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A FTIR method for determining the content of hexeneuronic acid (hexA) and Kappa number of a high-yield kraft pulp

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Abstract

Kappa number is a good indicator of chemical demand for bleaching. In the past, it was considered as an indirect measure of residual lignin, but was later realized to depend on both the residual lignin and hexA groups in pulps. Lignin has been characterized by FTIR spectroscopy and the intensity of its characteristic bands has been used to indicate the residual lignin and Kappa number but these previous FTIR methods were not reliable. In the current study, a number of high-yield kraft pulp samples with different Kappa numbers were produced by cooking pine chips in flow-through reactors. Based on the transmission FTIR spectra of dry pulps, a quick and reliable FTIR method was established using a multivariate analysis to take into account all the characteristic bands of lignin and hexA groups for the prediction of Kappa number and hexA content in pulp. The predicted values were found to be highly comparable with the measured values determined in the laboratory.

Keywords: FTIR; Transmission; Lignin; hexA; Kappa number; PLS

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1. Introduction

Kraft pulping has been used for production of high strength paper for many decades. Currently this process is used to produce more than 80% of chemical pulps worldwide. In both commercial practices and pulping research it is highly desirable to determine the amount of residual lignin in the pulps prior to bleaching and papermaking. Kappa number, which is the amount of permanganate consumed per unit of mass of oven-dried pulp, has been widely used to approximate the lignin residue.

Several FTIR methods have been developed to determine either the residual lignin or the Kappa number of chemical pulps. Marton and Sparks (1967) chose the multiple internal reflectance infrared spectroscopic (normally known as Attenuated Total Reflectance or ATR) method. This method required a pressure to keep the paper sample closely in contact with the crystal prism. The obtained spectra were normalized using the 1310 cm^{-1} carbohydrate peak as the internal standard. The intensity of the 1510 cm^{-1} peak, which is associated with lignin, from the normalized spectra was found to be approximately proportional to the Kappa number of the pulp in the low Kappa number range (<50), but no obvious correlation was found when Kappa number was above 50. It should be noted that the ATR method detected only chemicals at a certain depth of fiber wall. For this reason this method was valid only when the distribution of lignin is uniform through the fiber wall thickness. In a similar approach, Berben, Rademacher, Sell, and Easty (1987) used diffuse reflectance FTIR to obtain better signal/noise spectra. He subtracted the spectrum of cotton linters (a pure form of cellulose) from the spectra of unbleached pulp of different Kappa numbers. 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.

The use of a single band to represent chemical components of kraft pulps appeared not adequate. Schultz, Templeton, and McGinnis (1985) employed a stepwise regression analysis combining five diffuse reflectance FTIR

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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 (1994) took a similar approach, but chose the band at 1510 cm^{-1} as the internal standard instead of 1048 cm^{-1}.

Faix, Schubert, and Patt (1989) identified the absorption bands of lignin in the cooking liquors at 1494, 1466 and 1264 cm^{-1} and correlated the height/area of each of those lignin bands with the Kappa number of pulp during cooking. Using a curve fitting method Faix showed that FTIR spectral data of the cooking liquor could be used to predict the Kappa number of the pulp in the digester. Similarly, Michell (1990) described a method for estimating lignin content in spent liquors of the kraft pulping process. He selected the band at 1118 cm^{-1} to indicate the concentration of lignin in spent liquors. It was consequently found that the area under this band was linearly related to the Kappa number of pulp in the digester. These methods of indirect measurement of Kappa number could have large errors when liquor and pulp samples could not be collected simultaneously.

During the 1990s a group of Finnish scientists discovered the presence of a carbohydrate that also consumed permanganate during Kappa tests. Gellerstedt and Li (1995) and Gellerstedt, Pranda, and Lindfors (1994) confirmed that a substantial portion of the Kappa number in a birch kraft pulp was related to materials present in xylan chains. Further investigation discovered that kraft pulping of pine wood gives rise to hexA groups in the xylan by elimination of methanol from 4-deoxy-L-threo-hex-4-eno-pyranuronosyl groups (Teleman et al., 1995). hexA can be selectively removed using a mild hydrolysis with mercuric acetate solution (Vuorinen, Fagerstrom, Buchert, Tenkanen, & Teleman, 1996) and UV spectrophotometry can be used to quantify the dissolved hexA (Chai, Zhu, & Li, 2001). Previous results suggested that 10 μmol of hexA groups could raise the Kappa number by approximately 0.86 (Li & Gellerstedt, 1997).

