Application Note 116: Analysis of Barley on the Cropscan 1000B utilizing Multiple Calibration Selection.

NIR Technology Systems

Introduction:

The analysis of whole grain barley has been a problem using Partial Least Squares (PLS) calibration methodology. A single PLS calibration does not adequately compensate for all the spectral differences observed in barley samples. Artificial neural network methodology appears to resolve these problems by using the spectra to make decisions on the suitability of a calibration model and a sample.

NIR Technology Systems has developed a new methodology called Multiple Calibration Selection (MCS) that separates samples of barley into Type A and Type B.

This report shows the results of developing two separate calibrations for Type A and Type B barley and the improvements gained in prediction of barley samples.

Procedure:

Over two hundred and fifty barley samples were collected throughout Australia and analyzed for protein and moisture. These samples were scanned using the Cropscan 1000B Whole Grain Analyser. The Cropscan 1000B has a pour in/flow thru sampling system with a 18mm pathlength and scans over a wavelength from 720nm to 1100nm. 10 scans were taken for each sample and each sample was presented twice to the analyser. A separate set of 44 samples was also scanned in duplicate and used as a prediction set for the developed calibrations.

Figure 1 below shows the Near infrared Transmission (NIT) spectra for all of the barley samples.

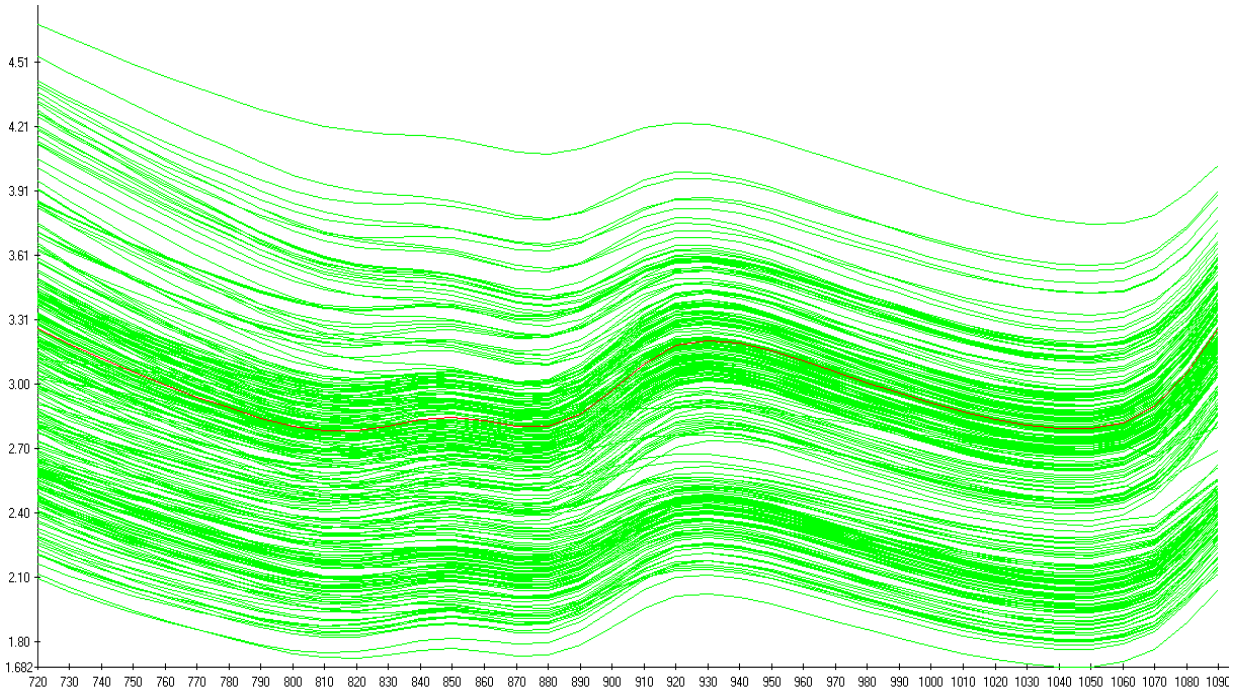

Figure 1: NIR spectra of scanned barley samples.

The spectra shown in figure 1 were used to create a new barley calibration for protein and moisture. The new calibration for protein had a Standard Error of Calibration (SEC) of 0.4 and a

correlation (R^2) of 0.87. For analyzing barley in the Australian market place this not completely acceptable.

