

EVALUATION OF A NEAR INFRARED SPECTROMETER FOR THE DIRECT ANALYSIS OF SUGAR CANE

L.R. Madsen II, B.E. White, and P.W. Rein

Audubon Sugar Institute
Louisiana State University Agricultural Center
Baton Rouge, LA 70803

ABSTRACT

A FOSS InfraCana Near Infrared (NIR) spectrometer was installed at a Louisiana mill for the 2001/02 crushing season to assess its suitability for direct analysis of cane delivered to the mill. Analysis of cane by both wet disintegration and core press methods were used as the primary measurements. Calibration equations for pol, brix, fiber, moisture and ash in cane were produced. Values of standard error were excellent, and the prospects for the use of such an instrument for the accurate direct analysis of cane look promising.

INTRODUCTION

Currently, the core-press method (CPM) of analysis is used in Louisiana for determination of sugar cane quality. The results of these determinations are used to calculate the theoretical recoverable sugar (TRS), in lbs sugar per ton of cane. TRS is used to determine how much a given grower will be paid for a consignment of cane. Methods similar to core press are currently used in many other cane-growing regions such as Colombia, Trinidad, and the Philippines (Edye and Clark, 1996). Core press analysis requires a team of at least three analysts per shift, for two eight-hour shifts. The time required for sample turn-around is roughly four hours. Since this method is intensive both in terms of time and labor, sampling every load is impossible. Usually, moisture % residue figures are not finally generated until the end of the shift; this means that the nature of the cane is not known until well after it has entered the mill. The goal of this investigation is to improve the quality of cane analysis whilst decreasing overall seasonal cost.

The cost of cane analysis consists of personnel, supplies, and utilities. Supply costs include Octapol and/or ABC juice clarifier, glassware, and utilities. Loss of profit can result from inaccuracies in cane quality data and losses caused by mill stoppage. Increased rate of sampling and quicker analysis would not only result in a greater likelihood of achieving representative sampling, but may decrease down times caused by foreign material entering the mill. While examining new methodology, modern technology and high-speed computing has rendered near infrared reflectance spectroscopy (NIRS) worthy of inspection. The InfraCana uses large samples (5 to 15kg) so that sub-sampling for increased precision is unnecessary (Berding and Brotherton, 1996). It is necessary to point out that NIR spectroscopy and chemometrics can provide a result that is only as good as the data put into it. When calibrated using quality data, these new

instruments promise high-speed, increased analytical precision, and long-term net savings. These savings would directly improve profitability for both the farmers and the mills.

NIR technology has been validated for quality control use in a wide variety of industries, including forage, fiber, grain, and cereal. FOSS provided a prototype InfraCana NIRS system to the Audubon Sugar Institute, which was installed at Cinclare mill in Louisiana for the 2001-02 crushing season. The instrument was calibrated using data acquired via Direct Analysis of Cane (DAC), as specified in the International Commission for Uniform Methods of Sugar Analysis (ICUMSA 1994). The DAC results were compared to results achieved using the core press method. The NIRS was calibrated for pol, brix, fiber, moisture, ash % cane, and TRS using the WinISI (Infrasoft) Chemometrics software package. The results of this calibration equation were subject to cross validation between laboratory results and the NIRS predicted values. The results of this cross-validation were key in the evaluation of the instrument as an alternative to CPM for purposes of cane payment.

MATERIALS AND METHODS

The NIRS



Figure 1. InfraCana Near Infrared Spectrometer.

The NIRS consists of four major components (Figure 1). The first, the sample conveyor, transfers a core sample evenly into the second component, the Jeffco Shredder. The fibrated sample is fed into component three, the read conveyor. Here, a cane-leveling device packs the cane into an even bed on a moving conveyor. When the cane bed is homogenous, infrared cane-height sensors tell the read head of the spectrometer to open, and to begin data acquisition. The average sample weighing 10kg will usually yield 60 total spectral replicates. Spectral scans are taken from 1100-2500nm until the cane height sensors indicate heterogeneity within the cane bed. The shutter on the read window snaps shut, a result “docket” is printed, and the fibrated cane is conveyed out of the instrument.

