PROGRESS IN IMPROVING LABORATORY EFFICIENCIES USING NEAR INFRARED SPECTROSCOPY (NIRS)

By

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Abstract

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. Based on development work conducted by the SMRI, the use of NIR spectroscopy has been approved for the analysis of C molasses for both factory control and cane payment purposes and has resulted in considerable savings in analytical costs. Development work is ongoing and samples of clear juice, syrup, B, C massecuite and A, B molasses have been analysed by traditional methods for sucrose, pol and brix, and the results used to develop NIRS calibrations for rapid multi-component analysis. The precision of the NIRS predictions appears to be excellent, comparable to the laboratory method tolerances, and it is suggested that this technology can be used by relatively unskilled personnel in a factory environment to produce reliable data at relatively low cost.

Introduction

The major sugar companies of South Africa have been expanding their operations in the Southern African sugar industry. The laboratories of the Sugar Milling Research Institute (SMRI) provide analytical services to the region and, with increased demand, it has been appropriate to develop near infrared spectroscopy **(**NIRS) methods for the rapid multi-component analysis of intermediate factory products.

Much of the earlier work at the SMRI was reported by Schäffler and De Gaye (1997) and Schäffler (2005) and was based on work initiated at CSM Suiker (de Bruijn, 1997).

A Foss NIR Systems 5000 spectrometer was used to acquire spectra but was prone to bias jumps and required adjustment, updating the calibration dataset and standardisation as the instrument was aging.

In the 2007–2008 season, the SMRI purchased a Bruker Near Infra-red Spectrometer and interfaced this with a Metrohm 838 auto sampler. No calibration modification was required when a major component such as a source lamp was replaced unlike previous experiences by Schäffler (2000).

Calibrations were developed for molasses and mixed juice and the comparison with earlier work was reported by Simpson and Oxley (2008). The NIRS analysis of molasses has subsequently been adopted for cane payment purposes by the South African sugar industry.

The implementation of NIRS analysis for molasses at the SMRI has resulted in major time and cost savings.

This coupled with the desire to provide analysis for factory control purposes performed by relatively unskilled laboratory staff has extended the scope of calibration development to include additional intermediate products and this work is the subject of this paper.

Experimental

Instrumental: Near Infra Red Spectrometer (NIRS)

The NIRS system is comprised of a Bruker Multi-purpose Analyser (MPA) fitted with a Metrohm 838 autosampler. No temperature control unit was attached to the MPA. However, the NIRS 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. The NIRS software used for spectral processing and calibration creation was OPUS Version 6.

This included Opus Lab, which provided a simple interface with mouse-click operations for controlling automated NIRS analysis. This interface was used throughout for sample analysis.

Samples

The 2008–2009 season weekly composite samples of clear juice, syrup, B, C massecuite and A, B molasses were sent to the SMRI from five different geographically located Southern African sugar factories *viz*. Malalane (ML), Felixton (FX), Noodsberg (NB), Nakambala (NK), Umzimkulu (UK). These samples were analysed for sucrose, pol (lead clarified) and brix.

Handling of clear juice and syrup samples

Weekly factory composites of clear juice and syrup samples submitted to the SMRI were analysed by NIRS. Syrup samples were diluted at 50 grams to 200 grams of which 150 grams was lead clarified for pol and the remaining 50 grams was filtered for brix. A 5 gram portion of syrup was diluted to 30 grams and analysed by gas chromatography (GC) for sucrose.

In addition, an unfiltered portion of the clear juice composite was submitted to the NIRS laboratory. Syrup samples were diluted at 20 g to 100 cm^3 for NIRS analyses. Each sample was analysed in triplicate and a NIRS spectrum for each obtained using Opus Lab. The predicted results from the three spectra were averaged to give the final predicted NIRS results.

All laboratory results were generated using the Official Methods (Anon, 1985 and 2005). Pol was measured on the Schmidt & Haensch Universal Polartronic using the wavelength 589 nm and lead clarification (Anon., 2005: Method 1.7). Brix was measured by refractometry. Sucrose was determined by gas chromatography (silylation-only) method (Anon., 2005: Method 1.9).

Handling of B, C massecuite and A, B molasses

Weekly composite samples of B, C massecuite and A, B molasses samples submitted to the SMRI were manually homogenised and sub-sampled. A single sub-sample was used for all test methods and the NIRS sample preparation. The samples were clarified and filtered for pol and brix analyses (Anon., 1985).

