AUTOMATED ROUTINE ANALYSIS OF QUALITY PARAMETERS IN SUGARCANE JUICES AND MOLASSES BY NIR

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Abstract

Previous work at the SMRI has shown that NIRS predictions based on calibrations produced from earlier datasets were often biased.

Bias-free NIR predictions were obtained by:

- daily adjustment of the instrument's wavelength (WL) constants to avoid instrumental bias
- incorporation of a repeatability file, containing three samples scanned at different temperatures. This file is added during calibration to compensate for sample/laboratory temperature variations
- adding three random samples from the previous week's samples to the calibration file.

The updated calibration equations were then used for the subsequent weekly samples. Results are described for both MJ and molasses for 17 weeks of the 2000/2001 season.

A Metrohm autosampler was added to provide unattended operation. Sampling rate is currently 20 samples per hour.

Keywords: accuracy, bias, repeatability, sucrose, transmission, autosampling

Introduction

As the demand for laboratory analyses continues to climb and the cost of conventional determinations spiral, it is imperative that research institutes and sugar companies move to more cost effective alternatives such as Near InfraRed Spectroscopy (NIRS).

These investigations were undertaken as there is limited information on the quality of day-to-day NIRS predictions.

Previous work at the SMRI has shown that NIRS predictions developed from calibrations based on earlier datasets were often biased (Schäffler, 2000). This work established that bias could be due to:

- temperature variations. A repeatability file, incorporating spectra of the same samples scanned at different temperatures dramatically improved subsequent predictions.
- small but significant changes in the NIR instrument's wavelength accuracy constants.

Both these factors were incorporated in the current work. Over 745 samples of juice and molasses were analysed over a 17 week period to simulate routine analytical conditions. Each week, the calibration data was updated with three randomly chosen samples, taken from the previous week's analyses, in an effort to improve the model's predictions.

Experimental

Samples

Samples of mixed juice (MJ) were scanned undiluted. C-molasses samples were diluted (16 g in 100 ml). The laboratory's air-conditioning system was on at all times. However, temperature and humidity were not monitored.

Analytes

Mixed juice samples were analysed for sucrose, glucose, fructose, pol, brix and sulphated ash. Molasses samples were analysed for sucrose, glucose, fructose, dry solids, sulphated ash, pol and brix.

NIRS

- A Foss NIRSystems 5000 spectrometer, with a scanning range of 1100 to 2500 nm, was fitted with a sample transport module. A 1 mm flowcell was used to scan juice samples. The lamp was left on at all times. Spectral noise tests ranged from 15 to 25 mA. Each day the wavelength accuracy constants were updated by using the suggested constants.
- The NIR 5000 instrument had previously been interfaced to an auto-flushing/auto-filling system (Schäffler, 2000). Although successfully used over many months, the main drawback of the system was manual presentation of the sample to the instrument. In order to automate this process, a Metrohm 673 Sample Changer and 664 Control Unit have been modified and interfaced with the NIR. Manual and automated operation of both pump and valve are possible. This modified unit has been successfully integrated into the NIR system allowing unattended operation of up to 10 samples at a rate of 20 samples per hour (see Figure 1).

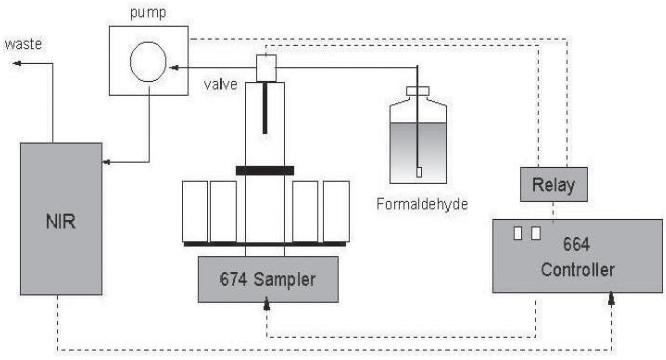

Figure 1. Schematic of the automated sampling and analysis system for factory liquors.

MJ and molasses calibrations

Samples, from previous seasons, were used to produce the initial generic calibration equations. A file containing spectra of a single sample scanned at 19 to 29°C was added during the calibration development stage.