Acquisition of Laboratory Data

Samples of billeted cane were acquired using an inclined coring machine. A core sample consists of billets up to twelve centimeters in length, a sample weighing between five and twelve kilograms. Two core samples per truck were taken. One core sample was fibrated using the existing hydraulic shredder. The material prepared this way has approximately 65% open-cells, and is referred to as Core Shredded Material (CSM) (Figure 2). This sample was subject to analysis via CPM. The second sample was shredded using the Jeffco shredder built into the NIRS. Material thus prepared has approximately 95% open-cells; it is referred to as Jeffco Shredded Material (JSM) (Figure 3). This sample was automatically transferred to a second conveyor where the NIR spectra were observed, and the data were saved to hard drive. The sample was conveyed out of the instrument, where it was collected and subject to DAC.



Figure 2. Core Shredded Material.



Figure 3. Jeffco Shredded Material.

Sample Analysis

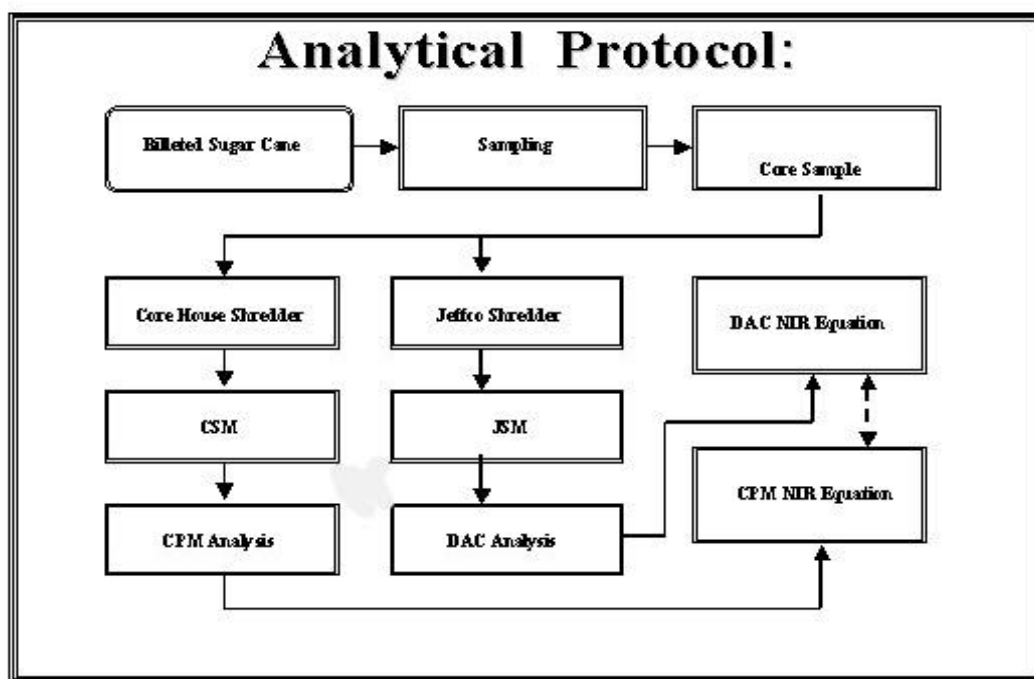


Figure 4. Flowchart of Analytical Protocol.

A flowchart describing analytical operations is included (Figure 4). A one-kilogram sample of JSM was weighed into a water-jacketed wet disintegrator pot. To this was added two kilograms of water. This deviation from ICUMSA DAC was necessary as Jeffco shredded material tends to absorb extraction water forming a sticky ball that does not macerate well; our wet disintegrator pot would not hold 6L. The sample was disintegrated for eight minutes at 7200 rpm. A 10g sample of the resulting extract was transferred into a 15mL conical centrifuge tube. This sample was centrifuged at 4000 rpm for ten minutes and analyzed for brix by refractometer. 100ppm Sodium azide was added as a preservative and sample was frozen. A 150mL sample of the extract was transferred into a glass jar. To the 150mL sample was added 19 grams of Octapol flocculent. The sample was shaken then filtered, whilst discarding the first 25mL of filtrate. The clarified filtrate was analyzed for polarimetric sucrose using an automatic saccharimeter. The frozen sample was taken back to the lab for sugar analysis (sucrose, glucose, and fructose) by HPLC. 500 grams of JSM were dried to constant weight, not to exceed -2g in 30 minutes (ICUMSA), at 105°C using a Deitert Moisture Teller forced draught air drier. The sample, once dried to constant weight, was placed into a plastic bag for storage and transport.

