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Determination of lignin content in high-yield kraft pulps using photoacoustic rapid scan Fourier transform infrared spectroscopy

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Abstract

The spectra of a number of kraft pulps from *Pinus radiata* with varying lignin content (Kappa number) were obtained using a rapid scan photoacoustic Fourier transform infrared (PAS-FTIR) spectrometer and a method was developed for the determination of lignin content. A partial-least-squares (PLS) model was established based on spectral data collected at different mirror velocities. The robustness of the model was statistically evaluated. The outcomes indicate that the PLS model can be used to predict Kappa number of kraft pulps with a high degree of accuracy provided that the moving mirror velocity is $\leqslant$0.5 cm/s.

Keywords: FTIR; PAS; PLS; Kraft pulp; Lignin

1. Introduction

The kraft pulping process is currently used to produce more than 80% of chemical pulps worldwide. High-yield kraft pulps have been commonly selected for the manufacture of high strength papers for containers. Kappa number, which represents the amount of permanganate consumed by pulp samples, has been used to determine the amount of residual lignin in kraft pulps. The residual lignin content of chemical pulps has been determined using several Fourier transform infrared (FTIR) spectroscopy methods. In one study using attenuated total reflectance (ATR) the obtained spectra were normalized using the 1310 cm^{-1} carbohydrate peak as the internal standard and the intensity of the 1510 cm^{-1} peak, associated with lignin, was found to be approximately proportional to the Kappa number of the pulp (Kappa < 50). However, the correlation was poor when Kappa number was above 50 (Marton & Sparks, 1967). Jaaskelainen et al. (2003) determined the lignin distribution in pulps using the ATR technique and a multivariate analysis after collection of 100–400 spectra for each sample using 30–200 μm distances between the spectral points. The penetration depth of the ATR technique is only sufficient for the measurement of lignin content in the outer layer of the sample, but not adequate for the determination of the average lignin content.

In one study using diffuse reflectance FTIR (DRIFTS) technique, the area under the characteristic lignin band at 1510 cm^{-1} of the resultant spectra was used to estimate the Kappa number and Klason lignin in the pulp. However, the use of a single band to represent chemical components of kraft pulps appeared inadequate (Berben, Rademacher, Sell, & Easty, 1987). Schultz, Templeton, and McGinnis (1985) employed a stepwise regression analysis combining several DRIFTS absorption bands (1514, 1034, 1216, 1151 and 1087 cm^{-1}) divided by the absorbance band at 1048 cm^{-1} to determine the lignin content in dried pulps. Grandmaison, Thibault, and Kaliaguine (1987) took a similar approach, but chose the band at 1510 cm^{-1} as the internal standard instead of 1048 cm^{-1}. The major drawback of DRIFTS is that it often involves particle size reduction and dilution of the sample from the preparation of KBr pellets, resulting in weak absorption bands.

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Transmission FTIR can be used but the obtained transmission spectra are normally weak due the high opacity of samples. For pulp and paper analysis, the opacity problem can be remedied by reducing the optical density of samples to a suitable level through reducing the grammage of paper samples. In a previous study, high-yield pine kraft pulp samples with different Kappa numbers were used for transmission FTIR study. A multivariate analysis was established, taken into account all the characteristic bands of lignin for the prediction of Kappa number of pulp. The predicted values were found to be highly comparable with the measured values determined in the laboratory. The method was limited to samples made from 40 gsm handsheets (Hoang, Bhardwaj, & Nguyen, 2005).

Since 1980s, photoacoustic spectroscopy (PAS) has become a valuable analytical tool due to the developments of FTIR, low noise electronics, high sensitivity microphones, and computerized data handling. PAS is unique as a sampling technique, because it does not require that the sample be transmitting, has low sensitivity to surface condition, and can probe over a range of selectable sampling depths from several micrometers to more than 100 μm. The photoacoustic signal contains information on the sample's absorption spectrum and on the depth below the sample's surface from which the signal evolves, allowing materials with layered or gradient compositions to be studied. The photoacoustic signal is generated when infrared radiation absorbed by the sample converts into heat within the sample. This heat (thermal waves) diffuses to the sample surface and into an adjacent gas atmosphere. As the thermal waves propagate from the region where absorption occurred to the sample's light-irradiated surface they decay rapidly. This decay process limits the depth beneath the sample surface from which signal generation occurs. This thermal diffusive depth, μ_t, is given by Eq. (1).

$$\mu_t = \sqrt{\frac{D}{\pi V v}} \tag{1}$$

where μ_t is the thermal diffusive length (cm); D is sample thermal diffusivity (cm^2/s); V is the moving mirror velocity (cm/s); v is the wavenumber (cm^{-1}).

