JACOBSON, BEVERLY J.*, JOSEPH H. WALLEVAND, TERRY D. McGILLIVRAY, AND C. GARY FISCHER, American Crystal Sugar Co., 1700 N. 11 St., Moorhead, MN 56560.
Overview of the development and application of near infrared spectroscopy at American Crystal Sugar Co.

ABSTRACT
This presentation describes the use of Near Infrared Spectroscopy (NIR) at American Crystal Sugar Company. It describes the use of on-line NIR in our Molasses Desugarization facility to determine sucrose, RDS, betaine, and solution absorbance. Our experience with implementation of AOTF technology is described. The development of calibrations for factory juices with both scanning and AOTF benchtop instruments is discussed. Experiences with transfer of the NIR technology to the factory laboratories are discussed.

INTRODUCTION
NIR has been used at American Crystal Sugar Company over the past several years in both benchtop and on-line applications. Both scanning and acousto-optic tunable filter (AOTF) NIR technologies have been used for both benchtop and on-line applications.

BENCHTOP APPLICATIONS
The objective of the project was to be able to determine a true sucrose measurement in the factory labs. True sucrose data is useful in factory accounting. Prior to implementation of NIR, true sucrose was measured using Ion Chromatograph (IC) at the research center. Use of IC in the factory labs proved to be difficult due to the level of complexity of the instrumentation. There are also time constraints at the factory labs, and the level of expertise of factory lab personnel is a factor.

NIR was chosen for determination of true sucrose measurements in the factory labs because of the ease of operator use and the speed of analysis. Initial calibrations and calibration maintenance were done by research center personnel.

Cossette Sugar Analysis by NIR
The first application that was implemented with NIR was cossette sugar analysis. Cossette extracts were prepared using the standard factory lab procedure of ½ normal weight solutions extracted with aluminum sulfate. Cossette extract samples were analyzed using IC for the NIR calibrations.

The spectrometer used was a NIRSystems (Silver Spring, MD) Model 5000 benchtop spectrometer in the transmission mode. This is a scanning NIR instrument. Initially, a liquid sample module was used with an open top 1mm pathlength quartz cuvette. Problems of cell breakage were experienced due to repeated handling of the quartz cuvette. Frequent cell breakage is undesirable because of cost of cells, and calibrations can change when using a new cell.
A closed cuvette with 1mm pathlength was used. This cuvette could be filled with a syringe while it remained in the cuvette holder. This minimized handling of the cuvette and also minimized cell breakage. The cell was cleaned by rinsing with water. Problems with bacterial

growth in the cell were experienced after prolonged use. It was very difficult to remove this bacterial growth due to the small pathlength of the cell.

A liquid sipper module was purchased to replace the original liquid sample module. This module has a peristaltic pump that allows a sample to be pumped into the cell. It also has a cleaning cycle in which the user is prompted to pump a cleaning solution through the cell. This liquid sipper module made the instrument easier to operate for factory personnel.

Both the liquid sample and the liquid sipper module have a heater in the sample compartment to maintain a constant temperature. The 40°C temperature setting was used because it was the lowest temperature that the unit could be set to. Samples had to be pre-heated before being pumped into the cell. The need to pre-heat the samples was a disadvantage.

The calibration equation that was developed for the cossette sugar application was based on 250 samples and was a 6 factor pls equation based on second derivative spectra. The wavelength regions used were 1136-1338 nm, 1510-1836nm, and 2100-2306nm. The regression coefficient was 0.95 and the standard error of prediction was 0.21. The lab error was 0.2. A plot of NIR predicted values versus lab values for cossette sugar analysis by NIR is shown in Figure 1. Figure 2 shows the residual plot for this data.