The results were used to calculate pol, brix, fiber, and moisture % cane. These figures were used to calculate TRS.

After the season, the stored dry matter was subjected to analysis for carbonated ash. All samples were analyzed in duplicate. The sample was placed into a tared dish, and a screen was placed over the top. The sample was incinerated at 650°C for 45 minutes. The sample was removed from the furnace, and allowed to cool to ~150°C. The screen was removed, and the dish containing the ash was weighed. The sample was carefully stirred and further incinerated at

650°C for ten minutes. The sample was removed from the furnace and allowed to cool. The sample was weighed, and transferred into a plastic bag for storage.

These data were used to calculate ash % cane. This number was subtracted from the fiber % cane to produce a figure for corrected fiber % cane.

The results from the core press analysis were provided by the mill administration. The given data provide pol and brix % juice, residue weight (from 1.0kg), and volumetric sediment. From these data were calculated pol, brix, fiber, and moisture % cane. These figures were used to calculate the TRS.

Calibrating the NIRS

Both of the data sets were entered into the WinISI software package. Here, the spectral results were matched to the laboratory data. Constituents for pol, brix, fiber, moisture % cane, and TRS were entered. The first derivatives of the spectral data were taken, and it was to these that the laboratory data is assigned. The data sets were regressed using a modified Partial Least Squares (PLS) algorithm. “Outliers” with a Global H value (distance from the global average) of more than three were re-evaluated. If the outlier was determined to result from anomalous spectral data, it was removed from the data set. For each constituent an equation was generated, and standard error of calibration (SEC) was calculated.

Ash % cane exhibits a logarithmic trend. To generate an equation that is not heavily biased by the average, this constituent was calibrated using the \log_{10} of the laboratory data. The instrument then predicts ash % cane as a logarithm. The anti-log is taken, and the result subsequently produced. SEC and r^2 are produced for the \log_{10} result.

The equations were used to evaluate a sample of the spectra. Here, lab results were compared with the NIR predicted values. This cross-validation is the final verification needed to determine if the equation produces representative predictions. The standard error of cross-validation (SECV) was used to determine the equation accuracy.

RESULTS

Laboratory results for DAC and CPM compared well. However, the pol % cane for CPM was always higher than that for DAC, as seen in Figure 5. This was attributed to extraction efficiency. DAC analysis used added water and provided more complete extraction. Fiber % cane for CPM values were, on average, between 10 and 17%. The DAC results displayed unusual spikes, ranging from 20 to 45%, as seen in Figure 6. Fiber % cane is a figure derived by difference from moisture and brix. As a result, any component other than water or brix will be seen as fiber % cane. Other components can include mud and/or trash. The spikes seen in the DAC-derived fiber % cane reflected the presence of mud, trash, or both.

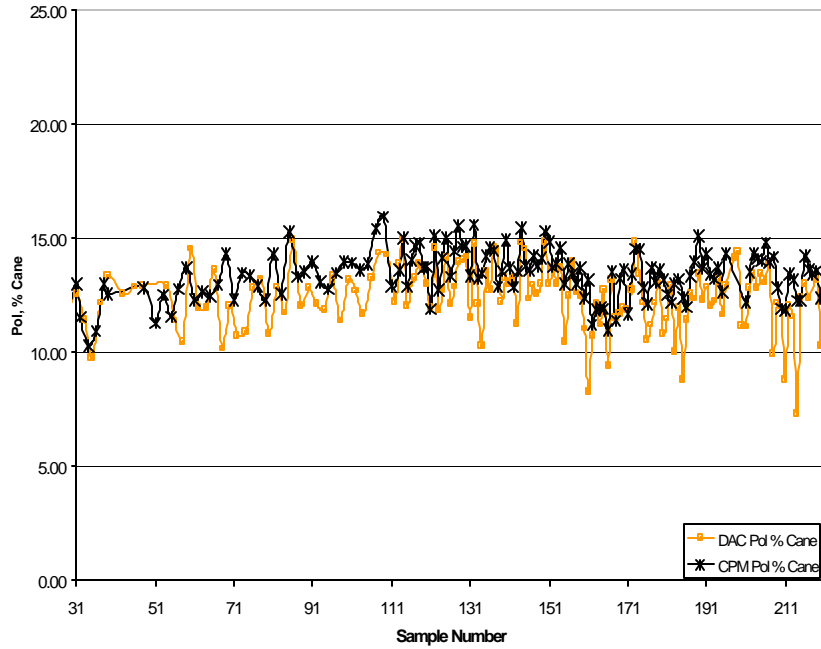


Figure 5. Pol % Cane, by core press method and by DAC. Arranged by parallel sample number.

