

RAPID NEAR INFRA-RED ESTIMATION OF MULTI-COMPONENTS IN MIXED JUICE AND FINAL MOLASSES: THE POSSIBILITY OF DAY-TO-DAY CONTROL OF RAW SUGAR FACTORIES USING NIR

KJ SCHÄFFLER AND MTD DE GAYE

Sugar Milling Research Institute, University of Natal, Durban, 4041

Abstract

More than 550 mixed juice (MJ) and over 900 C-molasses samples covering four seasons have been scanned using near infra-red spectroscopy (NIR). Fructose, glucose, sucrose, pol, brix and sulphated ash analyses were available for both products as well as dry solids for molasses. Mixed juice samples were randomly split into two sets. Partial least squares regression, together with principal component analysis, were employed to develop calibrations for all analytes in one of the sets. These calibrations were evaluated using the remaining set of samples. The splitting of the sample set into calibration and validation sets was repeated for the molasses samples.

For MJ, the NIR predictions were slightly less precise than the original laboratory results. The NIR estimates were nevertheless free from bias, with acceptable precision for day-to-day control (prediction standard errors for sucrose, brix and pol in MJ were all close to 0,1 unit). True purity in MJ could also be determined by NIR with good precision (prediction standard error = 0,8 unit of purity). As expected, NIR estimates for ash in juice were extremely poor.

For molasses, prediction standard errors for brix and dry solids were similar to the repeatability of the reference methods. The monosaccharides were also predicted with good precision and the results for sulphated ash were surprisingly good. The good estimates for ash are probably due to the low moisture content of C-molasses and individual ion-sugar-water associations. Ash analyses are tedious and these results indicate that the more easily obtained NIR predictions could be used for daily control. Sucrose and pol results were somewhat disappointing, with the standard error for sucrose being almost three times that obtained by high performance liquid chromatography (HPLC). The comparison of weekly target purity differences (TPD) by NIR with the official TPD results gave a standard error of approximately one unit. NIR determinations for all analytes (including TPD) can be carried out in less than 10 minutes. Averaging multiple samples is therefore suggested to increase NIR precision.

The excellent results can be attributed to the reliability of the laboratory data (weekly laboratory audits, replicate analyses) and to the wide spectral base of the NIR data (samples covering four seasons). The implications of using these global models and converting them to local calibrations with an NIR instrument installed in the mill laboratory are also discussed.

Keywords: NIR, mixed juice, molasses

Introduction

In South Africa, both mill and cane testing laboratories have been downsizing their operations in recent years in an attempt to remain competitive. This has led to:

- the remaining testers now having more analyses to perform, together with additional responsibilities. This has often resulted in hasty determinations with the resultant possibility of increased errors.
- less supervision with the concomitant lowering of laboratory protocols.
- the loss of competent staff who are often promoted out of the laboratory environment into process, leaving inexperienced staff to carry out the workload, again with the possible lowering of standards.

The major attractions of using NIR are the rapid estimations of multi-components in liquids, suspensions and solids with minimal sample preparation by relatively inexperienced staff. NIR has been used extensively for estimating analytes in sugarbeet and beet factory products (Jones *et al.*, 1994; Marchetti, 1990; de Bruijn, 1994; Edye *et al.*, 1994). NIR has also been used for the analysis of shredded cane (Berding and Brotherton, 1994; Berding, 1995; Clarke *et al.*, 1996; Schäffler and Meyer, 1996) and for front-end sugar cane juices (Berding *et al.*, 1991; Edye *et al.*, 1994).

There are only a few published reports on the use of NIR for back-end products from a raw sugar factory. Pax (1993) stressed the need for a rectilinear distribution of samples for the calibration set when analysing B-molasses. Only a limited number of samples spanning four weeks was used for this study. Clarke *et al.* (1995) looked at low purity streams from a sugar refinery which included run-off, remelt and final molasses. Nguyen and Player (1990) estimated sugars and fermentation yield in C-molasses. Once again the calibration set (N=45) and validation set (N=20) were limited, placing in question the robustness of the calibrations for future samples. In addition, only three wavelengths and not the entire NIR spectrum were used for their work.

