

Near-infrared spectroscopy for the analysis of wood pulp: quantifying hardwood—softwood mixtures and estimating lignin content

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ABSTRACT *A method has been developed for measuring the hardwood content of bleached hardwood—softwood pulp blends using near-infrared (NIR) spectroscopy. The procedure is useful over the range of 0% to 100% hardwood, and it yields results within 5% of those from the standard fiber microscopy technique. The NIR technique is faster than fiber microscopy, and it does not require that the analyst have special training.*

Near-infrared spectroscopy has also been used to estimate the lignin content of unbleached pulps. Separate calibrations were required for hardwood and softwood pulps; differences between Klason lignin and NIR values were usually less than 0.2%. Samples were air-dried and were fluffed prior to the NIR measurement.

KEYWORDS

Analysis
Hardwoods
Infrared
Lignin
Measurements
Pulps
Softwood
Spectroscopy

Our purpose was to explore the use of near-infrared (NIR) spectroscopy for the quantitative characterization of wood pulps. Much of the appeal of NIR for analyzing other substrates has stemmed from its utility for at-line and on-line analysis. Sample preparation is usually minimal, and rapid determinations can often be performed on aqueous solutions or solid materials that contain moisture. The effects of sample inhomogeneities are minimized because multiple spectra are obtained on the sample as it

is moved past the instrument viewport. A computer is used to control the spectrometer, collect the data, and analyze the spectra.

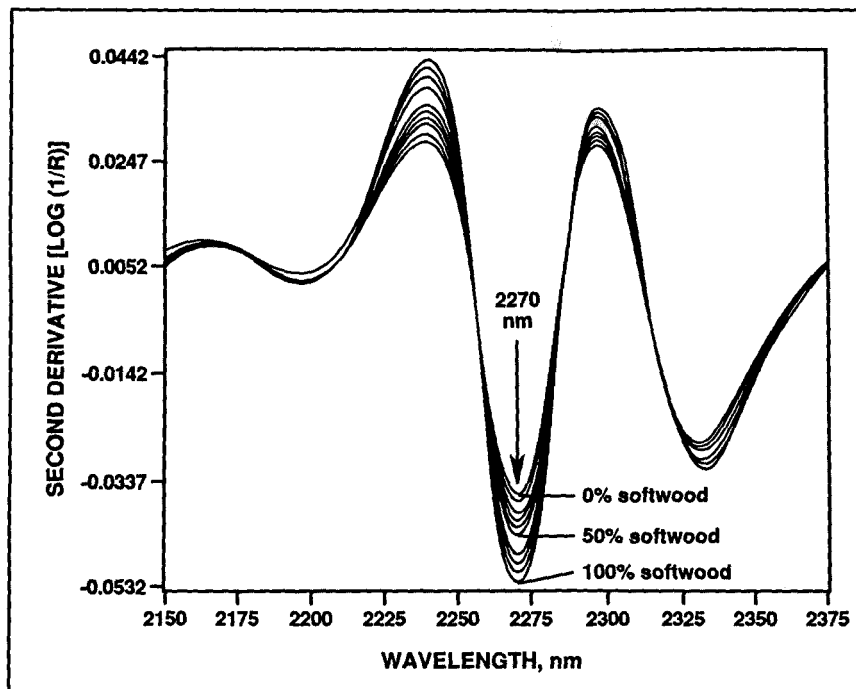
Principal early uses of NIR spectroscopy were the determination of water, protein, lipids, and other components of agricultural products (1, 2). Current applications include the analysis of materials as diverse as coal, textile fibers, plastics, and pharmaceuticals (3). Studies recently completed in other laboratories have compared NIR and mid-IR for analysis of lignocellulose (4) and have assessed NIR for estimating kappa number in paper handsheets (5, 6).

An earlier study in our laboratory indicated that Fourier transform mid-IR spectroscopy could be used to estimate the lignin content of unbleached pulps (7). The study present-