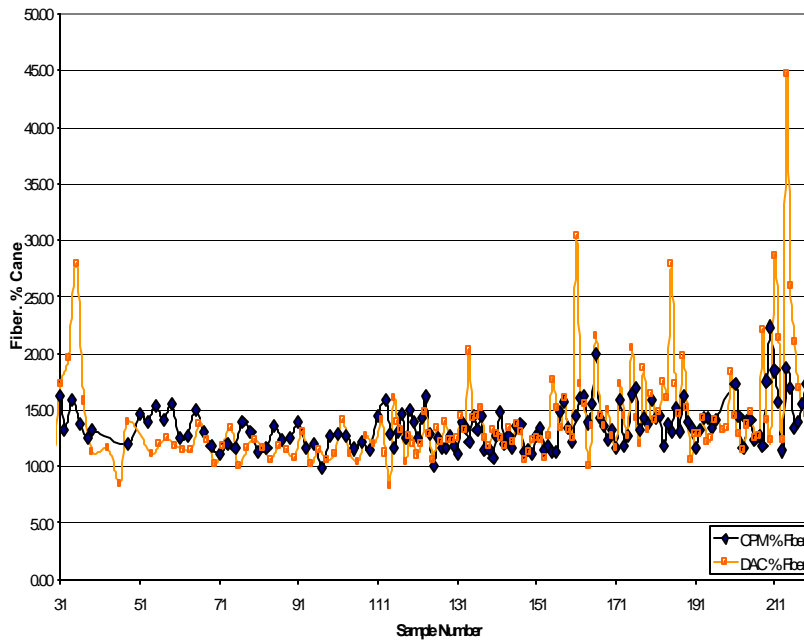


Figure 6. Fiber % Cane, by core press method and by DAC. Arranged by parallel sample number.

After calibration, the software calculated the standard error of calibration (SEC), and the square of the linear correlation coefficient r^2 (RSQ). The standard error of cross validation (SECV) refers to the compound error relating the differences between actual and predicted results. The constituent results for the calibration derived from DAC (Table 1) and CPM (Table 2) data sets demonstrated the effects of non-representative sampling. Both sets were based on the same spectra. Although laboratory data correlates reasonably well, SEC and RSQ demonstrate that the CPM results do not correlate well to the spectra.

The statistics for the DAC based NIR equation closely paralleled those found in literature (Table 3). A comparison of DAC results for SECV is given in Table 4.

The samples that were frozen were analyzed by HPLC for sucrose, glucose, and fructose. The results did not correlate with the pol sucrose. This effect was attributed to a lack of biocidal (NaN_3 , 100ppm) efficacy; the samples biologically degraded during processing, storage and transport.

Table 1. NIR equation based upon DAC analytical data. N is the number of samples used, SEC is the standard error of calibration, RSQ is the linear correlation coefficient, SECV is the standard error on cross validation; 1-VR relates to the correlation on population variance.

Constituent	N	Mean	SEC	RSQ	SECV	1-VR
Pol% Cane	180	12.90	0.237	0.961	0.325	0.927
Brix% Cane	183	15.44	0.246	0.966	0.427	0.898
Moisture% Cane	170	71.49	0.489	0.912	0.592	0.870
Fiber% Cane	171	12.91	0.518	0.901	0.699	0.818
CRFiber% Cane	170	11.17	0.411	0.907	0.488	0.869
Logash% Cane	185	0.228	0.082	0.870	0.099	0.811
TRS	173	216.7	5.31	0.948	7.14	0.905

Table 2. NIR equation based upon CPM analytical data.