PAS-FTIR technology has been used in a number of instances for wood analysis, for example, studying the effect of light-induced changes to surface properties of acetylated or polyethylene glycol-impregnated wood (Ohkoshi, 2002); comparing the spectral differences between red oak and redwood (Kuo et al., 1988); measuring depth profiles of puspa and kapur wood species exposed to various weathering environments (Yamauchi, Sudiyani, Imamura, & Doi, 2004).

Halttunen, Tenhunen, Saarinen, and Stenius (1999) investigated the applicability of PAS-FTIR depth profiling for the study of coated papers and presented a modified method for thickness calculation from spectral information. The PAS spectra were recorded using a step-scan FTIR. The penetration depth is given by Eq. (2).

$$\mu_t = \Delta\theta\sqrt{\frac{D}{\pi f}} \tag{2}$$

where $\Delta\theta = \theta v_b - \theta v_a$ is the phase difference between the bands at different wavenumbers of the surface and substrate; D is sample thermal diffusivity (cm^2/s); f is the modulation frequency (Hz).

The aim of this study is to evaluate the use of PAS-FTIR technique to quantitatively determine the residual lignin content (Kappa number) in chemical pulps. Two sets of spectral data, which included the characteristic bands of lignin, were collected. The first set was integrated with a multivariate analysis to formulate a model for correlating the selected spectral information with Kappa number of kraft pulps. The second set was used to validate the model.

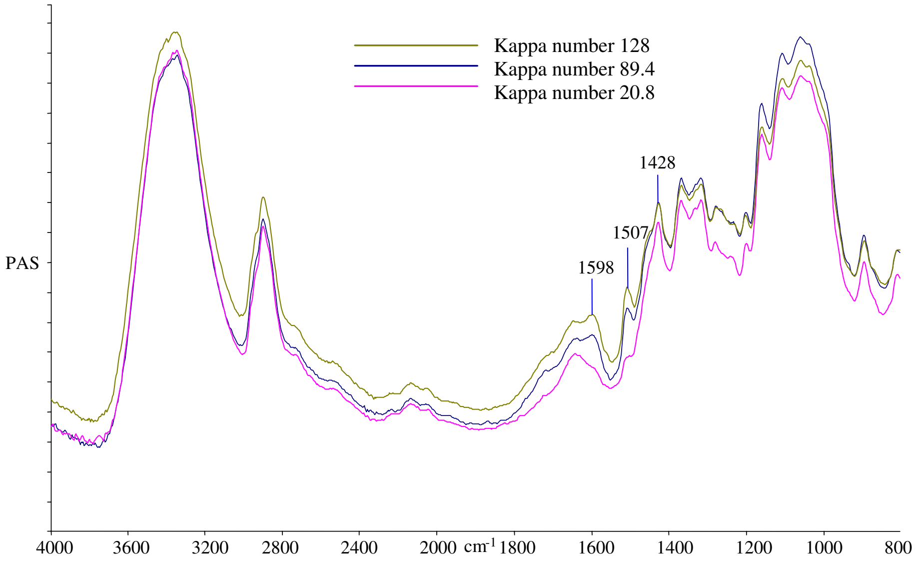

Fig. 1. PAS-FTIR spectra ($V = 0.05$ cm/s) of different *Pinus radiata* pulp samples (Kappa numbers 20.8, 89.4 and 128).

2. Experimental

2.1. Pulp samples

Twenty-six kraft pulp samples with different Kappa numbers were produced by cooking *Pinus radiata* wood chips in 2-L flow-through reactors at 0.5–1 M effective alkali as Na_2O and 30% sulfidity. The chips were first impregnated with the cooking liquor for 30 min at 108 °C before being cooked at 143–152 °C. Different cooking times were used to produce pulps of different Kappa number. The pulps were thoroughly washed and sieved through a screen with 0.15 mm slots prior to the measurements of Kappa number of pulp.

2.2. Measurement of Kappa number

TAPPI test method T236 om-99 was used to determine Kappa number of pulp samples. For various pulps, the Kappa number of the pulps is within the range 20.8–128. The Kappa number is in the range of 20–60 for twelve pulp samples, 60–100 for nine pulp samples and 100–128 for five pulp samples.