Kappa number is a good indicator of chemical demand for bleaching, and hexA is strongly associated with paper yellowing. Although these chemical components of kraft fibers are different, both are important to the production of fully bleached pulps. Unfortunately, both current tests for Kappa number and hexA have to be carried out separately, consuming a significant amount of time. In this study, we evaluated previous FTIR methods used for the Kappa number measurement of pulp and attempted to modify one of these methods for the determination of both Kappa number and hexA. Two sets of spectral data, which included the characteristic bands of lignin and hexA groups, were collected. The first set was integrated with a multivariate analysis to formulate a model for correlating the selected spectral information with Kappa number and hexA content of kraft pulps. The second set was used to test the accuracy of the model.

2. Experimental

2.1. Pulp samples

Ten kraft pulp samples with different Kappa numbers were produced by cooking pine chips in flow-through reactors at 1 M effective alkali as Na_2O. These chips were first impregnated with the cooking liquor for 30 min at 108 °C before being cooked at 152 °C. Different cooking times were used to produce pulps of different Kappa number. The pulps were sieved through a screen with 0.15 mm slots and were thoroughly washed with de-ionised water prior to the measurements of Kappa numbers and the hexA content in pulp.

2.2. Measurement of Kappa numbers

Determination of Kappa numbers of pulp samples was carried out following a standard procedure described in Tappi test method T 236 om-99.

2.3. Measurement of hexA groups

The determination of the hexA content in pulp was done by UV spectrophotometry. The hydrolysis solution was prepared, containing 22 mmol/l of mercuric chloride (0.6%) and sodium acetate (0.7%). Approximately 0.05 g of air-dried pulp handsheet with known moisture content was accurately weighed and placed in a 20 ml vial containing 10 ml of the hydrolysis solution. The vial was then sealed by a septum. Good mixing of the chemicals in the vial was obtained by hand shaking. The vial was then heated for 30 min in a water bath at 60–70 °C. After the solution was cooled to the room temperature, the UV absorption of the filtered solution was measured in a 10 mm path length silica cell at two wavelengths (260 and 290 nm) using a Shimadzu UV spectrophotometer (UV-1601). The same fresh hydrolysis solution was used as the blank in UV absorption measurements. The hexA content in pulp was calculated using the dual-wavelength formula as determined by Chai et al. (2001)

$$C_{\mathrm{hexA}} = 0.287\frac{(A_{260} - 1.2A_{290})V}{w}$$

where C_{hexA} is the content of hexeneuronic acid groups in pulp (mol/g); A_{260} and A_{290} are the measured absorption intensities at 260 and 290 nm, respectively; V is the volume of the hydrolysis solution (ml); w is the oven-dried weight of the pulp sample (g).

2.4. FTIR spectra

A handsheet of 40 gsm was made for each pulp sample. The FTIR spectra of these handsheets were scanned in the transmission mode using a Perkin Elmer FTIR spectrometer (GX model). The spectra were recorded in absorbance units. Each sample area was scanned eight times to obtain the average spectrum in the wavenumber range of 4000–800 cm^{-1}. The resolution of the scans was 4 cm^{-1} and the scan interval was 1 cm^{-1}.

A correlation between the transmission FTIR spectra and both the Kappa number and the amount of hexA groups in the pulp samples was established using the Partial Least Squares (PLS) regression. A general form of the PLS model is expressed as:

$$X = TP^{T} + E, \qquad Y = UQ^{T} + F$$

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

In this 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 $w^{T}w=1$ and $t^{T}t=1$ and the regression weight $b=t^{T}u$ 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 $Y=TBC^{T}$ 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 is chosen to perform this PLS analysis. Five samples were used for the calibration and other five remaining samples were used to verify the established model.

3. Results and discussion

The Kappa numbers of the pulp samples are presented in Table 1. These numbers are the averages of two tests. The Kappa numbers range from 20.8 to 84.8.

