SUGARCANE QUALITY ANALYSES BY NEAR INFRARED SPECTROSCOPY

LA EDYE AND MA CLARKE

Sugar Processing Research Institute, Inc., 1100 Robert E Lee Blvd, New Orleans, LA 70124, United States of America

Abstract

This presentation examines the use of near infrared (NIR) spectroscopic methods for the analysis of quality of the primary agricultural product of the cane sugar industry. The Louisiana sugarcane payment system is based on weight and on quality analysis of core samples from cane hauling bins. The conventional quality parameter of the Louisiana sugar industry, theoretical recoverable sugar (TRS), is calculated from the results of several analyses of the core samples (*viz.* sediment, refractometric dissolved solids and polarimetric sucrose in pressed juice, and moisture or fibre in the pressed cake of the cane sample). NIR calibrations have been developed for the prediction of individual core sample analyses (Brix, pol, sediment, and moisture), and for direct prediction of the calculated TRS value. In this study NIR spectroscopy has been used for direct prediction of TRS. Conventional analysis and NIR spectroscopic analysis of core samples for the past two sugarcane harvests are compared. The effect of cane preparation methods and sample presentation on NIR calibration development will be discussed.

Keywords:

Introduction

In Louisiana, the core/press method for cane quality analysis described by Legendre (1992) is an essential element of cane payment systems. In these systems, theoretical recoverable sugar or TRS is calculated empirically from the polarimetric sucrose, refractometric dissolved solids and sediment in expressed juice and the fibre content of a core sample of cane that is representative of the delivery. Similar core/press methods for cane quality analysis are utilised in many other cane growing regions (e.g. Brazil, Columbia, Trinidad and the Philippines). In general, cane payment systems based on quality, wherever they have been introduced, have been shown to effect an increase in the quality and sucrose yield in cane delivered to the factory. However, the core/press method and any other cane quality analysis based on extraction and analysis of juice and on analysis of residual fibre are labour intensive and also subject to sampling errors.

The obvious solution to random sampling errors is to obtain more samples so as to make the samples on average more representative. In Louisiana, at least, it is not feasible to increase the sampling rate of cane deliveries to the mill; most core labs operate efficiently but at maximum capacity. Neither is increasing the capacity of the core labs for analysis a solution since it would add significantly to the mill operating costs. Hence the development and adoption of a more rapid, less labour intensive cane quality measurement would be of great benefit to both the cane grower and the mill.

NIR multicomponent analyses of forage, fibre, grain and cereal are well documented (Williams and Norris, 1987; Murray and Hall, 1983). The possibility for application of NIR spectroscopy to cane quality measurement (for payment systems and for variety development) has prompted several feasibility studies on reflectance spectroscopy of finely chopped cane (Berding, *et al.*, 1991a, 1991b, 1994; Clarke, *et al.*, 1992, 1994; Edye, *et al.*, 1996; Anon, 1994-95; [1]personal communication). Berding *et al.* have concentrated on cane quality assessment for variety development using hand cleaned and finely chopped cane; the conventional analyses were performed in their own laboratory. These early studies used a scanning NIR instrument with a long light path that was affected by humidity variation. Clarke and Edye have concentrated on cane quality assessment for grower payment using cane samples and conventional analyses directly from a Louisiana core lab. Recently, the Sugar Milling Research Institute in South Africa has also taken an interest in NIR analysis (reflectance) of finely chopped cane for the prediction of DAC (direct analysis of cane; pol, Brix, moisture) analyses; their initial study on less than 200 samples without validation was encouraging (Anon, 1994-95) and further investigation of this NIR application will be reported at the 1996 South African Sugar Technologists' Association Congress. In the 1994-95 season the factory at Vale Do Rosario, Brazil, ran NIR parallel to core sample analysis systems (standard press method and hot water extraction) for NIR samples further shredded in a model shredder of South African design. The results were satisfactory and the factory now uses NIR analysis for cane payment ([1]personal communication). In general, similar success was reported for the NIR prediction of polarimetric sucrose and Brix in pressed or digested juice.

This report is concerned with the development of a NIR model for direct prediction of TRS, the calculated cane quality measurement upon which Louisiana grower payment systems are based. Over 3 000 samples have been collected at a single core laboratory (one factory) in the past three cane harvests. Each year cane preparation has been improved and the aims of the studies were more refined to obtain results that could be presented to growers and millers to convince them of the benefits of switching to an NIR based cane quality assessment system. Progress to this end forms the main body of this report.