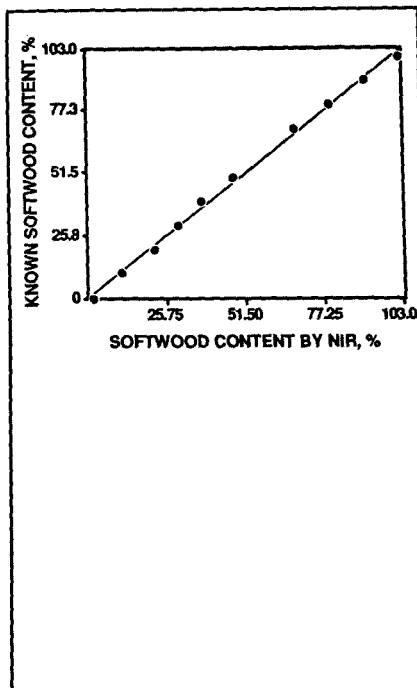
ed here was undertaken with the anticipation that NIR spectroscopy would demonstrate improved precision, fewer limitations on types and amounts of samples, and the ability to measure other pulp constituents. Of greatest potential importance in the current work is the finding that NIR could be used to measure the hardwood content of hardwood—softwood bleached pulp blends. These studies have also confirmed that NIR methods can estimate the lignin content of unbleached pulps, although the method was found to depend on wood species (hardwood vs. softwood), sample preparation, and moisture content.

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1. Expanded-scale, second-derivative NIR reflectance spectra of paperboard samples made from bleached hardwood—softwood pulp blends



2. Known softwood content of paperboard samples vs. softwood content computed from NIR spectra. ($R^2 = 0.996$. NIR calibration based on the band at 2270 nm.)



Development of quantitative NIR methods

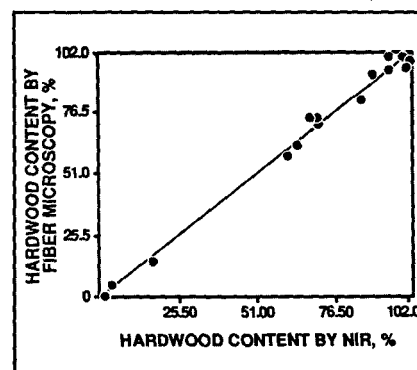
The first step in developing a quantitative NIR procedure is to calibrate the spectrometer by performing NIR measurements on real samples that have been characterized by primary, independent analytical methods. These methods often employ classical wet chemical techniques. The calibration of the instrument involves establishing a mathematical relationship, usually by using linear regression, between information in the NIR spectra and primary analytical data. The computer, which also runs the spectrometer, performs linear regression analysis on each wavelength in the spectra of the so-called "training set" of samples. The best wavelength or wavelengths are then selected for calibration, generating the calibration equation. This process is facilitated by using a dispersive NIR spectrometer and converting the spectra to their second derivatives (8). Peak intensities on derivatized spectra tend to be linear with concentration and more amenable to analysis by linear regression.

Derivatization is especially valuable when the NIR method employs reflectance measurements for analyz-

ing solid samples. Reflectance is affected by particle size variation, packing density, and other sample surface properties. The conversion of spectra to their second derivatives will often compensate for these factors by combining displaced or sloping baselines into a common, horizontal baseline. The residual, uncompensated differences between second-derivative spectra of repeated sample cell loadings of the same material must be established. Determining these sample reload errors is the second step in developing an NIR method for analyzing solids. Excessive reload errors may often be reduced by drying or grinding the sample in preparing it for analysis or by averaging spectra from multiple reloads of the same sample.

The final step in developing a quantitative NIR method is to test the method's ability to predict the composition of another sample population on which primary analytical data have been obtained. Although this cannot demonstrate that a calibration is universally valid, it will clearly reveal when a method has serious deficiencies. The calibration should be verified frequently if the NIR method is being used in a quality control laboratory. Calibration equations are

3. Pulp hardwood content from fiber microscopy vs. hardwood content computed from NIR spectra. ($R^2 = 0.992$. NIR calibration based on bands at 1752 and 2286 nm.)



usually quite specific for similarly treated samples.

Results and discussion

Quantification of hardwood—softwood mixtures

In initial studies of hardwood—softwood mixtures, we employed 10 paperboard samples made in the laboratory using a bleached hardwood pulp and a bleached softwood pulp in known proportions. In this work, the primary data were obtained by preparing the samples rather than by

I. Hardwood content of pulp blends measured by fiber microscopy and NIR spectroscopy

Sample	Microscopy, %	NIR, %	Difference, %
1	95.8	100.5	4.7
2	100.0	99.1	-0.9
3	100.0	94.5	-5.5
4	58.5	61.2	2.7
5	0	0.9	0.9
6	71.8	71.3	-0.5
7	5.0	3.7	-1.3
8	94.7	94.7	0
9	73.7	71.3	-2.4
10	15.0	16.8	1.8
11	63.0	64.7	1.7
12	82.0	86.0	4.0
13	92.3	89.4	-2.9
14	74.3	68.5	-5.8
15	98.2	101.8	3.6