Constituent	N	Mean	SEC	RSQ	SECV	1-VR
Pol % Cane	194	13.16	0.507	0.648	0.579	0.545
Brix % Cane	182	15.66	0.379	0.793	0.431	0.733
Fiber % Cane	171	16.74	0.844	0.777	0.908	0.743
% Moisture	186	71.19	0.872	0.604	0.933	0.546
TRS	192	215.7	11.51	0.526	12.50	0.442

Table 3. Results for DAC derived NIR equation and the average literature values (Bentley, Staunton, Atherton, and Henderson, 2001; Berding and Brotherton, 1999; Edye and Clarke, 1996; Larrahondo, Palau, Navarrete, and Ramirez; Johnson, 2000; Schaffler, Staunton, Lethbridge, Grimley, Streamer, Rogers, and Mackintosh, 1999)

Constituent	N		SEC		RSQ	
	Our work	From Literature	Our work	From Literature	Our work	From Literature
Pol % Cane	180	970	0.24	0.14-0.44	0.96	0.94-0.99
Brix % Cane	183	985	0.25	0.25-0.44	0.97	0.95-0.99
Fiber % Cane	171	745	0.52	0.52-0.56	0.90	0.87
% Moisture	170	622	0.49	0.57	0.91	0.92-0.95
Ash% Cane	185	1340	n/a	0.44	0.87	0.78
TRS	173	n/a	5.31	13.13	0.95	0.84

Table 4. Results for DAC derived NIR equation and the average literature value of SECV.

Constituent	N		SECV	
	Our work	From Literature	Our work	From Literature
Pol % Cane	180	970	0.33	0.18-2.10
Brix % Cane	183	985	0.43	0.25-0.70
Fiber % Cane	171	745	0.70	n/a
% Moisture	170	622	n/a	n/a
Ash% Cane	185	1340	n/a	0.50
TRS	173	n/a	7.14	13.62

DISCUSSION

As seen in Tables 1 and 2, NIR equations calibrated on DAC and CPM analytical data sets agreed poorly. We believe that this results from the sample-to-sample variation that occurs between two different core samples taken from the same load. The inclined core sampler was designed for use with whole cane, whereby a 23kg sample may be achieved. When this method is used for billets, the cutting head scatters some of the cane, while achieving a sample of only 5-15kg. The small sample size resulted in increased sample heterogeneity; in effect, the DAC and CPM analyses were performed on two different samples, albeit from the same truckload. NIRS is fast enough to compensate for small sample sizes by analyzing a larger number of samples.

For each constituent, a range of cited values was given; see Tables 3 and 4. When compared, the DAC derived SEC, RSQ, and SECV for each constituent were within the ranges seen in the literature. The DAC % of IIT refers to the result of our calibration relative to the

average of the cited range for a particular constituent. Based upon analysis of these figures, the DAC based NIR equation performed at least as well as the literature cited. The SECV achieved for DAC calibrations were within the ranges found in the literature. These equations provided accurate as well as precise predictions relative to the laboratory results, as seen in Figures 7- 9.

