

The Effects of Sample Presentation in Near-Infrared (NIR) Spectroscopy

NIR spectroscopy is a desirable methodology due to its unique ability to measure a wide range of different material types such as powders, liquids, solids, and slurries—often with little or no sample preparation. Users can measure these materials in their current states, saving analysis time and increasing sample analysis throughput. However, when developing a method for NIR spectroscopy, care should be taken to ensure that the sample presentation is both repeatable from user to user and is reproducible over time.

Variation in sample placement on the spectrometer can introduce unnecessary variance in the collected spectra. This can cause higher levels of error in any quantitative calibration model. The two greatest factors influencing sample presentation are particle size and compaction. When both compaction and particle size fluctuate,

the light in the NIR region interacts with the samples differently, introducing a scatter effect into the sample spectrum. Figure 1 demonstrates sample compaction effects of powdered sugar in a glass vial. Notice that as the sample is gradually packed into the sample vial, an offset is introduced into the collected spectrum.

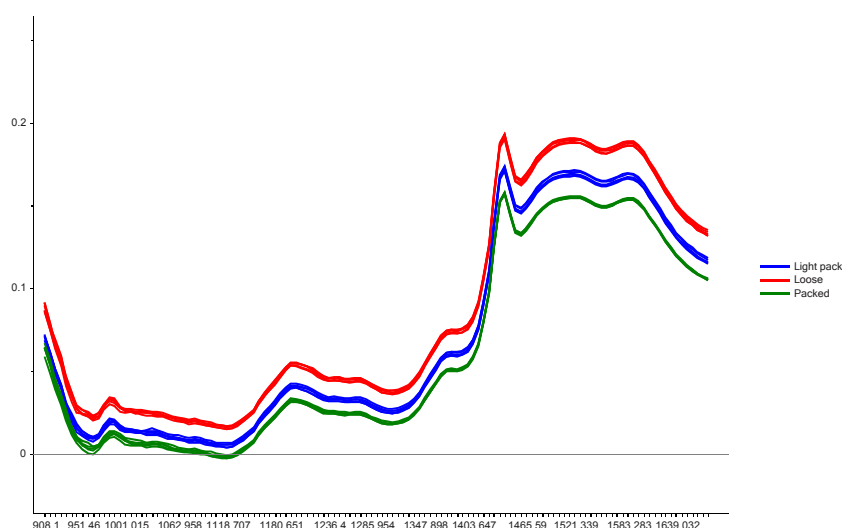


Figure 1. Powdered sugar spectra of a sample exposed to different levels of compaction

With particle size, the impact can be variable depending on the homogeneity of the sample. If the sample chemical makeup is consistent, then the particle-size effects are less severe and present themselves in a bias of the baseline from one sample to the next. For example, consider granular and confectioner's

(powdered) sugar. Chemically, the materials are the same with the difference being particle size. The particle size influences the light scattering within the sample. Figure 2 shows the spectral offset as a result of particle size.

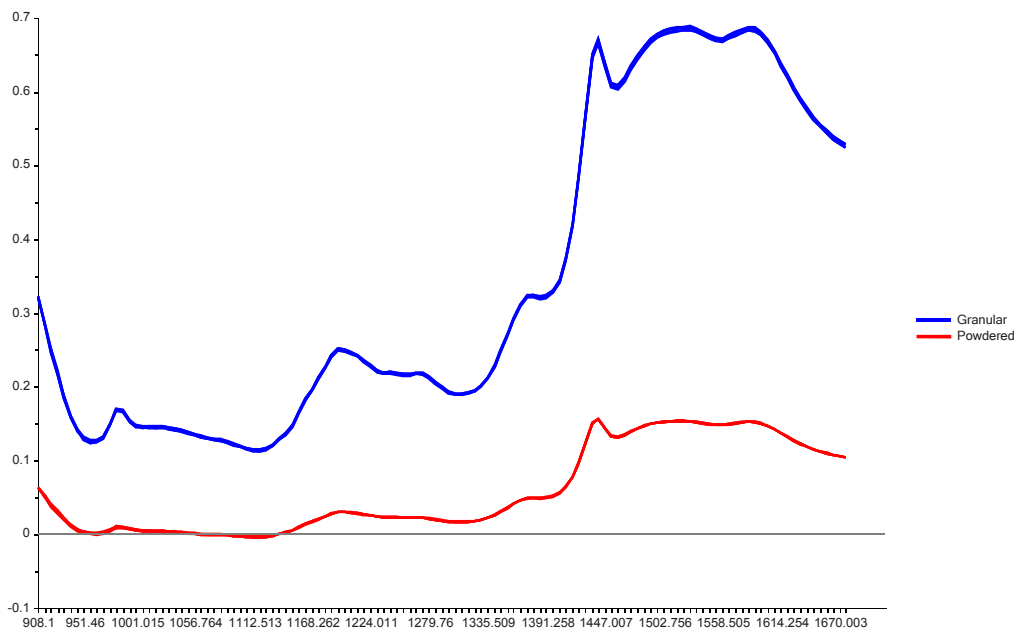


Figure 2. Comparison of granular and powdered sugar absorbance spectra

Figure 2 shows a loss in spectral specificity in the powdered spectra. While the major peaks are still visible, the smaller subtle peaks become less pronounced. When varying degrees of particle size are likely in the sample material, it is important to account for variation of particle size in a calibration model. Applying a baseline

correction and derivative to the spectral data can do a reasonable job of eliminating most of the particle size effects as shown in Figure 3. If a calibration model focuses on these less pronounced peaks, a separate calibration model may be required.

