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A REVIEW OF COTTON QUALITY FINENESS AND MATURITY MEASUREMENTS BY NIR HVI

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Abstract

Near infrared (NIR) spectroscopy has been a successful research tool for analyzing a wide variety of cotton fiber properties. These include, from sugar content, moisture effects on strength, water status, trash content, fiber fineness and maturity. Key findings of a literature review of this field are reviewed as related to a three variable model to help the cotton industry understand how changes in fineness and maturity produce spectral changes. For some in the textile industry, there are high hopes that nondestructive near infrared spectroscopy can be incorporated in High Volume Instrumentation, HVI, where fiber properties such as strength are currently measured destructively and fiber fineness and maturity are not measured. The following discussion will include a review of current literature regarding the use of NIR methods researched at SRRC to measure fineness and maturity.

Introduction

In the quest for accurate, rapid, reliable and nondestructive test methods in cotton fiber testing, the use of NIR has been a means of extracting a variety of information from cotton fibers. It has played a major role in quantifying insect sugar content of fibers (Brushwood and Han, 2000). With an ecological slant, NIR has assisted in the blending of recycled fibers by correctly identifying them (Thiemer, 2000). NIR has helped identify fiber damage caused by specific dyes (Bachmann et. al, 2000). NIR has also been used to detect changes in water status of cotton fibers (Wanjura et. al, 1999). The ability of cotton to be processed has also been simulated and analyzed by NIR methods (El Mogahazy et. al, 1998). The trash content of cotton fibers has also been measured by NIR (Taylor, 1996). Cotton fiber moisture's impact on strength has also been successfully measured by NIR (Knowlton, 1996). Also, NIR has been used to classify cotton fiber properties (Thomasson, 1995) and the application of NIR at SRRC to classify cotton fineness and maturity has been extensively reported.

Cotton Fineness and Maturity

There is a need for measurement of cotton maturity and fineness in the international marketing of cotton to demonstrate to the world that USA cotton is mature and fine. Maturity and fineness are important in dye uptake, fabric luster, nep formation, and strength and uniformity of yarn. Micronaire is an estimate of both maturity and fineness (Lord and Heap, 1988). The physical meaning of maturity and fineness can be defined in various ways related to the cross sectional dimensions of the fiber (Lord and Heap, 1988, and Ramey, 1982). In the context of this paper, the fundamental measures are used — wall thickness for maturity and perimeter for fineness.

A typical cotton NIR reflectance spectrum at infinite sample thickness is shown in Figure 1. The strong absorption band at about 1940 nm is due solely to moisture in the fiber. Using mid IR and NIR correlation spectra techniques, Himmelsbach et. al, showed that the band around 1500 nm is due to the O H stretch and at about 2100 nm it is due to the combination band of O H stretch. At about 2250 nm the band is due to the C C deformation band for cellulose (Himmelsbach et al, 1996). In fact, all of the bands can be assigned to water and carbohydrate absorption, and hydrogen bonding changes, and to a much less extent to fiber impurities.

Three Variable Model. A summary if SRRC research to rapidly measure maturity and fineness is shown in Table 1. Wall thickness and perimeter are sensed simultaneously and independently in the NIR region of the spectrum from 1100 nm to 2500 nm. In this spectral region, these two fiber properties govern the intensity of the absorption bands and the spectrum's baseline. The NIR reflectance spectrum of nineteen cottons was taken on a NIRSystems Model 6500 spectrophotometer placed under and off center to a 5" diameter rotating sample cell with quartz bottom (Montalvo et. al, 1994). Thirty grams of cotton was placed in the sample cell and the plunger was activated to press the cotton against the quartz window. Multiple spectra were taken during one revolution of the sample cell. The spectra were averaged and stored on a hard disk. Four average spectra were taken for each cotton, and the grand mean of the averaged spectrum produced to give a single spectra for each cotton. After NIR analysis, measurements for wall thickness and perimeter were made on the Arealometer (ASTM D1449 58). Ten replications were run on each cotton and the results were averaged to give mean wall thickness and perimeter values. Wall thickness and perimeter were fitted to the three variable model described below.