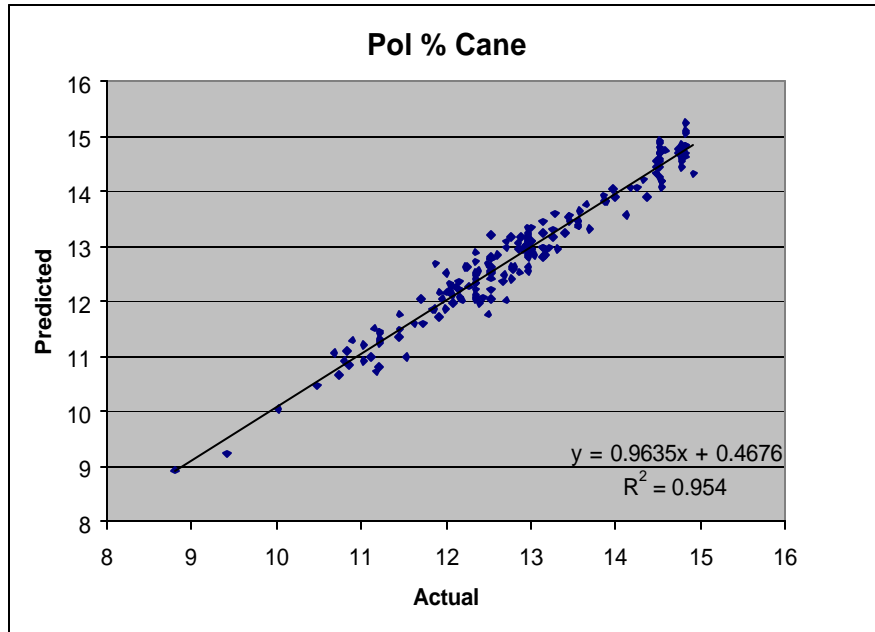


Figure 7. Pol % cane, DAC lab result vs. NIR prediction

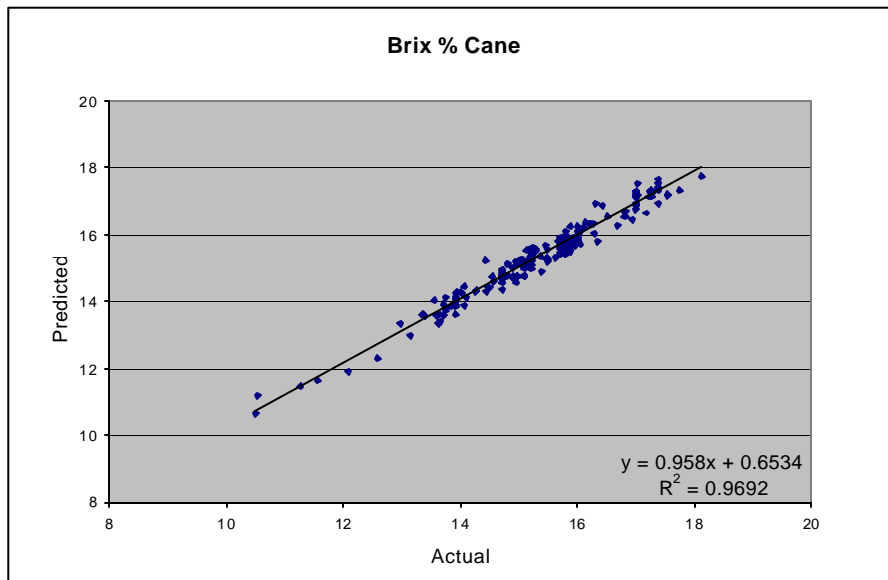


Figure 8. Brix % cane, DAC lab result vs. NIR prediction.

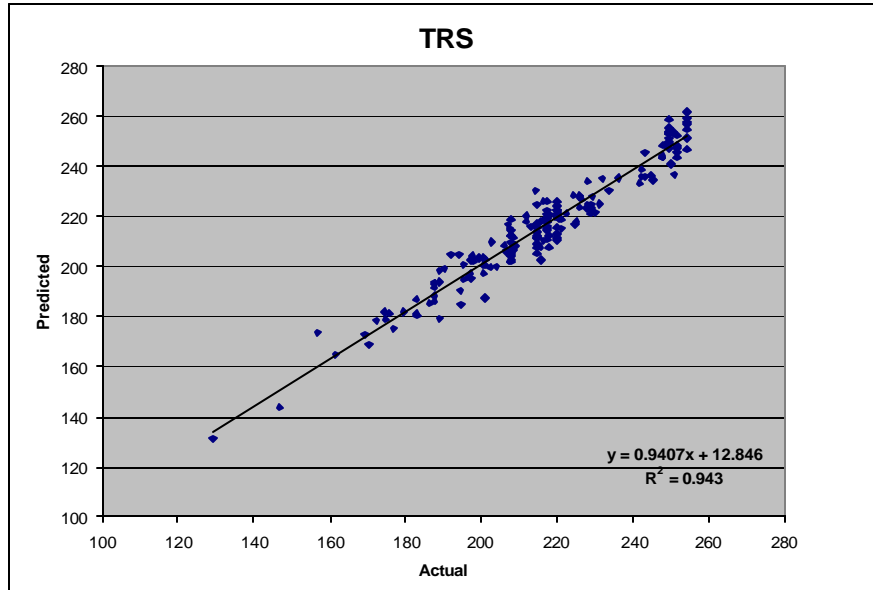


Figure 9. TRS, DAC lab result vs. NIR prediction.