2.3. Measurement of brightness

TAPPI test method T452 om-98 was used to determine the brightness of the handsheet under the directional reflectance at 457 nm.

2.4. PAS-FTIR measurements

All PAS spectra were obtained using a Perkin-Elmer FTIR (GX model) spectrometer equipped with MTEC300 photoacoustic cell using macro-sampling head. Prior to PAS measurement, it was necessary to purge moisture in the sample chamber. Successful purge increases the signal level by approximately a factor of 2–3. Purging was attained by using clean, pure and dry helium gas at a flow rate of 10–20 cc/s for approximately 10 s.

The reference spectrum was acquired by using the carbon black reference. The appropriate sizes of paper samples from 120 gsm handsheets were prepared using a hand punch for use in the macro-sampling head of photoacoustic cell for analysis. Each sample was scanned 8, 16, 32, 50 and 100 times using the moving mirror velocity of 0.05, 0.1, 0.2, 0.5 and 1 cm/s, respectively. The wavenumber range used is 4000–750 cm^{-1} with a resolution of 8 cm^{-1} and interval of 1 cm^{-1}.

3. Results and discussion

3.1. PAS-FTIR spectra

The characteristic bands of lignin such as aromatic skeletal vibrations have been previously found at 1605–1593, 1515–1505 and 1430–1422 cm^{-1} (Faix, 1992, chap. 4). The spectra of three pulp samples (Kappa numbers 20.8, 89.4 and 128) at $V = 0.05$ cm/s are presented in Fig. 1. The characteristic bands representing the vibration of aromatic groups in lignin compounds are noticed at 1507 cm^{-1} and two shoulders at 1598 and 1428 cm^{-1}. It is anticipated that these peaks are associated with the lignin content in the pulp. It is noticeable that the spectra show the characteristic bands of lignin with higher absorption intensity for pulps with higher Kappa number.

3.2. Multivariate analysis

The partial-least-squares (PLS) regression method was used to develop a correlation between the PAS spectra

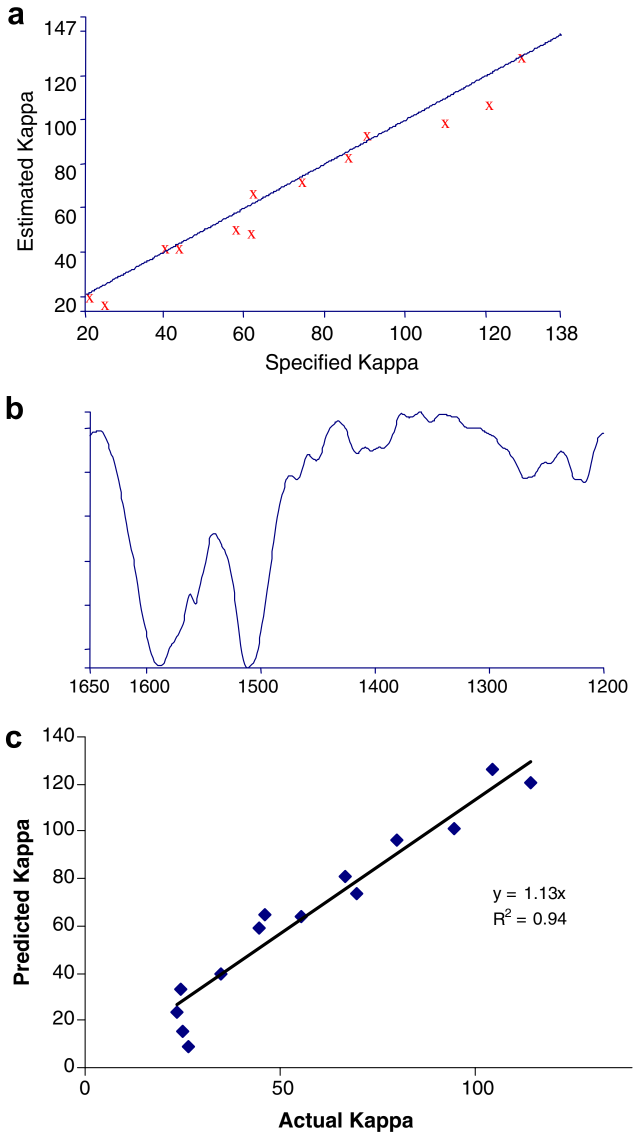

Fig. 2. (a) Calibration chart for Kappa number at $V = 0.05$ cm/s (b) Loading regression spectrum extracted from the PLS analysis ($V = 0.05$ cm/s). (c) PLS prediction ($V = 0.05$ cm/s) for Kappa number, predicted vs. Actual values.