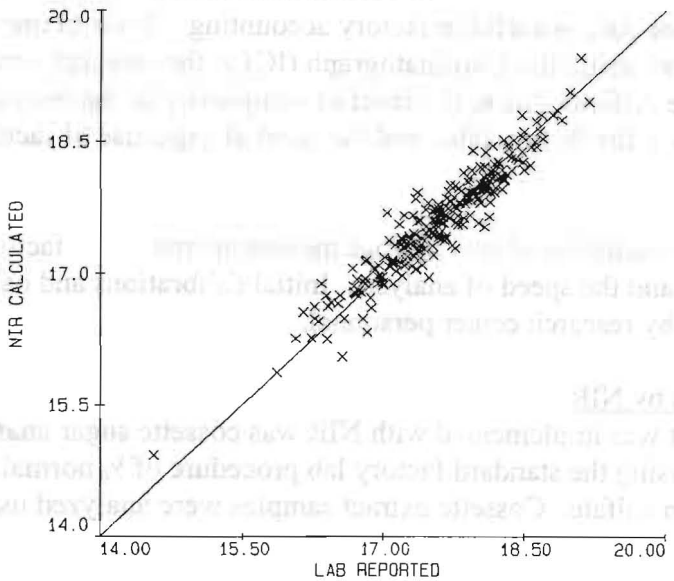

Figure 1. Cossette Sugar: NIR predicted vs. Lab

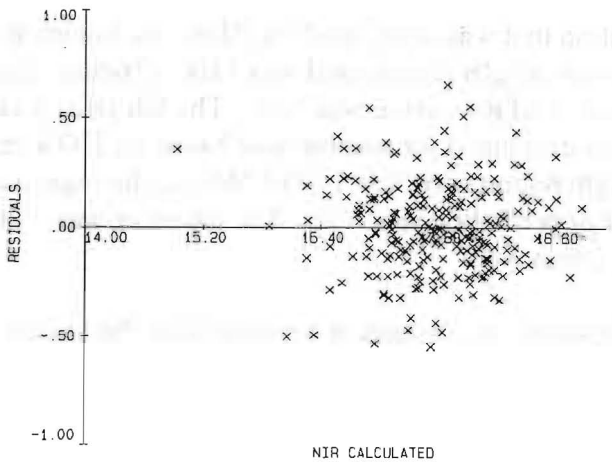

Figure 2. Cossette Sugar: Residual Plot

Cossette Purity Analysis by NIR

At the beginning of the 1999-2000 beet processing campaign, a new method of cossette purity analysis was implemented in the factory labs. For this method, 50% solutions of cossette extracts are prepared, which are extremely turbid and dark. These solutions are analyzed for purity using a polarimeter and refractometer.

NIR was selected to use to obtain true cossette purity analysis in the factory labs. The calibrations were based on IC sucrose measurement and refractometer measurement for RDS.

Because of the goal of having all five American Crystal Sugar Company factory labs capable of running true sucrose measurements, and because of the problems with the NIRSystems unit, a new NIR instrument was selected. Criteria for instrument selection included: ease of operator use, improved sample introduction system, instrument robustness in the factory environment, ease of calibration transfer between five instruments, and ability to analyze both liquid and solid samples on the same instrument.

A Brimrose Corporation (Baltimore, MD) Luminar AOTF-NIR Free Space spectrometer was selected. This instrument was custom designed for American Crystal Sugar Company to accommodate the need for a dual-purpose instrument for both liquid and solid samples, and ease of use for factory personnel. The instrument can be used in the transmission mode for liquid samples and the reflectance mode for solid samples. The instrument is equipped with a 1mm flow-through cell for liquid samples. The cell can be taken apart for cleaning if necessary. Liquid samples are simply poured through a funnel and scanned. The instrument has a rotating sample dish to accommodate solid samples.

The AOTF instrument is solid state and has no moving parts. It is not affected by vibration, which makes the instrument particularly well suited to factory environments. The instrument also has excellent wavelength repeatability which allows for easier calibration between multiple instruments.

The initial calibration equation that was developed for RDS was based on 200 samples and was a 6 factor pls equation. The wavelength region used was 1100-1760nm, the regression coefficient was 0.98, and the standard error of prediction was 0.13. The lab error was 0.10. The initial calibration equation that was developed for sucrose was based on 200 samples and was a 7 factor pls equation. The wavelength region used was 1100-1760nm, the regression coefficient was 0.91, and the standard error of prediction was 0.26. The lab error was 0.20. Plots for these calibrations are shown in Figures 3-6.

These calibrations will be updated for changes in the crop over the campaign, and also for future crops.