A three variable model was derived linking diffuse reflectance (*R*) as a linear function of wall thickness (*T*) and perimeter (*P*) (Montalvo et. al, Part III, 1991):

$$A = a + bT + cP + dTP$$

where *A* is the absorbance (*A* = log 1/*R*) and *a,b,c*, and *d.* are the regression (optical) coefficients at each wavelength. This work was published as a series of three papers in 1991 (Montalvo, Part I, 1991; Montalvo, Part II, 1991; Montalvo et. al, Part III, 1991).

This model is now used to help the cotton industry understand how changes in *T* and *P* produce a change in *A*. Figure 2 is a demonstration of a spectral match algorithm for estimating *T* and *P* for a test cotton using the three variable model. The procedure is as follows. The NIR spectrum of the test cotton is recorded. Then, wall thickness and perimeter are estimated simultaneously by iteratively selecting values of the two fiber dimensions that maximize the fit of the experimental spectrum to the model spectrum. The search for optimum values is found by minimizing the sum of the squares of the deviations between the experimental and model absorbances.

Figure 2 shows the superimposed experimental and model spectra. The curves are superimposed at wavelengths > 1440 nm; below 1440 nm the actual and simulated spectra are the upper and lower curves, respectively. Reference method and NIR predicted values are, respectively: perimeter, 51.3 μm and 49.2 μm; and wall thickness, 3.19 μm and 3.20μm. The good agreement between experimental and simulated spectra supports the use of the three variable model to understand how changes in *T* and *P* produce a change in *A*.

Relative Sensitivity. The relative sensitivity of the absorbance *A* to changes in wall thickness *T* and perimeter *P* as well as the variability of the relative sensitivity with wavelength is of interest. These sensitivities are important because the limit of detection by NIR is generally about 0.1% for a two component sample property.

Figures 3, 4 and 5 are intended to show simulated spectra by the three variable model to support answers to the given questions. Figures 3 and 4 show the family of spectra generated with one variable held constant at about the midpoint value in the range of values while the value of the other variable ranges from its lowest to highest value. These ranges for *T* and *P* correspond to the values found in the three variable model calibration set of samples. In both figures, the sensitivity of the *y* axis, absorbance, is the same to promote relative sensitivity evaluations.

Clearly, *A* is more sensitive to a change in *T* than to a change in *P*. To quantify the relative sensitivities and to examine these results across the spectrum, we used the ratio of partial derivatives, as shown in Figure 5. The equation for the change in *A* with respect to a change in *T* at constant *P* divided by the change in *A* with respect to a change in *P* at constant *T* is given in the figure. The equation is evaluated at the midpoint of *T* and *P* values in the set; *T* = 2.9 μm and *P* = 47 μm. The solid line is the model spectrum from the three variable model and the dashed line is the ratio of partial derivatives. At wavelengths < 1850 nm, this ratio is > 60:1 and drops to > 30:1 as the wavelength approaches 2500 nm. A ratio of 30:1 for a two component system corresponds to an equivalent "percentage" of 3.3% for P is and is about 33 times (3.3/0.1 = 33) more sensitive than the detection limit for NIR in percentage units. Thus, whether NIR calibration equations for routine analysis of *P* are based on multilinear or global (PCR and PLS) approaches, detection of both maturity and fineness in commercial cottons will be above the detection limit.

Spectral Pooled Standard Deviation. The pooled standard deviation of replicate spectra recorded on 189 raw cottons analyzed with the NIRSystems Model 6500 NIR instrument, 5" diameter sample cell, and 40 lbs force pressing the cotton against the quartz window has been reported (Montalvo et. al, 1994). The pooled standard error for the spectra was < 0.001 *A* (log 1/*R* units) at 1440 nm and increased to 0.002 *A* (log 1/*R)* units at 2500 nm.