Predictions

During the crushing season, weekly mixed juice (N=25) and molasses (N=20) samples from all South African mills are analysed at the SMRI. These samples were used for the current study. NIRS scans were carried out for 17 weeks (week numbers 19 to 35).

Results and discussions

Updating mixed juice and molasses calibrations

To ensure that the calibrations would continue to produce bias-free predictions, an on-going update of the calibrations was introduced (Table 1).

Mixed juice predictions

Predictions for the two monosaccharides and ash were very poor indicating that quantitative NIRS is not suitable for low concentration constituents (less than 0.5%). Predictions for the 17 weeks for sucrose, pol and brix in MJ samples are summarised in Table 2. The weekly variation in prediction data is also shown for sucrose in Figure 2.

Highlights from Table 2 and Figure 2 are:

- Excellent precision results, all three analytes produced SEP of better than 0.15 units.
- The target tolerance limits for bias were ±0.2 units. All three analytes were within these limits.
- Slope data were most acceptable (0.95 to 0.98).
- RSQ results were excellent (0.98 or better).
- The most pleasing part of the project was the excellent repeatability of the prediction parameters, week in and week out, indicating the robustness of the calibrations and the quality of the laboratory data (Figure 2).

Molasses predictions

The same weekly updating calibration procedure was used for molasses samples. Due to space limitations, results for only six analytes are included in Tables 3, 4 and 5. The predictions for brix and dry solids for the 17 week period were similar, only dry solids results are included.

A summary of the data in Tables 3,4 and 5 include:

- Good precision for the monosaccharides (SEP 0.2 to 0.5), bias is also low (-0.4 to 0.3).
- Precision and accuracy for sucrose and pol was similar (SEP = 0.8, bias = -0.2). Slope and RSQ were the least impressive of the seven analytes tested. However, a bias of 0.2 units (a relative error of less than 1%) is considered adequate for both research projects and factory backend products.

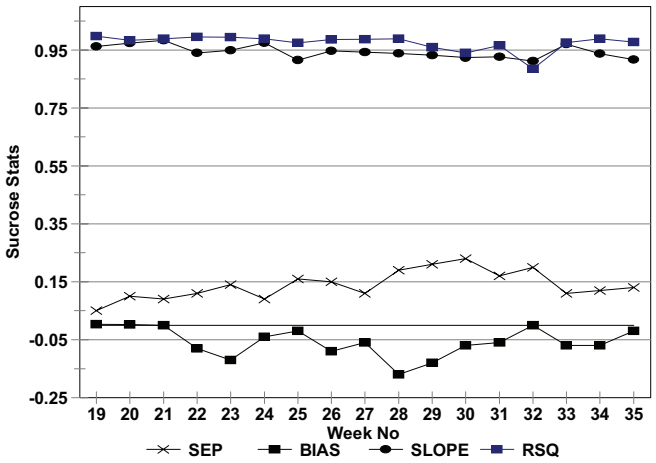

Figure 2. Sucrose in MJ, NIRS predictions for 17 weeks.

Table 1. Procedure for updating calibrations and for the monitoring of weekly NIRS predictions.

1. Analyse samples from first week (Week-19.cal) using the original global equations (e.g. global.eqa)
2. Select 3 samples at random from week-19 (wk19-rnd.cal)
3. Add these 3 samples to the original global calibration file (global.cal), new calibration data file is now glob-19.cal
4. Recalibrate using glob-19.cal and include the repeatability file (rep-all.nir), new calibration equation = glob-19.eqa.
5. Predict analytes in samples from week-20 using glob-19.eqa
6. Repeat steps 2, 3, 4 and 5 for samples from weeks 21 to 35

Table 2. Prediction results for sucrose, pol and brix in MJ samples, data averaged for weeks 19 to 35.

Analytes	SEP	Bias	Slope	RSQ
Sucrose	0.14	-0.14	0.984	0.975
Pol	0.14	-0.15	0.953	0.979
Brix	0.15	-0.06	0.948	0.978

- In mixed juice, there was virtually no correlation between ash and NIRS. In high brix, low purity products, ash is a major constituent and excellent statistical results were obtained for the 17 week period. The consistency of the ash predictions is highlighted in Figure 3.
- Karl Fischer dry solids is a tedious and expensive analysis. NIRS produced credible precision (SEP = 0.7 units in 72 to 86 units). Bias, slope and RSQ were also acceptable.

