USE OF NIR SPECTROSCOPY FOR ON-SITE BETAINE MEASUREMENT IN THE ACS HILLSBORO MOLASSES DESUGARIZATION PLANT

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Introduction:

Betaine content of the betaine-rich fraction from the first loop of American Crystal Sugar's (ACS) Hillsboro coupled-loop molasses desugarization (MDS) plant had previously been analyzed only with high performance liquid chromatography performed by a skilled operator and only at the Technical Services location. Feedback on betaine content was delayed since turnaround time for analysis was typically 2-3 days from the time of sampling.

The NIR spectrometer was calibrated for betaine and solids content in the dilute betaine-rich crossover non-sugars (CNS) stream and installed at the Hillsboro MDS laboratory in February 2008. Twice-daily analysis of betaine content is performed, allowing for timely adjustments to the separator controls to maximize betaine recovery. When combined with dry substance measurements, the betaine measurements are used to calculate an estimate of final product betaine concentration.

The Spectrometer and Calibration Development:

The instrument is a Foss NIRSystems Series 5000 benchtop spectrometer with Vision 3.4 software. A liquid sample module is installed and set at 40°C and a 2mm pathlength quartz cuvette is used. The data collection method is programmed to collect 32 scans per sample. The instrument is used in transmission mode over the 1100-2500 nm range. Relatively little maintenance is required. The bulb is left 'always on' and in our experience lasts as least as long as the 4000 hours specified by Foss. The cuvette is disinfected after each use to prevent microbial buildup. Internal performance checks are run periodically.

The reference method for the betaine calibration is high performance liquid chromatography (HPLC) and 150 samples were selected to cover the 0-20% betaine range. These samples were selected from the CNS and recycle cuts of the separator profile. The current calibration is a linear regression equation using a 2nd derivative pretreatment with a single wavelength associated with the first overtone of the methyl groups (~1660 nm). The coefficient of correlation is 0.997 and the standard error of calibration is 0.34 as opposed to the lab error of 0.17. (Figure 1)

The reference method for dissolved solids content is refractometer measurement. The 100 samples selected cover the range of 0-40% solids and were taken from the recycle and CNS cuts of the separator profile. The calibration is a multiple linear regression equation using a 2nd derivative pretreatment and two wavelengths associated with the water peak at 1400 nm. The coefficient of correlation is 0.9992 and the standard error of calibration is 0.34 as opposed to the lab error of 0.10. (Figure 2)

Figure 1 - NIR Predicted Betaine vs. Lab Value

$R^2 = 0.9976$
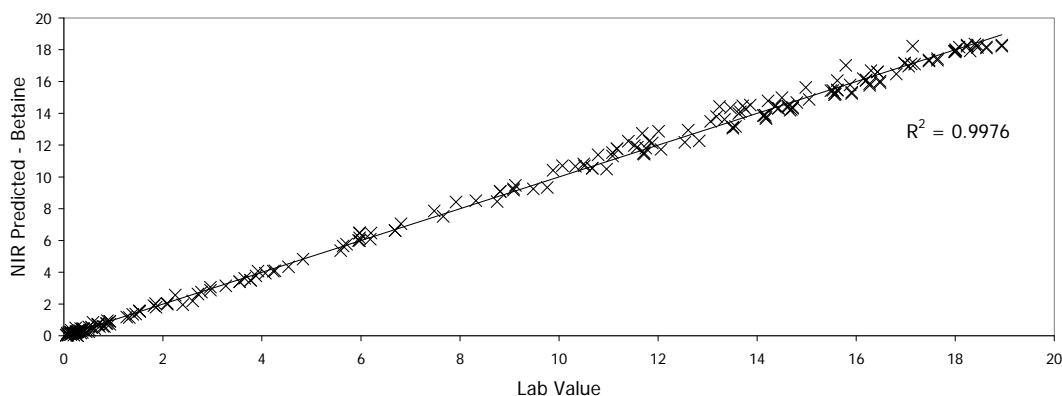
Figure 2 - NIR Predicted RDS vs. Lab Value