Experimental – methods and materials

Direct NIR analysis of finely chopped cane

Core samples from cane deliveries to a Louisiana sugarcane mill were subsampled prior to pressing and conventional analysis (polarimetric sucrose, refractometric dissolved solids and sediment of expressed juice, moisture in residual fibre). The cane subsamples were further ground (Jeffco cutter grinder, Wiley mill or Fitzpatrick mill) to a finely chopped consistency and the NIR reflectance spectra (400-2 500 nm) of the finely chopped cane samples were obtained using an NIRSystems 6500 scanning spectrophotometer with a coarse cell and a sample transporter (Perstorp NIRSystems Ltd., Silver Spring, Md, USA). The conventional analyses of the core samples, the calculated TRS values and the NIR spectra were used to develop chemometric models for prediction (NSAS and ISI software, Perstorp NIRSystems Ltd.).

[1] H Amorim, Fermentec, Ltda, Piracicaba (1996)

Determination of standard error of conventional core lab analyses

On each of three days, three core samples from the same delivery (*ca.* one hour before shift change) were mixed by hand and separated into four 1 kg subsamples. The subsamples (replicates) were analysed by the usual procedures of the core lab; the first two replicates by the evening shift and the last two by the morning shift. The results of all conventional core lab analyses were normalised to mean values and the standard error calculated as the standard deviation (ó) of the variances or residuals of replicates from mean values; standard errors calculated in this manner are directly comparable with standard errors of NIR analyses.

Results and discussion

During the 1993 sugarcane harvest the NIR spectra of *ca.* 200 core samples from a single factory were obtained. In this study the core samples from the pre-breaker (Cameco Industries, Thibodaux, Louisiana) were scanned without further preparation, and the sampling did not cover the entire harvest. However, the NSAS calibrations for the prediction of pol, Brix, fibre and TRS resulting from this preliminary study and a study at a USDA variety development laboratory (Clarke *et al.*, 1994) were sufficiently promising to warrant a more thorough investigation of this NIR application.

A more thorough investigation (with some modifications) of cane quality analysis by NIR spectroscopy was made at the same factory the following year (1994 harvest). In this study the core sampler cane was ground to a finer consistency in a Jeffco cutter grinder and *ca.* 1 000 samples were obtained at random over the entire harvest. The ISI chemometric software was preferred to the NSAS software for development of the statistical model. The two chemometric software packages will return the same statistical results on the training set of data. However, ISI can identify residual outliers (large differences between lab and NIR results) and spectral outliers (spectra that are significantly different from those used in the training set), but NSAS can only identify residual outliers. Spectral outliers identified at acquisition by principal components analysis and nearness tests can result from any incorrect packing of the sample cell (e.g. air or too much field mud at the NIR cell surface) or year to year changes in cane varieties, or perhaps even changes in general weather conditions (e.g. cane from a year of severe drought followed by cane from a year of good rainfall). These spectral outliers affect the stability or robustness of the NIR calibrations and must be managed (either deleted and sample rerun or added to the training set prior to recalibration). Fundamentally, for the aforementioned reasons, ISI is more suited to the reflectance spectroscopic analysis of agricultural materials where the statistical models are complex and have no physical explanation.

The statistical results of calibration or model development for the 1994 harvest are summarised in Table 1. These results and the 1995 results are reported without the removal of any residual outliers form the data set; removal of even 2 to 5% of residual outliers significantly improves the statistical results. The results from the determination of the standard error of conventional core lab analyses also are shown in Table 1. The pressed juice pol and Brix results are comparable with those that have since been obtained by other investigators and will not be further discussed, since this report is primarily concerned with the direct prediction of TRS by NIR spectroscopy. The calibration results are illustrated in Figure 1 (for comparison with the results of the following year). The standard error for NIR prediction of TRS was comparable with laboratory standard error, and the NIR analysis was well able to differentiate cane quality over the entire range of TRS values.