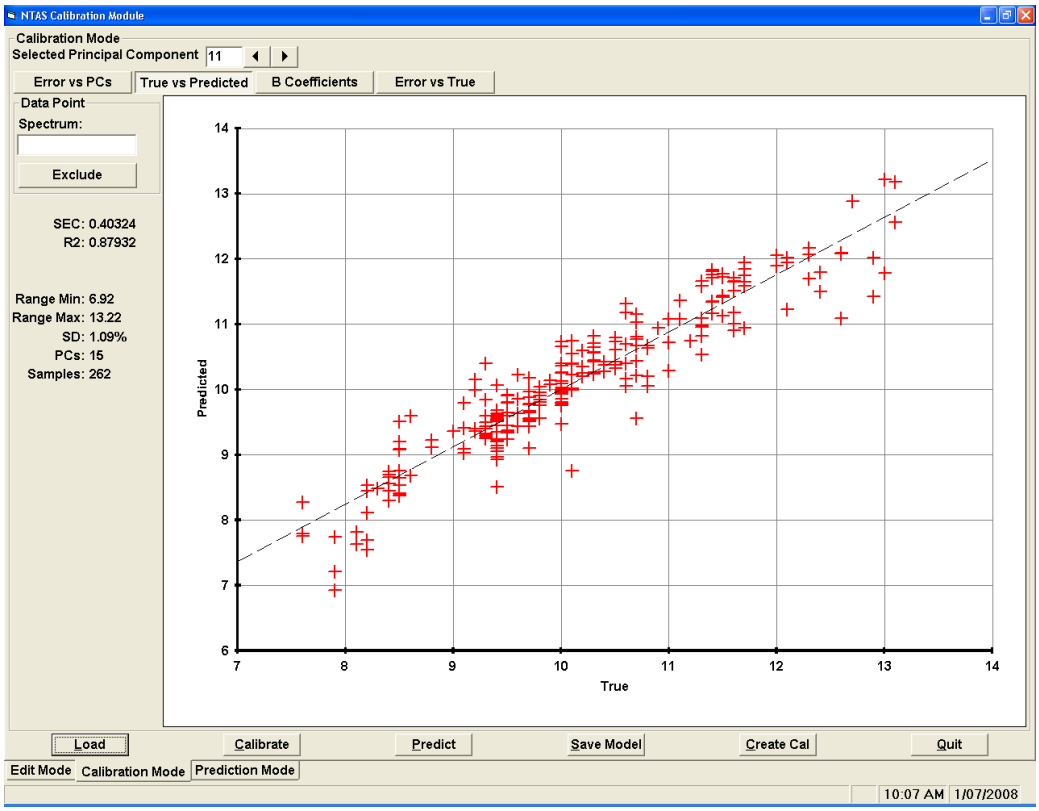

Figure 2: Calibration plot for Protein.

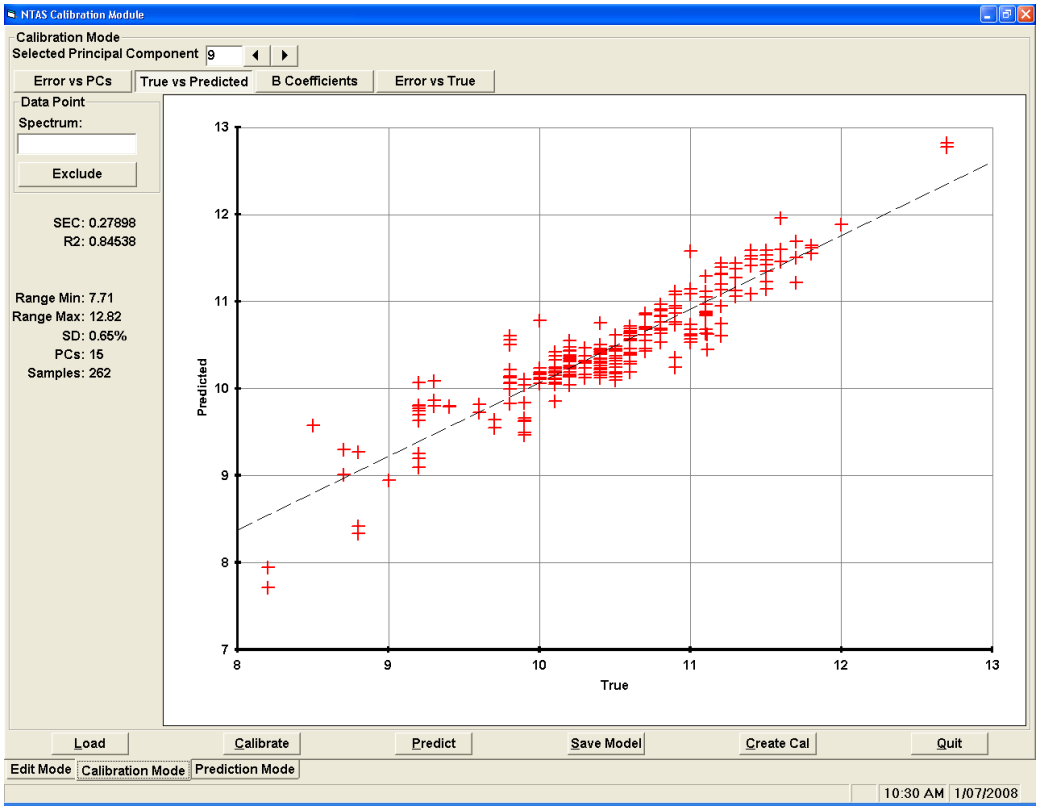

Figure 3: Calibration plot for Moisture

As can be seen in figure 3. the calibration for moisture is slightly better with a Standard Error of Calibration of 0.28 and a correlation of 0.85. Given the high SEC for protein than required, i.e., approx 0.25%, the barley samples were separated into two primary categories based on spectral

differences. The two types of barley shall be referred to as Type A and Type B for future reference.

The barley samples were separated based on differences in the earlier part of the spectra as seen below in figure 4. The lack of a “dip” in the spectral region of 810nm is the primary source for separation of the samples. Type A barley does have the indicated dip that the type B barley samples lack.

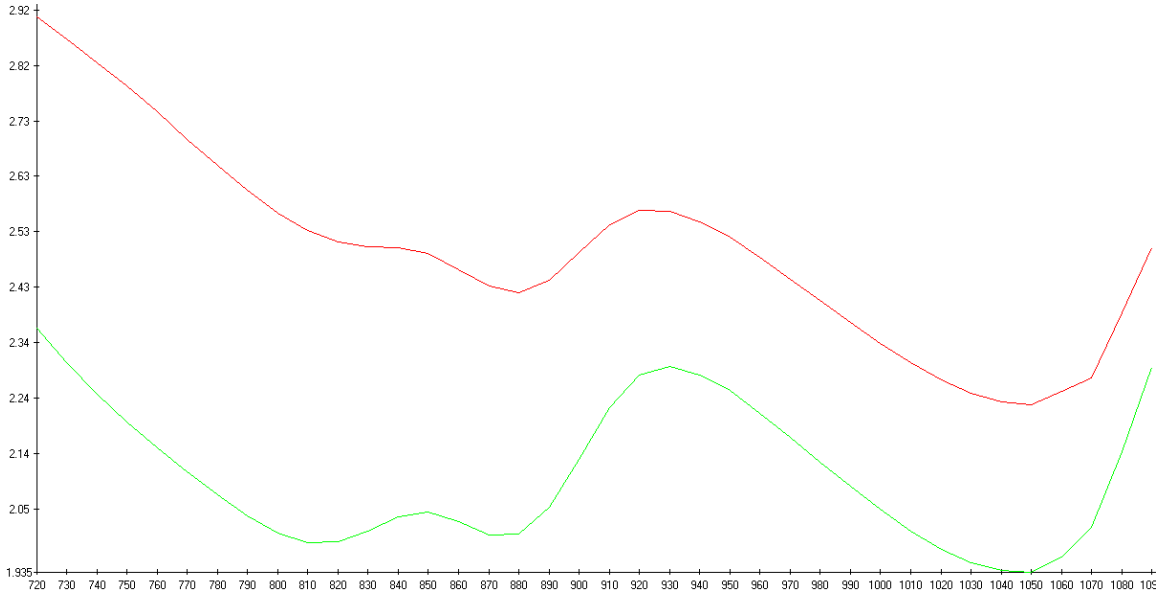

Figure 4: Spectral comparison between types A and B barley.

