Rapid Lignin Measurement in Hardwood Pulp Samples by Near-Infrared Fourier Transform Raman Spectroscopy

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FT-Raman spectroscopy is used for rapid quantification of hardwood pulp lignin. The ratio of the integrated area of the lignin band near 1600 cm^{-1} to that of cellulose in the region of 1200–1010 cm^{-1} behaves linearly with measured κ number for two separate sets of kraft hardwood pulp samples. Spectra and quantitative results of the hardwood samples, both with and without base line correction, are compared. Sources of error and measurement reproducibility are discussed. The method described shows potential for at-line process analysis of wood pulp.

Keywords: *FT-Raman spectroscopy; wood pulp; lignin; κ number*

INTRODUCTION

Measurement of the lignin content in wood pulp is important in manufacturing paper. The lignin content is typically measured in a commercial operation by the κ (or permanganate) number method (Biermann, 1993; Smook, 1989), which is an indirect measure of the lignin content. Since wood is chemically pulped to a target κ number, this is a key processing measurement. Unfortunately, κ measurement is time-consuming and labor-intensive and is also dependent on experimental conditions (TAPPI, 1991). Due to the critical importance of κ measurements on pulp manufacturing and the inherent problems with the current κ determination method, a recent industry workshop listed among "high priority research needs" the development of "on-line pulp characterization in real time of lignin content..." (PIRN, 1993).

Several spectroscopic techniques have been developed in recent years for at- or on-line secondary analysis of many products. A number of instrumental techniques which have the potential for rapidly measuring the κ number of pulp have been examined, including Fourier transform infrared (FTIR) (Schultz and Burns, 1990; Wallbäacks et al., 1991), near-infrared reflectance analysis (NIRA) (Birkett and Gambino, 1989; Olsson et al., 1995), and multidimensional fluorescence (MDF) spectroscopy (Oldham et al., 1993). Unfortunately, all these techniques have limitations such as lengthy sample preparation and moisture interference (FTIR), specificity of the sample type used in the calibration (NIRA), and poor reproducibility (MDF) (Oldham et al., 1993; Oldham and Schultz, 1995).

Raman spectroscopy can also be used for κ determination. This technique has several advantages including high spectral information, relative insensitivity to moisture and minimal sample preparation. The development of near-infrared (NIR) Fourier transform (FT) Raman spectroscopy greatly reduces any fluorescence background which often obscures spectral features when conventional Raman spectroscopy is used, and thus FT-Raman is rapidly gaining popularity for the study of wood pulps (Atalla et al., 1992; Evans, 1991; Ibrahim et al., in press; Kenton and Rubinovitz, 1990; Lewis et al., 1994; Stewart et al., 1995; Weinstock et al., 1993a & 1993b). Furthermore, in a previous study of softwood pulp it was observed that a simple ratio of the lignin band area near 1600 cm^{-1} to the cellulose band at 1200–1010 cm^{-1} behaved linearly with the κ number of those samples (Ibrahim et al., 1997). Use of this relatively simple and direct relationship avoided the use of multiple linear regression (MLR) or principal component analysis (PCA) techniques and, consequently, showed promise as a robust method for κ measurements.

The objective of this work is to further study the potential of FT-Raman spectroscopy for at-line κ analysis of pulp using hardwood pulp samples. To test the robustness of this procedure (insensitivity to feedstock source and processing), samples were obtained from kraft pulps prepared using different woods and at different locations.

EXPERIMENTAL PROCEDURES

Two separate sets of kraft pulp hardwood samples were obtained for these studies. Set 1, marked by * in Table 1, was obtained from mixed southern hardwoods pulped in a small research reactor. Samples from the second set were obtained from a commercial pulping operation using northern hardwoods as the feedstock.

Kappa numbers for all 36 hardwood pulp samples were determined by the standard TAPPI method (TAPPI, 1991). The 0.1000 N potassium permanganate volumetric standard solution was purchased from Aldrich. The 0.2000 N sodium thiosulfate standard solution was prepared from solid sodium thiosulfate pentahydrate (99.5%, Aldrich), and the 1.0 N potassium iodide solution was prepared from solid potassium iodide (99.0%, Aldrich). The 4 N sulfuric acid solution was obtained by dilution of concentrated sulfuric acid (95.0–98.0%, Fisher). All these chemicals were used without further purification.

Samples of set 1 were used directly for Raman measurement without any sample preparation. The samples of set 2 were very wet and thus were dried at room temperature in a ventilation hood for 24 h prior to measurement.