The development of rugged calibration models for analytes in complex products like molasses can be tedious and time consuming. However, once robust and stable calibrations have been developed, the routine estimation of brix, pol and moisture can be carried out by relatively unskilled staff. More sophisticated analyses (e.g. fructose, glucose, true sucrose, dry solids) demand considerable analytical skill and instrumentation, are time consuming and are virtually impossible to determine reliably in mill laboratories. With the necessary calibrations, NIR estimates for these components can be carried out easily by factory staff. These advantages, together with the problems discussed earlier on laboratory downsizing, make NIR an extremely attractive option.

Early NIR work on cane molasses carried out at the Sugar Milling Research Institute (SMRI) (Day-Lewis, 1994a; 1994b), highlighted the fact that calibrations, obtained from a limited number of samples (collected over a short period), could not be used to predict analytes accurately in samples that were scanned months or years later. For this reason, it was decided to scan samples at regular intervals over four seasons.

It was possible that calibrations developed from these samples would include spectral variations due to geographic, seasonal, varietal and other effects. Because of the number of samples involved, only mixed juice (MJ) and final molasses (FM) samples were scanned by NIR. The rationale behind this decision was that these two products included the range of factory intermediates, and analyses for the two products were available on a routine basis. This is an important advantage as laboratory determinations of individual analytes are far more time consuming than NIR scanning. If stable calibrations could be developed for these two streams, then training of NIR models for the intermediates should also be achievable. The present study is believed to be one of the most comprehensive investigations into the use of NIR for raw sugar factory products.

Experiment procedure

Mixed juice

Samples were obtained from the SMRI routine analytical programme. The SMRI contracts to do these determinations for the Cane Testing Service (CTS). Hourly MJ samples from each South African (SA) factory are rapidly deep frozen at individual CTS laboratories. These samples are transported weekly in special containers to the SMRI, where they are thawed and composited. Analyses of these weekly composites include pol, brix, sulphated ash, fructose, glucose and sucrose. Each week, the stability of these samples and the reliability of the individual CTS laboratories are checked by comparing their averaged results for pol and brix with the SMRI central laboratory. A NIRSystems 5000 spectrophotometer, with a scanning range of 1 100 to 2 500 nm, was fitted with a sample transport module. Duplicate aliquots of mixed juice samples were scanned in the transmission mode using a 1 mm cuvette.

Molasses

Again samples from the routine analytical programme were used for NIR development and testing. Weekly samples of final molasses from all SA factories were analysed for fructose, glucose, sucrose, pol, brix, sulphated ash and dry solids. Duplicate sub-samples were directly scanned by the NIRSystems 5000 in the reflectance mode using a 30 mm cuvette.

Software

Spectral data acquisition was achieved using NSAS version 3.25. Duplicate spectra from each sample were averaged and the individual files were merged for each product. The files were then converted to ISI's NIRS3 format. Calibration and validation sets were randomly generated (60:40). Calibration for each analyte was carried out as described in Table 1.

Table 1
Procedure for the calibration of analytes in mixed juice and molasses.

Description	Set points
Calibration type	Modified partial least squares
Scatter correction and detrend	On
Mathematical treatment	1, 4, 4, 1
Maximum number of terms	14
Number of wavelengths	231
Cross-validation groups	4
Critical T outlier value	2,5
Critical H outlier value	10
Critical X outlier value	10
Number of outlier passes	2

Results

Mixed juice and molasses samples were scanned by NIR for four consecutive seasons, details being given in Tables 2 and 3. A summary of the laboratory data for analytes in MJ and molasses for both calibration and validation sets are presented in Tables 4 and 5. Calibration and validation results for MJ and molasses are given in Tables 6 and 7 respectively.

Discussion

Sample selection

Berding and Brotherton (1994) eliminated samples with similar spectra from the calibration file. Pax (1993) also selected samples to produce a rectilinear distribution of samples across each analyte's expected range. The 'Select' program from ISI (Anon, 1993) was designed for this purpose. In the SMRI study, *all the samples* in the calibration set were retained because:

Table 2

Details of mixed juice samples used for NIR calibration and validation studies.

Year	Period	No. samples
1993	August to October	57
1994	October to November	132
1995	May to September	225
1996	April to June	148
Total		562
Randomly split into a calibration set (337 samples) and a validation set (225 samples)		

Table 3

Details of molasses sampled used for NIR calibration and validation studies.

