

RAPID ANALYSIS OF SUGAR PRODUCTS BY NEAR INFRA RED SPECTROSCOPY

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Abstract

The NIRSystems 6500 spectrophotometer has been used to study analytes in bagasse, shredded cane, direct analysis of cane extracts (DAC), mixed juice, molasses and raw sugar. Analytes included pol, brix, dry solids, moisture, sucrose, glucose, fructose, invert, ethanol, colour, ash and starch. Although Near Infra Red (NIR) is a secondary technique, relying on conventional laboratory procedures for calibration, the indirect technique was able to produce a surprisingly good estimate for many of the analytes tested. The results suggest that NIR could not replace conventional procedures where high accuracy is required (e.g. cane payment, factory balances and raw sugar sales). NIR is however able to produce results for multicomponents extremely rapidly and precisely, and therefore does appear to have a role to play in monitoring field and factory environments. Statistical comparisons between laboratory results and NIR are given for all analytes tested. NIR estimates for analytes in shredded cane and mixed juice from the 6500 spectrophotometer are

compared with those obtained from a filter instrument. Possible applications for NIR are also suggested.

Introduction

Absorbances in the NIR (800 to 2 500 nm) are due to overtones and combinations from fundamental vibrations in the infrared region (2 500 to 25 000 nm). As these NIR absorptions are much weaker and broader than those in the infrared, they are not much use for structural identification of organic molecules. The energy source for NIR is highly intense, and this coupled to extremely low noise detectors, make NIR an ideal quantitative technique. As the NIR region consists of many overlapping peaks, the technique is empirical. NIR is a secondary technique, dependent on laboratory methods to develop calibration equations for each analyte. The procedure depends heavily on statistics and regression analyses to produce a prediction for each constituent from the spectral data, and from the relevant cali-

Table 1
Overview of recent literature dealing with the use of NIR for sugarbeet and sugarcane products

Source	Application	Analytes	Instrument	Type
Ames <i>et al.</i> , 1989	Cane raws	P, M, RS, ash, Col, % fines	Bran & Luebbe 500	Scanning
Berding <i>et al.</i> , 1989	Shredded cane & juice	Bx, Cond, fibre, moisture, pol	Bran & Luebbe 450	Filter
Burzawa <i>et al.</i> , 1991	Beet juices, syrups & molasses	Bx, pol	On line, Bran & Luebbe 450	Filter
Clarke <i>et al.</i> , 1992a	Cane juice	Pol, Bx, Purity	NIRS model 6500	Scanning
Clarke <i>et al.</i> , 1992b	Cane juice	Pol, bx, purity	NIRS model 6500	Scanning
	Bagasse	Moisture, pol	NIRS model 6500	Scanning
	Beet juices	Pol, Bx	NIRS model 6500	Scanning
Dumoulin <i>et al.</i> , 1987	Beet molasses	Ethanol, total sugars	Bran & Luebbe 450	Filter
Edye <i>et al.</i> , 1992	Cane raws	Dextran, starch, invert, colour	NIRS model 6500	Scanning
Jones <i>et al.</i> , 1991	Thick juice & green syrup	Moisture, purity	On line, NIRS model 5500	Scanning
Meyer and Wood, 1988	Shredded cane & mixed juice	Pol, Bx, S, G, F	Bran & Luebbe 450	Filter
Nguyen and Player, 1990	Cane raws	Pol, Water, RS, ash, % fines	Bran & Luebbe 500	Scanning
	Soft brown sugar	Sucrose, moisture, RS, ash	Bran & Luebbe 500	Scanning
	Mill and refinery molasses	Total sugars, S, M, RS, ash, FY	Bran & Luebbe 500	Scanning
Stevens, 1988	Powdered and agglomerated sugars	Starch, moisture, invert	Dickey-john Instalab 610 (10 filters)	Filter
Vaccari <i>et al.</i> , 1987	Brei, raw/thick juice, molasses	Pol, Bx	Bran & Luebbe 450	Filter
Vaccari and Mantovani, 1988	Brei, raw/thick juice, molasses	Pol, Bx	Bran & Luebbe 450	Filter
Vaccari and Mantovani, 1989a	Cane raws	Moisture	Bran & Luebbe 450	Filter
Vaccari <i>et al.</i> , 1989b	Beet	Dry substance	Bran & Luebbe 450	Filter
Vaccari <i>et al.</i> , 1990	Raw/thin/thick - beet juices	Pol, Bx & nitrogen	On line, Bran & Luebbe 600	Filter
Vaccari <i>et al.</i> , 1992	Fermentation broth	Glucose, lactic acid, biomass	On line, Bran & Luebbe 600	Filter