and the lignin content in the pulp samples. A general form of the PLS model is expressed as:

$$X = TP^T + E \tag{3}$$

$$Y = UQ^T + F \tag{4}$$

where X is the variable predictor matrix (absorbance); Y is the variable response matrix (Kappa number); T and U are the X-score and Y-score matrices; P and Q are the X-loading and Y-loading matrices; E and F are the X-residual and Y-residual matrices.

In the PLS analysis, the matrices X and Y are initially column centered and normalized. PLS algorithm chooses successive orthogonal factors that maximize the covariance between each X-score and the corresponding Y-score. In order to specify T and U, two sets of weights w (X-weights) and c (Y-weights) are computed to create a linear combination $t = Xw$ and $u = Yc$ with the constraints that $w^Tw = 1$ and $t^{\mathrm{T}}t = 1$ and the regression weight $b = t^Tu$ be maximal. The columns of T are also called the latent vectors. When the first latent vector is found, it is subtracted from both X and Y and the procedure is re-iterated until X becomes a null matrix. Once the correlation is established, Y of the new sample is estimated as $Y = \mathrm{TBC}^T$ where B is a diagonal matrix with b as diagonal elements. The detailed PLS algorithm is well described by Geladi and Kowalski (1986). In this study, the Spectrum Quant+™ software was used to perform PLS analysis. Half of the samples was used for the calibration and the other half was used to verify the established model.

Prior to the PLS analysis, all spectra were automatically baseline corrected and then normalized at the cellulose peak at 1317 cm^{-1}. The PLS analysis was first performed using spectral data at the moving velocity of 0.05 cm/s within the wavenumber region 1650–1200 cm^{-1}. It is anticipated that all the characteristic bands of lignin are inclusive in this wavenumber region. Thirteen samples were used for the calibration. In choosing the calibration samples, it was important to include the extreme of the data (i.e., Kappa numbers 20.8–128). The PLS decomposition of the X and Y matrices resulted in three principle components (PCs) that can explain for 94% of the variance in the Kappa number. The relationship between the first set of spectral data and lignin content was established by the PLS analysis. The calibration chart extracted from Spectrum Quant+™ for $V = 0.05$ cm/s is presented in Fig. 2a. The regression spectrum is extracted and shown in Fig. 2b. This regression spectrum enables the viewing of features in the data that contribute to the model. The model was then validated by comparing the predicted values of Kappa number from the resultant model using the spectral data of the second set against the actual values of Kappa number. The regression coefficient R^2 value was 0.94 for $V = 0.05$ cm/s (Fig. 2c).

3.3. Effect of moving mirror velocity

The effect of mirror velocity on the obtained spectra was also investigated. In Fig. 3, the spectra of the pulp sample (Kappa number 26.4) using moving mirror velocity values of 0.05, 0.1, 0.2 and 0.5 cm/s are presented. It was found that at increasing mirror velocity, the spectra were shifted downward. It is anticipated that at increasing moving mirror velocity, the thermal diffusive depth will decrease in accordance with Eq. (1), hence yielding lower-intensity-signals.

It was found that the PLS analysis can also be used to calibrate and predict lignin content with a high degree of accuracy at different moving mirror velocities. Table 1 presents the calibration and prediction regression coefficients for Kappa number and under these different conditions. It was noted that at a higher moving mirror velocity (1.0 cm/s), the regression coefficient became lower due to

