Near-infrared spectroscopy for on-line analysis of white and green liquors

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ABSTRACT

Near-infrared (NIR) spectroscopy was investigated as an on-line method for measuring the composition of kraft white and green liquors. The results show that this approach can accurately predict concentrations of the three principal components in mill liquors: sodium hydroxide, sodium sulfide, and sodium carbonate. Effects of temperature on predicted composition can be quantified using any one of three suggested methods. The presence of trace components in mill liquors also contributes to prediction errors, but these effects can be quantified as offsets to adjust the model predictions. The feasibility of NIR spectroscopy as an on-line tool for analyzing white and green liquors was verified by testing liquors from three mills. Over long periods of on-line operation, occasional lab tests of liquor composition would be required to adjust the model offsets for gradual shifts in liquor composition.

Application:

Preliminary studies suggest that NIR spectroscopy can be used as an on-line tool to monitor the composition of kraft green and white liquors.

THE EFFICIENCY OF THE KRAFT process is largely dependent on the quality of the white and green liquors. White liquor, which is primarily sodium hydroxide (NaOH) and sodium sulfide (Na_2S), is used in delignification during the chip cooking cycle. Green liquor, which is primarily sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S), is generated during the liquor recovery cycle. White-liquor composition is very important in the control of pulp quality and uniformity. Green-liquor composition has a direct effect on the efficiency of the liquor regeneration process and determines the amount of makeup chemicals needed to guarantee the desired white-liquor composition.

Most mills still manually control the composition of white and green liquors. Liquor composition is measured in the lab, and the resulting values are entered into a control system, which makes appropriate adjustments. The standard lab procedure to determine liquor composition is the "ABC" titration test. This is a simple acid–base titration that yields values for sodium hydroxide, sodium sulfide, and sodium carbonate. Manual titration is only practical for occasional checks of liquor composition. Although the ABC test has been automated by the use of autotitrators, these devices require a significant amount of maintenance for continuous on-line operation. Some mills use conductivity sensors to measure white-liquor alkali concentration on-line *(1)*. This approach requires that sodium carbonate and sodium sulfide concentrations be known to eliminate their effects on the conductivity measurement. An automated sampling and analysis system, developed at Auburn University, is capable of measuring all three components *(2–4)*. However, this system requires a conductivity measurement, a refractive index or density measurement, and a UV analysis system. While this system is effective in a lab environment, implementation in a mill environment would require unacceptable levels of maintenance.

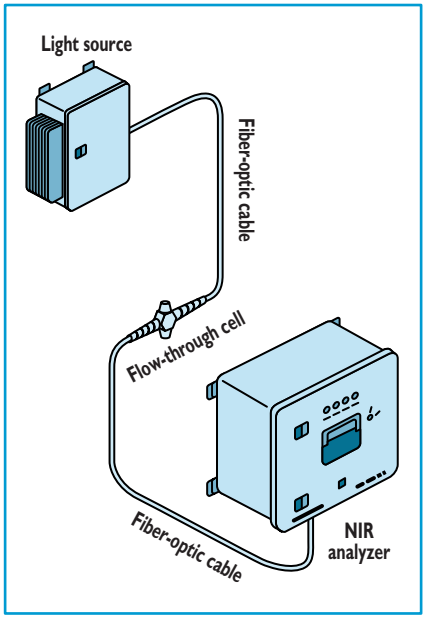
One approach that provides an attractive alternative is the use of spectroscopic measurement techniques. In particular, near-infrared (NIR) spectral analysis has been demonstrated to be a viable approach for measuring all three components *(5)*. The basic idea is to measure absorption values at a number of wavelengths in the NIR range and correlate these absorption values to the actual concentrations. This correlation can be derived using partial least-squares regression (PLS) or some other multivariable regression technique.

Correlations presented in this paper were developed using Rosemount's multicomponent liquid analyzer (MLA). **Figure 1** shows the basic components of this system.