Year	Period	No. samples
1993	July to November	106
1994	June to November	263
1995	April to September	266
1996-97	May 1996 to January 1997	286
Total		921
Randomly split into a calibration set (555 samples) and a validation set (366 samples)		

Table 4

Summary of laboratory data for analytes in MJ used for the NIR study (SD = standard deviation).

Analyte	Calibration (N=337 samples)			Prediction (N=225 samples)		
	Mean	Range	SD	Mean	Range	SD
Fructose	0,3	0,16 - 0,75	0,1	0,3	0,16 - 0,75	0,1
Glucose	0,3	0,13 - 0,81	0,1	0,3	0,14 - 0,81	0,1
Sucrose	9,7	7,1 - 12,9	1,2	9,7	6,6 - 12,8	1,3
Pol	9,5	6,9 - 12,6	1,2	9,5	6,5 - 12,6	1,3
Brix	11,5	8,7 - 14,9	1,3	11,5	8,2 - 14,5	1,3
Ash	0,5	0,3 - 0,6	0,1	0,5	0,3 - 0,6	0,1
Purity	83,9	76,6 - 90,1	2,5	83,9	77,9 - 90,0	2,5

Table 5

Summary of laboratory data for analytes in molasses used for the NIR study (SD = standard deviation).

Analyte	Calibration (N=555 samples)			Prediction (N=366 samples)		
	Mean	Range	SD	Mean	Range	SD
Fructose	7,6	4,3 - 13,4	1,6	7,5	4,2 - 13,2	1,6
Glucose	5,1	1,7 - 11,7	1,8	4,9	1,5 - 11,2	1,7
Sucrose	30,1	25,5 - 36,0	1,8	30,3	25,8 - 36,7	2,0
Pol	26,9	18,7 - 36,0	2,9	27,2	19,6 - 35,4	3,1
Brix	81,6	75,7 - 89,3	2,1	81,4	75,8 - 89,3	2,4
Ash	14,1	10,4 - 19,0	1,5	14,2	10,6 - 19,3	1,7
Dry solids	77,3	71,7 - 84,4	2,0	77,5	70,1 - 84,6	2,3

Table 6

Statistical summary of PLS calibration and prediction results for analytes in MJ (SEC = standard error of calibration, SEP = standard error of prediction, RSQ = correlation coefficient squared).

Analyte	Calibration set (N = 337)					Prediction set (N = 220, outliers = 2%)				
	SEC	RSQ	Factors	N	% outliers	Lab error	SEP	Bias	Slope	RSQ
Fructose	0,02	0,945	13	326	3		0,03	0,00	0,98	0,92
Glucose	0,02	0,950	14	321	5		0,04	0,01	0,98	0,89
Sucrose	0,06	0,997	10	319	5		0,09	0,00	1,00	1,00
Pol	0,06	0,998	12	318	6	0,07	0,08	-0,01	0,99	1,00
Brix	0,07	0,997	10	316	6	0,09	0,10	0,00	1,00	0,99
Ash	0,04	0,691	9	328	3		0,06	0,00	0,80	0,55
Purity	0,60	0,941	13	324	4		0,76	0,04	0,98	0,91

Table 7
Statistical summary of PLS calibration and prediction results for analytes in molasses (Lab error = repeatability standard deviation of reference method, TSAI = total sugars as invert, TPD = target purity differences).

Analyte	Calibration set (N = 555)					Prediction set (N = 366, outliers = 3%)				
	SEC	RSQ	Factors	N	% outliers	Lab error	SEP	Bias	Slope	RSQ
Fructose	0,4	0,94	12	533	4	0,15	0,5	0,01	1,00	0,91
Glucose	0,3	0,97	13	530	5	0,20	0,4	-0,01	0,98	0,94
Sucrose	0,5	0,91	13	532	4	0,25	0,8	0,07	1,00	0,84
Pol	0,8	0,92	13	529	5	0,20	1,2	0,03	0,95	0,85
Brix	0,3	0,98	13	523	6	0,50	0,5	0,03	0,99	0,96
Ash	0,4	0,92	14	532	4	0,20	0,6	0,01	1,00	0,88
Dry solids	0,2	0,99	14	530	5	0,25	0,3	0,01	1,01	0,98
Purity	0,7	0,91	14	532	4		1,0	0,05	0,99	0,82
TSAI	0,6	0,95	13	530	5		0,8	0,00	1,01	0,93
TPD	0,7	0,85	12	528	5		1,0	0,06	1,08	0,77

- analytical data were available for *all* the samples scanned by NIR; in other studies this is not always the case.
- the calibration process smooths out the random errors generated by the reference methods. This cancelling of errors will be greater for the original set than for a smaller set selected by the ISI software. Tables 4 and 5 show that the ranges, for each analyte in the calibration sets, are very similar to those found in the prediction sets. The use of ISI's 'Center and Select' software was used to remove samples with similar spectra from the calibration set. This reduced sub-set could not match the predictions from the original set.