By converting the spectra to 1st derivative spectra, this dip is observed as being a negative slope at pixel 11, i.e., 830nm. Type A spectra have a positive slope and Type B have a negative slope, as shown below.

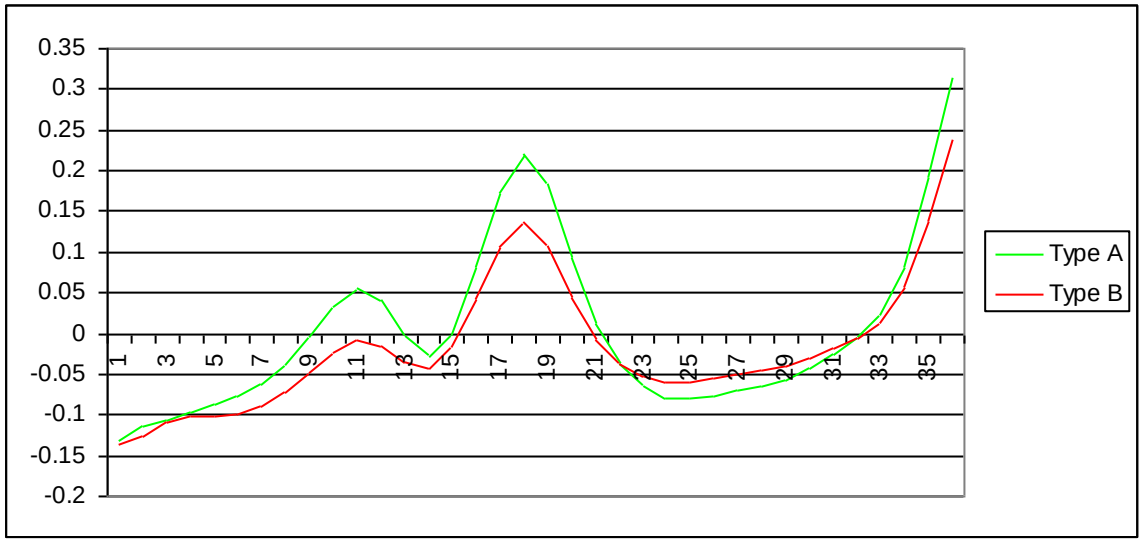

Figure 5. 1st Derivative Spectra showing Type A and Type B barley samples.

At this stage it is not understood why this difference occurs in the spectra. Darker coloured spectra and weather-damaged spectra appear to exhibit this phenomena more than normal malt grade barley. However this observation does not always hold since some light coloured barley samples may also be Type B.

After converting the barley spectra into the 1st derivative spectra and separating the barley samples into the Type A and Type B, new calibrations were developed for each type, with Type A containing the majority of the samples. Note that the absorbance spectra were still used for calibration. The 1st Derivative Spectra were only used to make the decision whether the barley was Type A or Type B.

As can be seen in the calibration plots below there are significant improvements for both protein and moisture. Protein is significantly improved with are Standard Error of Calibration of 0.28 and a correlation of 0.93. Moisture also improved with a Standard Error of Calibration of 0.22 and a correlation of 0.88.

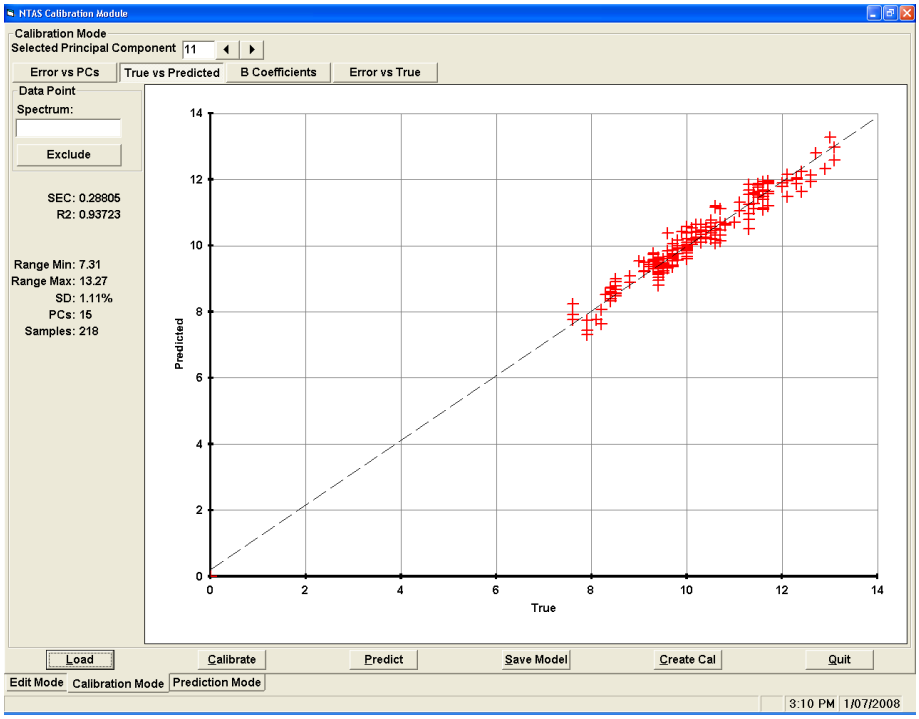

Figure 6: Calibration plot for protein in Type A barley.