Table 1
Kappa numbers of the pulp samples

Sample ID	Cooking time (min)	Kappa number
Sp1	120	61.2 ± 1.1
Sp2	235	25.1 ± 1.1
Sp3	245	23.7 ± 1.1
Sp4	255	20.8 ± 1.1
Sp5	100	84.8 ± 1.1
Sp6	140	69.6 ± 1.1
Sp7	170	57.0 ± 1.1
Sp8	200	44.7 ± 1.1
Sp9	220	42.9 ± 1.1
Sp10	230	34.9 ± 1.1

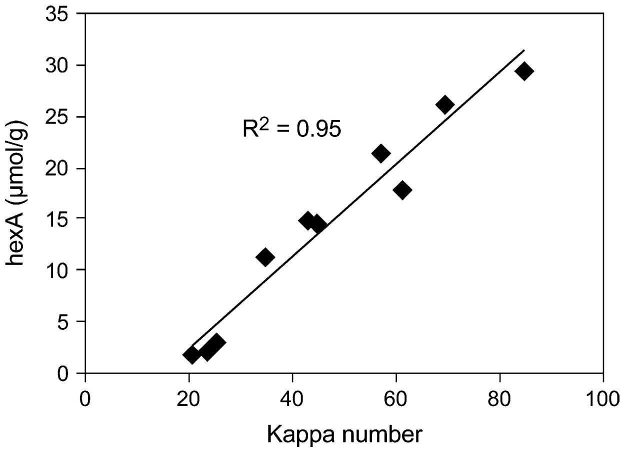

Fig. 1. Correlation of Kappa number with the hexA content of kraft pulps.

The hexA contents of the pulp samples, which are calculated from the UV measurements, are presented in Fig. 1. It is apparent that the hexA content has approximately linear relationship with the Kappa number. The regression coefficient, R^2, of this linear correlation is 0.95. It is noticeable that, when the Kappa number reduces to about 20, the hexA content becomes negligible.

Characteristic bands of lignin such as aromatic skeletal vibrations were previously found at 1605–1593, 1515–1505 and 1430–1422 cm^{-1} (Faix, 1992). The chemical structure of hexA consists of R–O–R links, –OH and –COOH groups, which normally show at 1270–1230, 1420–1250 and 1725–1700 cm^{-1}, respectively (Szymanski, 1964). Fig. 2 shows the spectra of three pulp samples with different Kappa numbers in the entire mid infrared range 4000–650 cm^{-1}. A change in the absorbance intensity is noticed for the peak at 1509 cm^{-1} and two shoulders at 1595 and 1466 cm^{-1}. It is anticipated that these peaks are associated with the lignin and hexA concentration in the pulp. In fact, the chemical structures of lignin and hexA are quite complex as they contain many functional groups, some of which are the same such as –OH groups and C–O–C links. Therefore in the finger print region (1333–667 cm^{-1}), it is extremely difficult, if not possible, to identify individual characteristic bands of lignin and hexA due to overlapping absorbencies.

Our results were used to test the method proposed by Marton and Berben. The Kappa numbers of the pulp samples are plotted against the intensity and area of the 1510 cm^{-1} band in Fig. 3. The plots indicate that the linear relationships suggested by Marton and Berben cannot be established.

In this study, multivariate analysis is carried out using all spectral data associated with lignin and hexA in the wave number range 1650–1200 cm^{-1}. Five samples were used in the calibration and a total of 451 points for