Key: P=pol, M=moisture, Col=colour, Cond=conductivity ash, Bx=brix, S=sucrose, G=glucose, F=fructose, RS=reducing sugars, FY=fermentation yield

bration equations. It is unlikely that NIR, in its present form, could be used to replace a laboratory method where extreme accuracy is required. There are however many applications where a rapid, unbiased result is more important than high accuracy. NIR can produce results for several analytes extremely rapidly, as sample preparation is often unnecessary. The sample can be present in either solid or liquid form. Quick results that are available on demand may, in certain instances, be more valuable to process personnel than accurate results that take hours or days to produce.

More and more reports describing the use of NIR spectroscopy for the analysis of constituents in sugar juices, factory intermediates and final products are appearing in the literature. Attempts to present an overview of recent and relevant NIR contributions to the sugar industry are shown in Table 1.

Scanning spectrophotometers are a relatively recent development for NIR analyses. Most of the earlier work with sugarcane was carried out on filter-based instruments (Meyer and Wood, 1988; Berding *et al.*, 1989). Several papers have claimed that scanning instruments, with their higher resolution, improved sample presentation and sophisticated chemometric software are capable of producing NIR estimates of greater accuracy than those derived from filter instruments (Anon, 1990, Clarke *et al.*, 1992a,b). This paper compares the results obtained from both filter and scanning spectrophotometers, for cane quality components in cane and mixed juice.

A NIRSystems 6500 instrument was evaluated for the determination of several analytes in a variety of sugar products. These are outlined in Table 2.

Table 2

Products and individual constituents analysed by conventional laboratory procedures and by NIR

Analyte	Bagasse	Cane	MJ	DAC	Molasses	Raws
Pol	Yes	Yes	Yes		Yes	Yes
Brix	Yes	Yes	Yes	Yes	Yes	
Dry solids					Yes	
Moisture	Yes	Yes				Yes
Sucrose			Yes		Yes	
Fructose			Yes		Yes	
Glucose			Yes		Yes	
Invert						Yes
Colour						Yes
Ash					Yes	Yes
Starch						Yes
Ethanol				Yes		

Experimental procedure

Bagasse

The NIRSystems 6500 spectrophotometer was installed in the mill laboratory at Maidstone, as moisture in bagasse is clearly susceptible to analytical and transport delays. Having the spectrophotometer on site made it possible for samples of bagasse to be taken from the factory floor whenever the analyst required a fresh sample. Duplicates of 72 samples of bagasse were placed in the special coarse sample holder.

This holder provides approximately 60 cm² of sampling area, reducing variations from sample packing and sample heterogeneity. In order to reduce sampling errors still further, each sample was scanned for one minute, using the reflectance mode, resulting in each spectrum consisting of approximately 30 scans. Each sample replicate was scanned from 400 to 2 500 nm, resulting in a total of 144 spectra. These were converted to their second derivatives before calibration.

Shredded cane

The experimental conditions were virtually identical to those for bagasse. Duplicates of 56 samples of shredded cane were compared with the conventional laboratory procedures. Thirty-five and 37 samples, respectively, were used in the comparison between the NIRS 6500 and the Bran & Luebbe filter-based instrument.

Mixed juice (MJ)

Mixed juice samples (35) were used for the calibration. Duplicate sub-samples were scanned twice, producing a total of 140 spectra. The narrow 1 mm cuvette was used with the 6500 in the transmission mode. Thirty-five and 90 samples, respectively, were used in the comparison between the NIRS 6500 and the Bran & Luebbe filter-based instrument.

DAC extract

DAC extracts (35) were used for the calibration. Duplicate sub-samples were scanned twice, producing a total of 140 spectra. The narrow 1 mm cuvette was used with the 6500 in the transmission mode.

Molasses

Molasses samples (40) were used for the calibration. Duplicate sub-samples were scanned twice, producing a total of 160 spectra. The large 30 mm cuvette was used with the 6500 in the reflectance mode.

Raw sugar

Samples of raw sugar (40) were scanned from 400 to 2 500 nm using the standard sampling cup with the 6500 in the reflectance mode.

Results and Discussion

Evaluating the NIR calibrations

It is common in NIR work to obtain a calibration equation using about 20-30 samples. This is then tested by scanning additional samples and comparing the NIR results with those obtained from traditional analyses. This approach could not be adopted for the current study as the NIRSystems instrument was available for only a short period. It has been observed however that the standard error of prediction (SEP) is often not significantly greater than the standard errors derived from the calibration (SEC) alone. A single set of calibrations obtained for mixed juice was used to predict pol and brix in first expressed juice samples.