$R^2 = 0.9991$
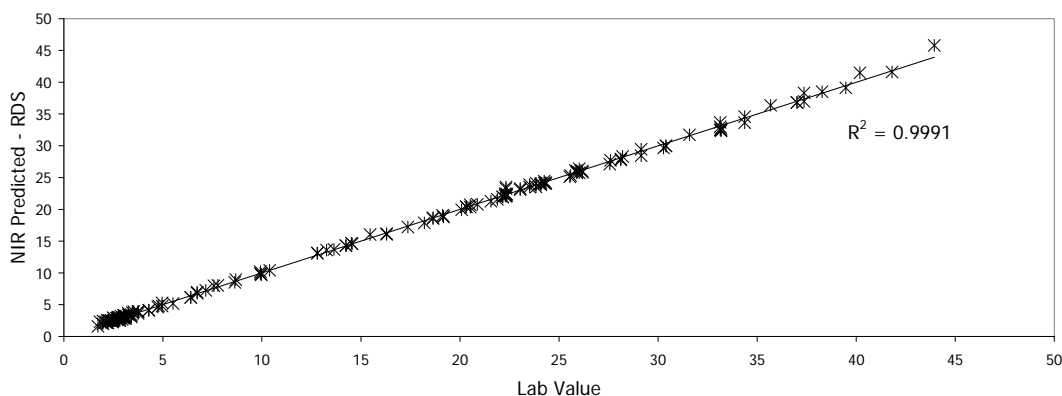
Calibration Updates/Expansion:

One of the advantages of NIR is that calibrations can be updated by expanding the analyte range and adding samples across the campaign and from year-to-year to make the equations more robust. This is relatively easy to do provided that the reference methods are readily available and relatively inexpensive. Updating calibrations follows the same method as the original calibration development except that more samples are added to the sample set and different wavelengths may be selected to optimize the equation.

We have found the need to update the equations three times in the year since the NIR was installed. Once was to voluntarily expand the sample range to include the recycle cut along with the CNS cut, another time was to correct a calibration shift due to a cuvette change and a third time to correct for a shift in the sample matrix.

The original calibrations were for the CNS cut only and done with single scans of samples hot from the separators. The calibrations were updated to include temperature variation (25-30°C vs. 55-60°C), duplicate scans and samples taken from the recycle cut. The NIR-predicted solids are still slightly temperature-sensitive at the higher concentrations, but agreement to the refractometer is good overall (Figure 3). As a rule, NIR repeatability is usually very good; duplicate scans agree well with each other and with the HPLC and refractometer (Figure 4).

Figure 3 – Betaine Separator Profile Samples Run Hot (55-60C) and Cool (25-30C) and Lab Values
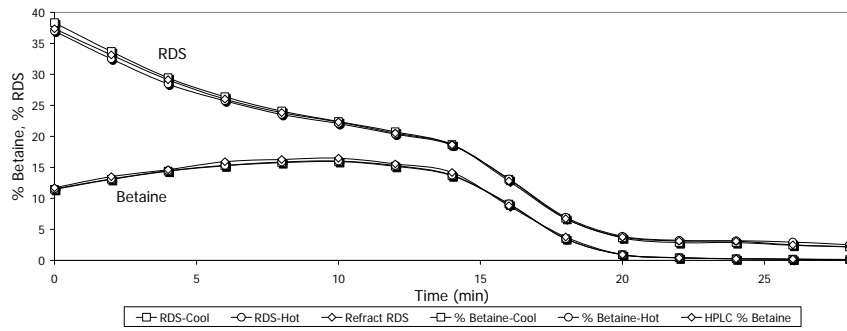

