Interactance–reflectance v. reflectance near infrared analysis of grains and ground animal feeds

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Introduction

The main applications of near infrared (NIR) spectroscopy for grains and powders have been done using reflectance and transmittance. During the past ten years, there has been an enormous development of fibre optic probes and cables. However, most of the applications of fibre optic probes have been done on suspensions, clear liquids and films, chemical and pharmaceutical products and also on fruits and animal products.

In the feed and milling industries, where several Tm. of material arrive and are processed daily, fibre optic probes and cables could represent an important saving in NIR analysis time (avoiding milling and packing in cups) and a useful interface to provide on- and in-line quality control at different key points at the processing plant.

At this moment, there are a large number of fibre optic styles and the choice of a given probe and fibre optic is primarily dependent upon sample type.[1]

The objective of the present paper is to compare the interactance–reflectance spectra of grains (barley, wheat and maize) and coarsely ground soybean meal v. the reflectance spectra of the same materials analysed after fine milling.

Material and methods

Samples

In this study, 60 barley, 45 maize and 47 wheat grain samples and 57 coarsely ground soybean meal samples were used for the interactance–reflectance analysis, while the reflectance analysis was performed on the same samples, but after grounding through a cyclone mill (1 mm screen).

NIRS hardware

A scanning monochromator, NIRSystems model 6500 (NIRSystems Inc., Silver Spring, MD, USA) with auto-gain detectors, was used to measure interactance–reflectance spectra from 400 to 2498 nm every 2 nm. The analysis was carried out using a fibre optic probe (NR-6775). Five spectra were collected for each sample at different locations, in order to calculate spectral repeatability.

For the comparison with the classical reflectance analysis, an NIRSystems 6500 without auto-gain-detectors and a spinning module, which uses standard ring cells was used.

NIR software

All manipulations and processing of the spectra were carried out with the ISI software NIRS3 ver. 4.0 and WINISI ver. 1.02 (Infrasoft International, Port Matilda, PA, USA).

Spectral repeatability was calculated as the root mean square (RMS) of the differences between each spectrum and the mean spectrum of sub-samples for all the log 1/*R* data points. The result is multiplied by 10^6, in order to simplify the expression. The RMS program of ISI software also gives the mean value (mean) and the standard deviation (STD). RMS value can be introduced as a limit in the SCAN program of the ISI software, so that spectra of sub-samples not significanty different in terms of RMS can be accepted and averaged.[2]

$$RMS\ (MEAN) = \sqrt{\frac{\sum_{i=1}^{n}\sum_{j=1}^{N}(Y_{if} - \bar{Y}_i)^2}{nN}}$$

Where:

Y_{ij}: log 1/*R* value for sub-sample *j* at wavelength *i*
$\bar{Y}_i$: Mean log 1/*R* value for all sub-samples at wavelength *i*
n: number of log 1/*R* reading points
N: number of sub-samples

Results and Discussion

The traditional methods used to obtain NIR spectra from grains and powders are reflection and transmission through the material. The basic principles of both types of radiation-sample interactions are well understood today.[3–6] However, less information is available from other radiation measurements such us interactance reflectance using fibre optic probes.

Figure 1 shows the mean reflectance spectra of fine milled grains (wheat, barley and maize) and soybean meal. Figure 2 shows the mean interactance–reflectance spectra of the unground grains and of coarsely ground soybean meal. As it can be seen on those graphs, the shape of the curves and the location and number of relevant peaks and troughs are similar for both analysis modes. So, both

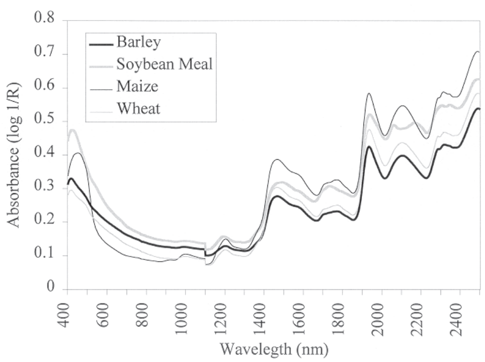

Figure 1. Mean reflectance spectra of fine milled grains (wheat, barley and maize) and soybean meal.