Bagasse

(a) Pol

From the second derivative spectra (Figure 1A) it can be seen that there is a strong band for sucrose (C-H combinations) at 2 250 nm. A standard regression (S Regr) indicated a strong correlation between pol and absorption at 2 250 nm. Results are summarised in Table 3A.

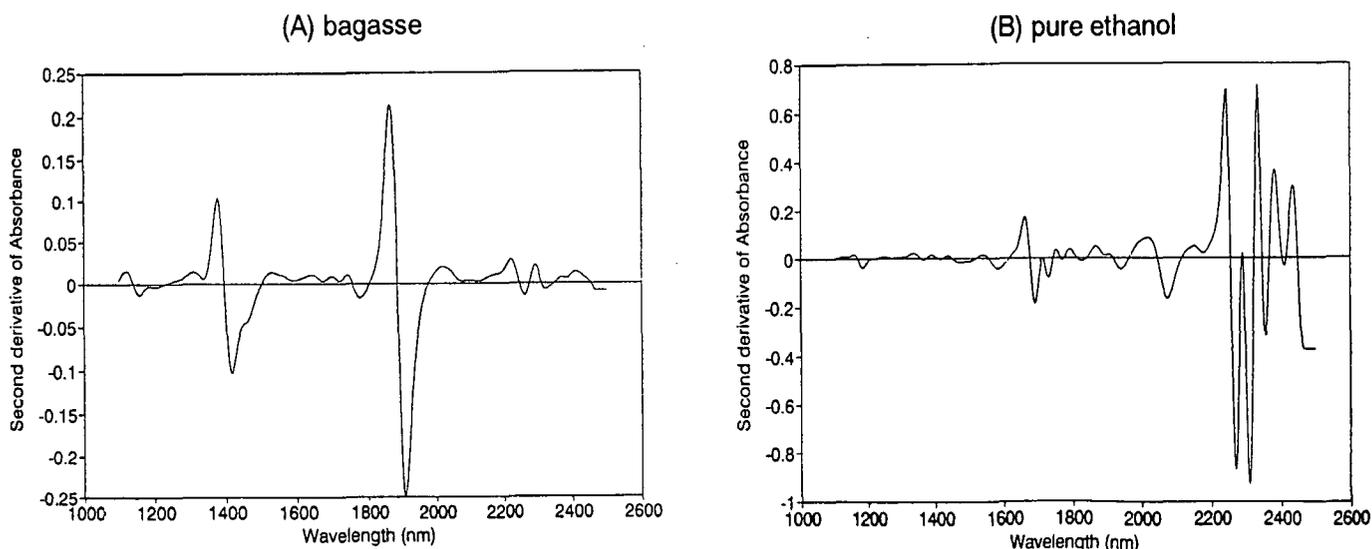


FIGURE 1 Second derivative NIR spectra.

Table 3

Comparison between laboratory data and NIR for pol, brix and moisture using simple regression and PLS in bagasse and shredded cane

(A) Bagasse

Analyte	Range	SD lab	Calibration method	Wavelength or factors	R	SEC	SD NIR replicates
Pol	0,25 to 1,39	0,09 ¹	S regr PLS	2250 nm 11	0,84 0,96	0,17 0,09	0,02
Brix	0,77 to 2,39	0,45 ¹	S regr PLS	2278 nm 13	0,84 0,97	0,25 0,11	
Water	50,9 to 65,0	0,90 ¹ 0,82 ²	S regr PLS	2274 nm 7	0,68 0,84	1,94 1,49	0,17

1 = Rein and Lamusse (1973). 2 = Excell and Koenig (1983).

(B) Shredded cane

Analyte	Range	SD lab	Calibration method	Wave-length	R	SEC
Pol	10,4 to 17,7	0,13 ¹	S regr PLS	2282 nm 11	0,96 0,97	0,43 0,42
Brix	14,1 to 21,1	0,15 ¹	S regr PLS	2280/2306 13	0,93 0,98	0,42 0,24
Water	62,4 to 74,2	0,39 ¹	S regr PLS	2224/952 8	0,88 0,93	0,86 0,81

1 = Brokensha (1990)

Pol in bagasse ranged from 0,3 to 1,4. A standard error of 0,17 may seem high, but this result is marginally better than the results obtained by Clarke *et al.* (1992b) for a smaller sample set (SE = 0,22, R=0,64, N=15). An improved correlation was obtained by carrying out a partial least squares regression (PLS) using 11 factors (Table 3A). The standard error obtained by PLS was identical to the precision obtained by polarimetry. The 95% confidence limits for pol in bagasse are therefore $\pm 1,96 \times 0,09 = \pm 0,18$.

