

Use of two-dimensional mid-infrared/near infrared spectroscopy to understand the correlation of near infrared spectra to physical parameters

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Introduction

The prediction of physical properties of cotton fibers by near infrared (NIR) has been pursued for the purpose of replacing a multitude of other measurements. Cotton mass has been predicted using NIR transmission measurements.¹ Cotton strength, length, color and Micronaire have been measured using visible/NIR reflectance spectroscopy.^{2,3} Specifically, the Micronaire measurement (considered a measure of fiber maturity and fineness) is a function of fiber wall thickness and cross-sectional perimeter. The Micronaire value is calculated from determining the pressure differential obtained when an air stream is forced through a sample of cotton of specified mass in a chamber of fixed volume. Buco and Montalvo² determined that using the NIR spectral region from 1100 to 2498 provided a better measure of Micronaire than using the visible region or a combination of visible and NIR. They were able to obtain a calibration for Micronaire, from 20 principal components, with an $R^2 = 0.910$ and a $SEP = 0.078$. This was stated to give about the same precision as that of the reference method. In these studies, little has been said about the nature of the NIR peaks that contribute to the calibrations. However, it has been recognized that the peak around 1932 nm is due to moisture and others are due to cellulose and impurities in the fiber matrix.

The mid-infrared region of the spectrum is less convoluted than the NIR region and is the source of the fundamental vibrations that give rise to the majority of the signals in the NIR region. Two-dimensional mid-infrared/NIR spectroscopy has been previously employed to assist in the determination of the nature of NIR signals.^{4,5} The current work was conducted to determine if two-dimensional mid-infrared/NIR spectroscopy could better identify the nature of the factors utilized in a NIR calibration for Micronaire value of cotton fibers.

Experimental

Samples

Cotton samples were obtained from the USDA Southern Regional Research Center in New Orleans, LA. They were from commercial sources and were provided on an “as ginned” basis. The sample set was 14 cottons from six different varieties with Micronaire values ranging from 2.6–5.5 $\mu\text{g/in/fiber}$.

Spectra

All spectra were obtained in the diffuse reflectance mode. NIR spectra were obtained using a NIRSystems 6500 grating monochromator system (NIRSystems Inc., Silver Spring, MD). The samples were packed in standard sample cups, scanned from 1100–2500 nm every 2 nm and averaged over 64 scans. Three sub-samples of the each of samples used for NIR were cut and mixed with KBr. These were then pressed into 13 mm metal cups that were used in Spectra Tech’s advanced diffuse reflectance accessory (Spectra Tech Inc., Shelton, CT). A “blocker” device was used to reduce scatter and the sample compartment was purged with N_2 to eliminate water and CO_2 interference. The mid-infrared spectra were obtained using a Nicolet model 740 Fourier transform IR spectrometer (Nicolet Analytical Instruments, Madison, WI) operated at 4 cm^{-1} resolution. The three sub-samples were averaged into one spectral file for each of the 14 samples.

Software/data processing

Data from both instruments was transferred to a PC compatible format and converted for use in GRAMS/386 (Galactic Industries Corporation, Salem, NH). The partial least squares type-1 (PLS1) method contained in the PLSplus package of GRAMS/386 was used to generate a NIR calibration to Micronaire. The two-dimensional correlation (2D) correlation between the NIR and mid-infrared spectral data was generated using the 2DCORR program, previously developed.⁴ The three-dimensional (3D) rendering was generated using GRAMS/3D.

Results and discussion

The NIR spectra of the 14 cotton samples were obtained under reduced moisture conditions to better approximate the conditions required to acquire mid-infrared spectra. The obvious difference among the set of NIR spectra is offset. The effect of fiber size differences may be analogous to particle size differences. Thus, this difference is not unexpected. Using a total of seven factors, a calibration between these NIR spectra and Micronaire was obtained with PLS1 giving $R^2 = 0.868$ and $SECV = 0.446$ when a sample rotation of 1 was utilized. Although this is not nearly as good a calibration as can be obtained using more samples and improved sampling techniques,² it sufficed for our comparative purposes here. The R^2 correlation plot of the NIR spectra (Figure 1) to Micronaire value indicates a correlation around water at 1930 nm, a correlation at 1680 nm and higher correlations from 1400–1100 nm. Obtaining a useful set of mid-infrared spectra of cotton fibers was difficult to accomplish. Only when three repetitions of the samples were averaged was it possible to get a usable set of spectra. The set of mid-infrared spectra, obtained on these samples (Figure 2), also indicate that the major difference was spectral offset. Signals in these spectra observed at 1600 and 1730 cm^{-1} were found to be due to absorbed water rather than carbonyls, as one might expect. Thus all of the water had not been eliminated from the samples, yet enough purging had taken place to remove water vapor problems in the mid-infrared spectra. A 3D rendering of the 2D correlation of the mid-infrared to NIR spectra gave a NIR projection (Figure 3) from the signals around 2200 cm^{-1} in the mid-infrared that mimicked the R^2 correlation between the NIR spectra and Micronaire values. The signals in the

