Progress in improving sugar factory laboratory efficiencies using near infrared spectroscopy

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Introduction

The laboratories of the Sugar Milling Research Institute have the responsibility of maintaining and improving the standards of analytical work within the SMRI and throughout the southern African sugar industry. The SMRI analytical laboratory has been exploring the feasibility of using NIR spectroscopy as a processing tool for intermediate products, following the successful implementation of this novel application for the analysis of C-molasses for both factory control and as part of cane payment during the 2009/2010 South African crushing season. The South African sugar mill and cane testing laboratories have, in recent years, strategically recognised the need to improve the cost effectiveness of their laboratories in order to remain globally competitive. The downsizing of their operations has put pressure on the remaining testers with an increased likelihood of analytical errors occurring. The ability of NIR spectroscopy to give rapid estimations of multiple components in liquids, suspensions and solids with minimal sample preparation by relatively unskilled staff prompted the SMRI to investigate this technique with a view to implementation in the SMRI, mill and cane testing laboratories. Calibrations for mixed juice and final molasses, developed by Simpson and Oxley[1] using a Bruker MPA spectrophotometer, culminated in the acceptance of a NIR spectroscopic technique for cane payment for molasses. The possibility of providing the process manager with a bouquet of calibrations from front-end to back-end of the raw sugar factory was an extremely attractive idea. The more sophisticated reference techniques to determine fructose, glucose, true sucrose and dry solids are virtually impossible to perform reliably in mill laboratories. The calibrations developed in the present study coupled with the calibrations available for mixed juice and molasses from a previous study by Simpson and Oxley[1] are believed to provide the most comprehensive range of NIR spectroscopic calibrations available for the analysis of intermediate products in raw sugar production.

Materials and Methods

Instrumental

Near infrared spectroscopy

The NIR spectroscopic system consisted of a multi-purpose analyser (MPA; Bruker Optics, Ettlingen, Germany) fitted with a Metrohm 838 autosampler. The NIR laboratory was maintained at 20ºC by air-conditioning at all times. All spectra were obtained in absorbance mode in the scanning range 800 to 2500 nm using a Hellma flow-through sample cell with a path length of 1 mm. When not in use, the cell is filled with 3% formaldehyde to ensure that the system remained bacteria free. OPUS version 6 (Bruker Optics, Ettlingen, Germany) was used to collect and process spectra, and also for generating calibrations. OPUS version 6 included OPUS Lab, which provided a simple interface with mouse-click operations for controlling automated NIR analysis.

Polarimeter

Reference pol values (i.e. sucrose content, °Z) were measured using a Universal Polartronic at 589 nm. Samples were clarified using the standard lead clarification method.

Refractometer

Reference Brix values (i.e. sucrose content, °Brix) were measured by refractometry using a RFM 500 refractometer.

Gas chromatography (GC)

Fructose, glucose and sucrose for clear juice and syrup were determined on a Varian 3900.

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High Performance Anion Exchange Chromatography (HPAEC)

Molasses and massecuite fructose, glucose and sucrose were determined on the Perkin Elmer 200 series, using a PE 200 pump, PE 200 autosampler and a Dionex II pulsed amperometric detector controlled by Peak-Simple chromatography software for data acquisition.

Samples

Weekly composite samples of clear juice, syrup, A-, B- and C-massecuite and A- and B-molasses starting from season 2007 to 2010 were sent to the SMRI from five southern African sugar factories: Malalane (Souht Africa), Felixton (South Africa), Noodsberg (South Africa), Nakambala (Zambia) and Umzimkulu (South Africa). These samples were analysed within the season they were obtained using the reference methodologies and NIR spectroscopy. Samples were scanned on the NIR spectrometer in triplicate and the spectra were averaged.

A quality control procedure was performed using three molasses control samples with compositions established by reference and NIR methods; control samples were run with each batch of samples tested. These were used to monitor NIR performance on a weekly basis. All laboratory results were generated using methods from the SASTA laboratory manual (Anon, 2005)[2] and SMRI test methods (SMRI TM300 and TM301, 2006)[3]. Table 1 summarises the dilutions for intermediate product analyses.

Table 1. Summary of dilutions for intermediate product analyses.