(b) Brix

When the Near Infra Red Spectral Analysis Software (NSAS) was allowed to find the best correlation between brix as measured by refractometry and absorbance, a wavelength of 2 278 nm (C-H combinations), was selected (correlation

coefficient = 0,84). This is similar to the calibration found for pol (both pol and brix approximate sucrose for high purity products). Clarke *et al.* (1992a) added an additional wavelength at 1 428 nm (O-H, water) to improve the correlation. In this work, the standard error and correlation coefficient did not improve when this wavelength was incorporated. Again a partial least squares procedure yielded the best results (Table 3A). A comparison between brix and NIR using PLS yielded a SE of 0,11 and a correlation coefficient of 0,97. The relationship between the two is shown graphically in Figure 2A. The 95% confidence limits for brix in bagasse are therefore $\pm 1,96 \times 0,11 = \pm 0,22$.

(c) Moisture

Water produces absorptions at 1 900-2 000 nm (O-H, combinations), at 1 400-1 450 nm (OH, overtones), at 960-970 nm (O-H, second overtone) and at 745-755 nm (O-H, third overtone). Some of these absorption bands can be seen in the second derivative spectra for bagasse (Figure 1). However, no meaningful correlation could be found between moisture by oven-drying and any of these wavelengths. A possible reason for this anomaly could be the extremely high moisture level. The 6500's detector had probably reached saturation and was unable to distinguish between high (50%) and very high (65%) moisture levels. A reasonable but indirect correlation was obtained between the laboratory value and NIR at 2 274 nm (SE=1,94 and correlation coefficient = 0,68). The best results were once again obtained using PLS (Table 3A). The 95% confidence limits for moisture in bagasse are therefore $\pm 1,96 \times 1,49 = \pm 3,0$. The standard deviation of the laboratory method for moisture was found to be 0,82. Although the NIR standard error is virtually double the SD of the laboratory method, NIR has definite potential, especially for high throughput rapid analyses.

Cane

Calibration data for pol, brix and moisture in shredded cane were carried out using both simple regression and PLS. The results are summarised in Table 3B. The relationships between NIR and moisture in cane are shown graphically in Figure 2B.

In general, PLS produced a better correlation coefficient and a lower standard error than simple regression. However the calculation time for PLS ($\pm 35-70$ minutes) is hardly worth the effort as the differences are marginal. For analytes at reasonably high concentrations, simple regression is ob-