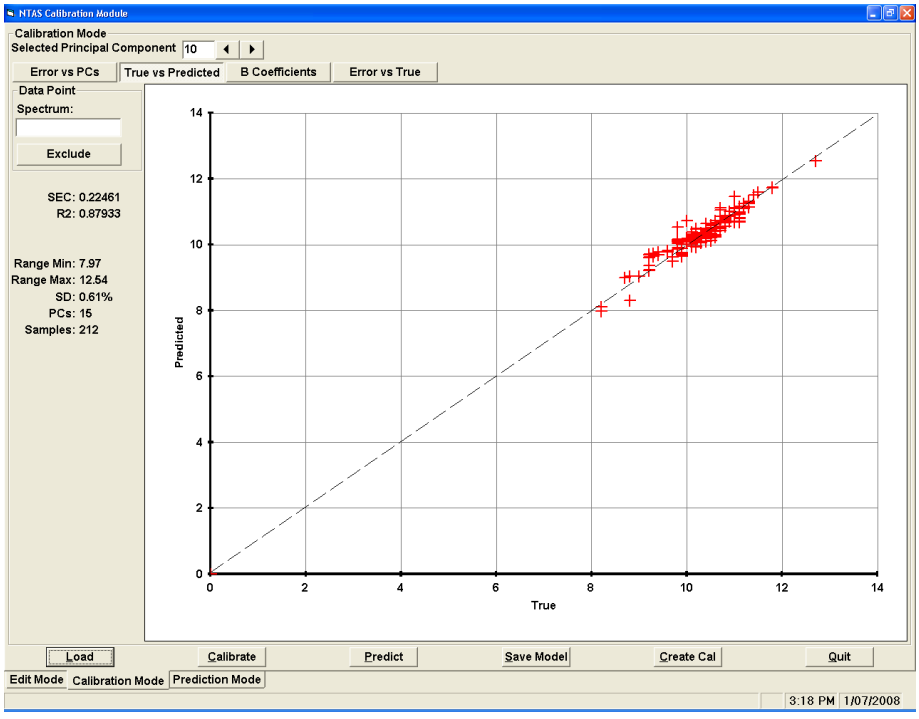

Figure 7: Calibration plot for moisture in Type A barley

The calibrations for the Type B barley were similar to the Type A barley calibration, however there were only 36 samples for the Type B barley calibration. This is not considered sufficient to develop a robust calibration.

Nonetheless, as can be seen in the following calibration plots for Type B barley, there were good improvements for both protein and moisture. Protein is significantly improved with a Standard Error of Calibration of 0.18 and a correlation of 0.95. Moisture also improved with a Standard Error of Calibration of 0.19 and a correlation of 0.87.

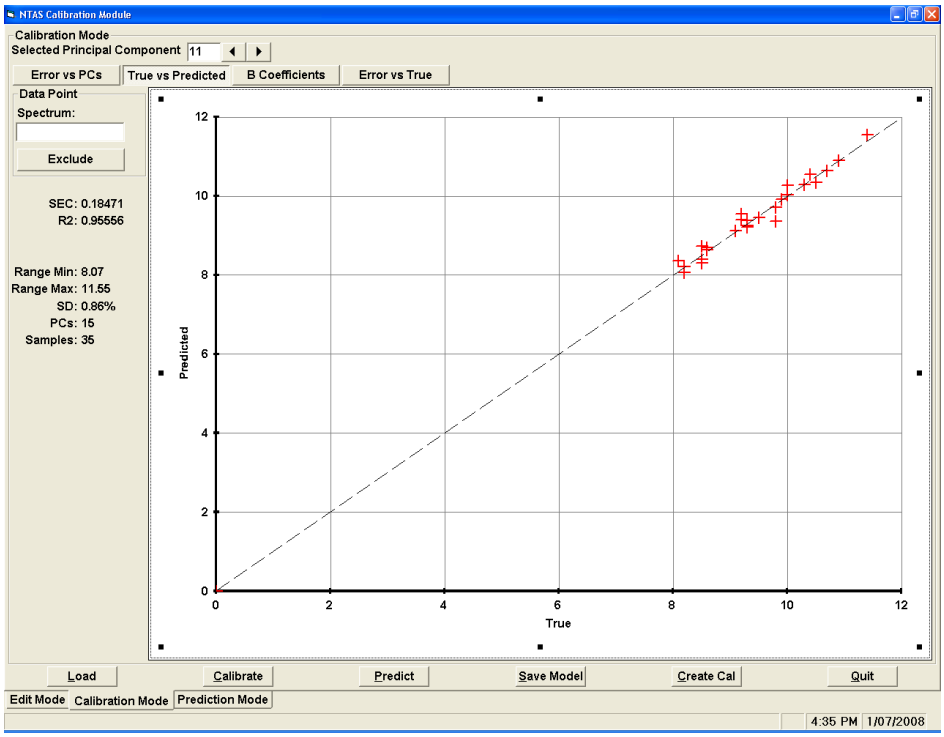

Figure 8: Calibration plot for protein in Type B barley.