	Pol & Brix	Fructose, glucose and sucrose (GC)	Fructose, glucose and sucrose (HPAEC)	NIR
Clear juice	150 cm^3	2 cm^3 (undiluted)	-	undiluted
Syrup	60 g to 240 cm^3	5 g to 35 g	-	20 g to 100 cm^3
A-massecuite	50 g to 250 cm^3	-	3 g to 100 cm^3	15 g to 100 cm^3
B-massecuite	50 g to 250 cm^3	-	3 g to 100 cm^3	14.5 g to 100 cm^3
C-massecuite	50 g to 250 cm^3	-	3 g to 100 cm^3	14 g to 100 cm^3
A-molasses	50 g to 250 cm^3	-	0.6 g to 100 cm^3	18 g to 100 cm^3
B-molasses	50 g to 250 cm^3	-	0.8 g to 100 cm^3	17 g to 100 cm^3

Calibrations

Calibrations previously generated for C- molasses were used to develop the intermediate product calibrations using OPUS QUANT (Bruker Optiks, Ettlingen, Germany). This software uses multivariate data analysis to combine a large amount of spectral information with the corresponding reference values. Partial least squares (PLS) regressions were used for generating calibrations. A calibration model was built using 50% calibration samples, and 50% of the test samples were used to validate the model. Cross validation was used to develop models when the number of samples was less than 300; spectra were added to the initial calibrations during the course of the seasons to make the models more robust.

Results

Clear Juice

The statistical results for over 300 clear juice samples showed excellent slope, correlation coefficient (RSQ) and standard error of predictions (SEP) between laboratory and NIR results for all analytes (Table 2). This calibration is a good example of the precision of NIR spectroscopy, especially where the sample solutions have minimal impurities. Clear juice samples require no sample preparation when scanned with NIR, and hence fundamental analytical errors are eliminated.

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Table 2. Summary of NIR spectroscopic predictions for clear juice.

Clear juice	Slope	RSQ	SEP (%)
Pol (°Z)	1.00	1.00	0.02
Brix (°Bx)	1.00	1.00	0.01
Fructose (%)	1.00	1.00	0.01
Glucose (%)	0.96	0.96	0.01
Sucrose (%)	1.00	1.00	0.07

SEP = standard error of prediction, RSQ = correlation coefficient squared

Syrup

The prediction data for syrup gave very good precision (SEP <0.13 units). The RSQ of 1.00 achieved for pol, Brix and sucrose were excellent. Figure 1 shows the comparison between the laboratory data and NIR predicted data for syrup pol, Brix and sucrose (SEP of 0.09%, 0.07% and 0.13%, respectively). The fructose and glucose achieved an RSQ of 0.94.

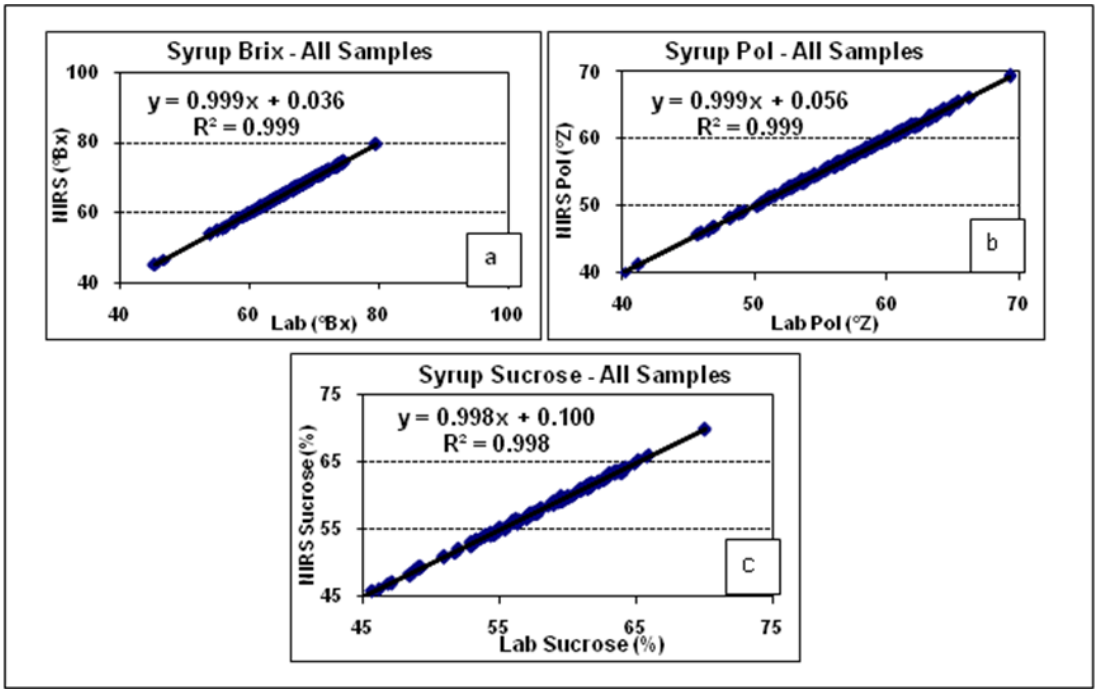

Figure 1. Conventional laboratory method and NIR correlation for syrup (a) Brix, (b) pol and (c) sucrose.