The standard error of prediction (SEP) and coefficient of determination (R^2) of wall thickness and perimeter was measured using a fast KES diode array NIR spectrophotometers in an HVI configuration. One second analysis was used in place of the 30 second analysis of the NIRSystems Model 6500 instrument (Buco et. al, 1998). The diode array manufacturer claimed that rotation of the 5" diameter sample cell was not necessary. The SEP for both wall thickness and perimeter was found to be smaller for a rotating cell compared to the stationary cell. For the stationary cell, R^2 was smaller for perimeter compared to wall thickness. This was attributed to poorer spectral precision with the stationary cell. The R^2 values for raw cotton between the diode array and FMT were shown in Table 2: wall thickness, stationary cell (0.949) and rotating cell (0.980); perimeter stationary (0.887) and rotating (0.911). Cleaning the cotton followed by analysis in the rotating cell gave slightly improved results. SEP values, shown in Table 3, were as expected as the % CV for the stationary and rotating cell respectively, were wall thickness (2.4 and 1.5) and perimeter (1.9 and 1.8). Note that the cleaned cotton analyzed in the rotating cell gave % CV comparable to the FMT analysis. Also included in Tables 2 and 3 are the results on other measures of fineness and maturity including micronaire.

Using the three variable model, the simulated spectra in Figure 6, after applying a subtraction spectrum to permit resolution of small spectral differences, show that a change in perimeter of about 1 µm gives an incremental change in *A* close to the expected spectral precision with the Model 6500 NIR instrument. It is important therefore, that spectral precision is optimized.

Variation of T and P at Constant Wall Area. Figure 7 simulated spectra shows the effect on *A* due to variation of both wall thickness and perimeter in opposite directions in order that wall area (*WA*)

$$WA = T(P \quad BT)$$

is maintained at a fixed value of 109 µm^2. For the family of model spectra, spectrum 1 represents a cotton with $P = 45$ µm and $T = 3.1$ µm and spectrum 4 represents a cotton with $P = 51$ µm and $T = 2.5$ µm. The relative maturity, *T/P*, decreases in the order shown in the graph.

The major changes in the simulated spectra are: (a) change in intensity of the absorption bands, (b) change in the overall baseline or spectral offset, and (c) change in the angle of the baseline relative to the *x* axis. Also note there are no changes in the number of absorption bands, gained or lost, with variation in maturity. Nonetheless, there are significant changes in the NIR spectra. As a consequence, with sophisticated algorithms, such as PCR and PLS, calibration equations can be developed and used to measure maturity of unknown cottons.

Diffuse Reflectance Optical Path. Embedded in the three variable model, however, is the mass of solid cellulose in the diffuse reflectance optical path. This parameter is included in the optical coefficients: *a*, *b*, *c*, and *d*. From another viewpoint, consider infinitely thin cross sections of fibers in the optical path. The *T* and *P* values are real but the spectral absorbance would approach zero due to the mass of cellulose in the optical path approaches zero.

In detailed work to probe the diffuse reflectance optical path, a red laser was used for visual observations (Montalvo, Part III, 1991). When pressure is applied to press a thick cotton sample against the quartz window in the NIR HVI, the total fiber length in the optical path is constant among cottons of the same perimeter. Also, at constant perimeter, the radiation propagation depth, seen as a red glow with the red laser source light, is independent of wall thickness and concomitant light absorption by the cellulose in the fiber wall and depends solely on scatter. Thus, in 3 D terms, changes in cotton fiber NIR reflectance spectra result from changes in the mass of cellulose in the diffuse reflectance optical path. This mass or volume of solid cellulose is dependent on the fiber's wall thickness, perimeter, and total fiber length illuminated.