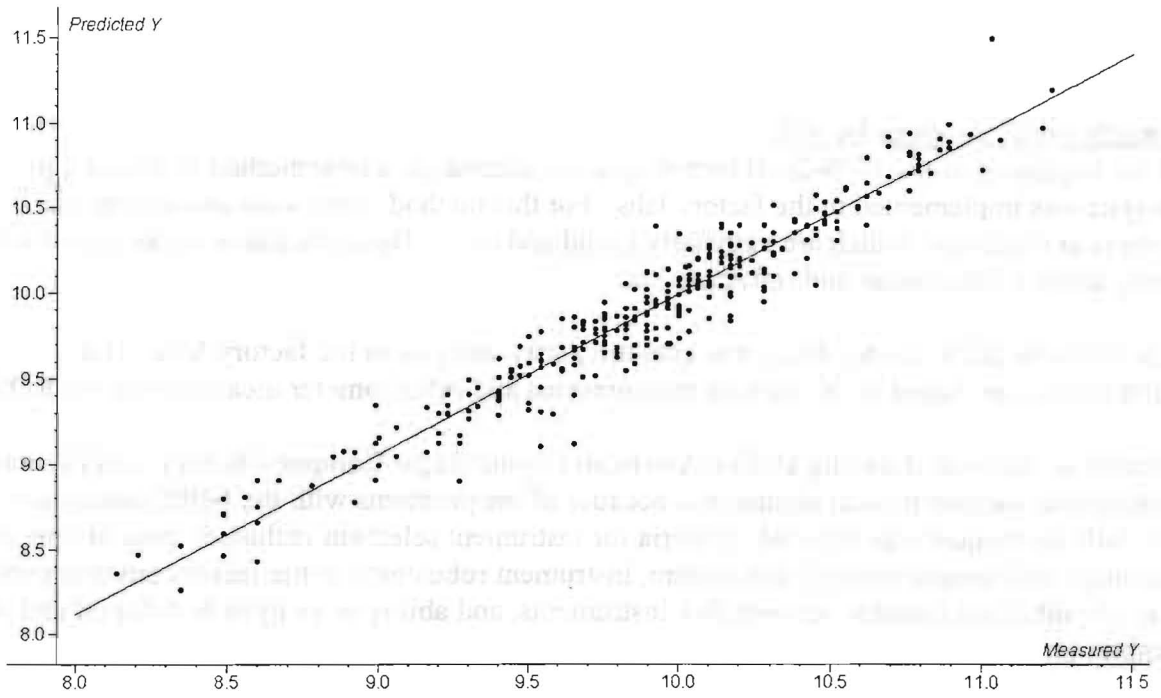

Figure 3. RDS: NIR predicted vs. Lab

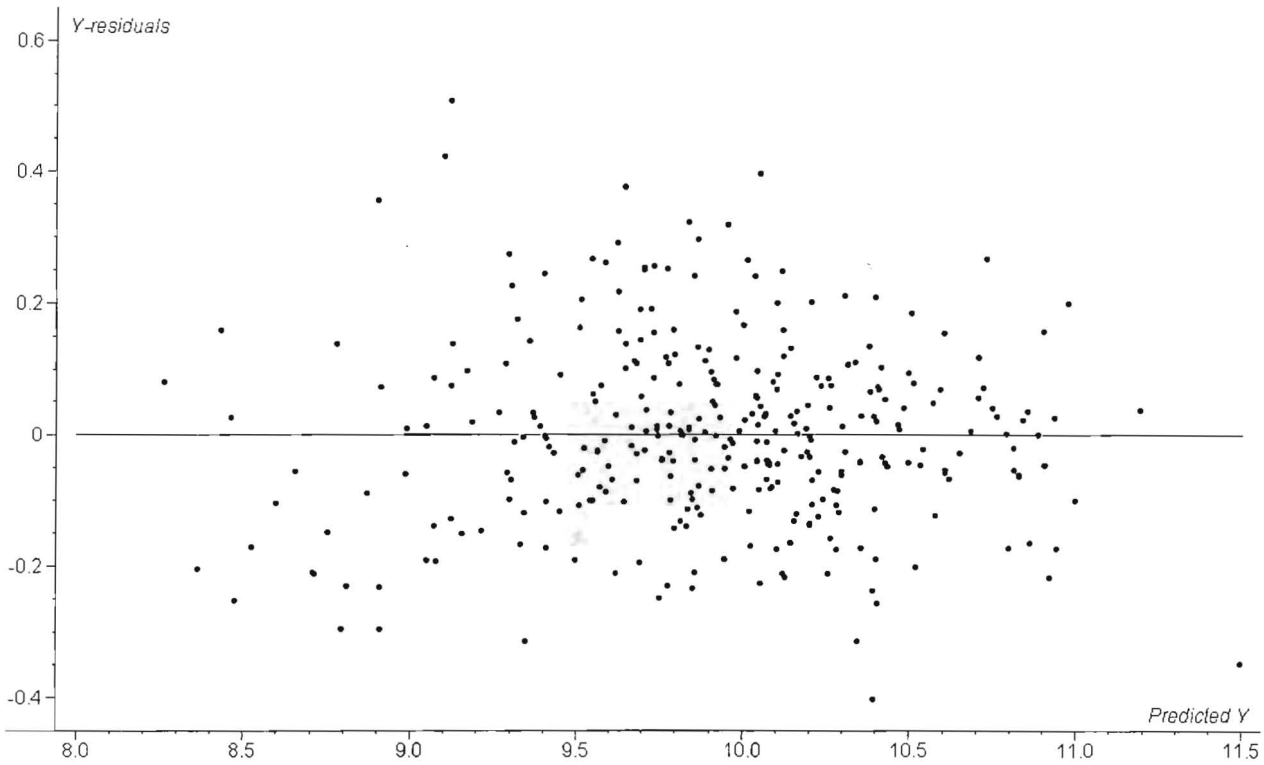

Figure 4. RDS: Residual Plot

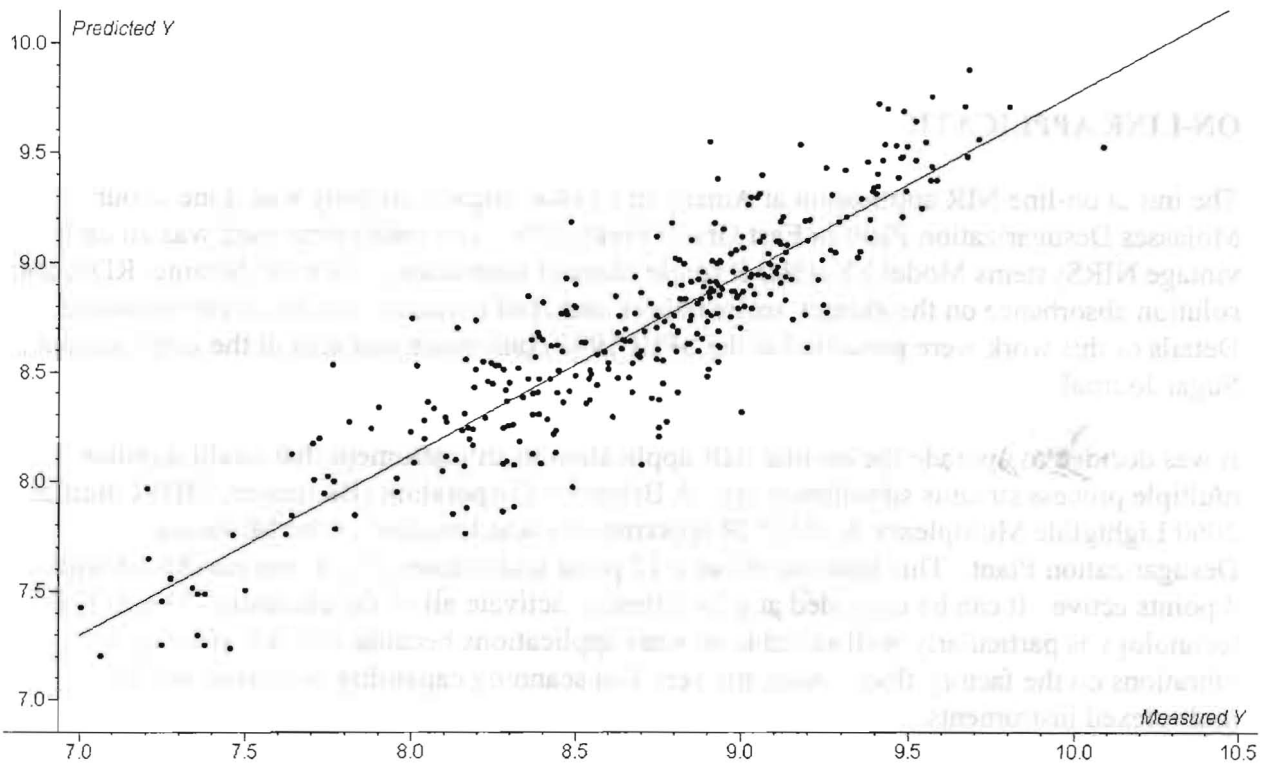

Figure 5. Sucrose: NIR vs. Lab

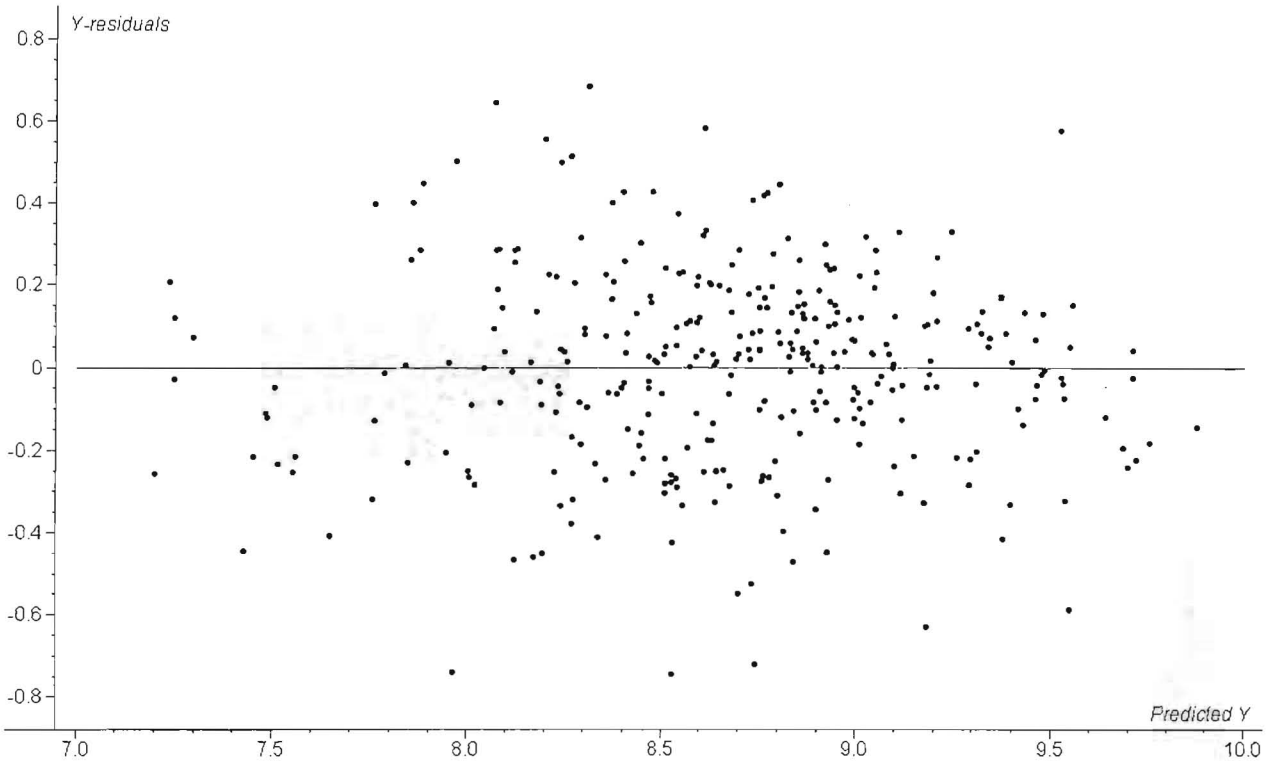

Figure 6. Sucrose: Residual Plot

ON-LINE APPLICATIONS

The initial on-line NIR application at American Crystal Sugar Company was done at our Molasses Desugarization Plant in East Grand Forks, MN. The instrument used was an early vintage NIRSystems Model SY-4500-P single channel instrument. Sucrose, betaine, RDS, and solution absorbance on the extract, recirculation, and feed molasses streams were measured. Details of this work were presented at the SPRI 1998 conference and also in the International Sugar Journal.