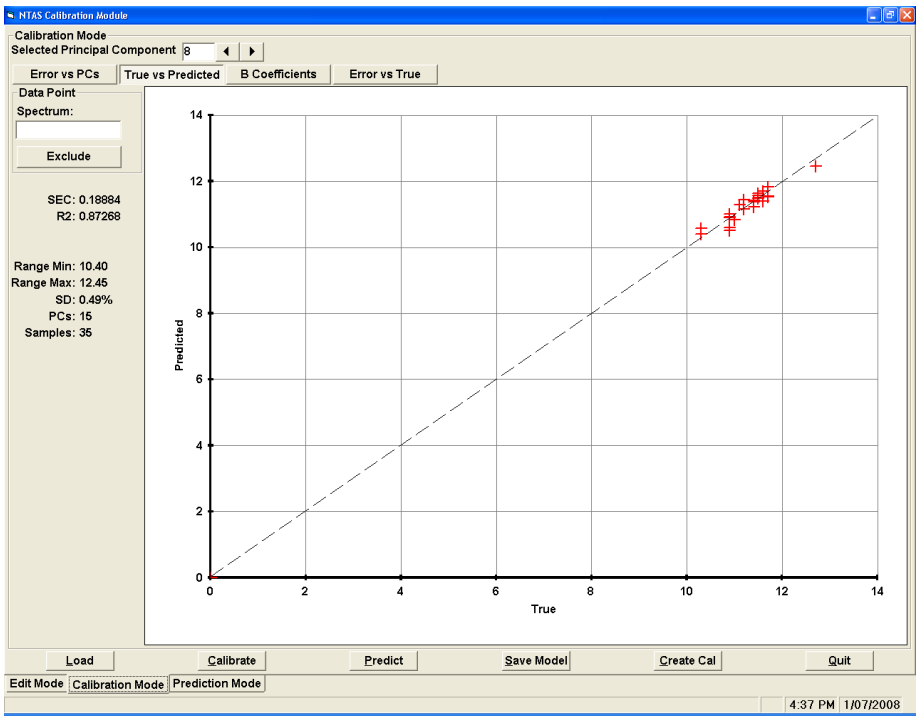

Figure 9: Calibration plot for moisture in Type B barley.

Prediction Analysis:

A new methodology called Multiple Calibration Selection (MCS) has been developed for the Cropscan 1000B and 2000B Whole Grain Analysers. This software makes it possible to install calibrations for both Type A and B barley in the Cropscan analysers under a master calibration called Barley (MCS). When Barley (MCS) is selected the analyser will scan the sample, convert it to the 1st Derivative spectrum and determine if the spectrum is positive or negative at pixel 11. Based on this computation, the analyser will decide whether to apply the Type A or Type barley calibrations the for each sample.

The MCS software is designed to separate out the two types of barley and thereby improve the prediction for both types.

A prediction set of 44 samples was run through the analyser initially use the initial barley calibration based on both Type A and Type B samples. The set was run again using Barley(MCS) calibrations to compare the prediction results based on the MCS vs. original PLS calibration.

Below is the prediction plot for protein using the calibration based on all samples, as per standard operation of the analyser. It can be seen from these plots that Standard Error of Prediction (SEP) for Protein is 0.37 with a correlation (R^2) of 0.93 for the combined prediction set.

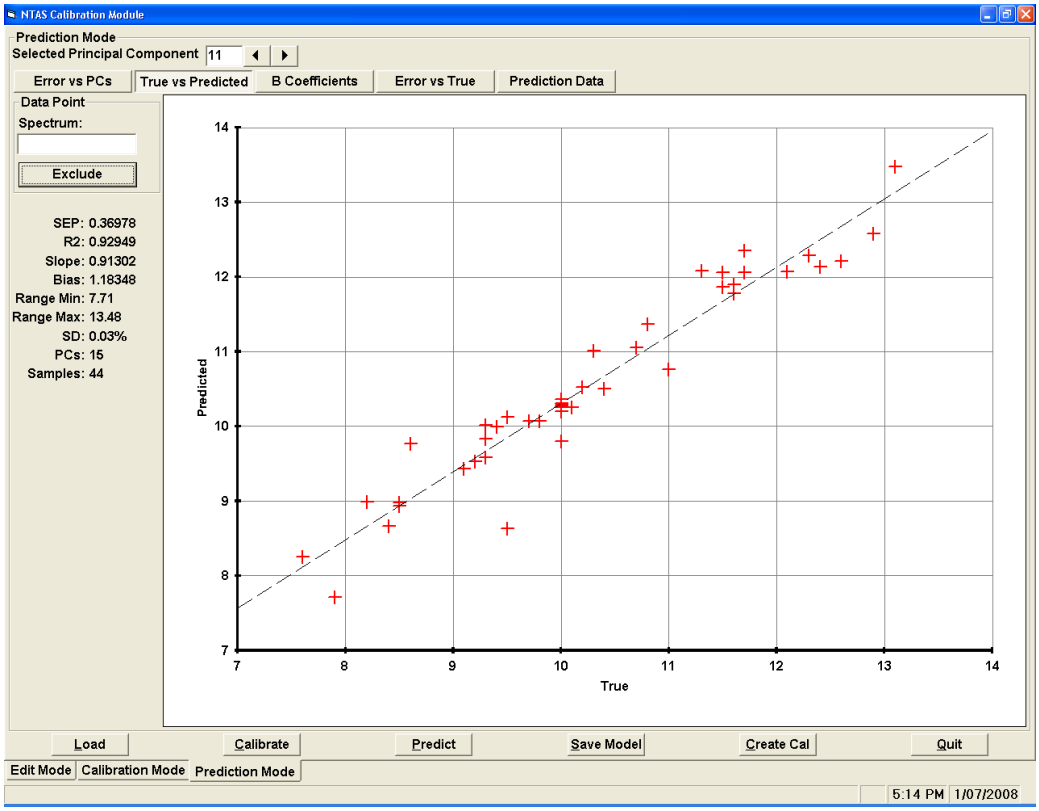

Figure 9: Prediction plot for protein for the combined prediction set.

However, when MCS is used to divide the prediction set the results improve for both types of Barley. As can be seen in the plots below the Standard Error of Prediction for protein in the Type A barley is 0.21 with a correlation of 0.97.

Whilst for the type B barley the Standard Error of Prediction for Protein is 0.35 with a correlation of 0.98. Note that there were only 4 Type B barley samples in the prediction set.