Outliers

Rejection of outliers was based on two criteria:

- if residuals between laboratory and NIR estimates were statistically significant ($T > 2,5$)
- if the spectral distance was too far from the spectral mean ($H > 10$), spectra were eliminated.

From Tables 6 and 7 it can be seen that flagged outliers ranged from 3 to 6 % of the total samples used for calibration. As many hundreds of samples were used for this investigation, it is obvious that:

- errors in laboratory analyses, scanning incorrect samples or clerical mistakes were bound to occur
- attempting to identify suspect samples was clearly impossible and therefore an outlier rate of 5% was considered acceptable.

Mixed juice

Sucrose, pol and brix. These three analyses are vital for factory control. Bias, slope and correlation coefficient squared (RSQ) data for these three analytes were impressive (see Table 6).

In Figures 1a, 1b and 2a scatter plots show excellent agreement between laboratory results and NIR predictions. The effectiveness of a NIR prediction is normally assessed by comparing NIR standard error of prediction (SEP) with the precision of the reference method. In the case of MJ, the South African sugar industry compares weekly averages of hourly MJ samples, carried out in individual CTS laboratories, with the weekly composite samples determined at the SMRI. The precision of this procedure was estimated by randomly selecting three MJ samples for each week of the 1996 season, and the 126 samples from the CTS and the SMRI were compared. The standard deviations (SD) of the mean difference were 0,07 and 0,09 for pol and brix analyses, respectively. The NIR-SEPs for sucrose, pol and brix were 0,09, 0,08 and 0,10 respectively. These NIR errors were remarkably similar to the laboratory errors. This fact, together with the lack of bias and excellent slope results (Table 6), illustrate that NIR is capable of producing excellent results for high purity juices. It must be pointed out that the exceptional agreements were due to:

- the high quality of the laboratory data. When a laboratory produces poor results this will be reflected in the NIR predictions. In the case of the MJ analysis for SA factories, weekly comparisons between individual CTS mill laboratories and the SMRI control laboratory ensure continuing high quality results.
- the absence of sample sensitivity of the calibration models due to the large and varied database covering four consecutive milling seasons (Table 4).

Fructose and glucose. These two sugars are minor constituents in MJ. They were included in this study simply because routine laboratory data were available routinely. Process staff regularly examine monosaccharide changes between MJ and final molasses as part of the undetermined loss programme and for