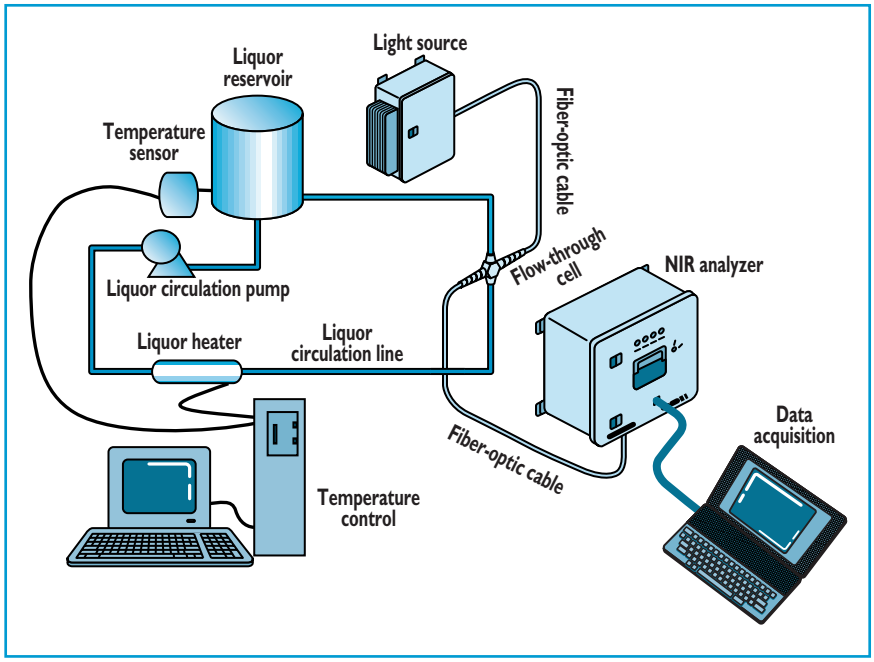
EXPERIMENTAL

To develop the correlations, stock solutions of sodium hydroxide, sodium sulfide, and sodium carbonate were prepared at varying concentrations using analytical-grade chemicals. The solutions were then introduced into a liquor circulation system, where 10 absorption scans per sample were collected. **Figure 2** shows the liquor circulation system.

Concentrations for the laboratory solutions were chosen so that there were multiple mixtures that had only one component varying in concentration while the remaining components stayed fixed. Sodium sulfide hydrolyzes to form sodium hydroxide and sodium hydrosulfide (NaHS), so calibration data were generated for varying concentrations of sodium hydrosulfide at constant



1. NIR detector and associated hardware



2. Data collection and calibration system

Component	TYPICAL LIQUOR COMPOSITION, g/L (as Na_2O) Lower Range	Upper Range
White liquor		
NaOH	50	100
Na_2S	5	40
Na_2CO_3	0	25
Green liquor		
NaOH	0	30
Na_2S	5	35
Na_2CO_3	65	105

I. Typical mill liquor concentration ranges

sodium hydroxide concentration. This approach generates a more robust data set, since the absorption of the hydrosulfide ion is isolated. Sodium hydroxide concentrations were varied from 0–14%; sodium hydrosulfide concentrations were varied from 0–5%; and sodium carbonate concentrations were varied from 0–16%. These concentrations correspond approximately to 0–127 g/L, 0–63 g/L, and 0–109 g/L (all as Na_2O) for NaOH, Na_2S, and Na_2CO_3, respectively. Typical concentration ranges for mill white and green liquors are given in **Table I**.

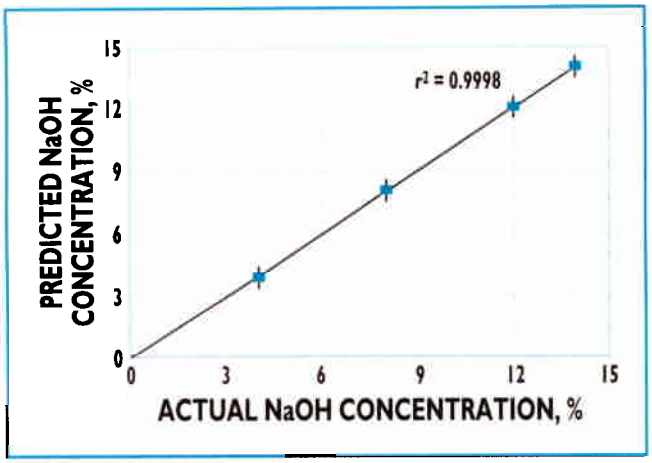
Development of a robust model requires the acquisition of pure-component absorption values as well as a uniformly distributed set of multicomponent absorption data. This data set should be designed such that the resulting model is interpolating instead of extrapolating when called upon to estimate the composition of an unknown liquor based on adsorption data. The interpolating model can then be used to predict any composition that lies within the bounds of the calibration data set. A robust data set that uniformly covers the range of desired concentrations requires a minimum of four different concentrations for each pure component and $4^3 = 64$ different combinations of the three components. This generates a data set of 64 + 12 = 76 unique liquor compositions that span the upper and lower concentration values of each component.