It was decided to upgrade the on-line NIR application to an instrument that could monitor multiple process streams simultaneously. A Brimrose Corporation (Baltimore, MD) Luminar 2060 Lightglide Multiplexer AOTF NIR spectrometer was installed in the Molasses Desugarization Plant. This instrument has a 12 point multiplexer, but it was purchased with only 4 points active. It can be upgraded at a later time to activate all of the channels. The AOTF technology is particularly well suited to process applications because it is not affected by vibrations on the factory floor. Also, the very fast scanning capability is convenient for multiplexed instruments.

The on-line instrument is installed on the extract, recirculation, feed molasses, and raffinate product streams. Calibrations are running for true sucrose, RDS, betaine, and solution absorbance. Data is output in real time to the factory Process Information Management System.

CONCLUSIONS

Benchtop NIR applications have allowed true sucrose measurement in the factory labs at American Crystal Sugar Company. The NIR method has been easier and faster for factory lab personnel to use than chromatographic methods. The on-line NIR applications have made available real time information for process decision making.

The calibrations that have been developed for the NIR applications will continue to be upgraded to include changes in the beet crop during storage, and also to include future crop years. This will result in making the calibrations more robust.

The development of the NIR applications will continue at American Crystal Sugar Company. Potential applications for NIR technology are abundant throughout the factory.

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