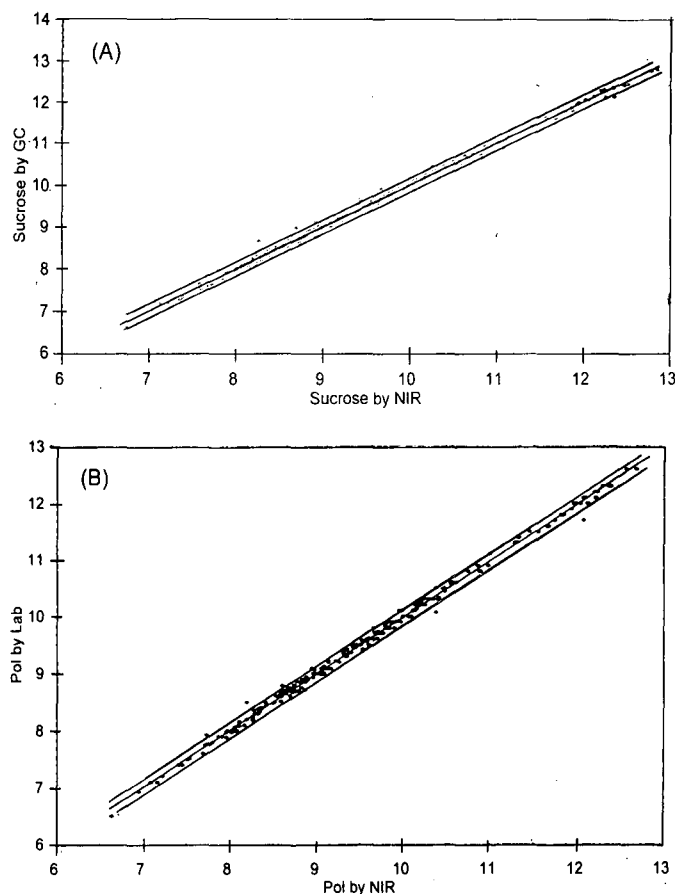


Figure 1. Scatter plots of NIR predictions of analytes in mixed juice. Regression lines, slope lines and 95% confidence limits are also included. A = sucrose, B = pol (220 samples used in prediction set, 337 samples used in calibration model covering 1993-96).

monitoring the Maillard reaction (Morel du Boil and Schaffler, 1978). Acceptable NIR estimates for these two sugars were not anticipated, as these two analytes are minor constituents of MJ. Results were, however, unbiased with low standard error of prediction (SEP) (0,04) (Table 6).

Ash. The NIR predictions for ash were extremely poor (slope = 0,80; RSQ = 0,55). This was expected, as:

- absorptions in the NIR region result from overtones and combinations from organic molecules.
- ash is a minor constituent in a dilute, high purity stream with little possibility of molecular associations with organic molecules.

True purity. Although purity can easily be calculated from the NIR results for sucrose and brix, true purity was included as a NIR calibration parameter. The prediction results are shown in Figure 2b. Good estimates were obtained (SEP = 0,76; bias = -0,04; slope = 0,98; RSQ = 0,91).

Molasses

Laboratory precision. The reliability of NIR predictions is often assessed by comparing NIR-SEP to the precision of the reference method. The precision of the reference methods, sometimes

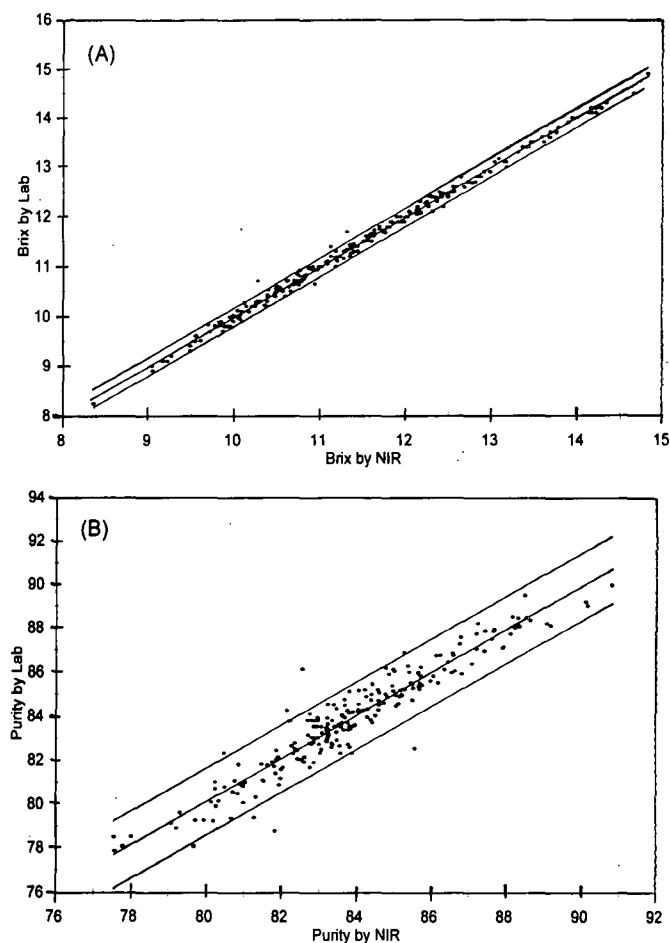


Figure 2. Scatter plots of NIR predictions of analytes in mixed juice. Regression lines, slope lines and 95% confidence limits are also included. A = brix, B = true purity (see Figure 1 for additional details).

described as the repeatability standard deviation, is included in Table 7. Precision data for fructose, glucose and sucrose were obtained from Anon (1994). Repeatability standard deviations for the other analytes were obtained from Mellet *et al.* (1982).