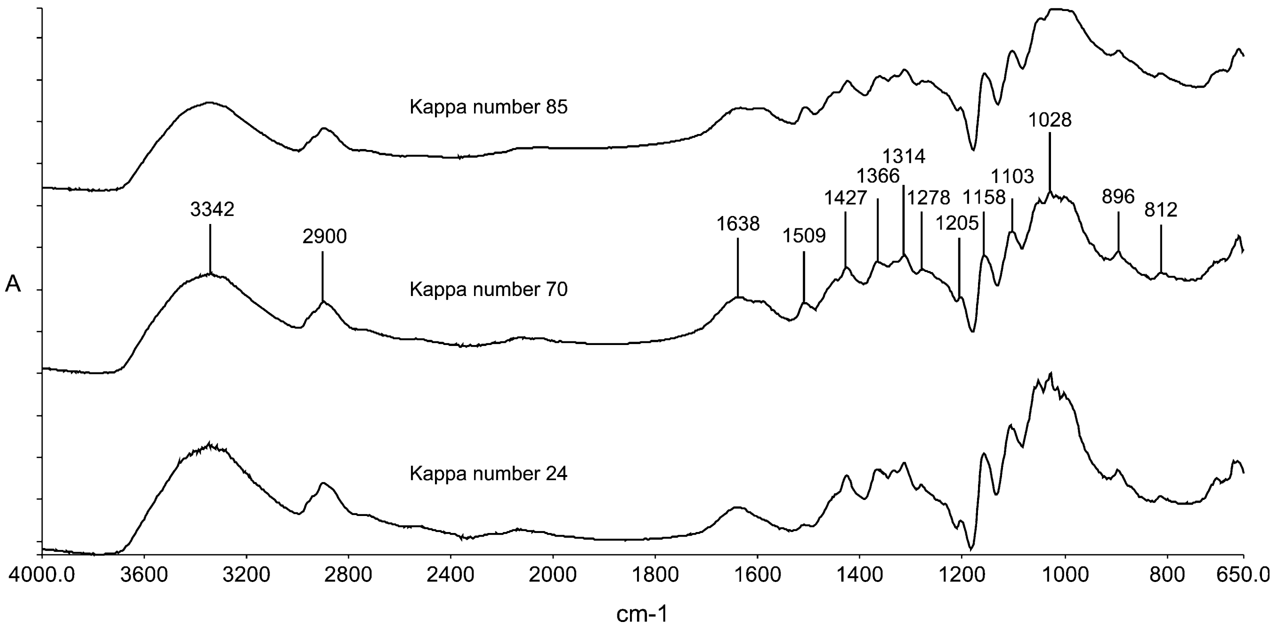

Fig. 2. FTIR spectra of the pulp samples with different Kappa numbers.

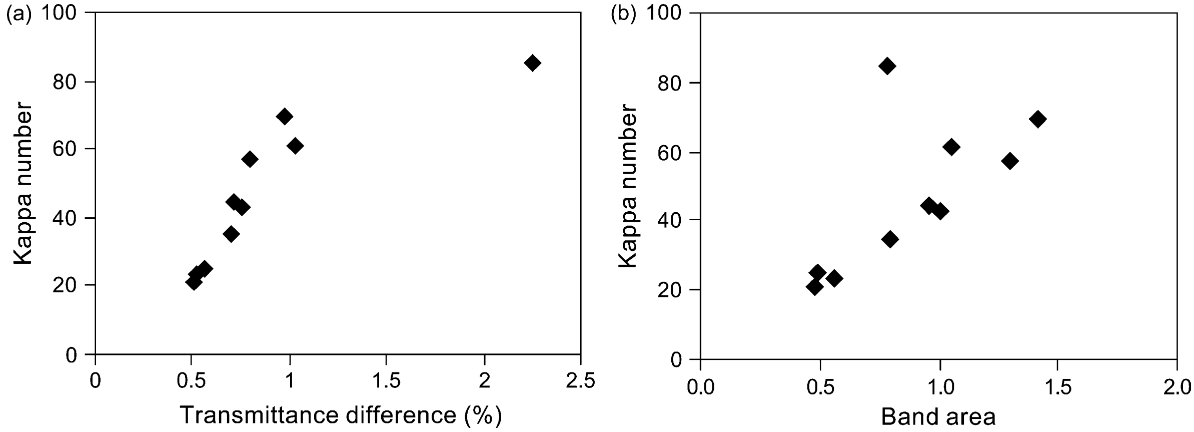

Fig. 3. (a) Kappa number versus transmittance difference at 1510 cm^{-1} (Marton's method). (b) Kappa number versus area of the 1510 cm^{-1} band (Berben's method).