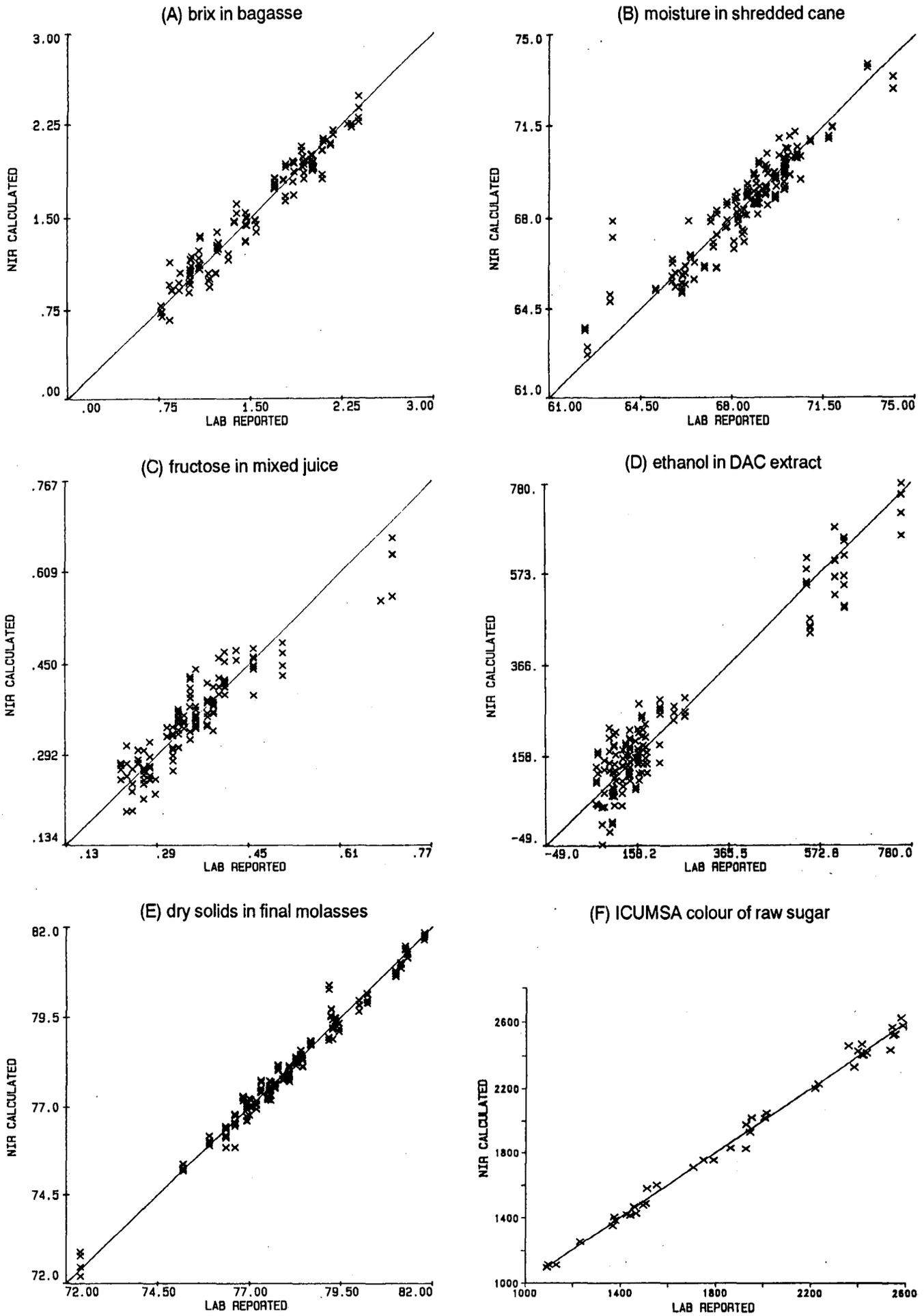


FIGURE 2 Using PLS, comparison between NIR and lab data.

viously adequate. The SEC for all three components is significantly higher than the SD of the laboratory procedures. It is obvious from the data that the use of NIR for cane payment is unrealistic. The method could however have application for evaluating trends and producing rapid routine results.

A comparison of the calibration performance of the NIRS 6500 and the Bran & Luebbe filter-based instrument (450) for measuring cane quality components of shredded cane are included in Table 4A. The main point of interest arising from this comparison, was that the NIRS 6500 produced results that were marginally better than the filter-based instrument.

Table 4
Comparison between the performance of scanning and filter NIR instruments

(A) for analysing shredded cane

Analyte	NIRS 6500			Bran & Luebbe 450		
	Wave-length	R	SEC	Wave-length	R	SEC
Bx % cane	1434 2082	0,90	0,45	2348 2270 1818 1759	0,88	0,47
Pol % cane	1198 2282	0,92	0,52	2270 1818 1778 1759	0,86	0,55
Purity % cane	2244 2140	0,87	2,06	2270 2138 1818	0,89	3,90
Dry matter % cane	2224	0,93	0,82	2270 2208 2180 2100	0,92	0,86
Fibre % cane	1838 1376	0,96	0,41	2336 2270 2208	0,87	0,69

(B) for analysing mixed juice

Analyte	NIRS 6500			Bran & Luebbe 450		
	Wave-length	R	SEC	Wave-length	R	SEC
Brix	1366 2160	0,99	0,15	2310 2270 2230 2180	0,97	0,35
Pol	2274	0,98	0,25	2348 2270 2208	0,98	0,32
Sucrose	2322	0,97	0,29	2310 2270 2230	0,97	0,31
Glucose	2342	0,77	0,05	2340 2310 2230	0,51	0,09
Fructose	2292	0,75	0,05	2348 2310 2230	0,54	0,07

Mixed juice

Calibration data for fructose, glucose, sucrose, pol, brix and sulphated ash in mixed juice were carried out using the standard regression and PLS options. The results are summarised in Table 5A.