The FT-Raman system was a Bruker RFS-100 that has been previously described (Ibrahim et al., 1997). Raman spectra

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Table 1. Data for Hardwood Kraft Pulp Samples[a]

K^b	$R_{nb}{}^c$	$R_b{}^d$	%PE[e]	%RSD[f]	K	R_{nb}	R_b	%PE	%RSD
*3.8	0.0166	0.0179	6.8	14	*15.6	0.0517	0.0455	1.6	1.6
*4.3	0.0232	0.0202	0.72	5.6	*15.6	0.0489	0.0457	1.1	1.6
*5.2	0.0272	0.0244	8.9	9.5	*15.6	0.0455	0.0419	9.4	2.9
*5.3	0.0246	0.0220	2.8	2.9	*15.8	0.0523	0.0473	1.3	4.4
*5.4	0.0295	0.0246	7.6	3.5	*15.8	0.0481	0.0442	5.3	2.6
*6.3	0.0297	0.0247	0.91	13	16.1	0.0532	0.0470	0.78	1.0
*6.8	0.0284	0.0253	3.0	3.6	16.2	0.0571	0.0507	6.5	2.1
12.9	0.0448	0.0391	2.4	3.6	16.3	0.0539	0.0485	1.4	1.9
12.9	0.0463	0.0409	2.2	2.7	16.4	0.0571	0.0490	2.0	4.4
*13.7	0.0459	0.0400	4.5	2.8	*16.5	0.0547	0.0478	1.0	8.1
13.8	0.0496	0.0411	2.4	8.0	16.8	0.0560	0.0494	0.87	4.0
14.4	0.0532	0.0442	1.7	2.4	17.0	0.0560	0.0480	2.9	0.98
*14.5	0.0484	0.0421	3.7	1.9	17.7	0.0569	0.0488	4.4	1.4
*14.7	0.0479	0.0429	2.9	1.3	17.9	0.0567	0.0515	0.018	5.9
15.0	0.0518	0.0451	0.56	1.6	18.4	0.0641	0.0521	1.0	2.2
15.1	0.0486	0.0449	0.40	1.8	18.7	0.0604	0.0530	0.61	3.1
15.2	0.0522	0.0442	2.4	3.3	19.4	0.0648	0.0547	0.41	2.1
15.3	0.0530	0.0467	2.6	2.0	21.1	0.0644	0.0572	2.8	1.0

[a] Samples marked with an * were obtained using mixed southern hardwoods pulped in a small research reaction, while the other samples were obtained from a commercial mill using northern hardwoods. [b] $K = \kappa$ number. [c] R_{nb} = average lignin-to-cellulose area ratio with no base line correction. [d] R_b = average lignin-to-cellulose area ratio with base line correction. [e] %PE = percent error between R_b and the calculated value based on $R = 2.24 \times 10^{-3} \times K + 1.08 \times 10^{-3}$. [f] %RSD = relative standard deviation $\times$ 100%.
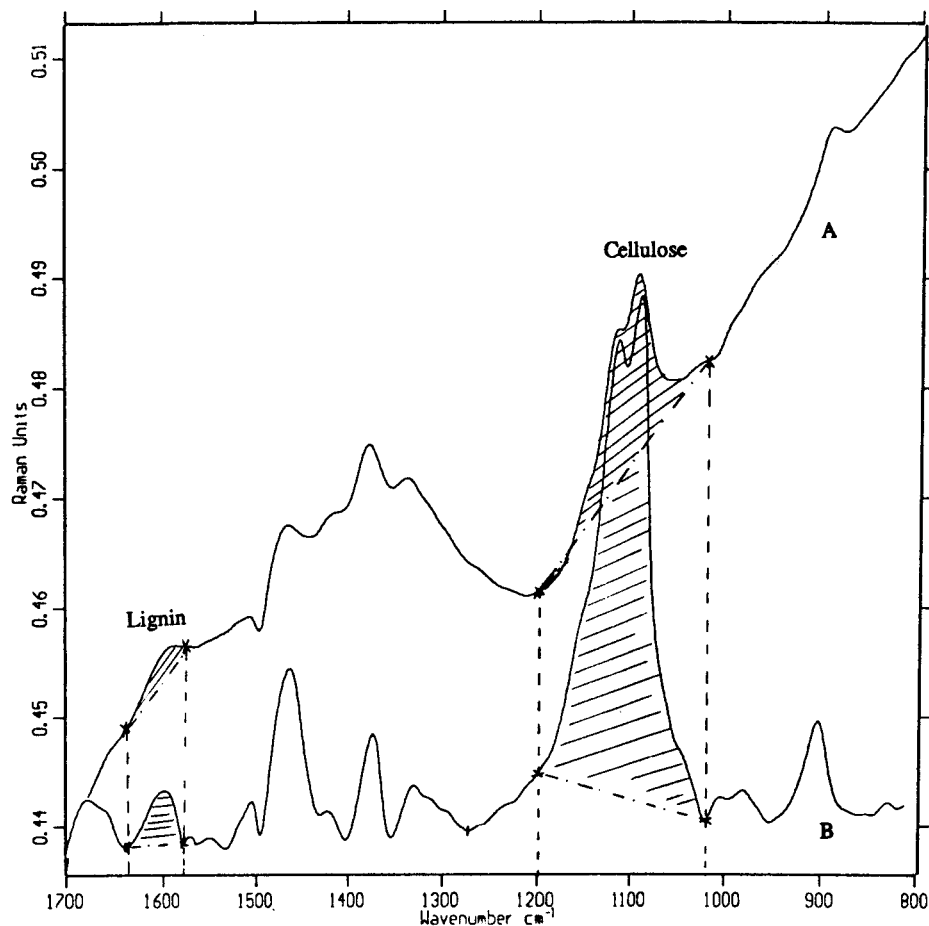