Partial least-squares (PLS) regression analysis was used to fit the collected data set. The PLS method was chosen because it reduces the dimensionality of the absorption data. Each absorption signature can have up to 256 discrete measurements spanning the 1.1–2.2-µm range. This generates a data vector of dimension 256. PLS effectively reduces this dimension by combining groups of similarly absorbing wavelengths and mapping the resultant group into a latent variable. Regression is then carried out on the set of latent variables. The number of latent variables needed for a robust calibration is a parameter that has to be optimized during the calibration process. The standard approach for doing this is to compute the prediction residual error sum of squares (PRESS). This approach divides the data set into two sets: one for building the calibration and one for testing the calibration. Predictions are made on the test set, with the error residuals squared and summed. The number of latent variables is increased until this sum is minimized *(5)*.

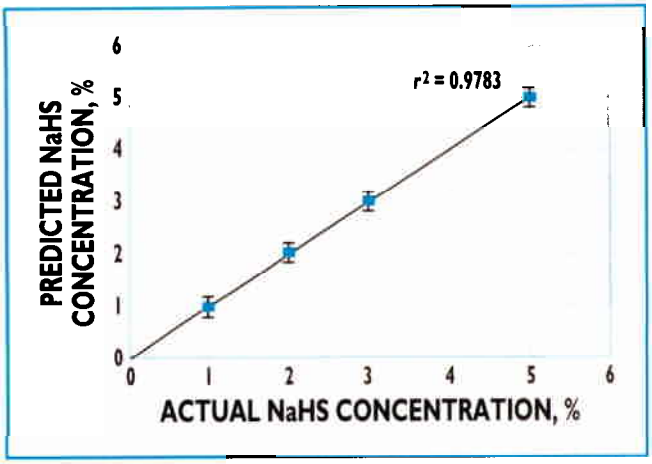
Figures 3–5 show calibration curves for each of the three components using the PLS technique. The PLS calibration required eight latent variables to achieve a minimum PRESS.

TEMPERATURE COMPENSATION

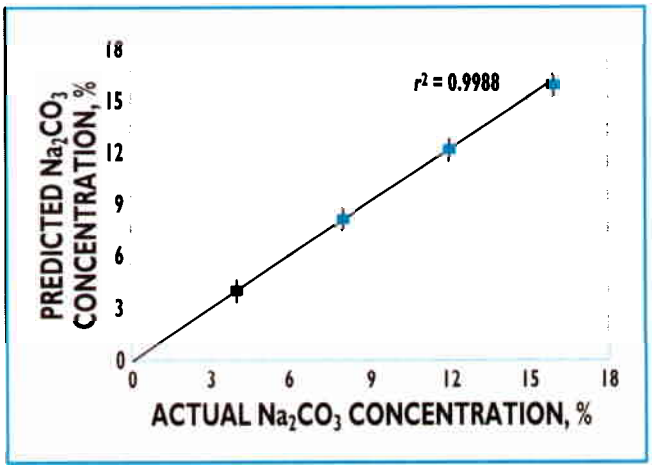
Temperature is a very important parameter that must be accurately controlled during the data collection phase. **Figures 6 and 7** show the effect of varying temperature for pure