Table 5

Relationship between laboratory data and NIR for fructose, glucose, sucrose, pol and brix

(A) Mixed juice

Analyte	Range	SD lab	Calibration method	Wavelength or factors	R	SE	SD NIR
Fructose	0,2 to 0,7	0,005 ¹	S regr	2342 2256 2294	0,81	0,06	0,03
			PLS	15	0,97	0,03	
Glucose	0,2 to 0,9	0,005 ¹	S regr	2342 2408 972	0,83	0,02	
			PLS	15	0,97	0,04	
Sucrose	9,7 to 13,9	0,02 ¹	S regr	2282 1708	0,97	0,27	0,05
			PLS	12	0,97	0,29	
Pol	9,5 to 13,8	0,004 ²	S regr PLS	2284 12	0,97 0,97	0,28 0,29	0,18
Brix	11,8 to 15,7	0,006 ²	S regr PLS	2270 10	0,97 0,97	0,25 0,28	0,07
Ash	0,4 to 0,6		PLS	7	0,77	0,05	

1 = Schäffler and Morel du Boil (1984). 2 = *Brokensha (personal communication)

*MA Brokensha, Manager, SASA Cane Testing Service

(B) Final molasses

Analyte	Range	SD lab	Calibration method	Wavelength or factor	R	SEC	SD NIR
Fructose	6,3 to 12,4	0,12 ¹	S regr	1230 nm	0,86	0,81	0,35
			PLS	14	0,97	0,41	
Glucose	2,4 to 13,9	0,09 ¹	S regr	1230 nm	0,87	1,33	0,52
			PLS	15	0,98	0,51	
Sucrose	26,6 to 33,0	0,10 ¹	S regr	1702 nm	0,75	1,1	0,4
			PLS	14	0,92	0,66	
Pol	22,9 to 32,3	0,14 ²	S regr	1704 nm	0,69	1,52	0,63
			PLS	14	0,91	0,90	
Brix	76,7 to 86,5	0,31 ²	S regr	1272 nm	0,87	0,95	0,43
			PLS	15	0,99	0,24	
Dry solids	72,4 to 81,8	0,18 ²	S regr	1268 nm	0,90	0,81	0,49
			PLS	14	0,99	0,29	
Ash	9,7 to 15,7	0,11 ²	S regr	1986 nm	0,69	1,00	0,48
			PLS	14	0,92	0,58	

1 = Schäffler and Morel du Boil (1984), 2 = Mellet *et al.* (1982).

Compared with sucrose, the two monosaccharides are relatively minor constituents in mixed juice. Their minimum and maximum concentrations range from 0,2 to 0,9%. Sucrose, on the other hand, has a low of 9,72% and a high of 13,9%. All three sugars absorb at similar wavelengths and, bearing in mind that these absorption bands are broad, it is not surprising that the correlation coefficients for the two monosaccharides, using only three wavelengths, were not as good as those obtained for sucrose. A PLS regression improved the correlations considerably (Figure 2C).

A standard error of 0,1 to 0,3 may still be too high for projects which demand a high accuracy (cane payment, factory losses). NIR may however be useful for rapidly screening juices to assess cane quality or in variety trials. An excellent correlation was obtained for sucrose in mixed juice and, as the purity of mixed juice is relatively high, good correlations were also obtained for pol and brix. Based on

these preliminary data, NIR could conceivably be used for routine mixed juice purity monitoring.

The NIRS was also compared with the Bran & Luebbe 450 for mixed juice analysis. A summary of the comparison can be found in Table 4B. The main points of interest were:

- Very similar results were obtained for pol, brix and sucrose.
- The 6500 produced superior results for the minor sugars with only a single wavelength being used, and produced even better results when the PLS procedure was used (Table 5A).

The calibrations produced by the 6500 for mixed juice were used to estimate pol and brix in 24 first expressed juice samples. Acceptable correlations were obtained for pol ($R^2 = 0,93$) and brix ($R^2 = 0,92$).

However, the SEP was almost three to five times higher than the SEC obtained for mixed juice. These results highlight the fact that the spectra of mixed juice and first expressed juice are not necessarily identical. Improved SEP will be obtained only with calibrations using first expressed juice.

Although sulphated ash is totally inorganic and should not produce absorptions in the NIR, several investigators have claimed a 'BLACK BOX' correlation for inorganic analyses. A standard regression between ash and NIR yielded poor results (SEC = 0,06 and R = 0,49). A PLS regression improved the agreement (SEC = 0,05 and R = 0,77).

DAC extract

Individual cane consignments from growers are tested by the direct analysis of cane procedure. Recently these extracts have been used to estimate the delays between cutting and crushing the cane. Ethanol is measured by GC to estimate the sucrose losses incurred from bacterial infection (Lionnet and Pillay, 1987; de Robillard *et al.*, 1990; Cox and Sahadeo, 1992). Ethanol levels in deteriorated DAC juices rise to significant levels (2 000-10 000 ppm on brix). Although ethanol analysis by GC is both simple and rapid, NIR is even faster. As the NIRSystems 6500 instrument was available it was decided to test the instrument's sensitivity, as most of the other analyses (brix, pol, sucrose and moisture) were not in the ppm range.