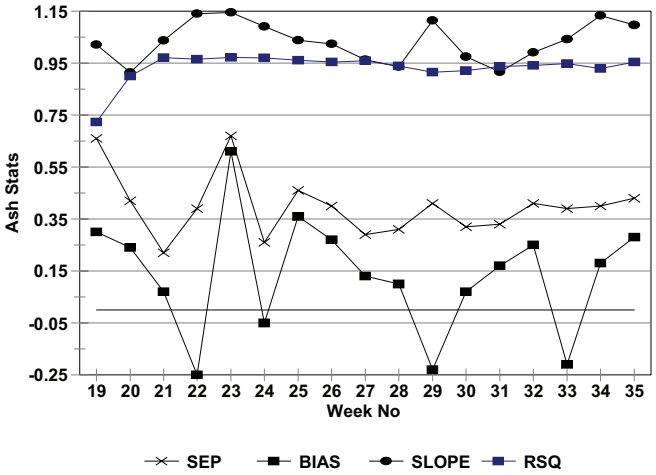

Figure 3. Ash in molasses. Predictions for 17 weeks.

Summary and recommendations

The predictions for the 17 weeks have established that the calibration procedure, developed at the SMRI, is capable of producing excellent routine results for analytes in both mixed juice and molasses. During this study a single analyst:

- analysed MJ samples from all South African mills in half a day.
- weighed, diluted and analysed molasses samples from all South African mills in a single day.
- collated laboratory data from 5-6 analysts and melded this information with the corresponding spectra in half a day.

The Foss 5000 NIR is to be relocated to Maidstone's mill laboratory during the 2002 season to:

- train analysts in scanning and predicting quality parameters in sugar liquors.
- use the NIRS to obtain parallel NIRS estimates for all routine and special samples.

Table 3. Prediction results for fructose and glucose in molasses samples, weeks 19 to 35.

	Fructose				Glucose			
Wk No	SEP	Bias	Slope	RSQ	SEP	Bias	Slope	RSQ
19	0.23	0.07	0.91	0.96	0.54	-0.44	0.90	0.94
20	0.41	-0.11	0.83	0.90	0.39	-0.22	0.88	0.95
21	0.34	-0.01	0.88	0.92	0.40	-0.09	0.83	0.94
22	0.30	0.11	0.91	0.90	0.37	0.12	0.94	0.89
23	0.29	-0.08	0.91	0.95	0.47	0.07	0.88	0.90
24	0.42	-0.27	0.85	0.89	0.26	0.00	0.96	0.95
25	0.38	-0.22	0.98	0.86	0.28	-0.06	1.08	0.95
26	0.28	0.02	0.93	0.89	0.39	-0.13	0.88	0.92
27	0.24	0.02	0.90	0.94	0.31	-0.08	0.98	0.93
28	0.22	0.07	0.90	0.94	0.37	-0.02	0.95	0.89
29	0.41	0.31	0.84	0.89	0.28	0.13	1.00	0.94
30	0.25	0.14	0.95	0.92	0.24	0.03	1.03	0.95
31	0.24	0.07	0.81	0.91	0.36	-0.23	1.02	0.91
32	0.28	-0.09	1.03	0.85	0.33	-0.23	0.95	0.92
33	0.34	0.11	0.72	0.71	0.30	-0.23	1.00	0.94
34	0.19	0.00	1.02	0.88	0.33	-0.26	1.01	0.94
35	0.31	-0.25	0.83	0.83	0.40	-0.31	0.96	0.91
Min	**0.19**	**-0.27**	**0.72**	**0.71**	**0.24**	**-0.44**	**0.83**	**0.89**
Max	**0.42**	**0.31**	**1.03**	**0.96**	**0.54**	**0.13**	**1.08**	**0.95**
Mean	**0.30**	**-0.01**	**0.89**	**0.89**	**0.35**	**-0.11**	**0.96**	**0.93**

Table 4. Prediction results for sucrose and pol in molasses samples, weeks 19 to 35.