Table 1a

PLS calibration statistical summary

Constituent	Mean	R	Std E	MSECV
Pol	67,43	0,94	2,00	2,10
Brix	20,46	0,95	0,58	0,70
TRS	219,31	0,84	13,31	13,62

Table 1b

Summary of statistical data from the determination of core lab error

	Moisture	Pol	Brix	Sediment	TRS	CRS
Mean (x_{all})	49,75	65,9	19,7	0,013	201,22	181,09
Range (R_{norm})	12,7	6,5	1,9	0,047	37,14	33,42
Std. dev. (ó)	3,37	1,75	0,63	0,0118	10,91	9,81

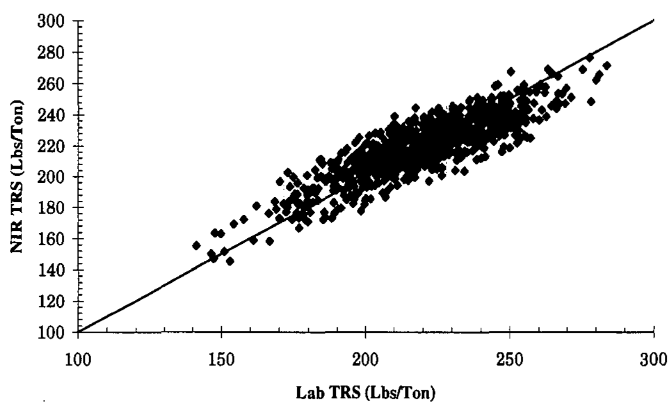

FIGURE 1

Since the 1994 harvest results were very encouraging the scope of the NIR study was expanded for the 1995 harvest. Rather than collect core samples at random for NIR analysis, initially eight growers (of varying size of production and varying historical cane quality) were selected to participate in the NIR study in order to determine whether a switch to NIR would affect individual grower payments. A Wiley mill was substituted for the Jeffco cutter grinder to improve cane preparation. For logistical reasons, after 14 days of sampling, the grower participant number had to be reduced to six and a more efficient Fitzpatrick mill was substituted for the Wiley mill.

By the end of the 1995 harvest over 2 000 NIR spectra had been obtained; the statistical results from a calibration model based on these spectra and the conventional determinations of TRS are shown in Table 2. The calibration results are graphically represented in Figure 2 (for comparison with the results of the previous year). A cursory comparison of statistical results from 1994 and 1995 harvests suggests that the 1995 outcome was not as good as that of 1994. In 1994 the NIR spectra were obtained in a somewhat timely manner by SPRI personnel and by a factory employee. In 1995 all spectra were obtained by a single factory employee and, on those occasions when the employee was called to other duties, some core samples sat at room temperature for up to two hours before NIR analysis. Significant cane deterioration and sucrose loss can occur in this time. This unfortunate circumstance would appear to explain the poorer results from the 1995 harvest.

Table 2

Comparison of calibration statistics for 1994 and 1995 harvests

Calibration	1994	1995
Mean (lab)	219	204
δ (lab)	22,3	28,6
Range (lab)	144-284	99-295
Standard error (lab)	10,91	n.a.
Spectral pretreatment	2,10,10,1	2,6,6,1
Correlation coeficient	0,70	0,68
SECV	12,33	15,97
SEP	13,62	18,75 (94 - 20,64)

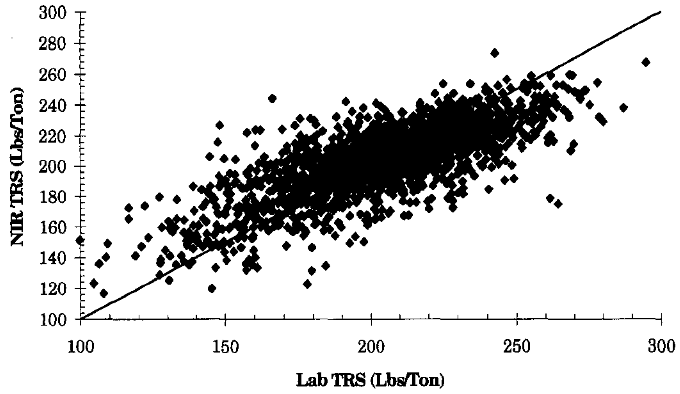

FIGURE 2

A more thorough investigation of the 1994 and 1995 data bases reveals that the results may in fact be very similar. The distributions of TRS residuals (lab TRS – NIR TRS) for 1994 and 1995 are shown in Figure 3; this is a representation of the standard error of prediction values and shows a broader distribution (and greater differences between NIR and lab results) of residuals for 1995. However, the range of conventionally determined TRS values also increased from 1994 to 1995 (see Figure 4) and, when the residuals are expressed as a fraction of the range of core lab TRS values, there is little difference between the two years. This conclusion could be supported by a comparison of results from the determination of standard error of conventional core lab analyses for the two years, but the analysis was not undertaken in 1995.