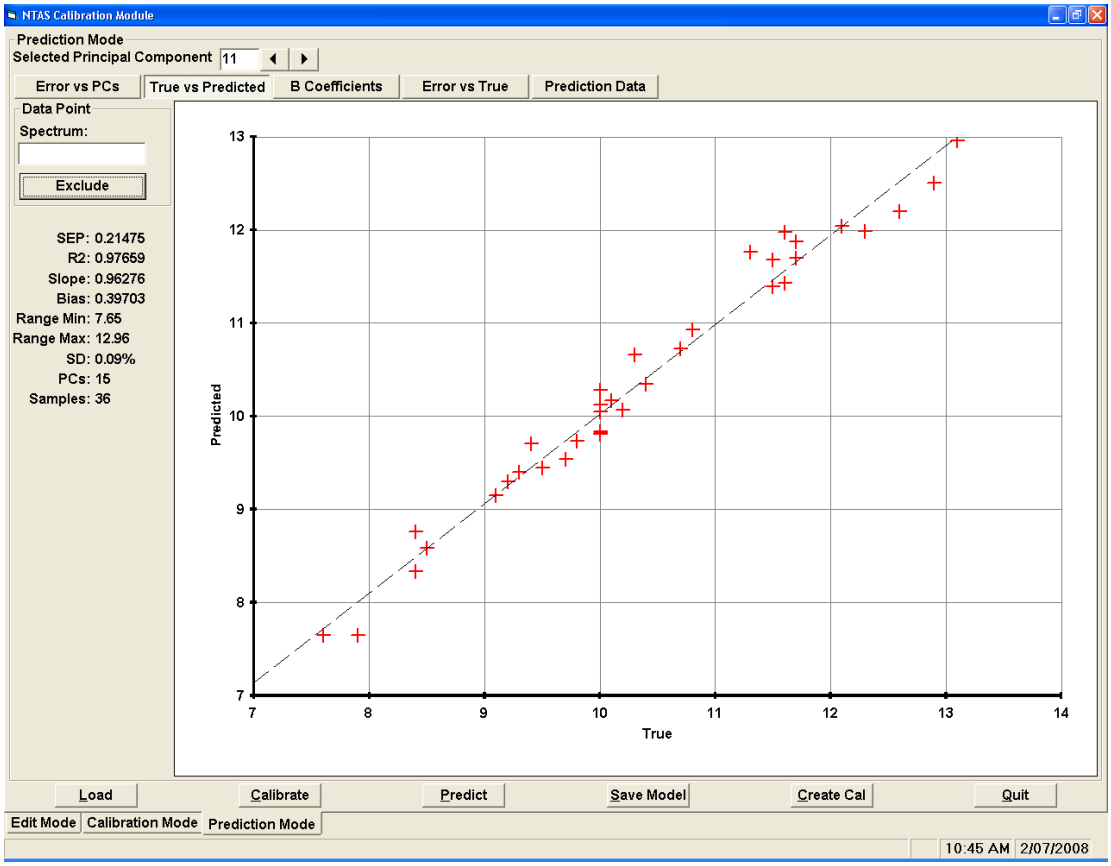

Figure 10: Prediction plot for protein in Type A barley.

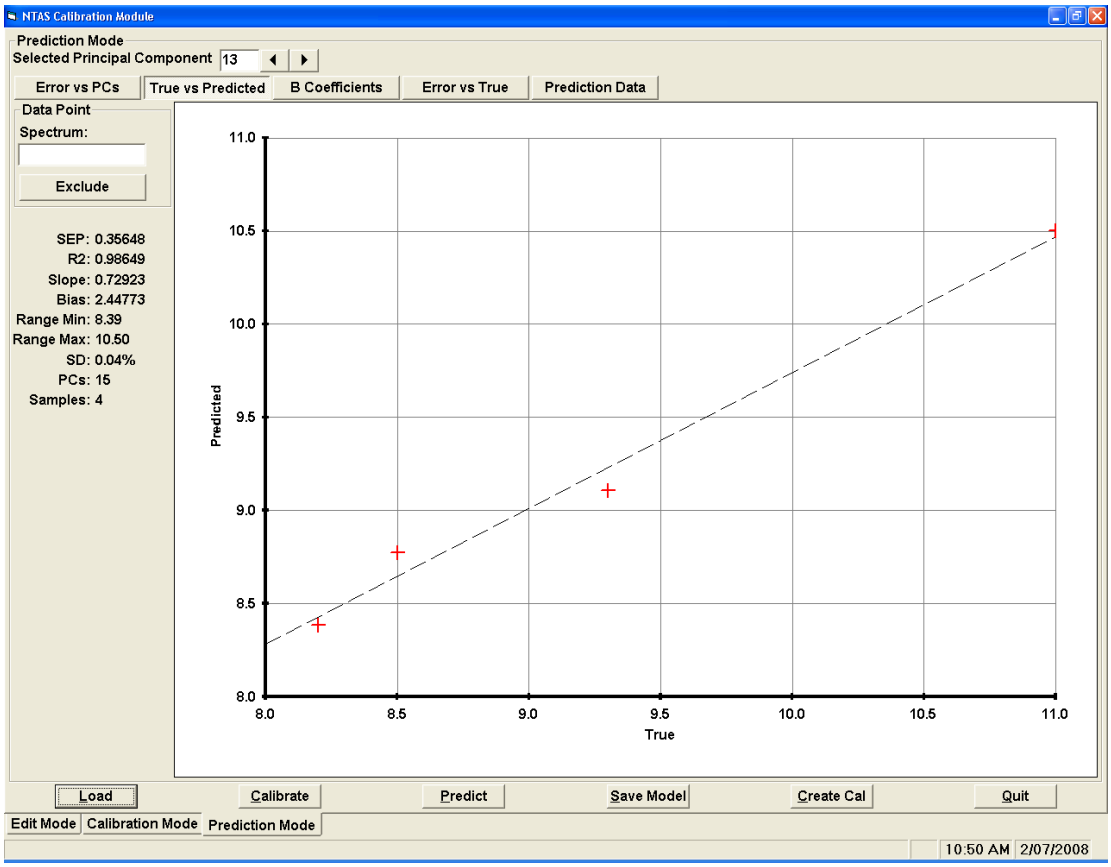

Figure 11: Prediction plot for protein in Type B barley.

Below is the prediction plot for moisture using the calibration based on all samples, as per standard operation of the analyser. It can be seen from these plots that Standard Error of Prediction (SEP) for moisture is 0.31 with a correlation (R^2) of 0.95 for the combined prediction set.