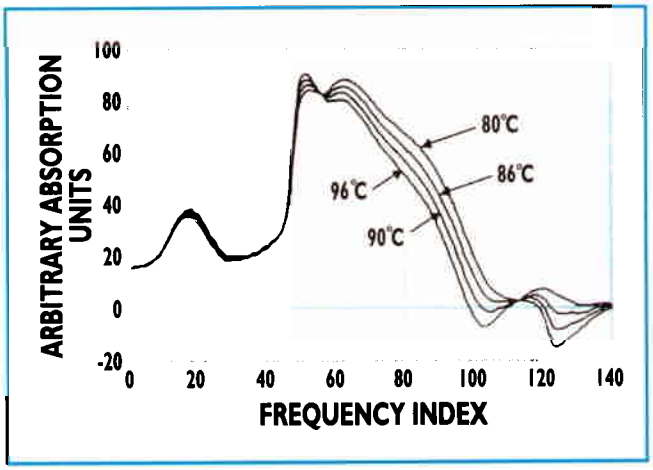
3. Calibration curve for NaOH



4. Calibration curve for NaHS (Na_2S)



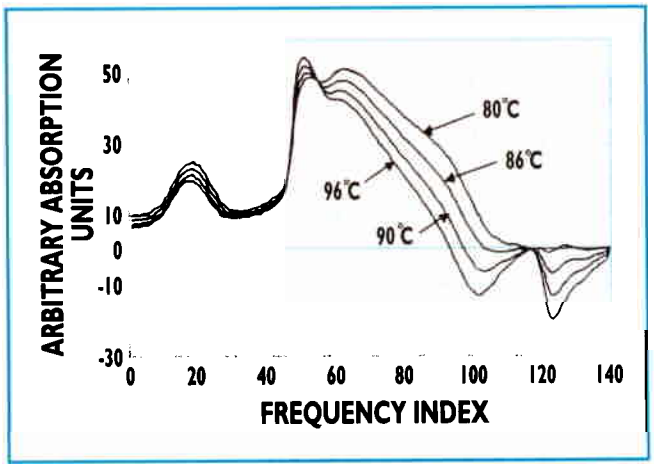
5. Calibration curve for Na_2CO_3



6. Effect of temperature on NaOH scans; [NaOH]= 45 g/L (as Na_2O)

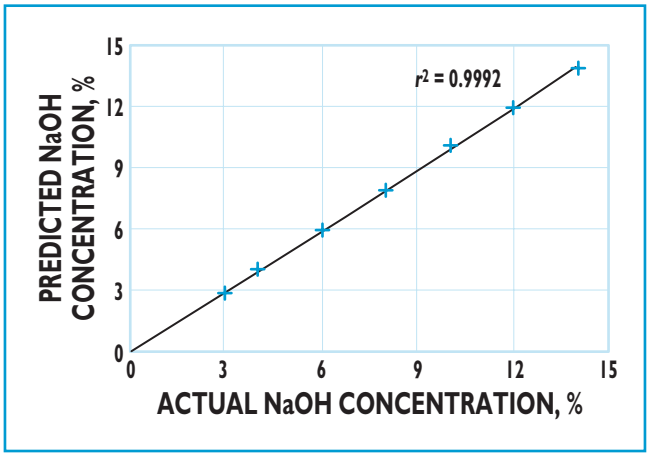
NaOH and Na_2S absorption signatures, respectively. Similar effects are seen for pure Na_2CO_3. Comparing the two sets of spectra, one can observe that the temperature effects are very similar. This is due primarily to the change in absorption characteristics of the water background. Changes in the absorption characteristics of the ionic species—OH^-, SH^-, and CO_3^{2-}—are present as well, but the bulk of the temperature effect manifests itself through changes in the absorption characteristics of the water.

Looking at the pure-component absorption data, one can see that there is significant overlap in the sodium hydroxide and sodium carbonate absorption spectra. The two spectra also have a very similar shape. This tends to produce a collinearity problem that makes distinguishing between the two components difficult. Once the calibration model has been developed, predictions are still quite sensitive to temperature variations. Sodium carbonate is underpredicted by approximately 1 g/L for every 0.1°C increase in temperature. Sodium hydroxide and sodium hydrosulfide are both overpredicted by approximately 0.2 g/L for every 0.1°C increase in temperature.