	Sucrose				Pol			
Wk No	SEP	Bias	Slope	RSQ	SEP	Bias	Slope	RSQ
19	0.91	0.77	0.89	0.92	0.74	-0.14	1.20	0.90
20	0.46	0.02	0.90	0.91	1.04	-0.01	0.97	0.74
21	0.58	0.11	0.91	0.89	0.90	0.33	0.95	0.83
22	0.89	-0.76	0.88	0.93	0.63	-0.13	1.08	0.92
23	0.74	-0.55	0.82	0.95	0.87	-0.07	0.91	0.82
24	0.63	-0.09	0.95	0.86	0.75	0.04	0.90	0.85
25	0.63	-0.09	0.87	0.81	0.77	-0.42	1.16	0.90
26	0.63	-0.45	0.84	0.93	1.26	-1.00	1.00	0.84
27	0.61	-0.43	0.88	0.92	0.75	-0.42	1.10	0.92
28	0.71	-0.50	0.73	0.89	1.11	-1.00	1.10	0.92
29	0.61	0.04	0.69	0.78	0.87	-0.67	1.03	0.86
30	0.48	0.03	0.81	0.82	0.56	-0.02	1.02	0.85
31	0.60	0.01	0.76	0.71	0.91	-0.58	0.91	0.73
32	1.05	-0.55	0.76	0.70	0.82	0.23	1.02	0.85
33	1.01	-0.89	0.82	0.92	0.45	0.07	1.03	0.94
34	0.75	-0.07	0.89	0.74	0.64	-0.27	0.87	0.90
35	0.71	0.12	0.85	0.93	0.70	0.03	0.90	0.81
Min	**0.46**	**-0.89**	**0.69**	**0.70**	**0.45**	**-1.00**	**0.87**	**0.73**
Max	**1.05**	**0.77**	**0.95**	**0.95**	**1.26**	**0.33**	**1.20**	**0.94**
Mean	**0.71**	**-0.19**	**0.84**	**0.86**	**0.81**	**-0.24**	**1.01**	**0.86**

Table 5. Prediction results for ash and dry solids in molasses samples, weeks 19 to 35.

	Ash				Dry solids			
Wk No	SEP	Bias	Slope	RSQ	SEP	Bias	Slope	RSQ
19	0.66	0.30	1.02	0.72	0.63	0.24	0.97	0.96
20	0.42	0.24	0.91	0.90	1.03	0.92	0.94	0.98
21	0.22	0.07	1.04	0.97	0.52	0.16	0.97	0.97
22	0.39	-0.25	1.14	0.97	0.41	-0.02	1.07	0.99
23	0.67	0.61	1.15	0.97	0.78	0.68	1.03	0.99
24	0.26	-0.05	1.09	0.97	0.73	0.48	1.09	0.99
25	0.46	0.36	1.04	0.96	1.10	0.24	1.00	0.91
26	0.40	0.27	1.02	0.95	0.97	0.74	1.09	0.97
27	0.29	0.13	0.96	0.96	0.55	-0.17	1.10	0.98
28	0.31	0.10	0.94	0.94	0.80	0.64	1.04	0.97
29	0.41	-0.23	1.11	0.92	0.63	0.30	1.06	0.96
30	0.32	0.07	0.98	0.92	0.63	0.32	1.00	0.97
31	0.33	0.17	0.92	0.94	0.98	0.77	1.05	0.96
32	0.41	0.25	0.99	0.94	0.76	0.47	0.99	0.97
33	0.39	-0.21	1.04	0.95	0.75	-0.51	1.04	0.98
34	0.40	0.18	1.13	0.93	1.12	0.94	1.09	1.00
35	0.43	0.28	1.10	0.95	0.60	0.45	1.08	0.99
Min	**0.22**	**-0.25**	**0.91**	**0.72**	**0.41**	**-0.51**	**0.94**	**0.91**
Max	**0.67**	**0.61**	**1.15**	**0.97**	**1.12**	**0.94**	**1.10**	**1.00**
Mean	**0.40**	**0.13**	**1.03**	**0.93**	**0.76**	**0.39**	**1.04**	**0.97**

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REFERENCES

Schäffler, KJ (2000). Trials and tribulations of implementing NIRS for raw sugar factory liquors. *Proc S Afr Sug Technol Ass* 74: 361-368.