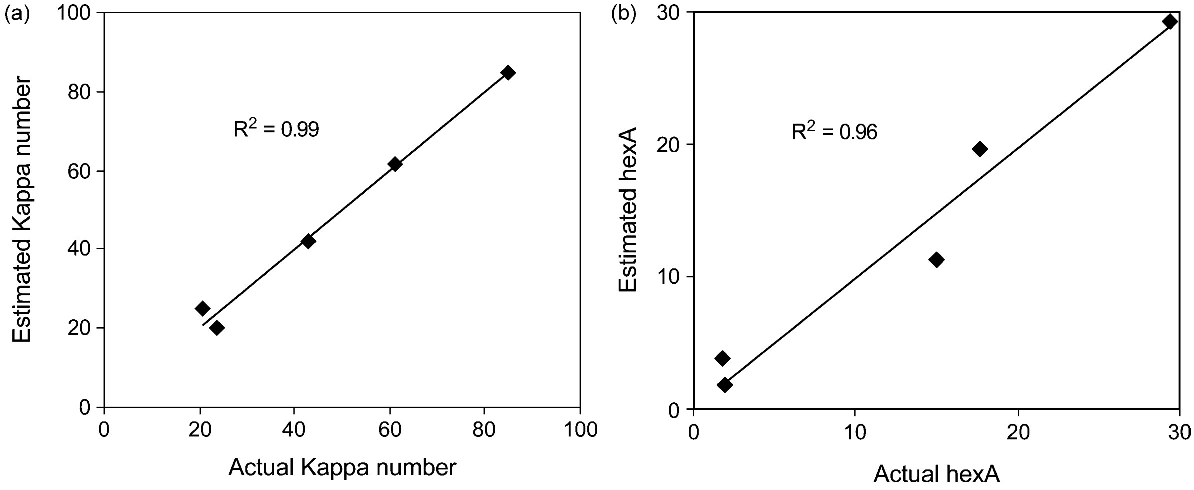

Fig. 4. Calibration of the PLS model. (a) Estimated versus actual Kappa number; (b) estimated versus actual hexA.

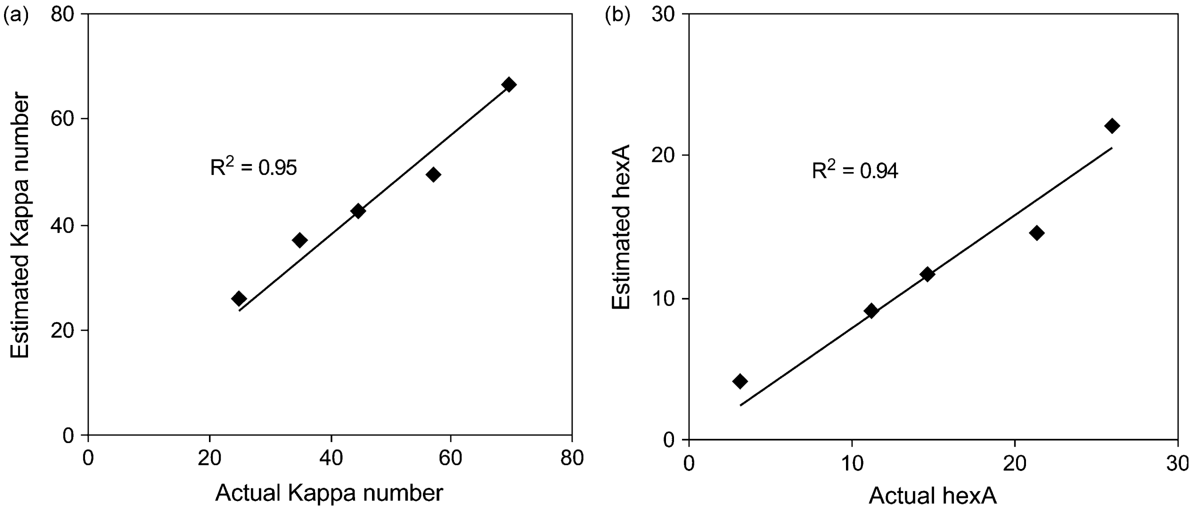

Fig. 5. Prediction of the PLS model. (a) Estimated versus actual Kappa number; (b) estimated versus actual hexA.

each spectrum was used in the analysis. The resultant *Y*-matrix has dimensions 5×2 and the *X*-matrix has dimensions 5×451. The PLS decomposition of the *X*- and *Y*-matrices resulted in two Principle Components (PC) that can explain about 99.9% of the variance in the spectral data and 99% of the variance in the Kappa numbers and 96% of the variance in the hexA content.

The relationship between the first set of spectral data and the Kappa numbers and hexA content are established by the PLS analysis. The calibration regression coefficients R^2 were 0.99 and 0.96 for the Kappa number and hexA content, respectively (Fig. 4a and b).

The accuracy of the model was then determined by comparing the predicted values of Kappa number and hexA content from the resultant model using the spectral data of the second set against the actual measurements. The regression coefficients of the comparison were 0.95 and 0.94 for Kappa number and hexA content, respectively (Fig. 5a and b).

4. Conclusion

This study describes how a PLS model can be established to correlate the FTIR spectral data in 1650–1200 cm^{-1} with the pulp Kappa number and content of hexA in unbleached kraft pulps.

If the model is properly calibrated, its prediction will be highly accurate, and the model can replace the time-consuming conventional methods for determination of Kappa number and hexA content in unbleached kraft pulp samples.

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