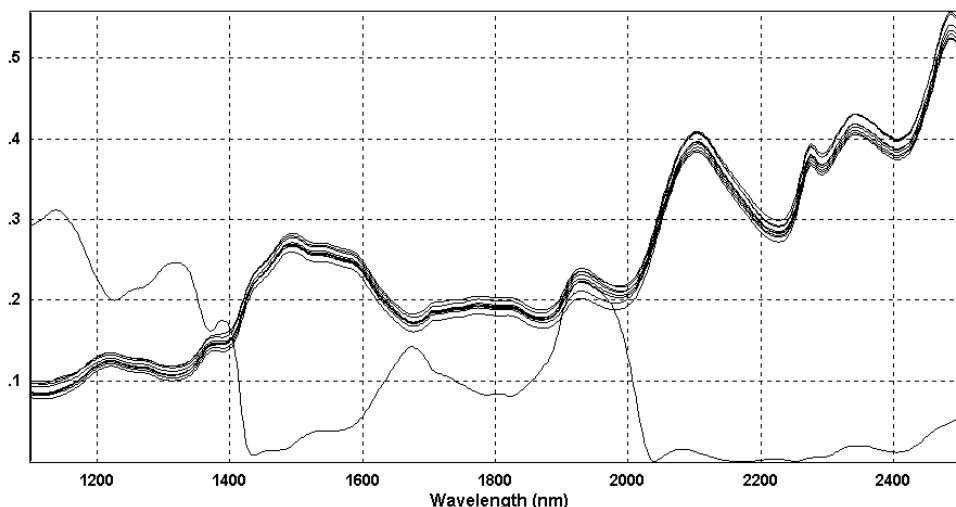


Figure 1. Plot of NIR spectra of 14 cotton samples at 10–15% moisture with R^2 correlation to Micronaire value.

2200 cm^{-1} region appear to arise as overtones or summation bands from signals around 1050–1150 cm^{-1} , in the mid-infrared, due to carbohydrate ring stretching and bridge C–O–C stretching. Changes in absorbances in 1050–1150 cm^{-1} region have been noted to occur for thin films of different thicknesses (2–6 μm) and are related to changes in hydrogen bonding in other regions.⁶ This is the first clue that there is more detail in these spectra and factors than previously observed. Factors 1, 2, 3 and 5 of the PLS calibration are most strongly correlated factors with Micronaire value (that can be understood). These four factors can be generally explained as free water, spectral

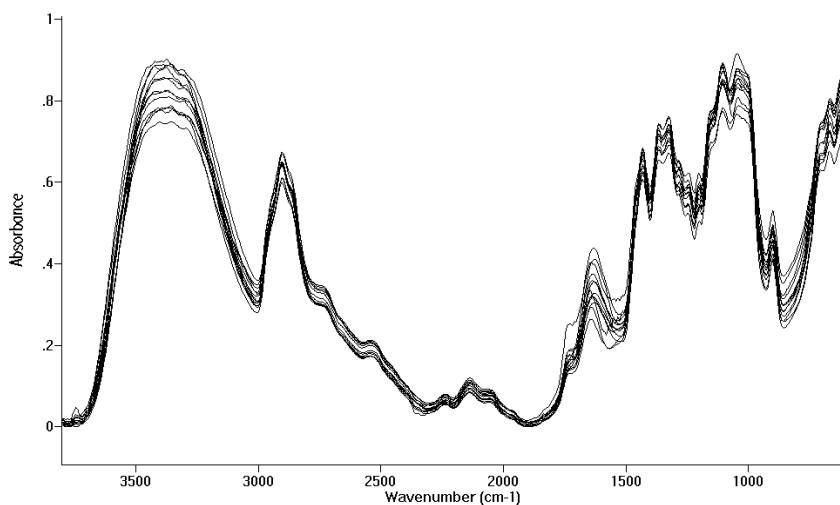


Figure 2. Plot of mid-infrared spectra from 14 cotton samples under N_2 purge.