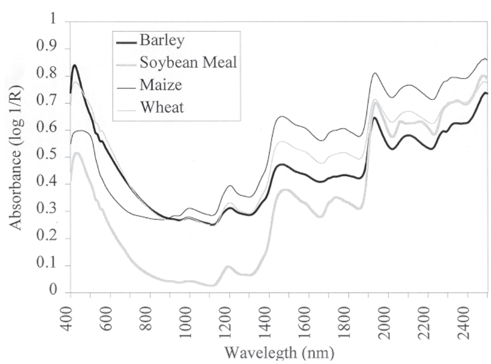

Figure 2. Mean interactance–reflectance spectra of the unground grains (wheat, barley and maize) and coarsely ground soybean meal.

interactance–reflectance and reflectance spectra should have similar analytical information and the analysis of grains and coarsely ground products by fibre optics could theoretically be feasible. Interactance–reflectance analysis of grains causes a reduction in the reflected energy (higher absorbance values) when it is compared to the reflectance analysis of the same products finely milled. The gross baseline differences could be due to changes in the optical properties of the samples associated with particle sizes differences. A change in particle size causes a change in the amount of radiation scattered by the sample. The larger particles do not produce many changes in the direction of incident radiation, so more is absorbed before leaving the sample, resulting in a higher log $1/R$ value. [5] In the case of the soybean meal, the physical state of the product analysed by reflectance and interactance–reflectance is very similar. Furthermore, the coarsely ground soybean meal could cause particles adhering to the window of the fibre optic to limit the penetration of the light into the sample, which would reduce the intensity of the absorbance bands at the lower wavelength regions (400–1400 nm).

One important factor when we work with fibre optics probes is to optimise the wavelength region for data treatment use. Manufacturers of the fibre optic probe used in the present paper recommend spectral data acquisition in the 800 to 2200 nm range. In order to confirm this suggestion, once the samples were scanned and the spectra were recorded from 400 to 2500 nm, the spectral data were examined for noise spikes by plotting the first derivative (1,1,1) of the spectra, [6,7] where spurious noise will appear as very sharp spikes. Figures 3 to 6 show the first derivative spectra for all the products analysed by the interactance–reflectance mode, where spectral errors at the beginning and at the end of the

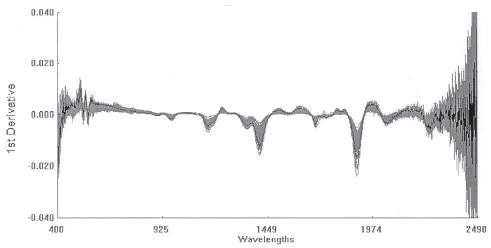

Figure 3. First derivative of the interactance–reflectance spectra of wheat grains.

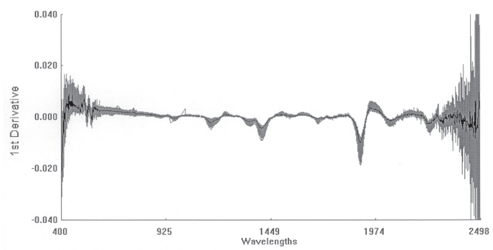

Figure 4. First derivative of the interactance–reflectance spectra of barley grains.

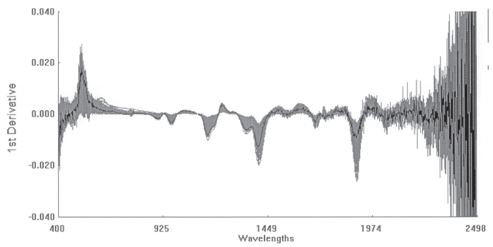

Figure 5. First derivative of the interactance–reflectance spectra of maize grains.

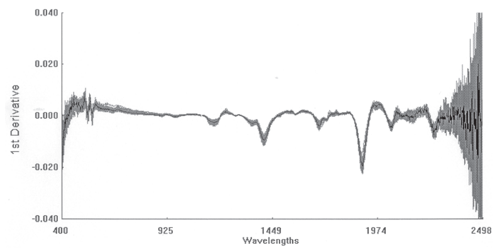

Figure 6. First derivative of the interactance–reflectance spectra of coarsely ground soybean meal.