Calibration of the NIRS for ash % cane required some special considerations. The NIRS reads samples containing soil. A viable method for quantitating soil in cane is combustion ash analysis. Samples containing soil reflected this as ash. WinISI software can only fit experimental data to a linear model, causing high ash % cane results to be discarded as outliers. This resulted in an equation that will not produce a predicted result in excess of the average global maximum (Figure 10), which in this case is ~5.0 %. To force the software to retain these points, the equation was linearized using the \log_{10} values of the laboratory data. The high results were no longer regarded as outliers, and the equation can, pending secondary calculation of the antilog, produce a predicted result that was between 87 and 117% of the actual value. The fit of the log equation to lower values was not jeopardized by these manipulations.

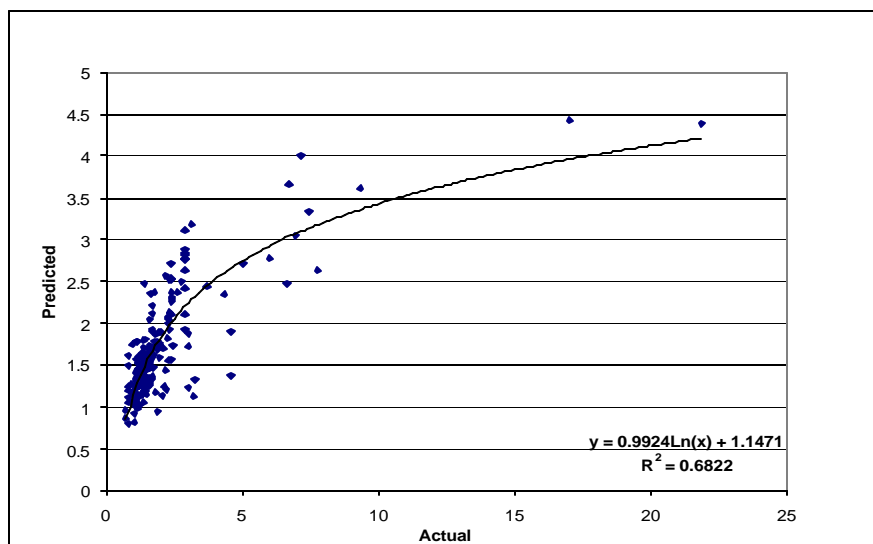


Figure 10. Prediction of ash % cane: the log curve fit has been added to demonstrate the distribution shape of the actual vs. predicted values.

Analysis of the lab data has clarified several questions. The fiber % cane includes the ash and soil present in the sample. It became obvious that CPM does not reflect this since mud fouls the press; juice cannot be expressed from mud without added extraction water. In addition to this, the mud must then be cleaned out of the press while accumulating a sample backlog. An NIRS instrument calibrated by DAC will be able to measure samples containing large amounts of soil. A more accurate fiber result is achieved by difference (Figure 11). This figure has been called “corrected fiber” (CRFiber, Figure 12) and has been added as a constituent to the DAC derived NIR equation set.

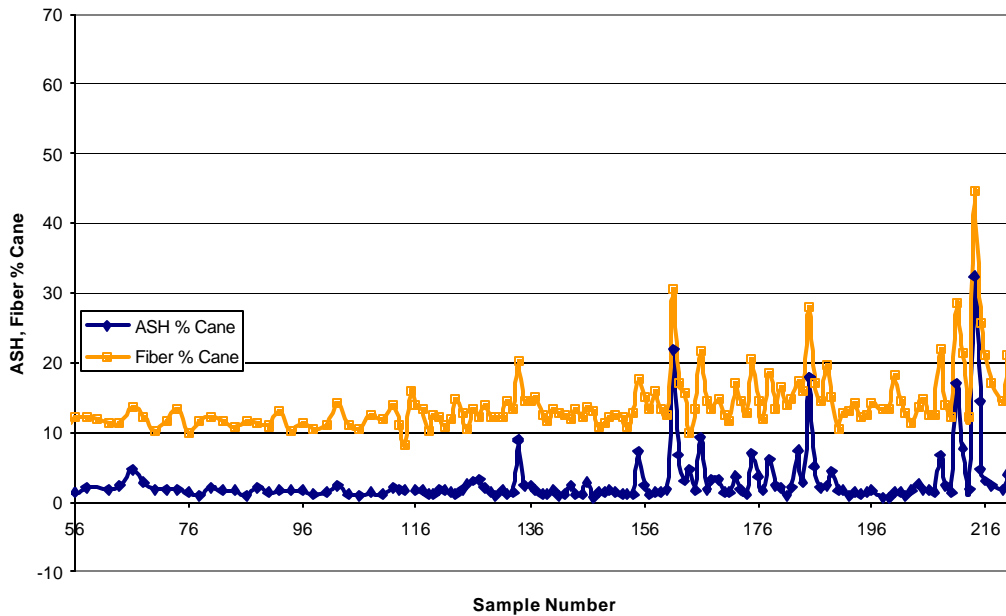


Figure 11. Ash % and Fiber % Cane Lab Data from DAC.

