

ABSTRACT

Separation of betaine during molasses desugarization has become more common in the industry with several companies doing so while using different separation technologies. ACS has two desugarization plants separating sucrose from molasses. Technologies used at the two locations are a simulated moving bed systems and a coupled loop system, both of which were developed by Amalgamated Research Incorporated. The coupled loop (newer technology) at our Hillsboro factory has been used to separate betaine for several years. Customers have requested a minimum concentration and RDS of product shipped, specifications that the plant has met. Because the plant lab does not currently have a means of determining the betaine concentration in material produced at the trains or after concentration at the evaporators, the plant generally has to exceed the minimum concentration by a large margin in order to ensure that the minimum concentration is met. Having an in-line or at-line instrument for determination of betaine will allow the production facility to ensure that they meet customer specifications and at the same time it may allow them to produce and sell more product at the agreed upon specifications.

HPLC is typically used for betaine determination, but an alternative technique is to determine betaine by NIR. ACS had a Foss NIRSystem 5000 NIR available for this purpose. The instrument is a scanning instrument using the wavelength range from 1100-2500 nm. The instrument is equipped with a heated sample compartment heated to 40°C. Foss Vision chemometrics software (version 2.11) was used for development of models for quantification and prediction of betaine in samples from the chromatographic separators. All spectra were mathematically processed to 2nd derivative form and that was used for calibration. Sample spectral data was treated in an analogous manner. All spectra reported in this work were taken using a 2 mm path length cell. Use of a 1 mm cell was not found to improve the precision of the analysis; the 1 mm cell was found to be more difficult to fill and empty than the 2 mm cell.

Samples were collected from the train during the betaine pick. Concentration of the samples ranged from 1.5-17 RDS and 0-13% betaine on sample. Several sets of samples were collected and analyzed by HPLC and by NIR. Calibrations were completed using both multiple linear regression (MLR) and partial least squares (PLS). MLR calibrations for betaine and RDS required the use of a single wavelength. Use of PLS algorithms did not improve the calibration and that method was not used for prediction. Wavelengths used for analysis were 1662nm for betaine and 1692nm for RDS. Correlations between the HPLC data and the NIR predictions were found to be very good with $R^2 = 0.9997$ for betaine and 0.9986 for RDS.

Given that a single wavelength was used for both calibrations, it may be possible to use a filter based NIR for determination of betaine in a chromatographic separator. Availability of a filter based spectrophotometer has not been investigated at the time this work was done.

Analysis of samples by NIR consisted of rinsing the cell with the sample, placing the sample in the sample holder and scanning the sample. This specific sample did not require sample dilution or filtration; the sample was analyzed as is. Total analysis time, including sample cell rinsing was one to two minutes.

Repeatability of the analysis was determined by analyzing samples in duplicate and calculating the pooled standard deviation for the group. Duplicate analysis was done in a

randomized manner so that each analysis required the rinsing, filling, and scanning of a sample. A sample was not analyzed twice in succession—there was always a another sample between duplicate analysis. The pooled standard deviation for RDS was 0.104 units and was 0.045 % for betaine. Repeatability was found to be very good.

Differences between the HPLC betaine and the NIR values are generally quite small. There is a slight bias between the two measures for betaine and that bias can be shown to be statistically significant; however, from a practical standpoint the difference is of no importance. For example, the difference between the HPLC betaine and the NIR predicted betaine for 28 samples averages 0.052%. A paired-t test of the data shows this difference to be significant with $p < 0.05$ for the case when the difference between the two tests is assumed to equal zero ($H_0 = 0$). Even though the difference is significant and the difference indicates a slight bias between the two measurements, the difference of 0.05% betaine is of no real importance with respect to control of the system. Similar results are observed for the RDS model using the same data set; the difference between the refractometer and the NIR value is -0.11%, a value significant at the 0.05 confidence level. Again, the difference is of little importance from a control point of view.

In summary, the NIR provides a rapid and precise method for determination of RDS and betaine in the betaine fraction from a molasses chromatographic separator. Accuracy and precision are adequate for ensuring the production of a betaine fraction that meets the customer specifications.