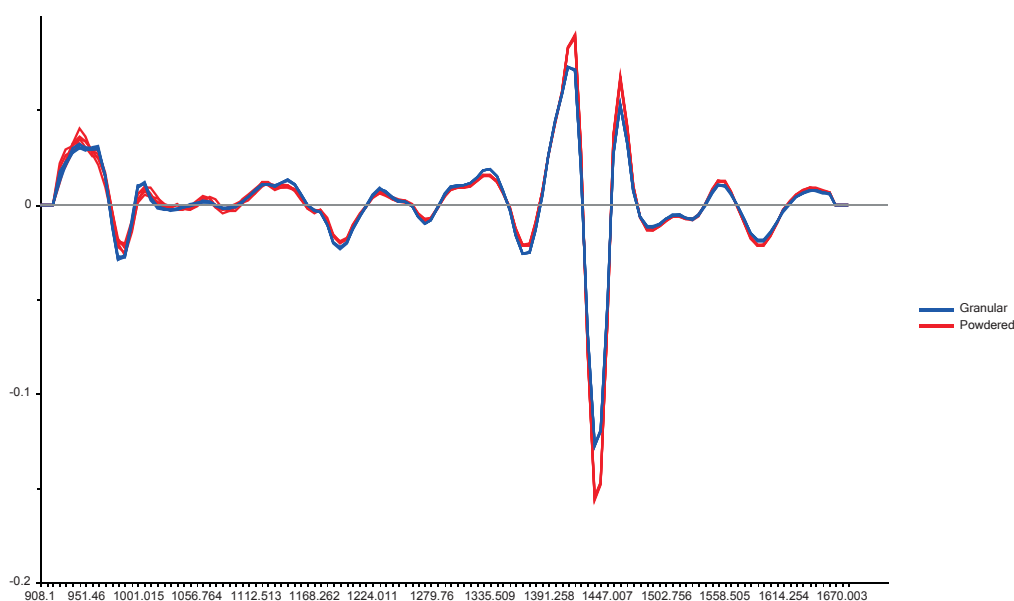


Figure 3. Baseline corrected 2nd-derivative spectra of granular and powdered sugar

For heterogeneous samples, such as biomass mixtures, feeds, or forages, particle-size effects become much more critical. The different particles can have very different chemical compositions, and accounting for this variability is important for calibration model deployment.

Figure 4 shows 10 different spectra collected on a sample of wood chips at two different time periods, time 1 and time 2. The variation across the spectra is extreme.

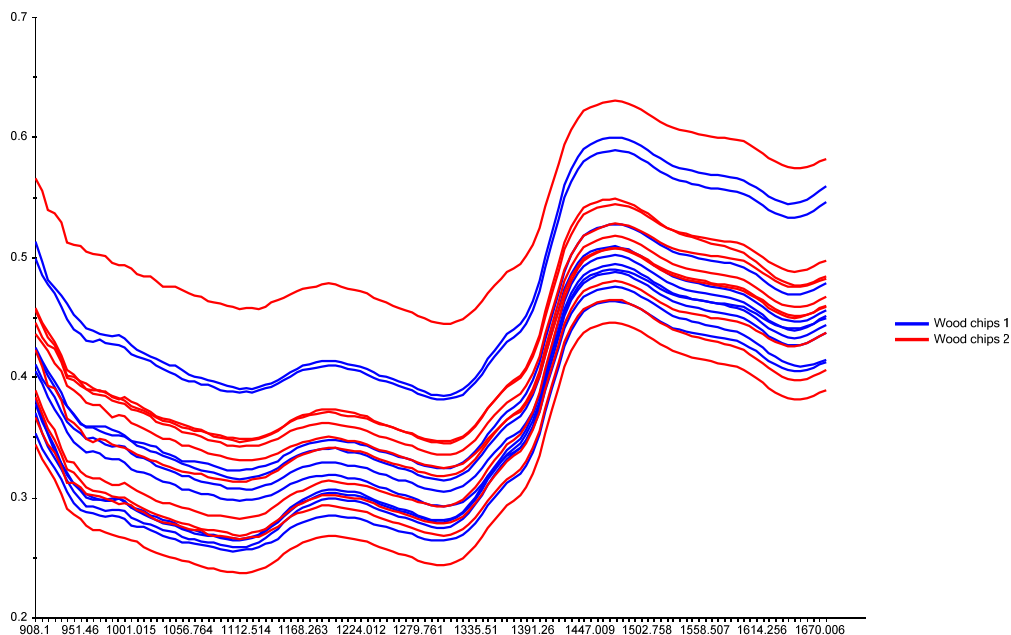


Figure 4. Absorbance spectra of wood chip samples

Averaging the 10 scans together creates a different view, as shown in Figure 5 and the baseline-corrected 2nd-derivative spectrum in Figure 6.