Brix and dry solids. Brix and dry solids determinations are essentially two different procedures for the determination of total dissolved solids. It is clear from Table 7 and from the scatter plots in Figure 3 that the NIR predictions are excellent. The SEP for brix (0,5) and dry solids (0,3) are very similar to the standard deviations of the laboratory methods (brix = 0,5 and dry solids = 0,25). NIR is a secondary technique relying on the original laboratory data. The question must then be raised, "Why are the NIR results equal to or better than the original results?" This issue has been raised by Dahm (1994). All laboratory procedures have random errors generated from the multiple steps required for each determination. Modern NIR on the other hand is extremely precise and the calibration process (in this case over 500 samples were used) results in an averaging out of the reference method's random errors. In this study brix and dry solids results were definitely the most precise NIR determinations. This was perhaps to be expected as these two constituents estimate total organic matter. Fructose and glucose, together with sucrose, should account for most of organic spectral

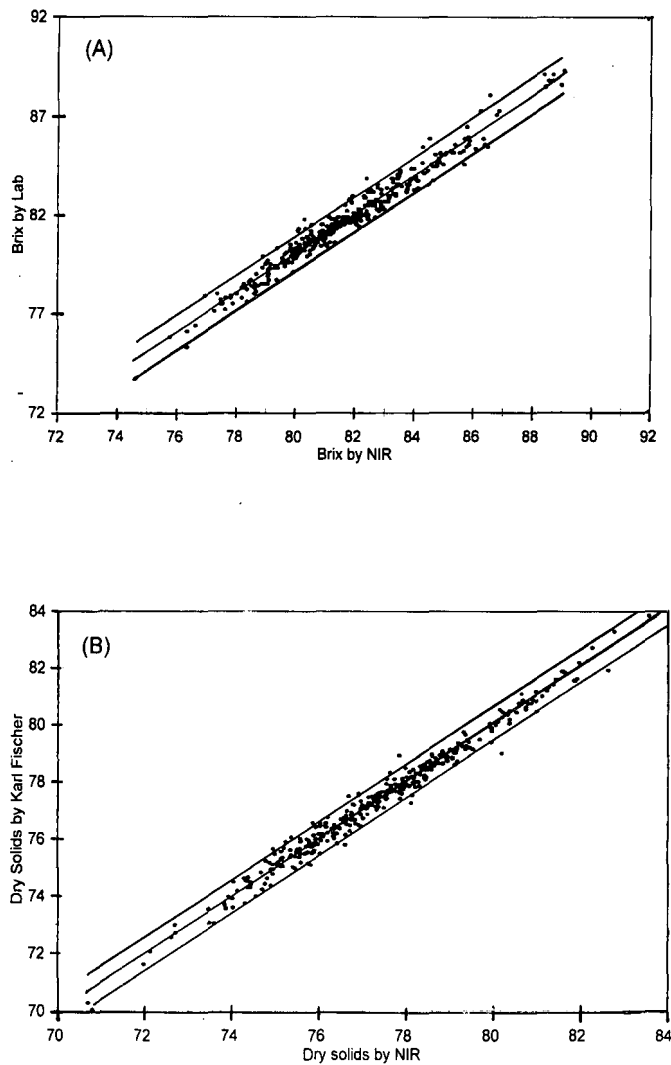


Figure 3. Scatter plots of NIR predictions of analytes in molasses. Regression lines, slope lines and 95% confidence limits are also included. A = brix, B = dry solids (366 samples used in prediction set, 555 samples used in calibration model covering 1993-96).

absorptions in NIR. This is borne out by one of the derived parameters (total sugars as invert, TSAI). It is clear from Table 7 that NIR would be most useful for molasses fermentation applications as the precision was similar to that achievable by HPLC.

Sucrose and pol. It is apparent from Table 7 and Figure 4a that SEP and RSQ were inferior to those obtained for dry solids, indicating that matrix effects adversely affected sucrose predictions. The higher NIR-SEP for both sucrose and pol is probably due to a slightly different composition of the monosaccharides (together with other NIR absorbing interferants) in the prediction set. Clearly the calibration set can account for most but not all of the variations in the prediction set. This problem will be addressed under the section of this paper headed, 'Future Work'. However, bias and slope data were acceptable for these two analytes. As the NIR standard error for sucrose is approximately three times greater than the HPLC procedure, future NIR estimates should perhaps consist of triplicate sub-samples and in this way increase NIR repeatability.