The massecuite and molasses samples were diluted and tested for fructose, glucose and sucrose by high performance anion exchange chromatography (Anon., 2005: Method 6.6). B massecuite was diluted at 14.5 grams to 100 cm^3 and C massecuite was diluted at 14 grams to 100 cm^3.

Each prepared sample was analysed in triplicate and a NIRS spectrum was obtained for each. The predicted results from the three spectra were averaged to give the final predicted NIRS results.

A quality control procedure was set up using three molasses samples of established composition with each batch of samples tested.

These were used to monitor the NIRS performance on a weekly basis. All laboratory results were generated using SASTA approved test methods (Anon., 2005). Polartronic measurements were made using the wavelength 589 nm and lead clarification (Anon., 2005: Method 6.1).

Brix was measured by refractometry in all cases (Anon., 2005: Method 6.1). Sucrose was determined by high performance anion exchange chromatography (Anon., 2005: Method 6.6).

Calibrations

Calibrations for C molasses were done with Bruker's *OPUS QUANT* Software. 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 to draw up the calibrations.

A calibration model was built using 50% calibration samples and 50% of the test samples were used to validate the model. Where the number of samples was less than 300, the method of cross validation was used to develop the equations. Spectra were added to the initial calibrations during the course of the season to make the models more robust.

Results and discussion

The cross validation results for clear juice, syrup, B, C massecuite and A, B molasses, presented in Tables 2 to 7 (Appendix A) show the correlation between laboratory and NIRS results for pol, brix and sucrose.

The prediction data are summarised in Table 1. The data from Tables 2 to 7 are presented graphically for sucrose in Figures 1 to 6, and the regression lines, slopes and 95% certainty limits for the respective analyses are given.

The results for sucrose were chosen to illustrate data as NIR prediction results for HPLC and GC analytical techniques are often not easy to reproduce with the required accuracy for payment purposes. The prediction data for clear juice gave excellent precision results as all three analyses produced a SEP of better than 0.08 units.

Excellent precision results were achieved for syrup pol and brix (SEP of 0.14 and 0.11, respectively). The RSQ of 0.995 for sucrose was most acceptable. Most products showed good overall predictions (SEP 0.02 to 0.45).

The tables in Appendix B illustrate excellent slope, bias and correlation coefficient squared (RSQ) statistics for the three components.

RSQ results were most acceptable (0.91 to 1.00). Comparing the standard error of prediction (SEP) to the precision of the laboratory method is a measure of the NIRS predictive capability and in all cases was found to be adequate for factory control purposes.

Table 1—Prediction results for pol, brix and sucrose.

Product	Analyte		
	Pol	Brix	Sucrose
RSQ			
Clear juice	0.996	1.000	0.997
Syrup	0.998	0.998	0.995
A Molasses	0.990	0.950	0.985
B Molasses	0.937	0.991	0.985
B Massecuite	0.986	0.949	0.927
C Massecuite	0.989	0.910	0.952
SEP			
Clear juice	0.082	0.021	0.066
Syrup	0.139	0.112	0.214
A Molasses	0.225	0.220	0.323
B Molasses	1.249	0.225	0.308
B Massecuite	0.221	0.152	0.447
C Massecuite	0.170	0.170	0.288

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

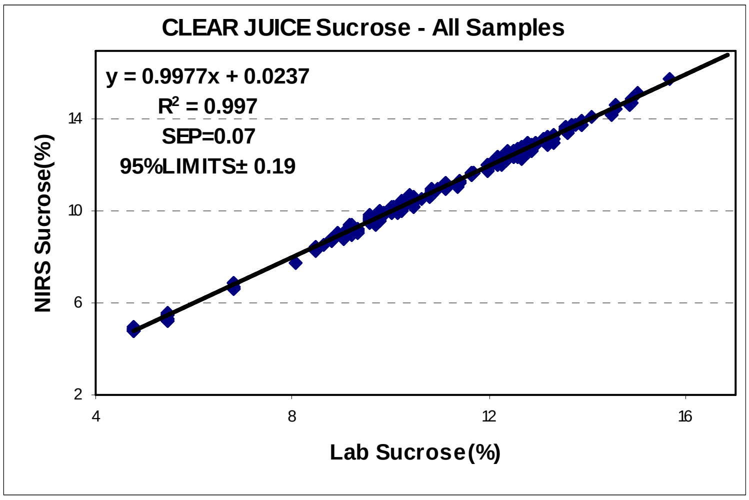

Fig. 1—Conventional laboratory method and NIRS correlation for sucrose in clear juice.