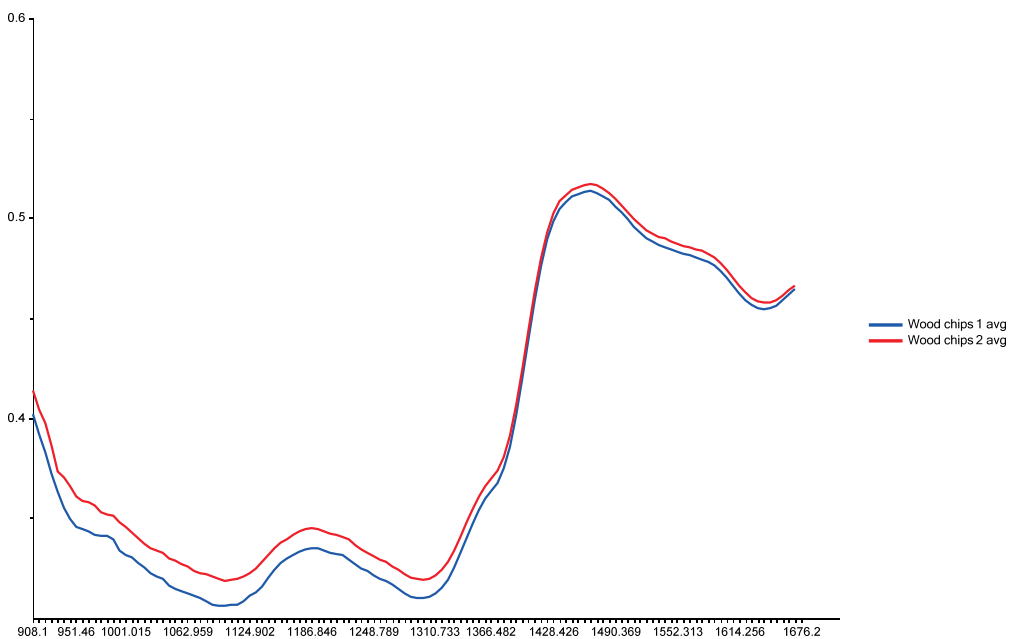


Figure 5. Averaged absorbance spectra of wood chip samples

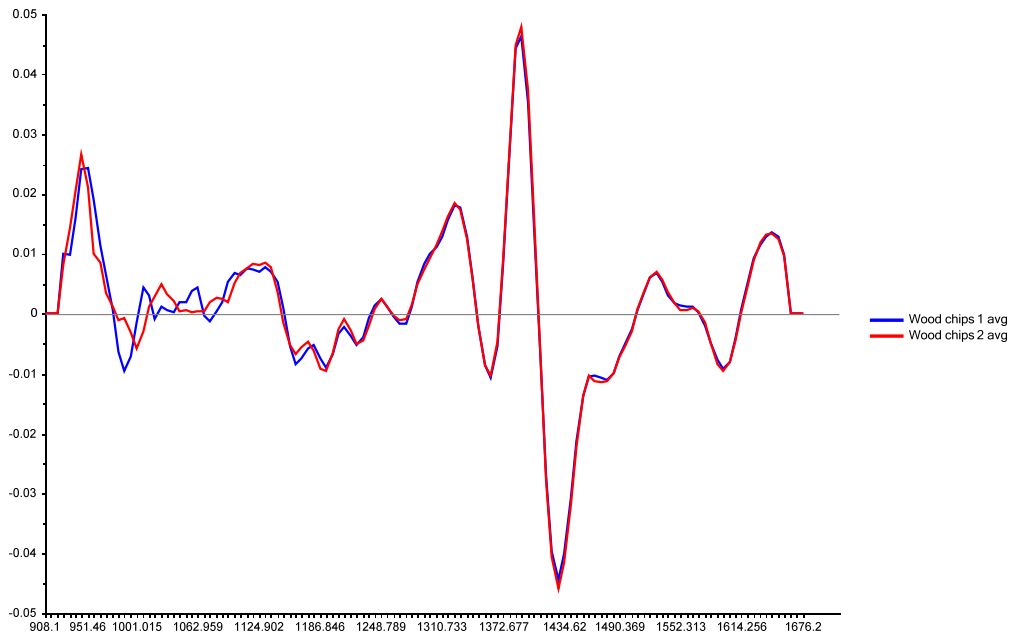


Figure 6. Baseline-corrected 2nd-derivative of average wood chip samples

When dealing with heterogeneous samples, sufficient replicate averaging must be explored to account for the sample heterogeneity. Failure to investigate this component of sample variability will introduce unnecessary variance into the calibration model and subsequently affect overall model performance and accuracy.

To summarize, sample presentation to a NIR spectrometer is an important attribute for superior model performance. Proper care should be taken to fully understand any effects of sample compaction, particle size variation, or sample presentation to the spectrometer. Properly accounting for these effects in the calibration model will generate superior results and more robust and reliable prediction accuracy.