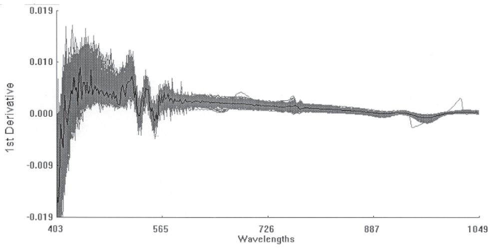

Figure 7. Amplified plot corresponding to the first derivative of the interactance–reflectance spectra of barley grains (lower wavelengths).

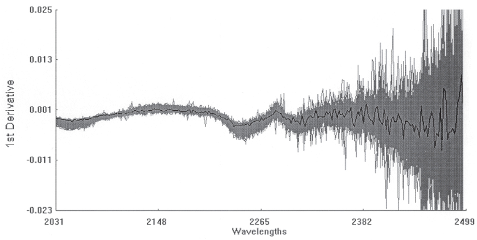

Figure 8. Amplified plot corresponding to the first derivative of the interactance–reflectance spectra of barley grains (higher wavelengths).

spectra are evident. The same type of graph was also obtained for reflectance spectra (not shown). In this case, errors at the end of NIR region were not detected.

Manufacturer recommendations are quite adequate, as wavelengths between 800 and 2200 nm seem to be free of very sharp noise spikes. Figures 7 and 8 illustrate the amplified plots for the extreme wavelengths, confirming that a cut-off point for the visible region could be located around 800 nm. Below 800 nm, there are some samples which exhibit a noisy spectra. As stated by Tkachuck,[6] the presence of even one small noise spike in one sample can have a dramatic effect on the calibration. Cut-off for the NIR region could be established around 2100–2200 nm. Despite the fact that some noise spikes could still be observed in this region, it is expected that they can be removed by mathematical data treatment or by improving spectral repeatability during scanning.

Based on the author's experience it can be said that obtaining highly repeatable spectra for grains using fibre optic it is not easy. Spectral repeatability was calculated using the RMS program of the ISI software. Table 1 shows the mean RMS values obtained from spectra of five sub-samples for each sample analysed. These calculations were done working with two spectral ranges (full spectrum or 800 to 2200 nm) and comparing results for log 1/*R* v. first derivative spectral data. In this table, it can be seen that no improvement is achieved when spectral range is reduced for crude spectra. However, reduction of spectral range applied to first derivative spectra leads to a 30% improvement in spectral repeatability, as an important part of spectral variability due to scatter effect is eliminated with the mathematical treatment. Coarsely ground soybean meal was the product with the best repeatability, while the highest RMS values were obtained from maize, the grain that shows the largest size and the most heterogeneous shape. Table 2 presents the RMS values for five sub-samples of different samples of each material. The comparison of data from Table 1 and Table 2 reveals that, when working with the complete

Table 1. Mean RMS Values calculated from five sub-samples for each sample: two spectral ranges and two mathematical treatments.

Spectral Range	Math treatment	Barley (grain)	Maize (grain)	Wheat (grain)	Soybean meal
400–2498 nm	None	103326	185061	99069	50825
	1st Deriv.	2043	4168	2438	2057
800–2200 nm	None	100222	187761	97396	48291
	1st Deriv.	1350	2883	1920	1320

Table 2. Mean RMS Values calculated from groups of five sub-samples corresponding to five different samples: two spectral ranges and two mathematical treatments.

Spectral Range	Math Treatment	Barley (grain)	Maize (grain)	Wheat (grain)	Soybean Meal
400–2498 nm	None	108636	226833	99795	56185
	1st Deriv.	2292	4787	2628	2130
800–2200 nm	None	104454	228185	97240	53964
	1st Deriv.	1446	3426	2139	1381

range (400–2498 nm) the intra-sample errors are even, in some cases, higher that the inter-sample errors. However, after reduction of the range to 800–2200 nm and after derivation, intra-sample errors are lower than inter-sample errors in all the materials analysed. The highest errors are always obtained for maize and the lowest for coarsely ground soybean meal.

Conclusions

The NIR analysis of whole grains and animal feed meals commercialised after a coarse grinding is feasible using a fibre optic probe. However, efforts should be made to get a repeatable spectrum. Further work is in progress to establish an RMS limit for each material. The RMS limit will be used during the scanning process avoiding the presence of spurious noise.

Acknowledgements

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