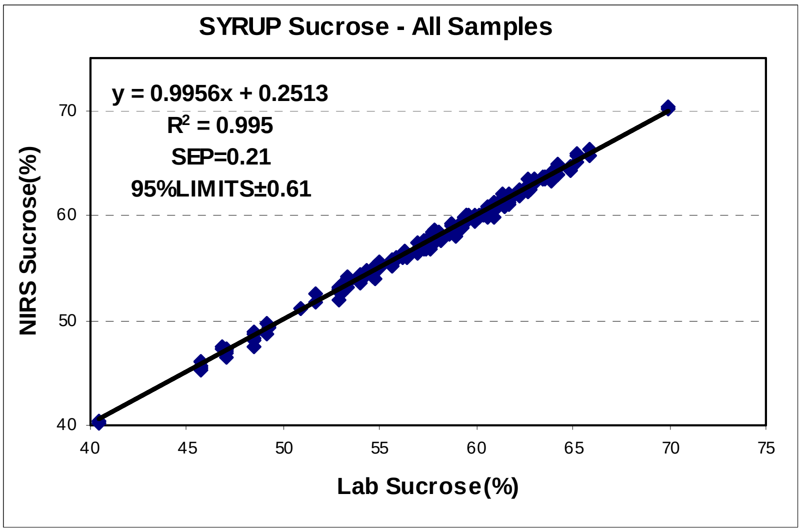

Fig. 2—Conventional laboratory method and NIRS correlation for sucrose in syrup.

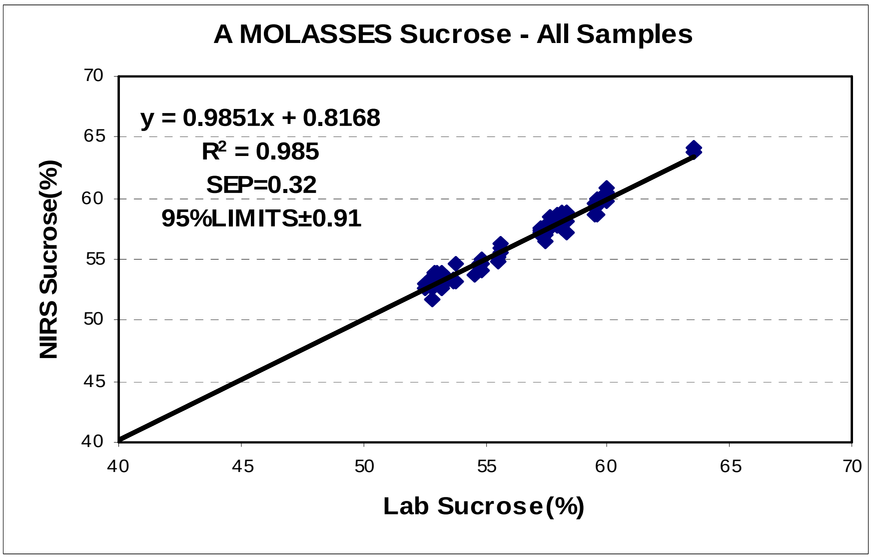

Fig. 3—Conventional laboratory method and NIRS correlation for sucrose in A molasses.

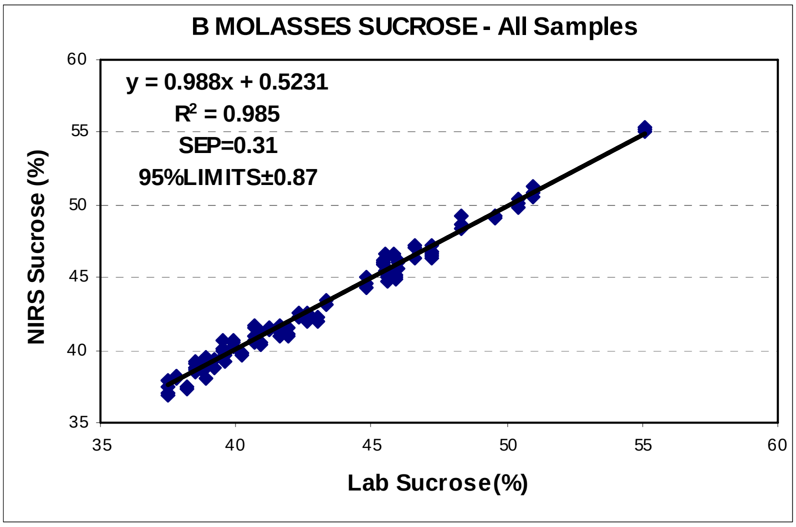

Fig. 4—Conventional laboratory method and NIRS correlation for sucrose in B molasses