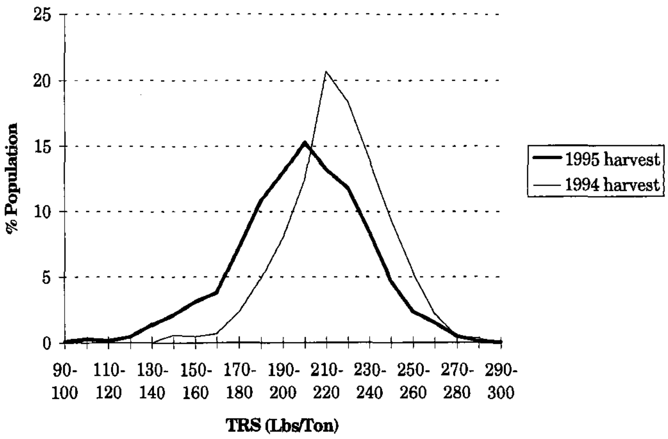

FIGURE 4

Certainly, the comparison of conventional TRS results for the two years leaves some doubt about the accuracy and precision of the TRS measurement and appears to place a limit on the best possible outcome of NIR statistical modeling of this data. However, the regression process for generating a NIR calibration model will, with a sufficient number of samples, automatically average out most of the random error in the lab values but incorporate any systematic lab error. The residuals in the validation step (from which the standard error of prediction is obtained) are apparent validation errors and are the sum of errors in the lab values and inherent errors (or appropriateness) of the model. Therefore, it is possible for NIR predictions to outperform conventional analyses. However, if the validation set has similar errors to the calibration set, the hypothesis that NIR predictions outperform conventional analyses can never be tested or confirmed (DiFoggio, 1995). Therefore, the TRS calibration from a large training set with an apparently large standard error of prediction may be more reliable for measuring cane quality than the conventional core lab, but it cannot be proven by validation using only conventional core lab results.

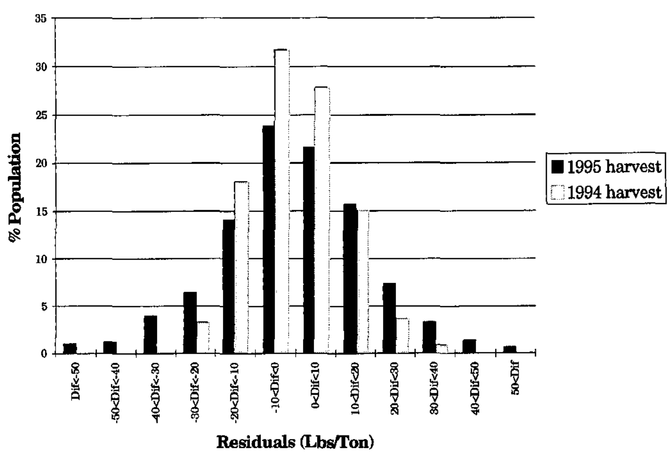

FIGURE 3

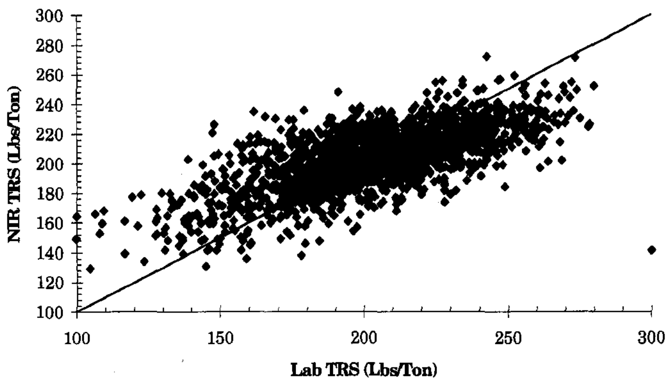

FIGURE 5

Perhaps the most convincing argument for the superiority of the NIR method over the conventional method for cane quality or TRS measurement is that the NIR calibration for 1994 and 1995 were similar; both were PLS calibration models based on second derivative spectra (the 1994 calibration used more smoothing, i.e. fewer data points than the 1995 calibration) and the weightings and loadings were similar. This is a remarkable outcome since the cane preparation changed from 1994 to 1995, and since the lag prior to NIR analysis was variable in 1995. In fact the 1994 calibration can reasonably predict the 1995 TRS values (see Figure 5 and compare with Figures 1 and 2) even though the cane preparation changed.

Conclusion

A major contributor to the seemingly less than satisfactory agreement between NIR and conventional core lab TRS values is the error in the conventional method. The NIR method appears to be more precise than the conventional analysis, and it is certainly clear that NIR analysis is a valid assessment of cane quality.

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