Summary

A review of the development of cotton quality measurements by NIR HVI in research laboratories is presented for fineness and maturity assessments. A simple three variable model is described to help the cotton industry understand changes in NIR reflectance spectra of cotton as a function of the fiber's fundamental cross sectional dimensions, wall thickness and perimeter. Furthermore, a red laser source light can be used to understand the amount of cotton in the diffuse reflectance optical path.

References

Bachmann F; Dannacher JJ; Freiermuth B; Studer M; Kelemen J. 2000. Vat dye sensitised fibre damage and dye fading by catalytic and activated peroxide bleaching. Journal of the Society of Dyers and Colourists. 116(4): 108 115.

Brushwood DE; Han YJ. 2000. Characteristics of entomological sugars applied to the surface of raw cotton. Proceedings Beltwide Cotton Conferences Vol. 2; (1522 1527).

Buco SM; Montalvo JG; and Faught SE. 1998. Analysis of cotton maturity and fineness by multiple NIR HVIs. Part I. Data analysis. Proceedings Beltwide cotton conferences. Vol 2: (1289 1290).

El Mogahzy Y; Broughton R Jr; Guo H. 1998. Evaluating staple fiber processing propensity. Part I: Processing propensity of cotton fibers. Textile Research Journal.68(11): 835 840.

Himmelsbach, D. S., Barton, II, F. E., and Montalvo, J. G., Jr. Use of two dimensional MIR/NIR spectroscopy to understand the correlation of NIR spectra to physical parameters, pp. 20 25. In Davies, A. M. C. and Williams, P (eds.) Near Infrared Spectroscopy: The Future Waves. NIR Publications, 742 pp. 1996.

Knowlton JL. 1996. Effect of moisture on cotton fiber strength. Proceedings Beltwide cotton conferences. Vol. 2; (1300 1305).

Lord, E. and Heap, S. A. The origin and assessment of cotton fiber maturity. Published by the International Institute for Cotton, Manchester UK. 38 pp. 1988.

Montalvo, J. G., Jr. Faught, S. E., and Buco, S. M. A comparative study of diffuse reflectance of cottons grouped according to fiber cross sectional dimensions. Part I. Fundamentals. Applied Spectroscopy 45 (5):779 789. 1991.

Montalvo, J. G., Jr. A comparative study of diffuse reflectance of cottons grouped according to fiber cross sectional dimensions. Part II. Optical path simulations. Applied Spectroscopy 45 (5):790 794. 1991.

Montalvo, J. G., Jr. Faught, S. E., and Buco, S. M. A comparative study of diffuse reflectance of cottons grouped according to fiber cross sectional dimensions. Part III. Experimental. Applied Spectroscopy 45 (5):795 807. 1991.

Montalvo, J. G., Jr., Faught, S. E. , Grimball, R. and Buco, S. M. How to improve spectral precision on VIS/NIR spectroscopy of raw cotton. NIR News 5 (4):9 11. 1994.

Ramey, H. H. Jr. The meaning and assessment of cotton fiber fineness. Published by the International Institute for Cotton, Manchester UK. 19 pp. 1982.

Standard Method of Test for Specific Area and Immaturity Ratio of Cotton Fibers (Arealometer Method). American Society for Testing and Materials, D1449 58.

Taylor RA. 1996. Measuring leaf, bark and grass particles in cotton with NIR imaging. Beltwide cotton conferences. Proc. conf. Nashville. Vol. 2; (1705 1708).

Thiemer R. 2000. Fibre recognition by neurochip. Chemical Fibers International. 50(1): 40 42.

Thomasson JA; Shearer SA. 1995. Correlation of NIR data with cotton quality characteristics. Transactions American Society of Agricultural Engineers. 38(4): 1005 1010.

Wanjura DF; Upchurch DR. 1999. Cotton response to abrupt change in water application. Proceedings Beltwide Cotton Conferences. Vol. 1; (380 387).

Table 1. Summary of SRRC research in NIR HVI to rapidly measure maturity and fineness.

