore the TPD results will all be affected in the same way if the ICUMSA conductivity ash method is used in preference to the SMRI sulphated ash analysis. Furthermore, the seasonal profile for molasses TPD is identical, whether based on the SMRI sulphated or ICUMSA conductivity ash results. Figure 6 represents the situation for a mill where a poor correlation exists between TPD results derived from using the SMRI sulphated and ICUMSA conductivity ash results. Both the seasonal trends and the scatter plot illustrate this. Figure 7 depicts the situation for a mill where a good correlation exists between the respective TPD results.

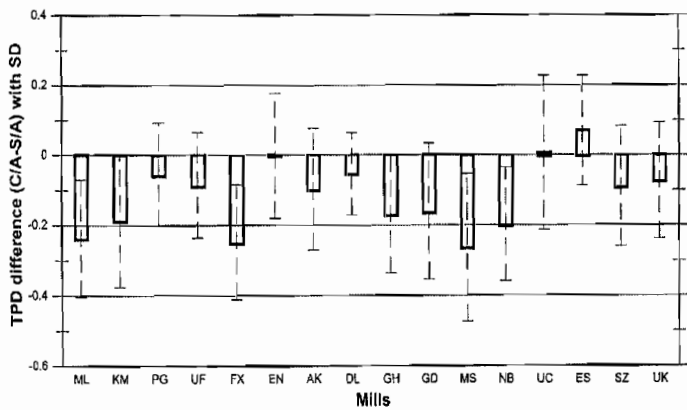


Figure 5. Mean TPD differences of the South African mills for the 1997-98 season.

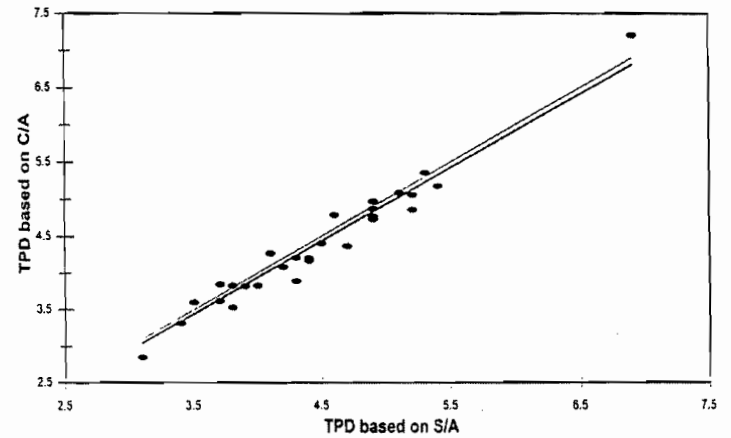
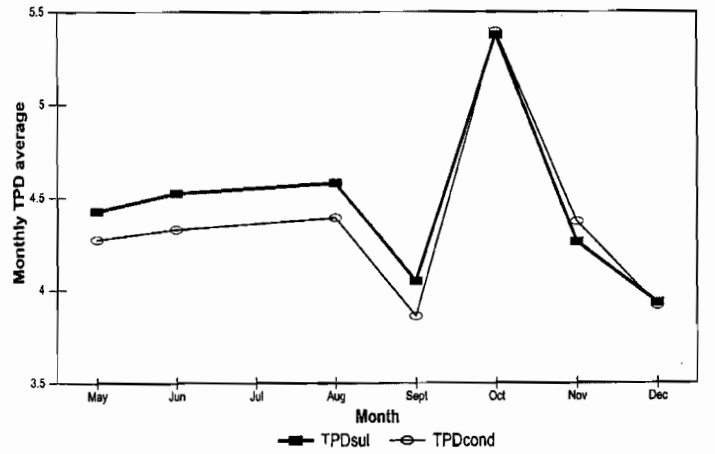


Figure 6. Poor correlation between TPD results.

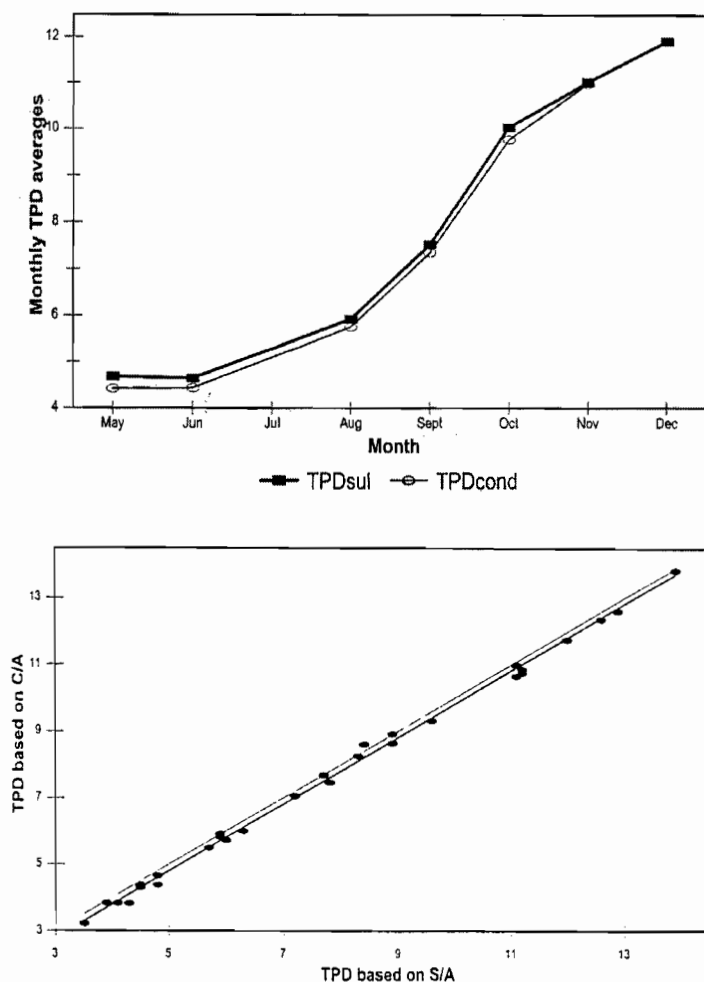


Figure 7. Good correlation between TPD results.

Conclusions

The results obtained from these studies show that an effective conductivity method for determining ash in molasses has been developed by ICUMSA, and that this method could replace the use of the environmentally hazardous sulphated ash analysis without affecting the TPD results considerably. To evaluate the ICUMSA conductivity ash method further, the conductivity and sulphated ash analyses of the weekly mixed juice and molasses samples from all South African

mills will be run concurrently for the 1999-2000 season. This method will not be re-evaluated for South African raw sugar samples, since a comprehensive study by Chou and Altenburg (1996) and Nguyen (1998) has shown that excellent agreement exists between the ICUMSA conductivity and sulphated ash methods for raw sugars. Studies are also in progress to evaluate the effect of sample deterioration on conductivity ash results of molasses and mixed juice samples.

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