II. Comparison of Klason lignin and lignin content estimated from NIR spectra (hardwood pulp)

Sample	Klason lignin, %	NIR, %	Difference, %
Aspen 4-1	5.10	5.08	-0.02
Aspen 4-2	2.70	2.88	0.18
Aspen 4-3	1.90	1.69	-0.21
W. Oak 4-4	6.90	6.85	-0.05
W. Oak 4-5	4.20	4.25	0.05
W. Oak 4-6	1.90	1.86	-0.04
W. Oak 4-7	1.40	1.48	0.08

analysis. NIR spectra were obtained on the paperboards, were converted to their second derivatives, and were examined for bands with intensities that correlated with the known differences in composition. **Figure 1**, an expanded scale portion of the second-derivative spectra, reveals a band at 2270 nm with intensity proportional to softwood content. (Note that a positive spectral peak becomes a negative peak between positive lobes in the second derivative.)

A more intense band had previously been found in the NIR spectrum of cotton linters, suggesting that the 2270-nm peak could be attributed to cellulose. The calibration equation was developed using linear regression of second-derivative 2270-nm band intensity on known softwood content; it was then used to estimate the softwood content of each of the paperboard samples. **Figure 2** shows the relationship between the known softwood contents of the paperboards and the softwood content computed from the NIR spectra. This was the first evidence that NIR could be used to determine hardwood—softwood content (9).

The continued study of hardwood—softwood mixtures was directed toward establishing the general utility

of the NIR technique. Because prepared mixtures were used in the initial study, any difference between the two pulps composing the mixtures would vary in a regular manner and would appear as a difference between hardwood and softwood. Consequently, in further work, we employed a variety of bleached kraft hardwood—softwood pulp blends from mills throughout the United States. These pulps had been submitted to the IPC Fiber Science Laboratory for determination of the hardwood—softwood ratio by fiber microscopy, and the results were used as the primary analytical data.

NIR spectra were obtained on 15 commercial pulp blends, were converted to the second derivatives, and were examined visually and via computer for potentially useful bands. Although the 2270-nm band appeared to be of value, the best calibration, with a correlation coefficient of 0.996, was based on bands at 1752 nm and 2286 nm. The selection of these bands was empirical; they most likely represent differences in the carbohydrate composition of hardwood and softwood pulps. **Figure 3** is a plot of percent hardwood from fiber microscopy vs. percent hardwood from the NIR calibration equation. Tabulated

data are in **Table I**. Maximum differences between microscopy and NIR values are 2–5%, and this is comparable to the accuracy of the microscopic technique cited in TAPPI Test Method T 401.

Fiber microscopy is a time-consuming procedure that requires the analyst to possess considerable expertise. Results of this study have revealed the potential of NIR spectroscopy for generating analytical data of comparable accuracy to fiber microscopy on hardwood—softwood blends.

Estimation of lignin content

As in our earlier studies of hardwood—softwood blends, we employed mixtures of known composition in the initial work on lignin estimation. An unbleached pulp was mixed with known amounts of cotton linters to produce pulps of varied lignin contents. Sample reload errors were excessive when NIR spectra were obtained on pieces of dried pulp, but after fluffing in an Abbe mill, the samples gave acceptable data. A band at 1680 nm was found to vary with kappa number, as shown in **Fig. 4**. Spectra of cellulose (linters) and lignin (Indulin) indicated that the 1680-nm peak probably is a carbo-

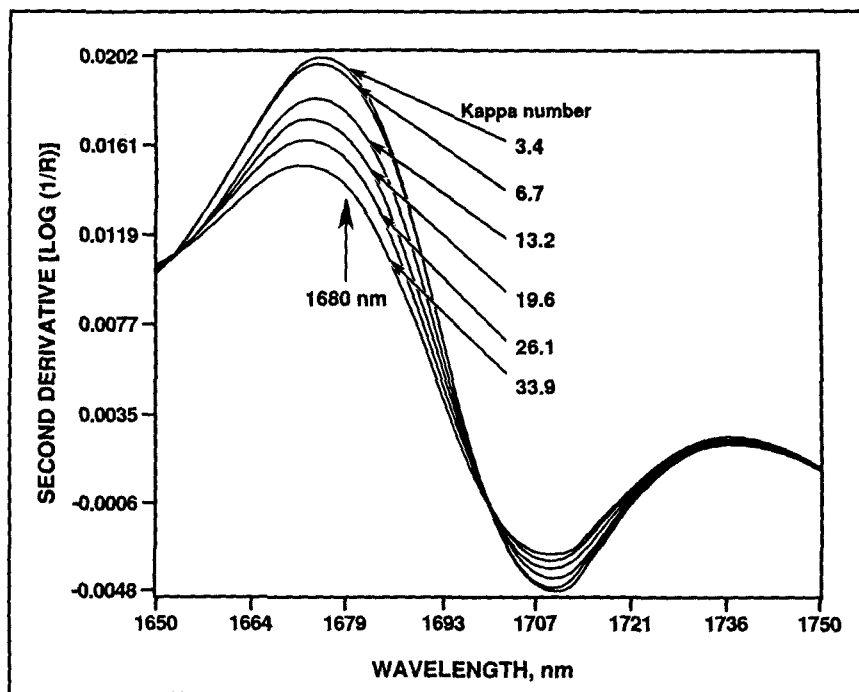
hydrate band reduced in intensity by the lignin in the samples. The usefulness of an NIR calibration for estimating kappa number based on the 1680-nm band is shown in Fig. 5.