Topic	**Accomplishment**
Sensing mechanisms	Identified fundamental cross sectional properties detected.
Absorption band assignments	Two dimensional mid IR/NIR provided definitive band assignments
Reference methods data diagnostics	Developed split half test statistics to measure reliability a priori of NIR calibration.
Reference methods and calibration cottons	NIR HVI calibrated with SRRC upgraded FMT; 12 new calibration cottons analyzed by independent reference methods used to calibrate the FMT (10, 11).
Physical standards	FMT developed headspace resistance standards (HRS); NIR HVI in progress.
Adjunct measures of maturity, fineness	Used wall thickness and perimeter to deconvolute NIR HVI errors.
Improve spectral precision	Sample presentation: 5" diameter sample cell that rotates over the optics; applied pressure of 40 lbs
Effects of variety and crop year on NIR calibration equations	NIR calibration equations must be derived from commercial varieties and across several crop years.
Sample heterogeneity	NIR calibration, validation, and check cottons, use cleaned and blended samples only. Routine NIR HVI analysis, use raw or opened raw or cleaned or cleaned and blended?
Rapid blender	In progress
Specific NIR calibration equations	Global (PCR, PLS) has provided best correlation statistics.
Speed of analysis	Reduced from 30 to 1 second measurements.
Spectral modeling	Needed to help cotton industry understand how changes in maturity and fineness produce a change in the reflectance spectra.
Round robin evaluation	TBA

Table 2. Cross validation statistics, R^2, on DA HVI #1 (100 Cottons, FMT reference Method).

Property	Raw Static	Raw Rotating	Clean Rotating
Perimeter	0.887	0.911	0.910
Wall thickness	0.949	0.98	0.989
Fineness	0.940	0.957	0.963
% Thick	0.912	0.958	0.967
Maturity ratio	0.912	0.961	0.970
Micronaire	0.953	0.981	0.988

Table 3. Cross validation statistics, CV (%), on DA HVI #1 (100 Cottons, FMT reference Method).

Property	Raw Static	Raw Rotate	Clean Rotate	Clean FMT
Perimeter	1.9	1.8	1.8	1.8
Wall thickness	2.4	1.5	1.1	1.1
Fineness	2.8	2.3	2.2	2.0
% Thick	3.5	2.4	2.2	2.5
Maturity ratio	2.7	2.0	1.7	2.0
Mic.	2.9	1.8	1.4	1.2

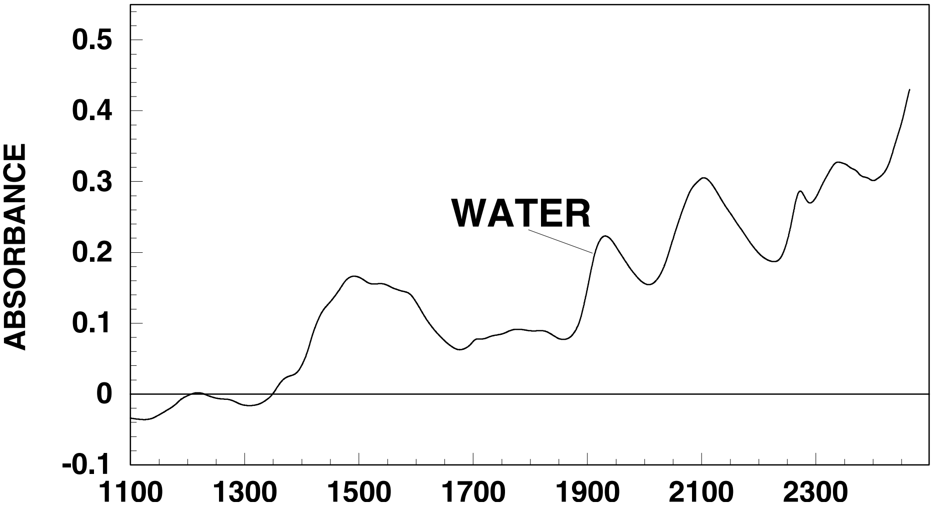

Figure 1. Typical NIR reflectance spectrum of cotton, arrow points to water band.