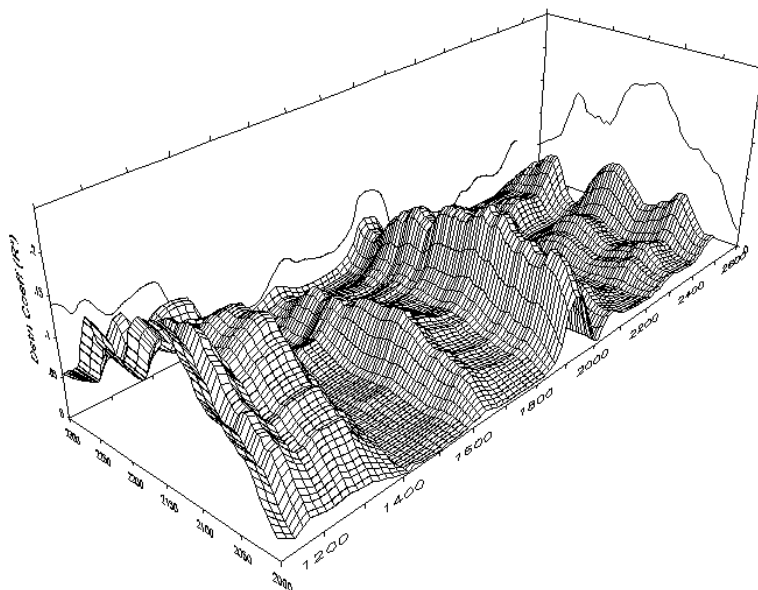


Figure 3. Three-dimensional rendering of the R^2 correlation of the 2000–2300 cm^{-1} region of the mid-infrared to the entire NIR spectrum.

offset, water with some carbohydrate and mostly carbohydrate (respectively). Factor 5, which looks much like a carbohydrate spectrum (Figure 4), contains the most detail and has sharp correlations in the 1450–1600 nm region and around 2100 and 2270 nm. These are the general areas for the 1st overtone of O–H stretch, the combination band of O–H stretch and O–H deformation and combination band of O–H stretch and C–C deformation for cellulose (respec-

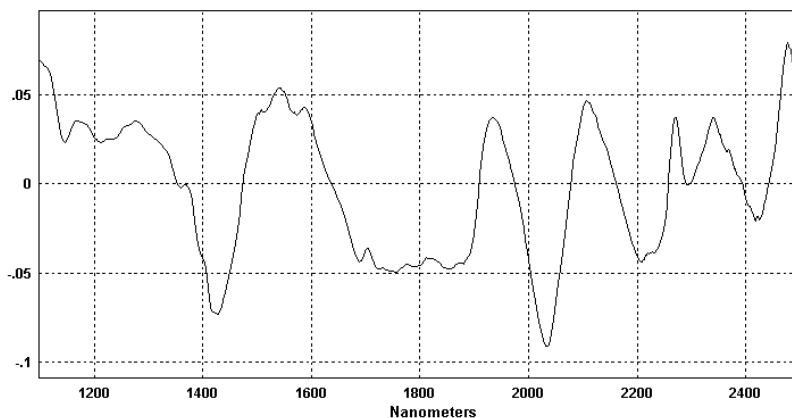


Figure 4. Plot of factor 5 from the PLS1 calibration of the NIR spectral correlation with Micronaire value.