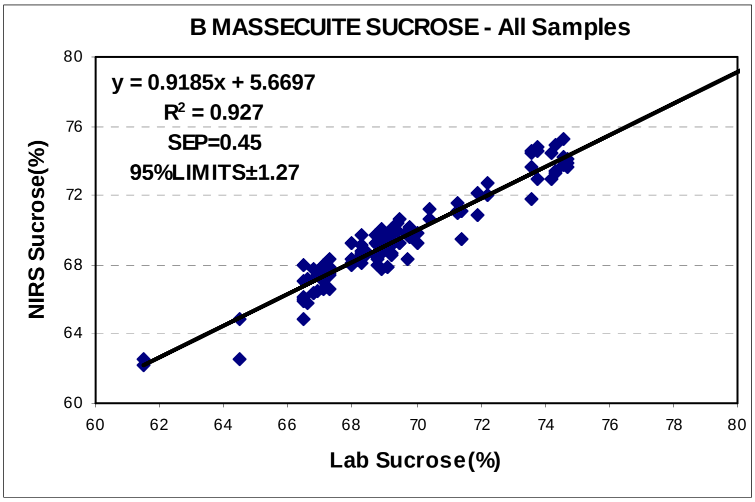

Fig. 5—Conventional laboratory method and NIRS correlation for sucrose in B massecuite.

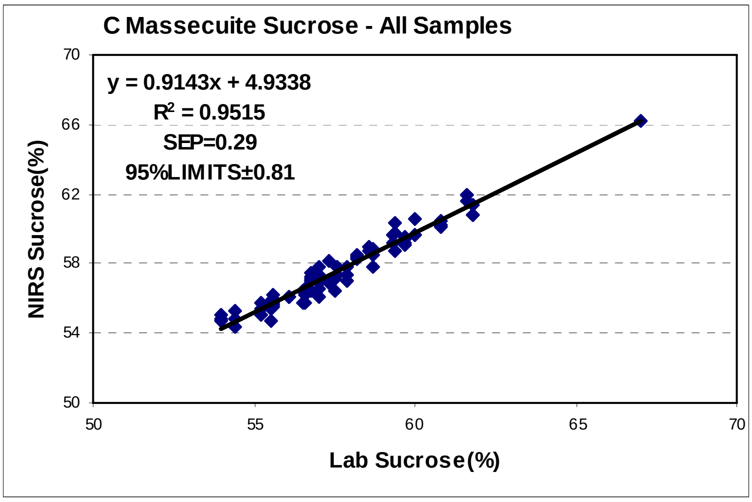

Fig.6—Conventional laboratory method and NIRS correlation for sucrose in C massecuite.

Future work

- Develop fructose and glucose calibrations for all intermediate factory products.
- Improve the A massecuite sample preparation to develop better correlations.
- Install the NIRS at a mill laboratory with the SMRI universal calibration. This equation would need to be adjusted for local conditions to avoid any bias and maintain the 95% confidence limits with weekly quality control checks. These checks would be based on samples with the conventionally established composition.
- Develop a proposal for implementing the NIRS in a factory laboratory for assessment on the economic impact and the potential for online use. Investigate a 'master-slave' relationship between the SMRI and the mills as an option to maintain and update calibrations.

Conclusions

The implementation of routine mixed juice and molasses analysis by NIRS is expected to reduce the time spent by the SMRI laboratory analysts by 80 percent *i.e.* from 128 hours per week to 24 hours per week and has already been implemented for final molasses at the SMRI. However, factory process managers will also benefit immensely from reliable data produced in a fraction of the time taken for conventional analysis. This work shows that calibrations can be developed for a number of intermediate factory products. The maintenance of the calibrations would require technically competent individuals but routine analysis could be done by relatively unskilled personnel. Due to the geographical location of the mill laboratories, the transportation of samples, particularly those that deteriorate is problematic and expensive. Provided that the mill laboratory has a NIR spectrophotometer, samples could be scanned and spectra sent to the SMRI for interpretation of the results, if technically competent staff are not initially available.

Results would then be returned to the mill laboratory via the internet. 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. It would also allow benchmarking based on sucrose for the entire region and not only the South African mills.

Acknowledgements

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Appendix A

Table 2—Clear juice pol, brix and sucrose correlations.

Clear juice			
	Pol	Brix	Sucrose
No. of samples	256	242	396
Slope	0.997	1.000	0.998
RSQ	0.996	1.000	0.997
Bias	0.000	0.000	0.002
Range	0.081	–0.088	–0.370
SEP	0.082	0.021	0.066

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

Table 3—Syrup pol, brix and sucrose correlations.