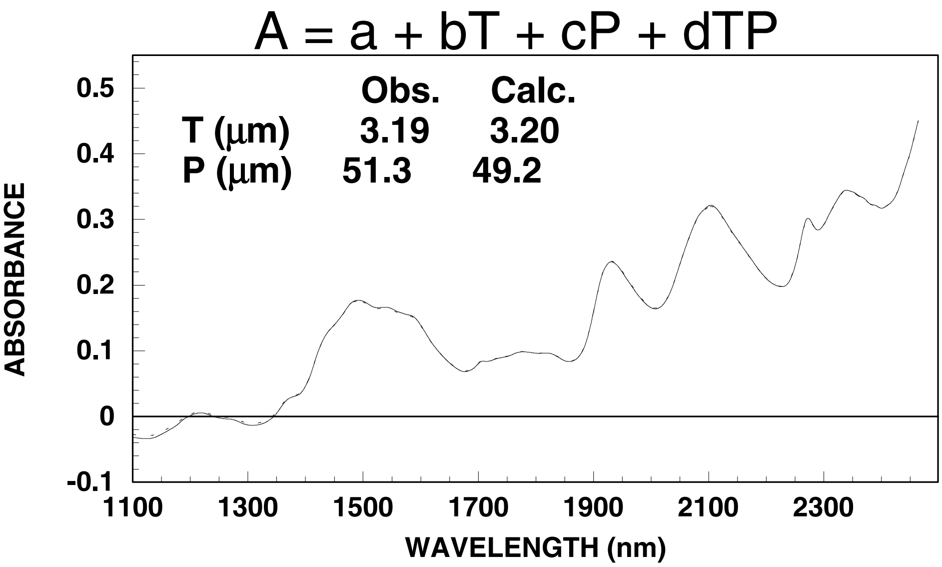

Figure 2. Demonstration of spectral match algorithm.

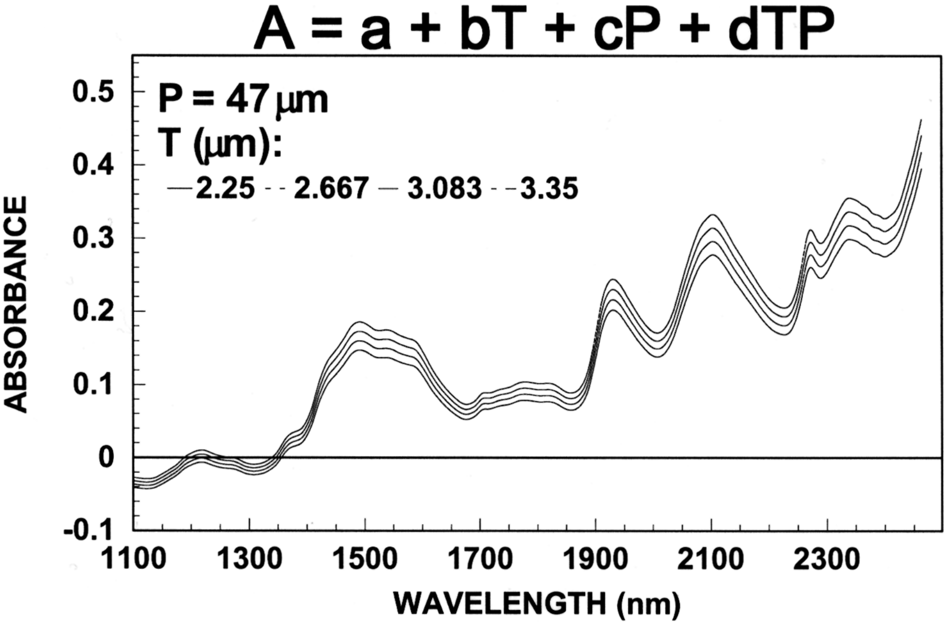

Figure 3. Simulated reflectance spectra at constant perimeter.