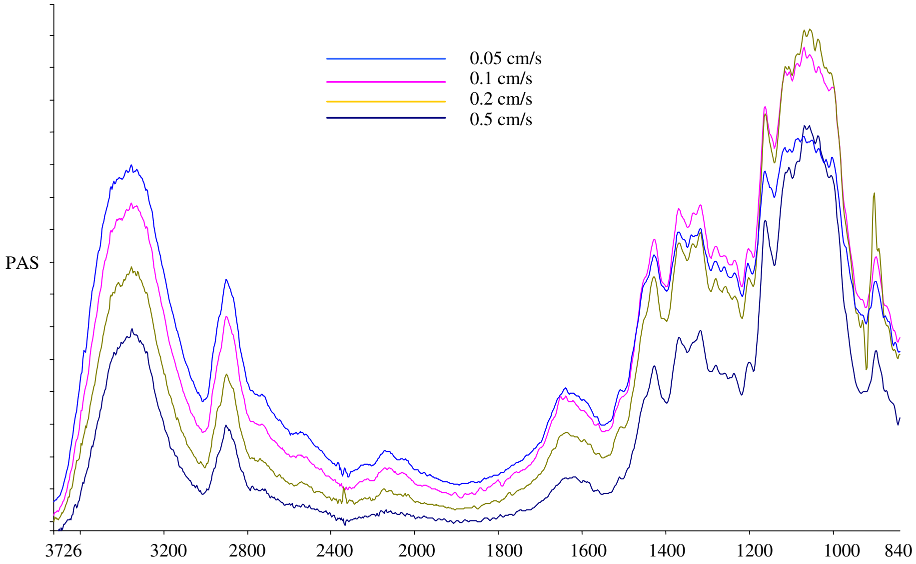

Fig. 3. Effect of mirror velocity on the spectra of pulp sample (Kappa number 26.4).

Table 1
Regression coefficients derived from PLS analyses applied to spectra obtained at different moving mirror velocities

V (cm/s)	Calibration R^2 (PC used)	Trendline equation	Prediction R^2
0.05	0.94 (3)	$y = 1.13x$	0.94
0.10	0.95 (3)	$y = 1.13x$	0.95
0.20	0.97 (3)	$y = 1.12x$	0.92
0.50	0.95 (3)	$y = 1.03x$	0.94
1.00	0.97 (3)	$y = 1.08x$	0.68

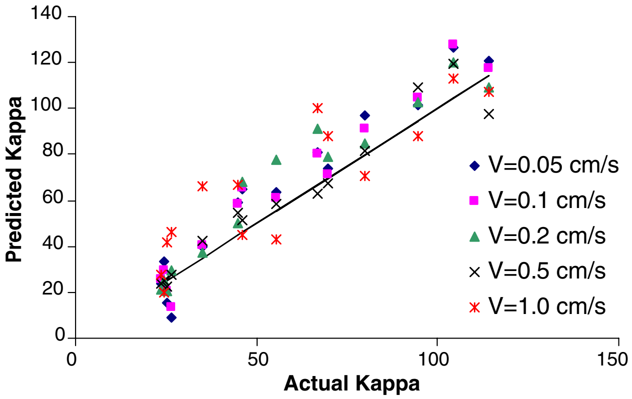

Fig. 4. Kappa number prediction at different moving mirror velocities.

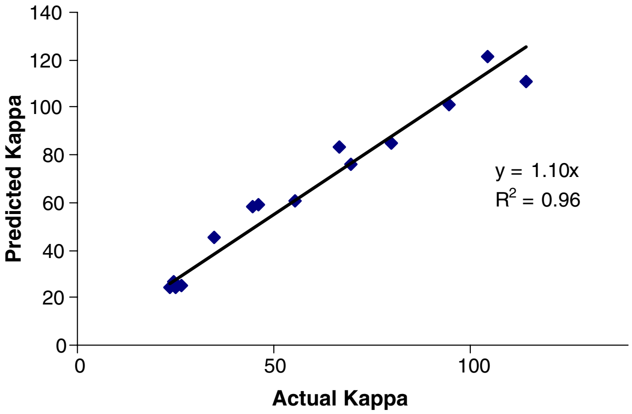

Fig. 5. PLS prediction for total Kappa number, predicted vs. actual values.

the fact that the scanned depth was not adequate to represent the average lignin content in the samples. Fig. 4 represents the prediction of Kappa number at different moving mirror velocities.

As lignin distribution could be random in different layers of pulp handsheet, taking the sum of all spectra measured at different mirror velocity provides a better representative signal for the calibration and prediction of lignin content in the pulp. In doing this, the prediction was improved, as shown in Fig. 5, with a regression coefficient, R^2, of 0.96. It is satisfactory that the PLS model can accurately predict the total Kappa number in pulp samples by scanning samples at different moving mirror velocity and then using the total spectra for calibration and prediction. The results lead to the conclusion that PAS-FTIR represents a reliable alternative to other FTIR methods.