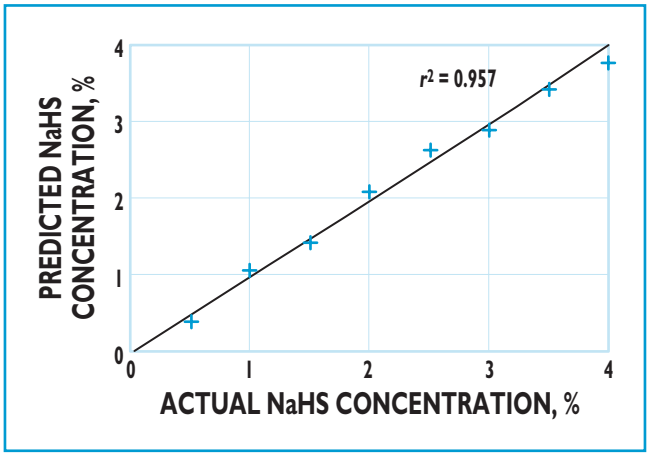


7. Effect of temperature on Na_2S (NaHS) scans; [Na_2S] = 45 g/L (as Na_2O)

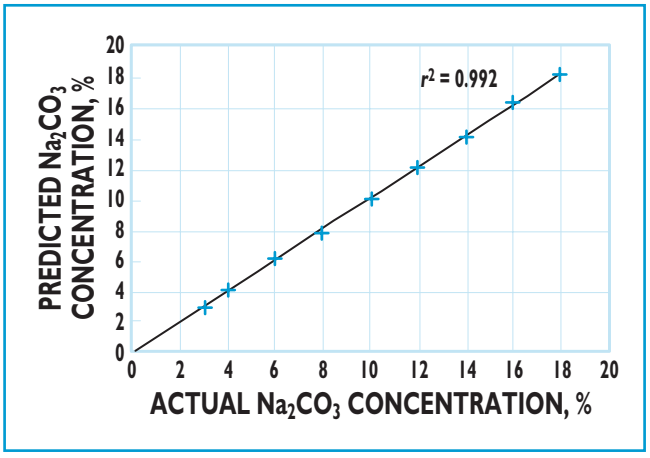
Corrections for temperature variations can be obtained in three different ways. Each has advantages and disadvantages.



8. Prediction performance for NaOH



9. Prediction performance for NaHS (Na_2S)



10. Prediction performance for Na_2CO_3

1. The most straightforward approach is to add temperature-corrected offsets to the predicted values. These correction offsets are a function of temperature only and require measuring the liquor temperature immediately after it exits the flow-through cell. Once the calibration model is built at a given temperature, predictions of known liquor concentrations can be performed in the presence of temperature variations. These values can then be used to compute offsets as a function of temperature. The main advantage of this approach is that a model can be built at a single temperature. This significantly reduces the amount of data needed for a robust model compared with the next approach. The main disadvantage is that an accurate temperature measurement has to be taken at the sample cell outlet.
2. Another approach to dealing with temperature variations is to include absorption data over the range of temperature variation for the pure-component and multicomponent liquors. This essentially adds another component to the system. If four different temperature values are used that span the range of temperature variation, then the data set required for a robust model becomes $3 \times 4 \times 4 + 4^4 = 304$ unique combinations of the three components and temperature. This approach has been used on liquors with only sodium hydroxide and sodium carbonate with excellent results.
3. The final approach investigated is a hybrid of the two previous approaches. Since variations in water absorption characteristics with temperature are responsible for the bulk of the prediction errors, absorption data of pure water in the presence of temperature variations can be included into the calibration set. This requires only four extra scan sets to be added to the single-temperature data set. Although this does not eliminate all temperature effects, it greatly diminishes the effect of temperature, and the corresponding temperature-correction offsets are not nearly as sensitive to temperature variations.

CALIBRATION TEST RESULTS

The robustness of the calibrations was verified by testing synthetic liquor samples containing only the three principal components: NaOH, Na_2S, and Na_2CO_3. **Figures 8–10** show the predicted vs. actual values for the three components. Standard deviations for the three components were 0.56 g/L for NaOH, 2.12 g/L for NaHS, and 0.78 g/L for Na_2CO_3 (all as Na_2O).

INDUSTRIAL LIQUOR PREDICTIONS

NIR spectroscopy and PLS modeling worked well for predicting concentrations of synthetic liquors containing only the three components of interest. However, actual industrial liquors contain trace amounts of other components that can degrade the prediction performance of the liquor calibration. These "interfering" liquor compo-

nents include sodium thiosulfate, sodium sulfate, chloride, potassium, and suspended solids. Sodium thiosulfate and sodium sulfate (at respective concentrations of 10 g/L) had a slight effect on liquor predictions, producing an approximate 0.5-g/L underprediction in NaOH, a 0.4-g/L overprediction in NaHS, and a 1.1-g/L overprediction in Na_2CO_3.