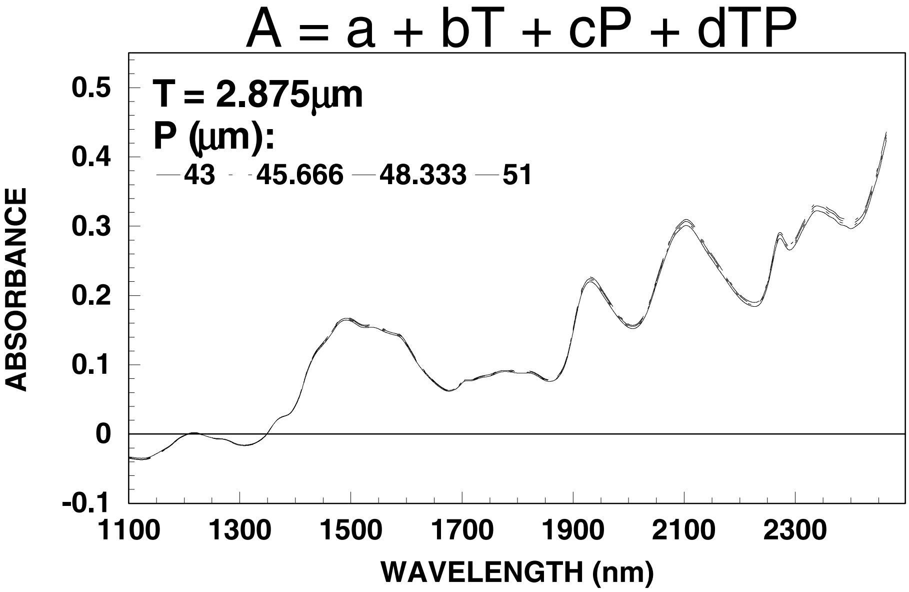

Figure 4. Simulated reflectance spectra at constant wall thickness.

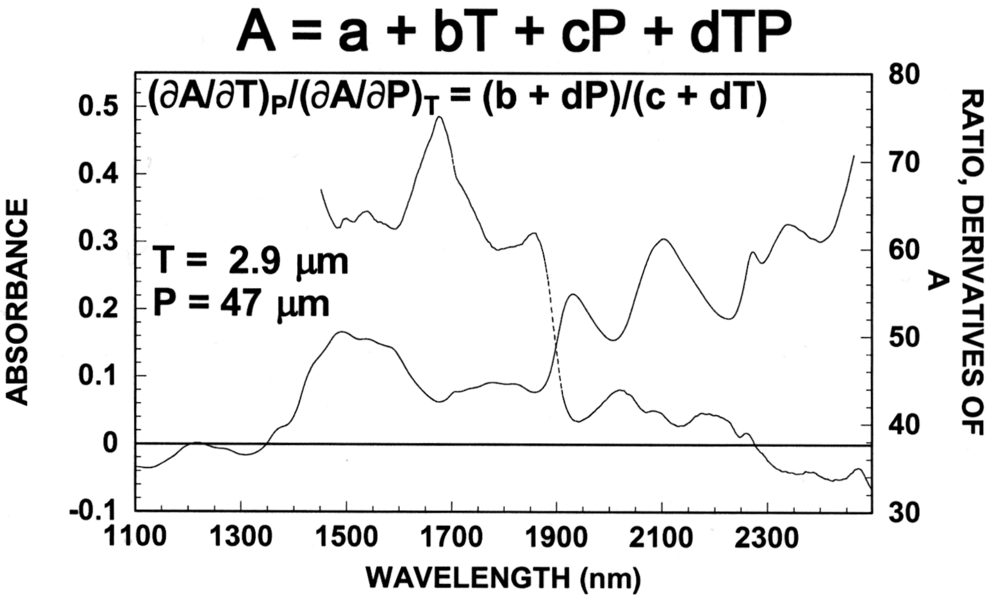

Figure 5. Relative sensitivity of simulated reflectance readings.