Syrup			
	Pol	Brix	Sucrose
No. of samples	295	313	229
Slope	0.998	0.999	0.996
RSQ	0.998	0.998	0.995
Bias	0.000	0.000	0.000
Range	–0.470	–0.050	–0.670
SEP	0.139	0.112	0.214

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

Table 4—A molasses pol, brix and sucrose correlations.

A molasses			
	Pol	Brix	Sucrose
No. of samples	298	300	79
Slope	0.988	0.954	0.985
RSQ	0.990	0.950	0.985
Bias	0.002	–0.002	0.009
Range	0.560	–1.090	–0.880
SEP	0.225	0.220	0.323

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

Table 5—B molasses pol, brix and sucrose correlations.

B molasses			
	Pol	Brix	Sucrose
No. of samples	294	293	116
Slope	0.937	0.992	0.988
RSQ	0.937	0.991	0.985
Bias	0.022	0.000	–0.007
Range	–4.770	–0.640	–0.950
SEP	1.249	0.225	0.308

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

Table 6—B Massecuite pol, brix and sucrose correlations.

B massecuite			
	Pol	Brix	Sucrose
No. of samples	289	293	110
Slope	0.987	0.934	0.919
RSQ	0.986	0.949	0.927
Bias	–0.002	–0.005	–0.008
Range	–0.120	0.190	3.470
SEP	0.221	0.152	0.447

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

Table 7—C massecuite pol, brix and sucrose correlations.

C massecuite			
	Pol	Brix	Sucrose
No. of samples	229	257	85
Slope	0.990	0.904	0.914
RSQ	0.989	0.910	0.952
Bias	0.000	0.001	0.014
Range	0.090	0.050	1.110
SEP	0.170	0.170	0.288

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

AMÉLIORATION DE L'EFFICACITÉ AU LABORATOIRE À L'AIDE DE LA SPECTROSCOPIE INFRAROUGE PROCHE (NIRS)

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MOTS-CLEFS: NIRS, Mélasse, Massecuites, Sirop, Jus Clarifie.

Résumé

LES LABORATOIRES du Sugar Milling Research Institute ont la responsabilité de maintenir et améliorer les normes du travail analytique au sein du SMRI et dans les industries sucrières du sud de l'Afrique. Un travail de développement mené par le SMRI a permit l'utilisation du NIRS pour l'analyse de la mélasse C pour le contrôle en usine et pour le paiement de la canne; ceci a donné des économies considérables dans les coûts d'analyse. Le travail de développement continu; des échantillons de jus clarifie, sirop, massecuites B et C, et mélasses A et B ont été analysés par les méthodes traditionnelles pour déterminer le saccharose, le pol et le Brix; les résultats ont étés utilisés pour développer des étalonnages pour le NIRS, donnant ainsi des analyses multiples rapidement. La précision des résultats du NIRS semble être excellente; elle est comparable à la précision des méthodes conventionnelles de laboratoire. On suggère que cette technologie peut servir pour un personnel relativement non qualifié dans un environnement d'usine, pour produire des résultats fiables à coût relativement faible.

PROGRESOS EN EL MEJORAMIENTO DE LAS EFICIENCIAS DE LABORATORIO CON EL USO DE ESPECTROSCOPÍA DE INFRAROJO CERCANO (NIRS)

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PALABRAS CLAVE: NIRS, Mieles, Masas Cocidas, Meladura, Jugo Clarificado.

Resumen

LOS LABORATORIOS del SMRI (Sugar Milling Research Institute) tienen la responsabilidad de mantener y mejorar los estándares del trabajo analítico dentro del Instituto y en toda la industria azucarera sudafricana. Con base en trabajo de desarrollo dirigido por el SMRI, el uso de espectroscopía NIR ha sido aprobado para el análisis de mieles C tanto para control fabril como para fines de pago de caña y ha generado considerables ahorros en costos de análisis. El trabajo continúa y muestras de jugo clarificado, meladura, masas B, C, y mieles A y B se han analizado con métodos tradicionales para sacarosa, pol y brix y los resultados se usaron para generar calibraciones de NIRS para análisis rápido multi-componente. La precisión de las predicciones del NIRS fue excelente, comparable a las tolerancias del método de laboratorio y sugirió que esta tecnología puede ser usada por personal relativamente inexperto en un ambiente fabril para producir datos confiables a un costo relativamente bajo.