Potassium levels in industrial liquor can be as high as 3000 ppm, which is approximately 3 g/L of K^+. At these levels, potassium introduces prediction errors in much the same way as sodium sulfate and sodium thiosulfate. Potassium does not directly absorb, but there is a depression effect on the spectral absorption of water, which again introduces errors in predictions for all three components. At 3 g/L, potassium ion prediction errors account for approximately a 0.45-g/L underprediction in NaOH, a 1.34-g/L overprediction in NaHS, and a 1.31-g/L overprediction in Na_2CO_3. Chloride ions are present to a much lesser extent than potassium ions and do not account for any appreciable prediction errors.

Suspended solids exist in both industrial white and green liquors in the form of carbon particles in green liquor and lime mud in white liquor. These particles do not absorb nor do they affect the absorption of other components. However, these solids tend to shift the entire spectral signature down by electromagnetic scattering.

Obviously, it is not practical to model all of the trace components that can introduce errors in the predicted compositions. The most practical approach to obtaining reliable composition predictions is to build a calibration based on the three components of interest and then using an offset to adjust to the actual composition. In a mill environment, this amounts to installing the analyzer and letting it make predictions.

Mill No.	LAB TEST VALUES NaOH	Na_2CO_3	Na_2S	PREDICTED VALUES NaOH	Na_2CO_3	Na_2S	ERROR NaOH	Na_2CO_3	Na_2S
1	110.14	9.00	16.32	109.21	8.31	18.25	0.93	0.69	–1.93
2	110.34	37.00	34.88	111.43	35.88	33.01	–1.09	1.12	1.87
	105.00	30.27	38.54	104.38	28.95	35.76	0.62	1.32	2.78
3	109.39	11.47	32.51	108.21	10.67	31.23	1.18	0.80	1.28

II. Prediction of mill white liquors, g/L (as Na_2O)

Mill No.	LAB TEST VALUES NaOH	Na_2CO_3	Na_2S	PREDICTED VALUES NaOH	Na_2CO_3	Na_2S	ERROR NaOH	Na_2CO_3	Na_2S
1	27.43	67.46	32.37	27.70	67.59	32.04	–0.27	–0.13	0.33
2	29.47	60.74	28.45	30.97	58.94	33.01	–1.50	1.80	–4.56
	29.24	67.31	30.42	30.55	65.45	32.76	–1.31	1.86	–2.34
3	31.20	63.46	30.51	31.99	64.39	31.23	–0.79	–0.93	–0.72
	32.06	72.21	30.68	32.37	74.72	32.88	–0.31	–2.51	–2.20

III. Prediction of mill green liquors, g/L (as Na_2O)

Then, take a liquor sample and perform the ABC titration test and offset the predictions to the correct values. This works well as long as there are no significant changes in the composition of trace components.

Some preliminary tests on actual mill liquors have been performed, and the results are presented in **Table II** (white liquors) and **Table III** (green liquors). Predictions were made without using any offset corrections. Mill 1 liquor tested well for the one sample available. Mill 2 requires some offset in all three components. Mill 3 requires some offset in sodium carbonate and sodium sulfide. Over long periods of on-line operation, occasional lab tests would need to be performed to recalibrate the offsets so that they reflect any changes in the liquor composition.

CONCLUSIONS

Near-infrared (NIR) spectroscopy provides a reliable means of determining the concentrations of the three key components—NaOH, Na_2S, and Na_2CO_3—in white and green liquors using a single instrument. The method has the advantage of simplicity and reliability. Sodium hydroxide and sodium carbonate predictions are in excellent agreement with actual values. Sodium sulfide predictions do not perform as well, but they are within acceptable limits.

Instrument calibration requires the collection of large quantities of data in a very well-controlled environment. Temperature effects are present in any spectroscopic application, but they are especially noticeable in this one because of the high degree of overlap in the absorption signatures of the three components of interest. Three approaches were investigated for dealing with temperature effects. The most time-consuming approach involves the collection of data at varying temperatures as well as varying compositions. However, this approach has the desirable property of creating a standalone liquor analyzer, since no temperature measurements have to be taken and no external calibrations have to be generated.

The NIR spectroscope was calibrated using synthetic liquor samples. Predictions for these synthetic liquors were in excellent agreement with actual values. Of course, mill liquors contain trace quantities of other components that affect composition predictions. However, lab results show that these disturbances are not excessive and can be dealt with in a straightforward manner on a mill-by-mill basis.

The proposed technique was used to analyze liquors from various mills, with promising results. The next step is to implement NIR spectroscopy in a mill environment for a long-term run. **TJ**

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