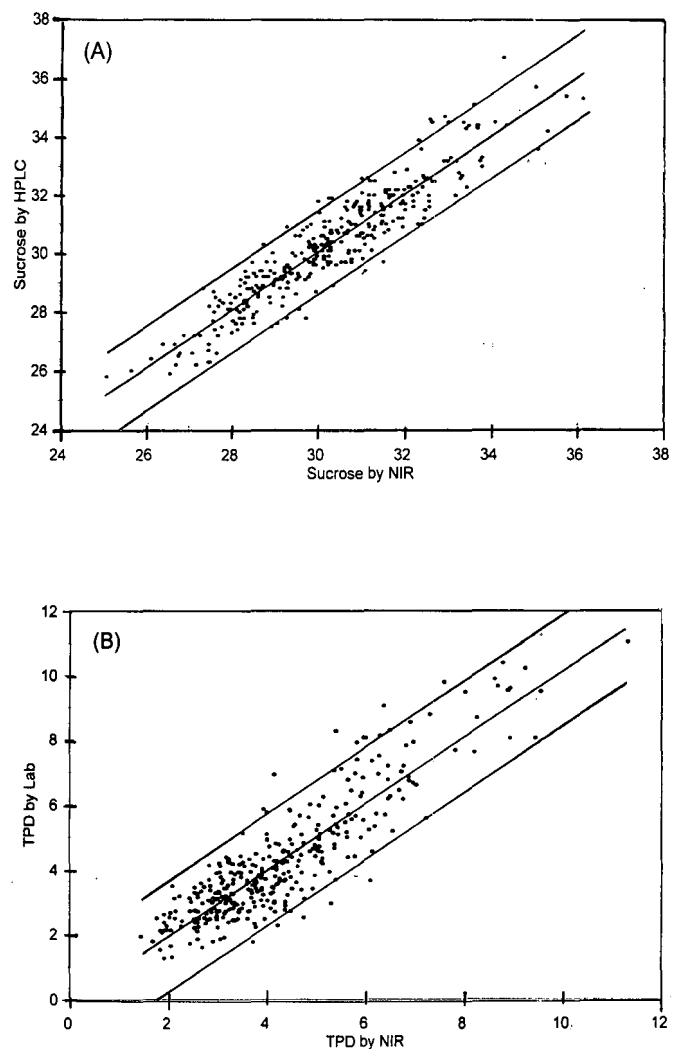


Figure 4. Scatter plots of laboratory versus NIR predictions for molasses, sucrose and target purity differences results. Regression lines, slope lines and 95% confidence limits are also included (see Figure 3 for additional details).

Fructose and glucose. These two sugars are concentrated during the crystallisation process. The NIR statistics were very good for the two analytes (bias $\pm 0,01$; slope = 0,98 to 1,00; SEP = 0,4 to 0,5).

Ash and TPD. NIR results for ash in MJ were poor. This was expected as MJ is a dilute, high purity product. The results for molasses were rather different (bias = 0,01; slope = 1,00; SEP = 0,6). The improved NIR results were attributed to the low water content of C-molasses, where ionic-sugar associations could be responsible for the improved results (Allen and Wood, 1974; Rendleman, 1966). These preliminary results are important as sulphated ash analysis is a tedious, difficult determination where toxic sulphuric acid fumes are released into the atmosphere. The introduction of NIR into mill laboratories could also provide process staff with a tool for determining true purity and target purities. A scatter plot of laboratory versus NIR derived target purity difference is shown in Figure 4b. The SEP for TPD was 1,0 unit. TPD can also be calculated from the individual NIR estimates rather than directly as a TPD constituent. However,

the two NIR-generated TPD values were virtually identical, with similar prediction statistics. The magnitude of this error and its significance for day-to-day control needs to be addressed. The error in determining TPD, using laboratory results, has not been evaluated. Molasses exhaustion is currently determined by a target purity formula (Smith, 1995) where:

$$\text{TPD} = \frac{\text{True sucrose}}{\text{Dry solids}} - [43,1 - 17,5 \{1 - \exp(-0,74(F+G)/\text{Ash})\}]$$

It is clear from the TPD equation that the following procedures both contribute to the overall error when determining TPD:

- the errors incurred during the development of the formula (exhaustion procedure, range of analytes in molasses, analytical errors)
- the errors in determining the five analyses prior to calculating TPD.