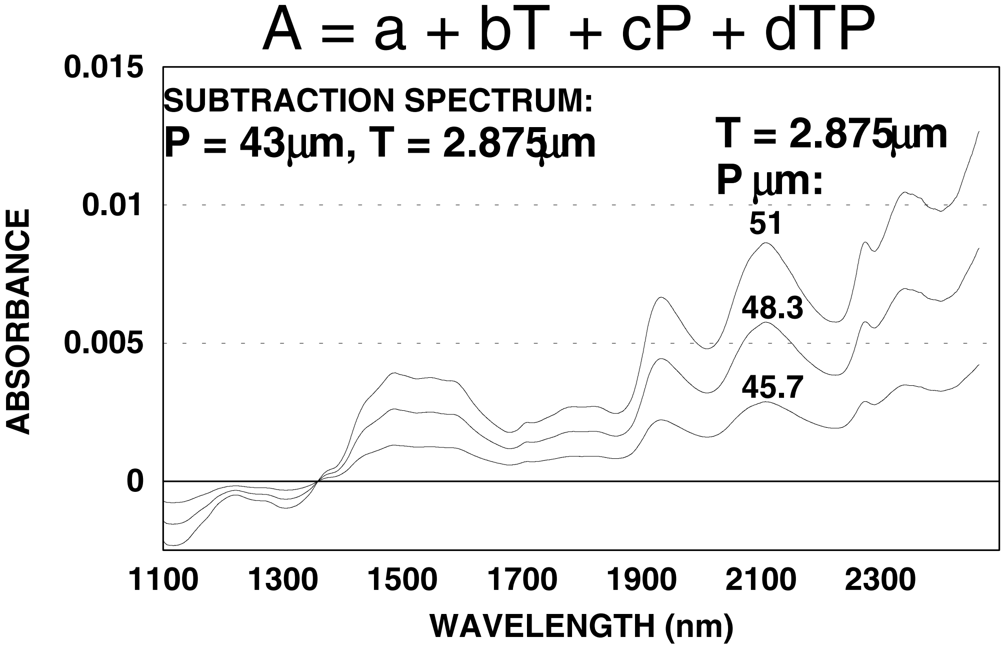

Figure 6. Improved resolution of simulated spectra at constant wall thickness.

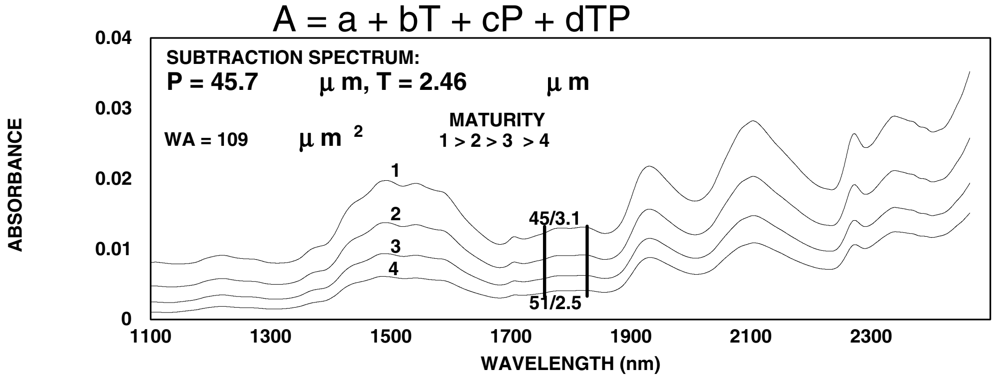

Figure 7. Improved resolution of simulated spectra at four levels of maturity.