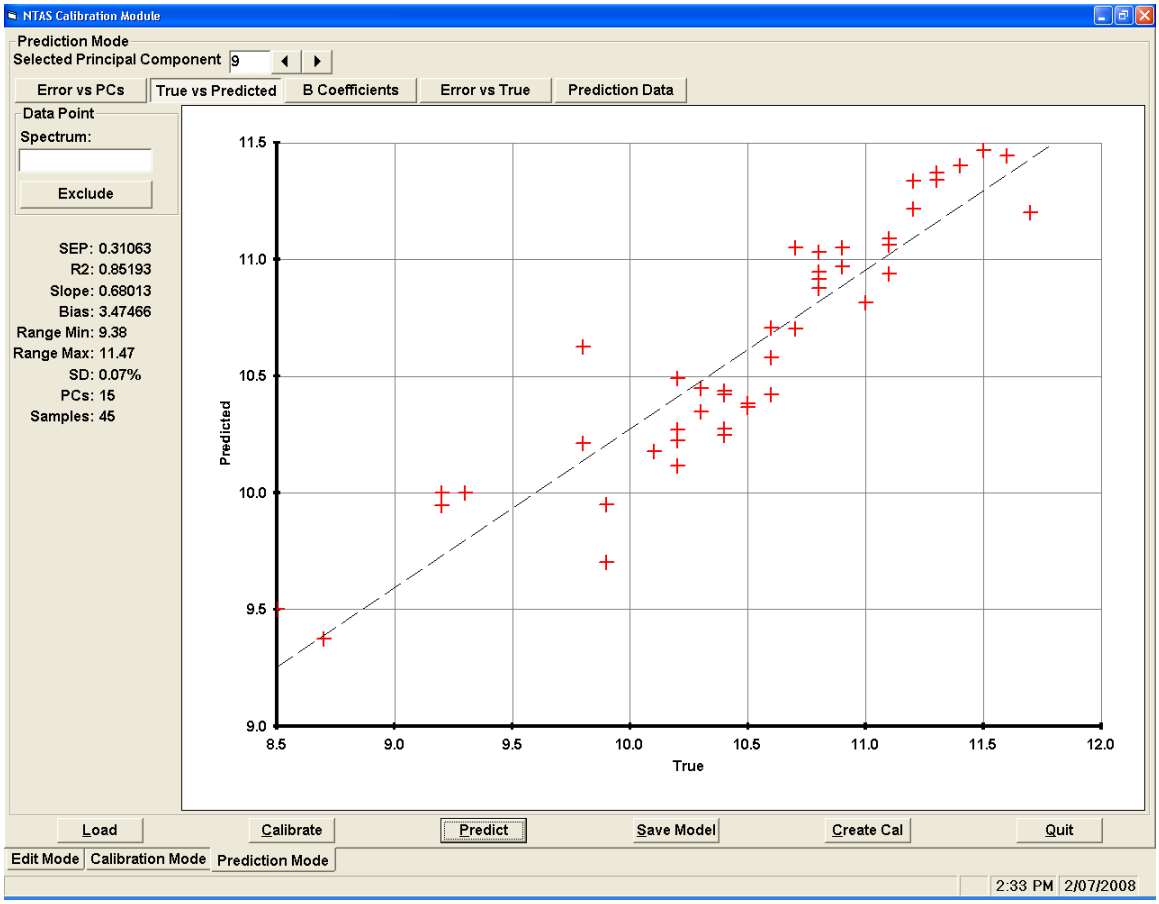

Figure 12: Prediction plot for Moisture for the combined prediction set.

When MCS is used to divide the prediction set the results improve for both types of Barley. As can be seen in the plots below the Standard Error of Prediction for moisture in the Type A barley is 0.23 with a correlation of 0.85.

Whilst for the Type B barley the Standard Error of Prediction for Moisture is 0.10 with a correlation of 0.88. While this seems to be very good it must be noted that there are only a very small number of Type B barley samples in the prediction set.