In subsequent studies, the accuracy of lignin estimates in commercial pulps was unacceptable, and we suspected an effect attributable to differences between hardwoods and softwoods. Hardwood and softwood pulps with varied lignin contents were prepared and were subjected to Klason lignin determination and NIR analysis. Calibrations for estimating lignin content in the hardwood and softwood pulps were developed using NIR bands at 2144 nm and 2180 nm, respectively. Substantial spectral differences between lignin and bleached pulps had previously been observed at these wavelengths. Figures 6 and 7 show plots of Klason lignin vs. lignin estimated by NIR. Tables II and III contain the tabulated data from this study; differences between Klason lignin and NIR values were usually less than 0.2%. Thus, NIR could effectively estimate lignin contents when separate calibrations were developed for hardwood and softwood pulps.

The need for separate NIR calibrations for hardwoods and softwoods reflects the differences in the pulps' overall composition. Because NIR bands from lignin are broad, overlapping those from carbohydrates, the sensitivity of lignin estimations is influenced by the variability of the carbohydrate substrate. Spectral differences between species provide the basis for measuring hardwood—softwood ratios, but they add to the complexity of estimating lignin content. Thus, it seems unlikely that a single NIR calibration can be developed for estimating lignin in all types of pulps without a means for correcting for carbohydrate differences.

An additional effect of carbohydrates on lignin estimations arises from the hygroscopic nature of the carbohydrates. Larch pulps (Table III) were conditioned to about 15% moisture; NIR spectra were obtained, and lignin contents were estimated using the calibration developed for air-dried pulp. Lignin estimates were consistently low (Table IV), indicating the significant impact of pulp moisture content on the NIR method.

4. Expanded-scale, second-derivative NIR reflectance spectra of pulps made from mixtures of an unbleached kraft pulp and cotton linters



In general, band intensities in NIR spectra of wood pulps are greatly reduced at high moisture contents. This drop in intensity is probably caused by changes in the scattering properties of the fiber mat and the resultant altering of the depth of penetration of the NIR beam. Although lignin can be estimated in dry pulps by NIR, a way to correct for moisture is needed to fully utilize the technique.

Experimental procedures

Paperboard samples for the initial hardwood—softwood studies were approximately 1 mm thick and were prepared with softwood contents at 10 levels between 0% and 100%. In later work, we employed commercial bleached kraft pulps with hardwood and softwood contents determined by fiber microscopy (TAPPI Test Method T 401).

In the orienting study on lignin estimation, we used an unbleached kraft pulp mixed with cotton linters to produce pulps with kappa numbers from 3.4 to 33.9. For subsequent studies, aspen, white oak, and larch wood samples were kraft cooked in the laboratory to yield pulps with varied Klason lignin contents, with the

results shown in Tables II and III. The pulps were air dried and fluffed in an Abbe mill.

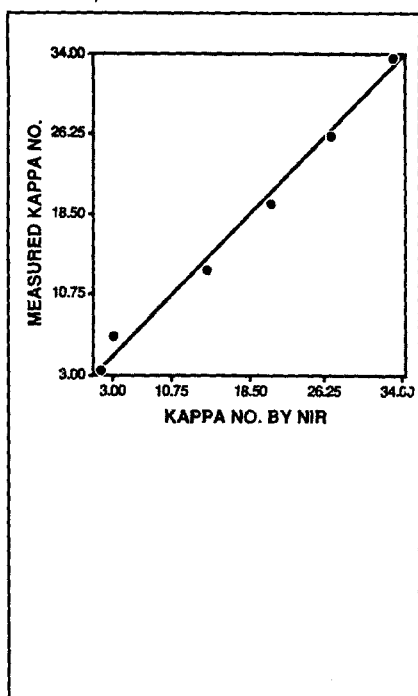
NIR spectra were obtained on a Pacific Scientific (NIR Systems) Model 6250 spectrometer operated through an IBM PS/2 Model 50 computer. Samples were placed in an elongated cell with quartz windows and a 1-cm path length. Fluffed pulp filled the cell, and paperboard samples were mounted with a black foam backing. Fifty reflectance spectra from 1100 nm to 2500 nm were obtained in about 10 s as the sample was transported through the NIR beam. The area of the sample scanned by the beam was about 70 cm².