(a) Brix

A comparison between brix and NIR was carried out as the ethanol results are normally reported on a brix rather than on a sample basis. The brix/NIR comparison could also act as a control in the event of questionable or outlying ethanol results. A standard regression using a single wavelength (2 276 nm) produced a standard error of 0,18 and a correlation coefficient of 0,89. The standard deviation of NIR replicates was 0,07. These results are very similar to the results obtained for mixed juice.

(b) Ethanol

A second derivative spectrum of pure ethanol showed weak absorption at 1 690 and 2 074 nm. There were strong absorptions at 2 272, 2 308 and 2 354 nm (Figure 1B).

A PLS regression, however, produced the best results. A standard error of 60 ppm was obtained with a multiple correlation coefficient of 0,96. An ethanol by GC versus NIR comparison is included in Figure 2D. It is obvious that NIR lacks the sensitivity of GC (pooled standard deviation of replicates about the mean = 5 ppm, Schäffler, 1993). Scatter is also high (± 60 -100 ppm). However, NIR could possibly be used to distinguish between low and high levels of ethanol.

Improved ethanol results could be expected if the calibration data were more evenly distributed (Figure 2D). In this case, NIR would produce a qualitative rather than a quantitative indication of cane deterioration.

Molasses

As final molasses is one of the output streams of a raw sugar factory, considerable effort was made to establish correlations between individual constituents and NIR. Both simple and PLS regressions were carried out for fructose, glucose, sucrose, pol, brix, dry solids and sulphated ash. The relevant correlations are shown in Table 5B.

In general, simple regression produced disappointing results. Correlation coefficients were usually less than 0,9 (range 0,69-0,90). SECs were also disappointing, being 3-15 times larger than the standard deviations for the laboratory analyses. This is in contrast to the mixed juice estimates. The lower purity of final molasses is probably responsible for the weaker NIR associations. PLS produced far better results where 14-15 factors were used for each calibration. Excellent correlations were obtained when the PLS technique was used (range 0,91-0,99). SECs were also much improved. NIR results for brix and dry solids in particular were excellent, with SECs very close to laboratory standard deviations; see Figure 2E for the dry solids/NIR comparison.

Pol by NIR was disappointing (SEC = 0,90). However, this analysis is severely affected by changing monosaccharide composition, and the poor results are perhaps not unexpected. The relatively good results for sulphated ash were also surprising, as ash is an inorganic component. The improved calibration for ash in molasses compared with that obtained for mixed juice could possibly be due to the concentration effect across the boiling house.

From the results obtained, it is clear that NIR could be a useful tool for carrying out trend analyses (e.g. monitoring molasses feedstock prior to fermentation; hourly or daily checks on molasses exhaustion; the comparison of different vacuum pans or crystallisers, etc.). An hourly analysis of all seven constituents could be carried out in about 10 minutes.

Raw sugar

For raw sugar analyses, the special spinning sampler cup was used. This module rotates the sample for diffuse reflectance measurements and produces a sample averaging effect. This averaging improves sampling precision and compensates for particle size variations. The quality of the NIR estimates for pol, moisture, reducing sugars, starch and conductivity ash are presented in Table 6.

It can be seen that acceptable correlations were obtained for all six analytes. The standard error for estimating pol was somewhat disappointing at almost five times greater than the SD for determining pol in sugar. It is obvious that NIR could not be used for raw sugar sales. The standard errors for the other five components, on the other hand, were very similar to the precision of the laboratory methods. The NIR results for colour were particularly pleasing. A graphical comparison between colour and NIR is shown in Figure 2F. It is obvious from Table 6 that NIR can produce a vast amount of analytical information in a matter of minutes.