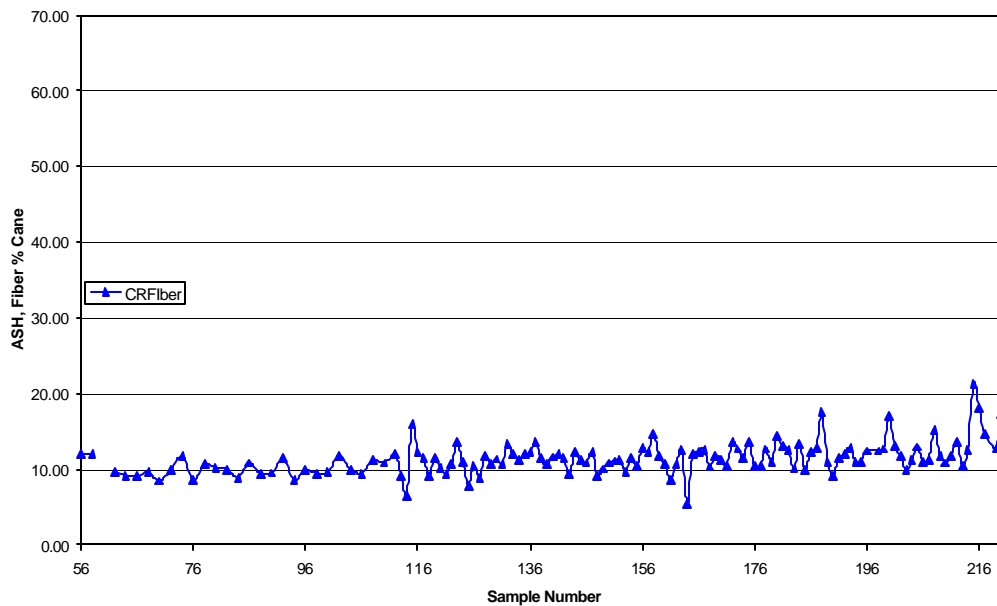


Figure 12. Corrected Fiber % Cane, taken by difference from the DAC results for fiber and ash % cane.

Actual data from a Louisiana core lab showed costs of ~\$85,000 per season on employees and supplies. The same lab, using the NIRS might have spent ~\$14,000 per season. A net saving of ~\$70,000 per season may be achieved. At an initial cost of \$160,000 dollars, a NIRS system of this type could be paid for in less than 3 years. Savings resulting from accurate data have not been assessed, but are likely to be even more significant.

If NIRS is installed, a qualified technician may manage continuing calibration verification (CCV), once per week. This technician should serve to monitor the instrument, update calibration, and to serve as liaison for support in the event of technical difficulty. For Louisiana, serving 15 mills, only one liaison technician should be required, and could be subcontracted as an independent body.

CONCLUSIONS

The instrument was able to meet or exceed calibration values found in the literature for fibrated cane. Analysis of core-sampled cane can be completed within 120 seconds, while providing accurate results for pol, brix, fiber, moisture, ash % cane, and TRS. The possibility of discriminating and quantitating “trash” from mud has been realized, and may be exploited in the future. Increased throughput will allow for more comprehensive sampling. Improvement in sample representation will result in accurate payments. Immediate knowledge of excessive mud or “trash” at the weighbridge might be used to decrease the amount of foreign material entering the mill, reducing mill stoppage.

The instrument needed no mechanical maintenance (other than routine cleaning) during the course of this trial, even under the most hostile ambient conditions. Use of the InfraCana will require only one operator per shift, rather than 3-5 per shift as at present, and is not subject to experimental error. In light of these developments, it can be concluded that the InfraCana NIRS may be proven a viable alternative to current core press method of cane analysis.

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