The photoacoustic probing depth should be determined from the shorter of the thermal diffusive length μ_t and the optical wave decay length μ_β. The thermal diffusive length can be controlled by the moving mirror velocity as described in Eq. (1). In a previous study by Lima et al. (2000), the thermal diffusivity of kraft pulps were correlated with pulp brightness. In our study, we used these correlations to estimate the thermal diffusivity of pulps. The estimated thermal diffusivity is plotted against the Kappa number as shown in Fig. 6. It should be noted that the brightness of an unbleached kraft pulp can vary a lot depending on the pulping condition such as the residual alkali at the end of the cook. Therefore, the estimated thermal diffusivity is only used to approximate the thermal diffusive depth in this study, which was based on the wavenumber associated with the characteristic band of lignin (1506 cm^{-1}).

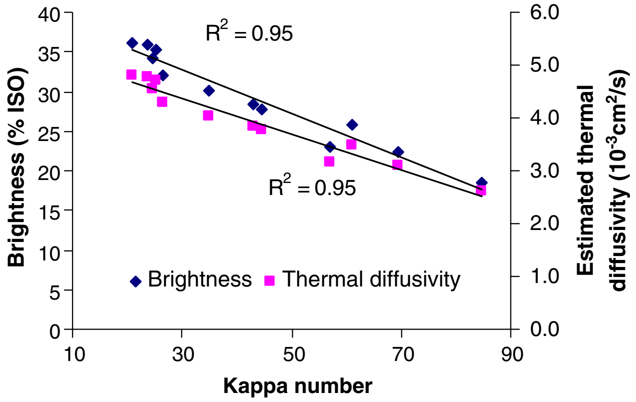

Fig. 6. Correlation between Kappa number and brightness and estimated thermal diffusivity of kraft pulps.

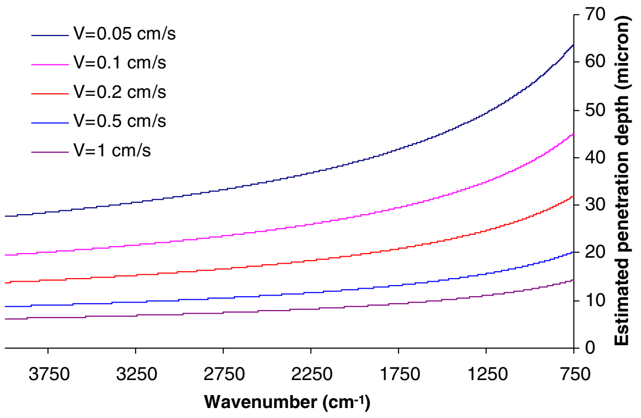

Fig. 7. Estimated thermal penetration depth as a function of wavenumber.

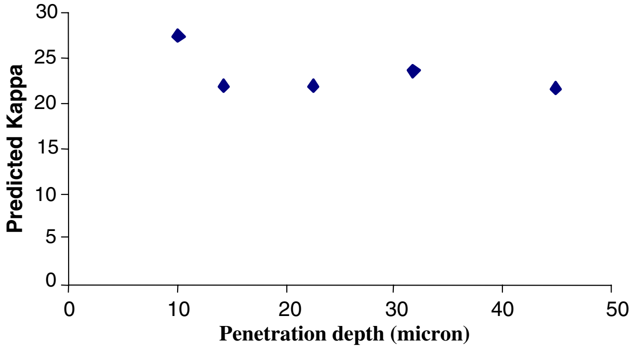

Fig. 8. Kappa number profile from the surface of pulp sample (Kappa number 23.7).

Using an estimated thermal diffusivity value of $4.78 \times 10^{-3}\,\mathrm{cm}^2/\mathrm{s}$ for the pulp sample (Kappa number 23.7), the penetration depth could be determined using Eq. (1), and shown in Fig. 7. Assuming each penetrated layer could be used to approximate the Kappa number of pulp, the established PLS models were used to predict the Kappa numbers in these layers and plotted against the average estimated depth (Fig. 8). The results confirm that the variation of lignin content at different depth in this pulp is not significant when the estimated depth is greater than 12 μm, suggesting that the method is acceptably accurate when the mirror speed is $\leqslant 0.5$ cm/s.

4. Conclusion

This study describes how PAS-FTIR can be used to determine the lignin content in kraft pulps. The spectral data in 1650–1200 cm^{-1} region are found to have strong correlations with the average Kappa number of kraft pulps, provided that the scan depth is adequate.

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