Costs

Compared with the older filter-based NIR instruments, the NIRSystems 6500 is not cheap. Current capital outlay is about R250 000. However, the 6500 uses a grating monochromator to provide excellent spectral resolution (2 nm),

Table 6

Calibration of NIR for the analyses of pol, moisture, reducing sugars, colour, starch and conductivity ash

Analyte	Range	SD of lab	Calibration method	Wavelength or factors	Correlation coefficient	Std error of calibration
Pol	97,6 to 99,6	0,02	S regr	2308 1946 nm	0,99	0,09
Moisture	0,06 to 0,46	0,02	S regr	1902 nm	0,98	0,03
Red. sugars	0,09 to 1,05	0,02	PLS	11	0,98	0,03
Colour	1090 to 2600	35	PLS	12	0,99	40
Starch (ppm)	50 to 262	9	PLS	11	0,97	13
Cond. ash	0,09 to 0,33	0,01	PLS	14	0,98	0,02

and the entire spectrum from 400 to 2 500 nm can be scanned in less than 2 seconds. The drift is reduced still further by internal referencing and scanning each sample about 30 times. The use of either the coarse sampler or the spinning cup reduces sampling errors from particle size variations. This feature was used by Jones *et al.* (1991) to monitor water and sugar contents on-line, using a fibre optic bundle to connect the system to the sample stream. To reduce noise from aeration, 320 scans were taken for each data sample.

The NSAS software also employs a sophisticated partial least squares method that uses all the information in the spectrum. Filter-based instruments cannot provide this sort of additional information. Although the filter instruments produced results comparable to the 6500, the latter came into its own when analytes of low concentration in complex mixtures were determined. Acceptable NIR estimates were obtained for fructose and glucose in mixed juice and molasses as well as colour, ash and starch in raw sugar.

It must also be remembered that the combined costs of a polarimeter, refractometer, liquid chromatograph and many other laboratory instruments and peripherals far outweigh the cost of a single NIR. It is not inconceivable that eventually a central facility (e.g. Sugar Milling Research Institute (SMRI) or South African Sugar Association Experiment Station (SASEX)) could provide mill and other laboratories with the necessary calibration data for multi-component analyses. Cheaper filter instruments could be used for routine process monitoring. This implies that routine monitoring by conventional procedures would not be necessary. The savings in man-hours and the increase in reliability would however need further investigation. Possibly the area that needs the greatest attention is the role of physical and chemical characteristics of each product on the robustness and stability of calibration curves; geographical and seasonal variations are expected to produce the biggest problems in calibration validity. The range of each analyte, the number of samples and the frequency of quality control checks all need careful attention.

Conclusions

- (a) Although excellent correlations were obtained between laboratory determinations and NIR, the standard errors were generally too large for applications where high accuracy is required (e.g. cane payment and raw sugar sales).
- (b) The procedure produces results for multicomponents extremely rapidly. For example, pol, moisture, invert, colour, starch and ash in raw sugar could all be obtained in about 10 minutes.
- (c) For routine factory control (e.g. bagasse moistures, MJ purity, molasses brix and sugar colour) NIR has definite potential.
- (d) Sample pre-treatment is not normally required. Bagasse and shredded cane can be analysed without extraction. Molasses is analysed without any dilution. Raw sugar is not dissolved prior to analysis.
- (e) The partial least squares procedure generally produced better calibrations than simple regressions. This is especially true for low purity products (e.g. final molasses). It must be pointed out that, although calibration using the PLS procedure is time-consuming, subsequent estimates using the PLS-based calibrations are rapid.
- (f) Due to the high moisture contents of bagasse and cane, NIR predictions of moisture were determined indirectly from C-H type absorptions and not from O-H type absorptions, as the NIR detector appeared to be saturated at these high moisture levels.
- (g) Ethanol in DAC extracts does not appear to be viable. The low ethanol concentrations produced high scatter. This was considered to be due to the low sensitivity of NIR when compared with GC. NIR could probably be used to give a qualitative rather than a quantitative estimate of cane deterioration.
- (h) Although the 6500 produced results that were marginally better than the Bran & Luebbe 450 for cane quality components, the values obtained on the two instruments were remarkably similar for most of these components. The 6500 did however produce better correlations and lower standard errors for fructose and glucose.
- (i) NIR, using the partial least squares technique, produced useful information for all major sugars in molasses. The correlation diagrams indicated little or no bias in the NIR estimates, implying that provided enough samples are taken, NIR should provide reasonable estimates for these analytes.
- (j) As the test period was limited, further testing of NIR should be carried out, to determine the long term quality of the NIR calibrations.
- (k) Once accurate calibrations have been obtained for the different factory streams, NIR should be run in tandem with conventional analyses in order to determine long term reliability.
- (l) As the NIRSystems instrument is rather expensive, parallel tests with available filter instruments should be carried out to compare the results from both types of instruments.

- (m) New developments in optical fibre and diode technology will be closely watched. Potential applications include continuous on-line monitoring of raw sugar quality and *in situ* sucrose testing in plant breeding selection programmes using portable NIR analysers.
- (n) SMRI and SASEX should draw up a programme of work, which should clearly identify areas where NIR will have the greatest benefit.

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