Figure 4 – Betaine Separator Profile Samples Scanned in Duplicate and Lab Values
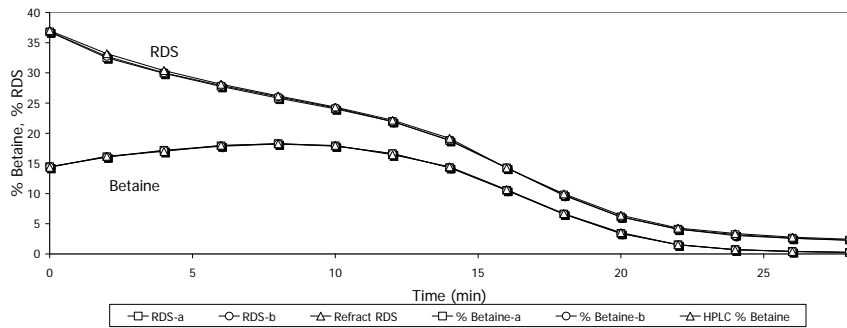
A precision study was done to determine standard deviation by refilling and scanning the cuvette twenty times with the same sample. The average and standard deviation of the predicted values were $6.75 \pm 0.05\%$ for RDS and $3.77 \pm 0.02\%$ for betaine. The residuals from this testing are displayed in Figure 5.

Figure 5 – Precision Study Residuals
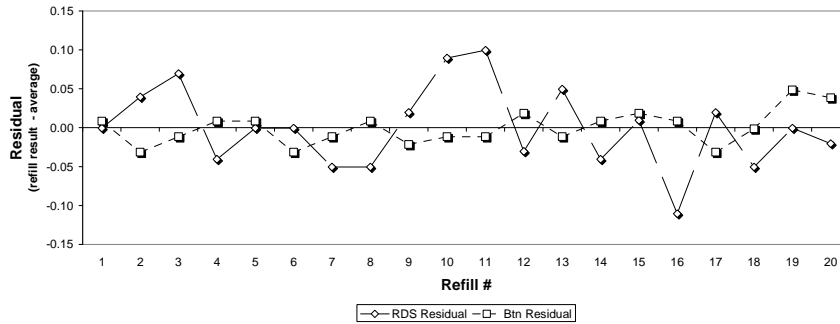
Calibration Shifts – Cuvette:

An update of the calibration equation for RDS was necessary when a new cuvette was put into service. Three cuvettes have been used since installation. No shifts were observed when the original cuvette was replaced, however when the current cuvette was put into service, the NIR-predicted RDS immediately jumped one point over the lab value. There was no obvious shift in the betaine data.

The 2nd derivative spectra of water scans in the different cuvettes show a difference in shapes at the wavelength of the first term of the RDS calibration equation. NIR is very sensitive to absorbance changes and this may have been enough to introduce a bias. A similar shift in the betaine calibration was not observed and there was no difference in the 2nd derivative spectra at the betaine wavelength of the calibration being used at the time. (Figure 6)

Figure 6 - 2nd Derivative Spectra of Water in Two Different Cuvettes
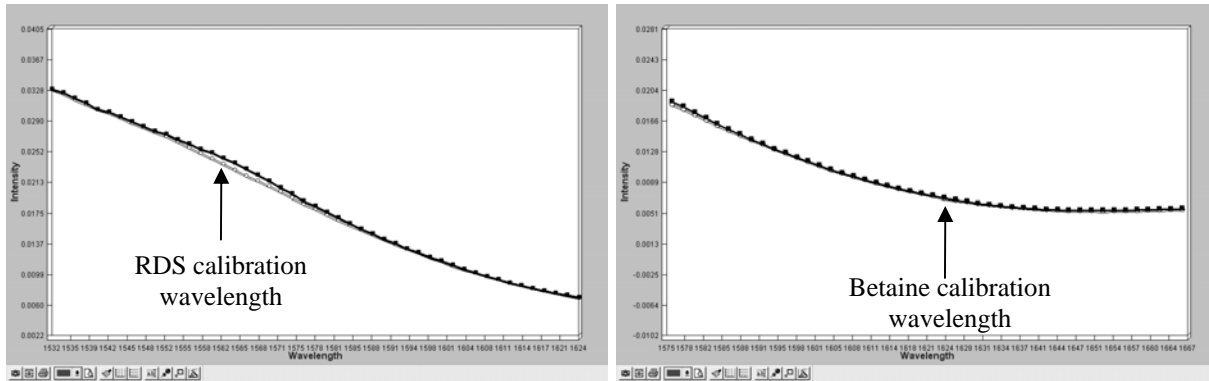
Calibration Shifts – Sample Matrix:

Another update of the RDS calibration was needed due to a shift in the sample matrix. Due to backwash water availability constraints at the MDS plant, the resin in the first loop hadn't been backwashed in over a year. After a water reclamation system was installed, all cells in the loop were thoroughly backwashed to remove resin fines. After the backwashed resin was returned to service, the separation profile changed slightly. Since the NIR is matrix-dependent, any slight differences in the product scan may bias the calibration. There was no change in absorbance at the calibration wavelengths like that seen when the cuvette was changed, but sample spectra scanned in the same cuvette before and after backwashing are different, as evidenced in Figure 7.