Figure 1. Illustration indicating spectral regions used for calculation of lignin and cellulose band area. A. FT-Raman spectrum of a hardwood pulp sample without base line correction. B. FT-Raman spectrum of the same hardwood pulp sample with base line correction.

were obtained with a Nd-YAG laser operating at 1.064 μm. The laser power was set at 600 mW which provided 473 mW at the sample with a 0.1 mm spot size. Because hardwoods are no more susceptible to thermal decomposition than softwood (Lewis et al., 1994), and the Nd-YAG laser in the FT-Raman spectrometer is a low-energy light source, no sample burning was observed with a laser power of 600 mW. Each pulp sample was divided into three portions and measured separately using a 180°, focused-mode Raman scattering geometry. The spectra were recorded at 8 cm^{-1} resolution,

coadding 1000 scans, over the wavenumber range $\Delta\nu = 50-3500$ cm^{-1}. Under these conditions, 15 min was required to obtain each spectrum.

RESULTS AND DISCUSSION

Figure 1 highlights the 1620−1580 cm^{-1} region used to indicate lignin content and also the cellulose peaks in the 1200−1010 cm^{-1} region which served as an internal reference. A multipoint base line correction
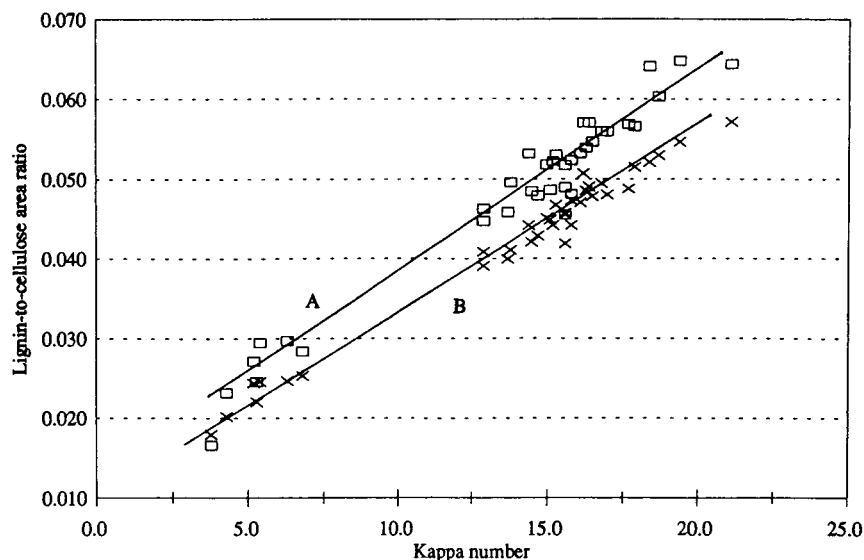
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Figure 2. Plot of κ number *vs* average lignin-to-cellulose area ratio for 36 hardwood pulp samples with and without base line correction of the original spectra. (A) Without base line correction; (B) with base line correction.

(Ibrahim et al., 1997) was used on the original Raman spectra of all hardwood pulp samples to remove fluorescence background, as illustrated in Figure 1. This method is an interactive base line correction which fits line segments between multiple points along the wavenumber axis. Figure 1 also shows the method used to calculate the integrated area of the lignin and cellulose bands in the spectra both with and without base line correction. The base line correction method did not significantly affect the profiles of the lignin and cellulose bands for the corrected Raman spectra, but simply improved the aesthetic quality of the spectra.