A-, B-, C-massecuite

The prediction data for A-, B- and C-massecuite presented in Table 4 shows the correlation between laboratory and NIR results for pol, Brix, fructose, glucose and sucrose. The massecuites showed good overall predictions (SEP 0.02% to 0.68%). With the exception of A-massecuite glucose and C-massecuite fructose, the massecuites illustrated excellent slope and correlation coefficient (RSQ) statistics for all components. RSQ results were acceptable (0.91 to 1.00). The NIR spectroscopic predictive capability was found to be adequate for factory control purposes. Although the SEP for A- and C-massecuite glucose and fructose is acceptable at 0.15 and 0.19 respectively, additional samples could to be taken to widen the range of analyte values and to improve the correlation between NIR and conventional laboratory testing.

A- and B-molasses

Table 4 presents the predictions for A- and B-molasses (RSQ 0.93 to 1.00). The high SEP of 1.55 for B-molasses pol is attributed to analytical errors in laboratory analyses associated with sample heterogeneity as some B-molasses samples contained crystals. The 95% confidence limits achieved by NIR for B-molasses pol was better (±0.94) than that achieved by the reference method (±0.97).

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Table 3. Summary of NIR prediction results for A-, B- and C-massecuites.

	Slope	RSQ	SEP (%)
A-massecuite			
Pol (°Z)	0.96	0.96	0.27
Brix (°Bx)	0.97	0.96	0.10
Fructose (%)	0.91	0.91	0.09
Glucose (%)	**0.80**	**0.80**	0.15
Sucrose (%)	0.93	0.93	0.68
B-massecuite			
Pol (°Z)	0.99	1.00	0.13
Brix (°Bx)	0.99	0.99	0.08
Fructose (%)	0.94	0.94	0.07
Glucose (%)	0.95	0.95	0.08
Sucrose (%)	0.95	0.95	0.56
C-massecuite			
Pol (°Z)	0.99	0.99	0.02
Brix (°Bx)	0.93	0.93	0.15
Fructose (%)	**0.76**	**0.76**	0.19
Glucose (%)	0.95	0.95	0.11
Sucrose (%)	0.97	0.97	0.29

Discussion

The benefits to the mill from NIR spectroscopy

Figure 2 is a schematic of a sugar process flow showing areas where rapid NIR spectroscopic predictions could be used. All products shown with a tick indicate where an NIR multi-component calibration could be used to predicate product values. Benefits are summarised as follows:

- Comparison across unit operations could be used for rapid purity profiles, inversion losses, exhaustions and purity rise predictions.
- Although fructose and glucose are two minor constituents of juices and syrup, process staff regularly examine fructose:glucose ratios before and after evaporators. Acquiring these results in minutes can quickly reveal potential inversion problems across evaporators.
- Massecuite analyses for exhaustion calculations would be rapid, enabling rapid monitoring of pans, crystallisers and centrifugals. Process managers would be able to make adjustments accordingly, rather than having to wait for the weekly figures.

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Table 4. Summary of NIR prediction results of A- and B-molasses.

	Slope	RSQ	SEP (%)
A-molasses			
Pol (°Z)	1.00	1.00	0.13
Brix (°Bx)	0.99	0.99	0.09
Fructose (%)	0.99	0.99	0.03
Glucose (%)	0.99	0.99	0.02
Sucrose (%)	0.98	0.98	0.33
B-molasses			
Pol (°Z)	0.93	0.93	1.55
Brix (°Bx)	1.00	1.00	0.09
Fructose (%)	0.98	0.98	0.05
Glucose (%)	0.98	0.98	0.08
Sucrose (%)	0.99	0.99	0.29