Lionnet (1981) established that true purity calculated from the regression formula had a confidence interval of $\pm 0,7$ unit of purity. Although the analyses required to calculate TPD have repeatabilities well below one unit, error variances are additive and hence TPD calculation errors will be greater than those for individual analyses. The 95% confidence limits for the TPD-NIR-LABORATORY comparison shown in Figure 4b may be fairly wide; however, bias is low ($-0,6$) and slope is reasonable (1,08). Frequent NIR-TPD determinations (e.g. every hour) could be used to produce a daily or weekly average. The NIR-TPD result will also be available to process staff immediately and not a week later (as at present). Factory staff may then be able to make more timeous and effective changes to back-end processing.

Future work

During the 1997-98 season a NIRSystems 5000 NIR spectrophotometer will be installed in a mill laboratory for an extended period to:

- train laboratory staff in routine NIR work and to establish how the instrument tolerates day-to-day mill laboratory conditions.
- monitor MJ and molasses calibrations. As each season appears to produce samples that are marginally different from those in previous years, bias (especially for sucrose and pol) will be inevitable. Once an NIR instrument has been installed in a mill laboratory, the SMRI global calibrations need to be adjusted for local conditions. This can be done by taking several samples for a short period to adjust any bias found in the global calibrations. The localised equations can then be monitored with the use of control charts. As purities and non-sucrose change slowly, this can be done by analysing laboratory samples at reduced frequencies to ensure that NIR/laboratory differences lie within the 95% confidence limits.
- establish whether at-line derived parameters (true purity and TPD) are useful daily process control tools. NIR-TPD results will be compared with the official SMRI exhaustion data.

Summary and Conclusions

At this early stage, no effort has been made to calculate possible laboratory savings or other benefits. This study has concentrated on the suitability of the current NIR calibrations for day to day factory control.

The main findings of this work are:

- NIR predictions for sucrose, pol and brix in MJ were impressive (SEP $\pm 0,1$; bias $\pm 0,00$; slope $\pm 1,00$; RSQ $\pm 1,00$).
- NIR estimates for brix and dry solids in molasses were also excellent, with SEP similar to the precision of the reference methods (SEP $\pm 0,4$).
- Although sucrose and pol estimates for C-molasses were free from bias and slope errors, SEP was three times higher than the laboratory results. Until these predictions can be improved, triplicate sub-samples will be used in an attempt to reduce NIR errors.
- The NIR estimate for sulphated ash in molasses was good, which is in direct contrast to that of MJ. The improved results were attributed to the low moisture content of molasses and ionic-sugar associations. Ash predictions by NIR are rapid and free from the disadvantages of conventional sulphated ash analysis.
- NIR results for TPD produced a SEP of 1,0 unit. The magnitude of the error for laboratory generated TPD is not known; however, it must certainly be greater than 0,5 unit. Regular comparisons between the two TPD results are planned for 1997-98.

The excellent prediction results were due to a number of factors:

- NIR spectra are an accumulation of broad absorptions from a variety of non-sucrose components that overlap those due to sucrose. NIR spectra of MJ and molasses have been scanned for the past four years. This approach was taken to ensure that NIR spectral variations due to geographic, seasonal, varietal and other effects were included in the calibration and prediction sets. This strategy has lead to prediction results that are generally free from bias with low SEP.
- The chemometric software from ISI for the detection of outliers and for the construction of the calibration models has been a major improvement over earlier procedures.
- The reliability of the laboratory data. NIR is a secondary technique and calibration is totally dependent on laboratory results. The laboratory information used in this investigation was of excellent quality due to continuing sound laboratory practices.

A NIRSystems 5000 spectrophotometer will be installed at one South African mill for the 1997-98 season, when the accuracy of current calibrations for both MJ and molasses will be assessed. In addition, mill staff training will be initiated. The global

calibrations, developed at the SMRI, will be used initially to produce local calibrations for the mill where the NIR instrument is installed. The control chart principle will be used to monitor the accuracy of these local calibrations. The suitability of the instrument and improvements to sampling will be evaluated.

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