The spectral band assignments used in this study have all been previously established in the literature (Atalla et al., 1992; Ibrahim et al., 1997; Weinstock et al., 1993a & 1993b). The lignin band in the region $1620-1580$ cm^{-1} arises from the aromatic ring stretching mode of phenol groups in residual lignin within the pulp. In the native lignin structure, approximately one in ten phenylpropane subunits has phenolic groups and many contain α-hydroxyl moieties in the propyl side chain. For kraft hardwood pulp during the pulping and bleaching process, chemical reactions of lignin may produce quinones from phenols and/or carbonyls from benzylic alcohols (Weinstock et al., 1993b). The produced quinones or carbonyls will broaden the $1620-1580$ cm^{-1} lignin band with shoulders on the low or high frequency sides. To reduce these effects, only the lignin band in the region of $1620-1580$ cm^{-1} was considered.

The results for the 36 hardwood pulp samples are shown in Table 1 and Figure 2. Each sample was divided into three parts which were separately measured. Thus, the lignin-to-cellulose area ratios (R) in Table 1 are the average values of three separate analyses where the ratio of the integrated area of the lignin band at 1600 cm^{-1} to that of the cellulose bands in the $1200-1010$ cm^{-1} region was measured. The difference between R_{nb} and R_b is that R_{nb} indicates the lignin-to-cellulose area ratio with no base line correction while R_b is the ratio with base line correction. Plots of R_b and R_{nb} against κ number (K) are depicted in Figure 2. Statistical evaluation of these data resulted in a correlation coefficient (r) of 0.983 for a linear model with base line correction and 0.962 for that without base line correction. The two calibration curves are represented by the following equations:

$$R_b = 2.24 \times 10^{-3} \times K + 1.08 \times 10^{-3} \qquad (1)$$

$$R_{nb} = 2.60 \times 10^{-3} \times K + 1.16 \times 10^{-3} \qquad (2)$$

From Table 1 it is observed that R_{nb} is slightly higher than R_b for the same sample except the sample with a κ number of 3.8. This can be easily seen in Figure 1. The four points, which are starting and ending points for lignin and cellulose bands in the spectrum, give the base line for these two bands which were used to measure the lignin and cellulose band areas. For the cellulose bands in the spectrum without base line correction, a portion of the band area is excluded due to the nonlinear base line which results in a reduced area compared with the spectrum with base line correction. There is no such problem for the lignin band. Therefore, the lignin-to-cellulose ratio R_{nb} increases relative to R_b.

Since the cellulose peaks were used as an internal reference, the lignin-to-cellulose area ratio appears to be relatively insensitive to experimental conditions. Consequently, error due to the experimental conditions is insignificant and can generally be neglected. We believe that the existing error in this method primarily comes from two sources. One originates from insufficient sensitivity to accurately measure the smaller lignin bands which occur with the smaller κ number samples. As shown in Table 1, the sample with the κ number of 3.8 not only had the largest relative standard deviation (14%) and one of the largest percentage error (6.8%), but also had an abnormal R_{nb} value which was lower than R_b. The other samples exhibited $R_{nb} > R_b$. For the 36 samples measured, 7 exhibited κ numbers below 10. It was observed that these samples had average percentage error of 4.4% and average relative standard deviation of 7.4% that were much higher than the average percentage error (2.8%) and average relative standard deviation (3.7%) of all the samples. The other source of error is believed to be due to the chemical heterogeneity of the sample. After the pulping process of kraft pulp, the residual lignin differs in structure from the native lignin. So wood pulp of different κ number likely has different lignin structure which may cause different Raman response.

As previously mentioned, two separate sets of pulp samples representing different hardwoods obtained by

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different processes were pooled. In comparison of their independent regression eqs 3 and 4, the correction across sample sets is excellent. Thus, this method appears to be robust and applicable for measuring lignin content in hardwood kraft pulp samples typically required in the industry.

$$R_b = 2.15 \times 10^{-3} \times K + 1.13 \times 10^{-3}$$

$$\text{(for the samples of set 1)} \quad (3)$$

$$R_b = 2.14 \times 10^{-3} \times K + 1.28 \times 10^{-3}$$

$$\text{(for the samples of set 2)} \quad (4)$$

CONCLUSION

This work demonstrates the ability to use FT-Raman spectroscopy as a rapid method for the measurement of lignin content in hardwood pulp. In the laboratory, the time required for Raman determinations was about one-third of the time required by the traditional permanganate titration method. Furthermore, this technique is nondestructive, direct, and requires minimal sample handling as compared to the traditional method and appears to be relatively robust providing accurate lignin measurements for two totally unique sample sets. Therefore, it demonstrates excellent potential for at-line process analysis of wood pulp. Further work is needed to increase the sensitivity for low κ number samples and further reduce the fluorescence background. Eventually, a prototype Raman spectrometer (designed for the pulp mill environment) will be required to evaluate the practical application of these measurements. Additionally, this work has shown the negative interference from fluorescence background to be minimal, although more work is needed to optimize the most appropriate background correction method.

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