Figure 7 – 2nd Derivative Spectra of Samples Taken Before and After Thorough Resin Backwash
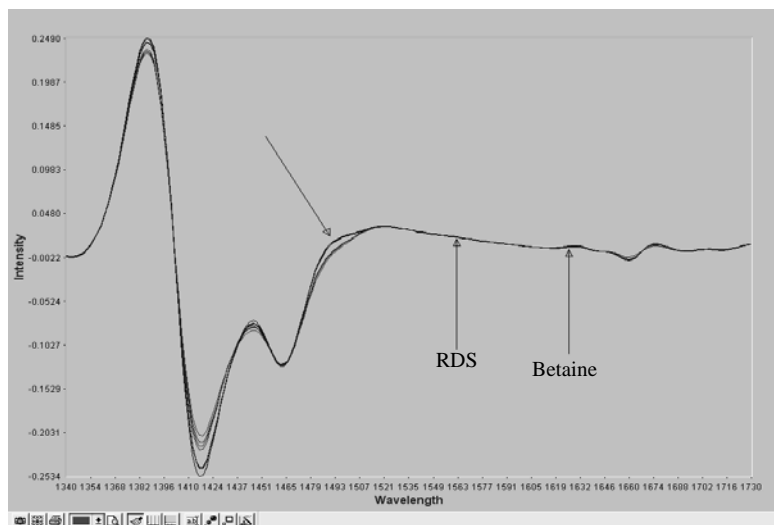
Utility of On-Site Measurement:

Previously, betaine data was available only from weekly composites. Weekly composite data smoothes the variation and is not effective for day-to-day optimization. Composites may not be completely representative, either, if the analyst elects not to composite a sample during a process upset. Routine twice-daily monitoring of the betaine content from the separators gives the operators advanced warning of changes in betaine content so that they can optimize the separators for betaine recovery.

The betaine profile moving through the separators can be characterized by taking samples every 2-3 minutes throughout the recycle and CNS cuts. These profile surveys are useful in determining if the cuts are occurring in the right place within the separator profile to maximize betaine recovery without sacrificing sucrose. Samples across these two phases can be taken in thirty minutes and can be read in thirty minutes; results are obtained in one hour as opposed to 2 days minimum.

Three-point picks are an abbreviated form of the betaine profile; samples are taken at the beginning, middle and end of the CNS cut. With experience, one can determine from these samples if the cut is occurring in the appropriate place to maximize betaine recovery.

The twice-daily betaine readings are also used to estimate betaine concentration in the final product. The betaine value of the dilute sample is multiplied by the solids content of the final product and divided by the dilute solids content; essentially a mathematical 'brixing up' of the dilute process stream. This gives the operators an approximate value of betaine content in the saleable product which can be used to adjust separator parameters or to segregate or blend final product as needed. There is a word of caution: mathematically concentrating the dilute stream also magnifies the NIR error. For example, a ±0.1% NIR error translates to ±0.9% difference in a 7% RDS stream concentrating to an RDS of 60%. Reducing the NIR error to more closely match the laboratory error helps minimize this magnification.

Conclusion:

In the past, separator controls have been set based on solids and apparent purity data; the addition of betaine to the sample protocol allows the operators to fine-tune separation for betaine itself. Since the installation of the NIR, the variability in the betaine concentration of our final product has been reduced. The standard deviation has been reduced from ±3.0% to ±1.6% and the 95% confidence interval has been reduced from 11.6 units to 6.1 units wide. With tighter control and reduction in variability, the target set point can be reduced, maximizing betaine recovery while still maintaining the minimum guarantee betaine concentration.