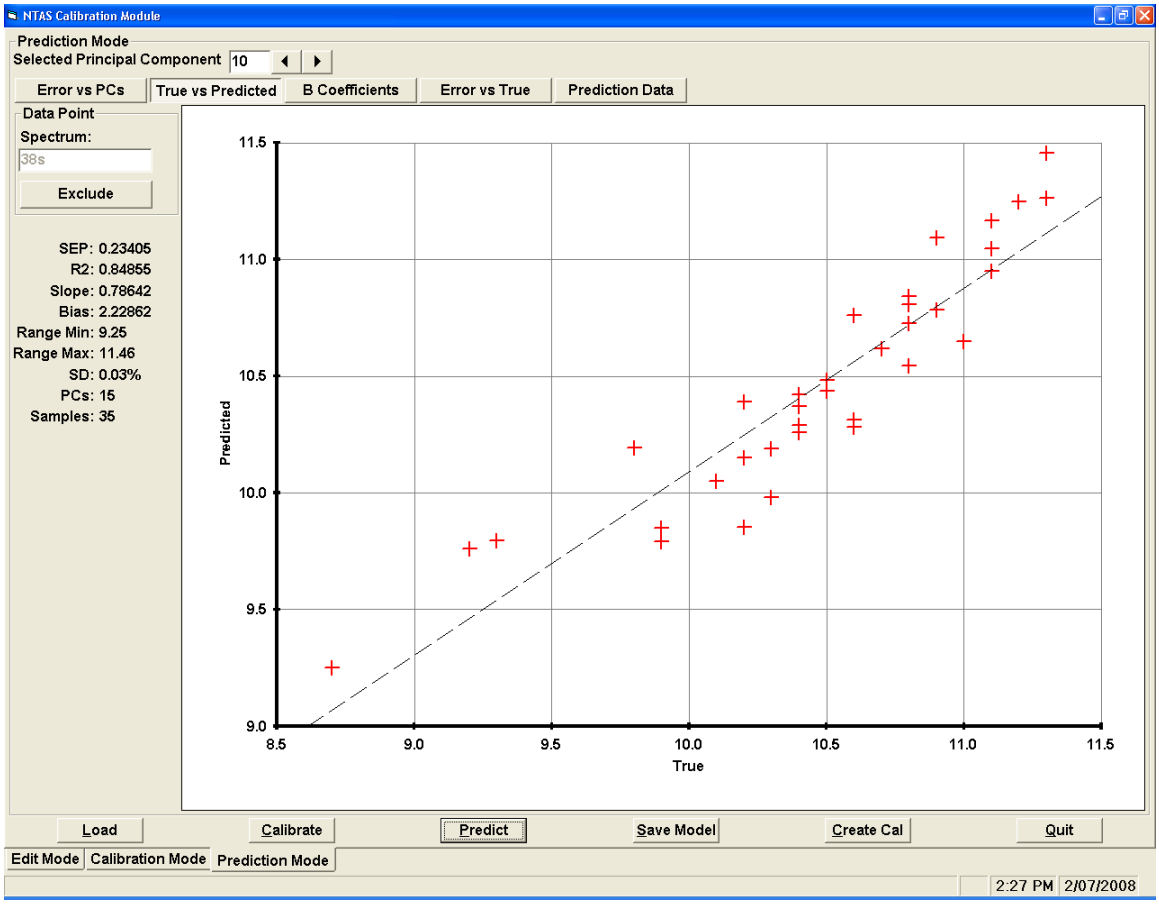

Figure 13: Prediction plot for moisture in type A barley

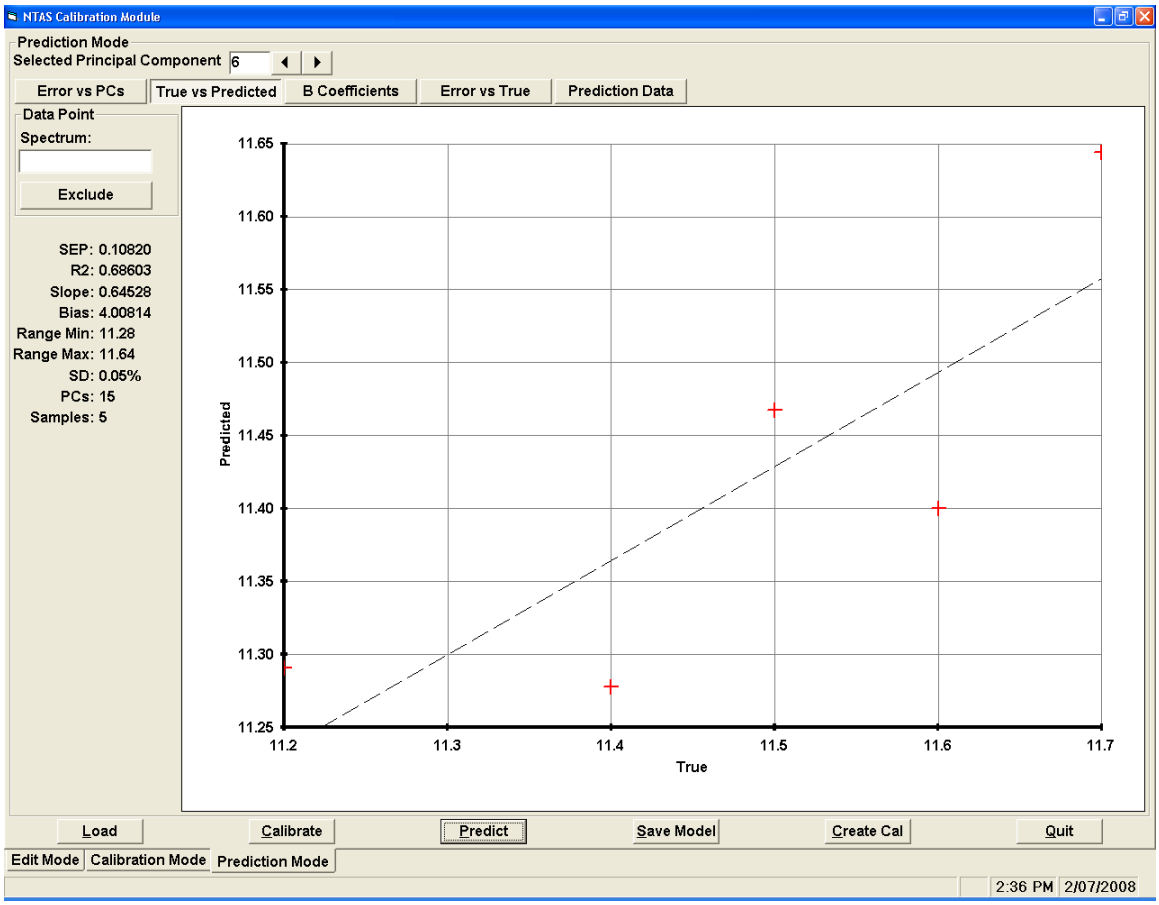

Figure 14: Prediction plot for moisture in type B barley.

Conclusions:

The use of MCS shows significant improvements over standard calibrations for Type A barley, with a reduction in the SEP of almost 40% for protein and 30% for moisture. However, for Type B barley the reduction in SEP was about 10% for protein and 60% for moisture. It is considered that this would most likely change if the prediction set had a greater number of Type B samples. As the prediction set had only a handful of Type B samples it is not a true statistical representation of Type B barley.

Analysis of numerous records show that the presence of type B barley in the general population of barley samples is only about 10-15% of samples. This low representation in the general population clearly demonstrates that type B barley samples are the exception to the norm.

Therefore, it can be concluded that the enhancements to the standard calibration by use of MCS is highly valuable for the greater majority of barley samples. With continued collection of more Type B barley, a better calibration can be expected and therefore a better prediction SEP can be expected.

NIR Technology Systems
366 Edgar Street, Condell Park, NSW, 2200, Australia
Tel: 612 9771 5444, Fax: 612 9771 5255
Email: nirtech@nirtech.net, Web: www.nirtech.net