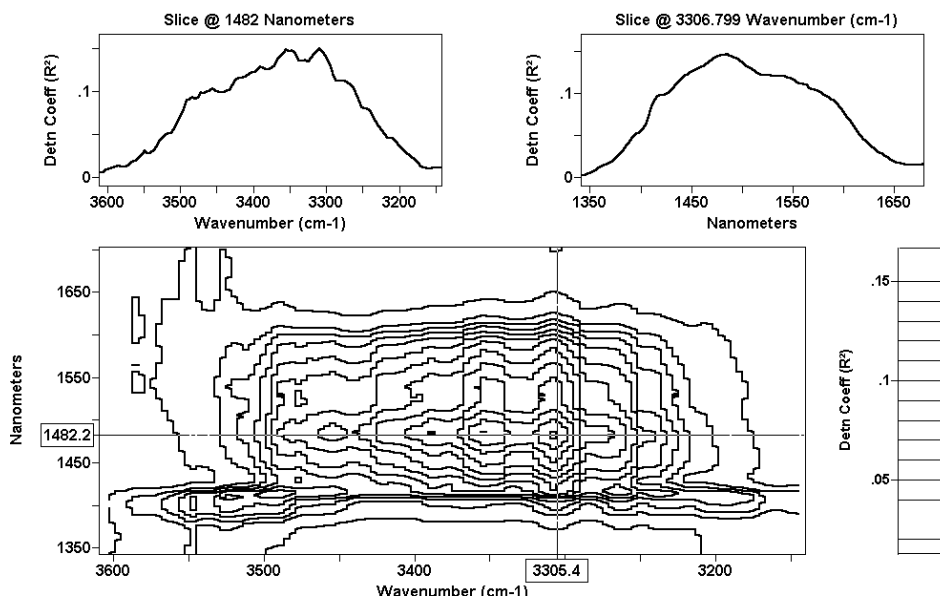


Figure 5. 2D contour plot of the mid-infrared/NIR correlation map of the mid-infrared O–H stretch region ($3500\text{--}3200\text{ cm}^{-1}$) to the NIR region ($1370\text{--}1700\text{ nm}$) with slices taken at 3305 cm^{-1} and 1485 nm , respectively.

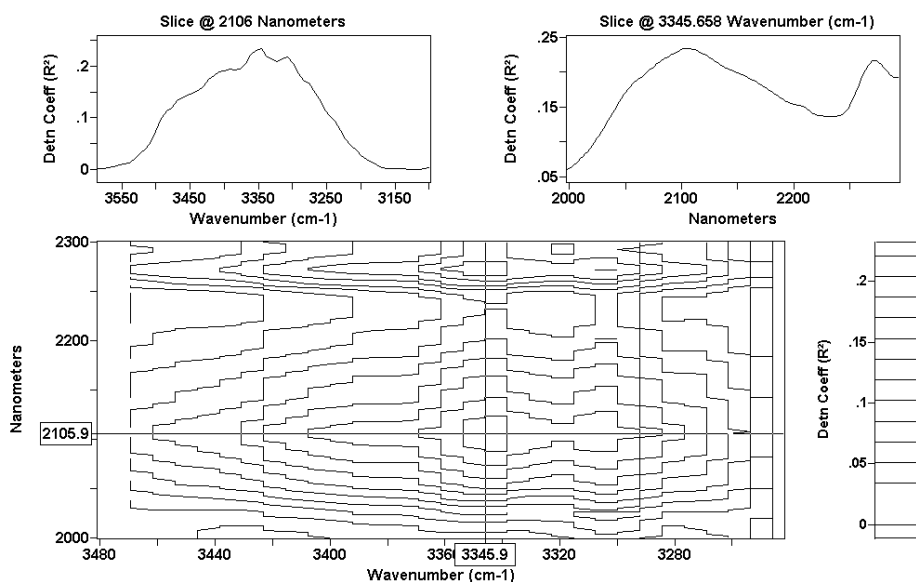


Figure 6. 2D contour plot of the mid-infrared/NIR correlation map of the mid-infrared O–H stretch region ($3500\text{--}3200\text{ cm}^{-1}$) to the NIR region ($2000\text{--}2300\text{ nm}$) with slices taken at 3346 cm^{-1} and 2106 nm , respectively.

tively). If hydrogen bonding changes occur, they should be reflected in these regions. Figure 5 shows the correlation of the fundamental O–H stretches for intra- and intermolecular hydrogen bonds at 3350 and 3305 cm^{-1} (respectively) in the mid-infrared to the corresponding signals in the NIR at 1485 and 1540 nm in the overtone region. Figure 6 shows the correlation of the fundamental O–H stretches in the mid-infrared to the combinations bands for O–H stretch around 2100 and 2270 nm in the NIR region. With this type of detail being detected in the loading factors for the calibration and in the correlations between the NIR and mid-infrared spectra, it is likely that differences in hydrogen bonding and other subtle interactions play a role in the measurement of physical parameters. Wall thickness and perimeter of fibers are two parameters that appear to generate similar effects to those observed with changes in film thickness.

Conclusions

The technique of 2D mid-infrared/NIR can be employed to gain insight into the factors that are involved in the correlation of NIR spectra to physical parameters. In particular, changes in hydrogen bonding and other related effects appear to be involved in measurements such as fiber wall thickness or perimeter. The employment of improved sample handling techniques for fibers in both the NIR and mid-infrared regions would go a long way in making these types of studies more accessible. Additional approaches need to be explored so that the advantages of these types of correlations can be further exploited.

References

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