Spectra were obtained on a ceramic reference prior to running each sample; sample and reference spectra were then ratioed, and the spectra were converted to their second derivatives. Multiple sample cell reloads were analyzed to determine reload errors. NIR Systems NSAS software was used to perform linear regression analysis on the spectra and the primary data in order to identify analytical wavelengths and compute the calibration equations. □

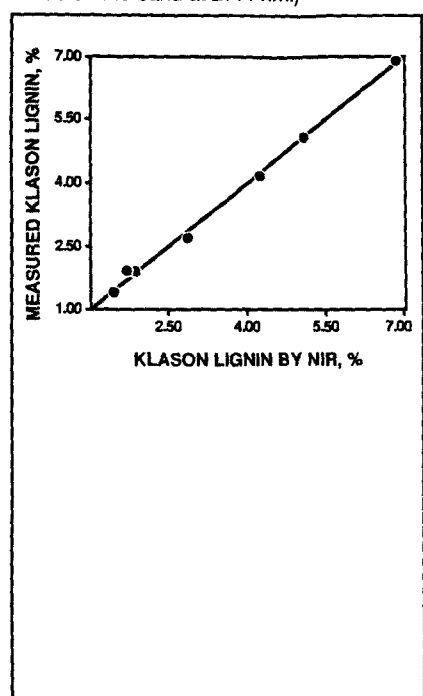
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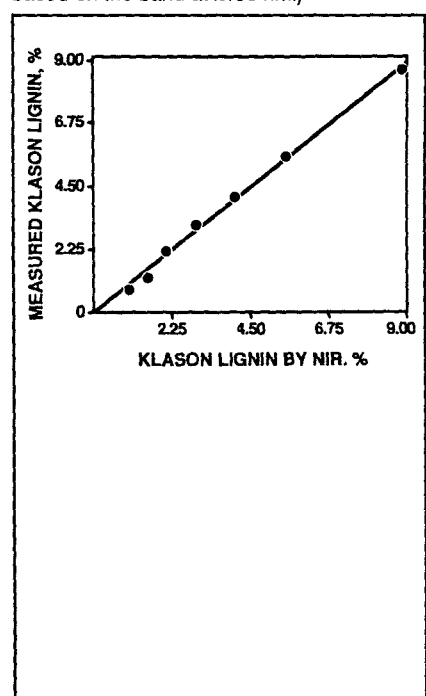
5. Measured kappa number vs. kappa number estimated from NIR spectra. ($R^2 = 0.990$. NIR calibration based on the band at 1680 nm.)



6. Measured Klason lignin content of hardwood pulps vs. lignin content estimated from NIR spectra. ($R^2 = 0.996$. NIR calibration based on the band at 2144 nm.)



7. Measured Klason lignin content of softwood pulps vs. lignin content estimated from NIR spectra. ($R^2 = 0.996$. NIR calibration based on the band at 2180 nm.)



III. Comparison of Klason lignin and lignin content estimated from NIR spectra (softwood pulp)

Sample	Klason lignin, %	NIR, %	Difference, %
Larch 5-1	8.72	8.84	0.12
Larch 5-2	5.56	5.50	-0.06
Larch 5-3	4.12	4.04	-0.08
Larch 5-4	3.14	2.93	-0.21
Larch 5-5	2.22	2.04	-0.18
Larch 5-6	1.26	1.53	0.27
Larch 5-7	0.86	1.00	0.14

IV. Comparison of Klason lignin and lignin content estimated from NIR spectra using air-dried pulp calibration (softwood pulp, 15% moisture)

Sample	Klason lignin, %	NIR, %	Difference, %
Larch 5-1	8.72	6.50	-2.22
Larch 5-2	5.56	3.69	-1.87
Larch 5-3	4.12	2.06	-2.06
Larch 5-4	3.14	0.75	-2.39
Larch 5-5	2.22	-0.44	-2.66
Larch 5-6	1.26	0.22	-1.04
Larch 5-7	0.86	-1.44	-2.30

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