- Monosaccharide changes between mixed juice and final molasses may be examined, as part of the undetermined loss programme. For example, if a factory is experiencing a 2.5% undetermined loss, their objective would be to achieve the benchmark of 2%. By conducting the analyses mentioned above, they could identify sources of loss. For a 300 tons cane per hour factory, reducing undetermined losses by 0.5% would result in savings as follows:
  - 300 tcph ≈ 30t of sugar per hour;
  - 0.5% of 30 t = 0.15 t;
  - Assume 90% of saving is sugar;
  - Sugar saved = 0.135 t of sugar per hour = 3.24 t per day of sugar;
  - At R3000 per tonne this equates to savings of R9720 per day.
- Tracking glucose and fructose values across the boiling house could also reveal the occurrence of Maillard reaction *i.e.* where glucose is being destroyed.
- With the development of sucrose calibrations, factories could convert from pol to sucrose based performance/payment calculations without costly and complex GC or HPAEC analytical requirements.
- The SMRI analytical laboratory has experienced significant improvement in operational efficiencies following the implementation of routine molasses analysis by NIR spectroscopy in the 2009/2010 season and the development of calibrations for intermediate products will certainly add to the laboratory efficiency. With a complete set of intermediate product calibrations, factory process managers will benefit immensely from reliable data produced in a fraction of the time taken for conventional analysis.

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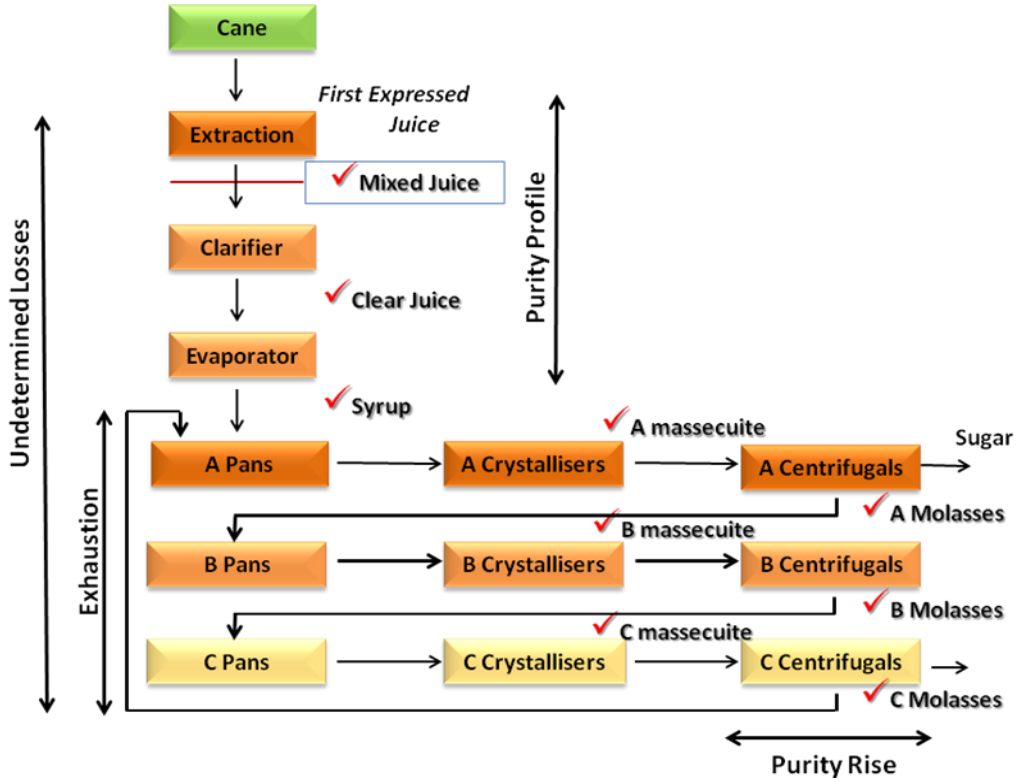

Figure 2. Schematic of a sugar process flow showing areas for rapid NIR spectroscopy predictions.

Conclusions

NIR spectroscopy is capable of providing an analytical prediction tool suitable for sugar factory process control. The method, compared with conventional analysis, would allow for a larger number of analyses and eliminate the need for hazardous chemicals. The availability of results in a fraction of the time by NIR spectroscopy would represent a significant change in the quality and the speed of information available from the sugar mill laboratory in order to make informed decisions concerning factory performance. The benefits to the mills as outlined suggest that this analytical tool will be incorporated into the mill laboratories within the Southern African Development Community (SADC) countries and will offer these mills a competitive advantage.

Acknowledgements

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