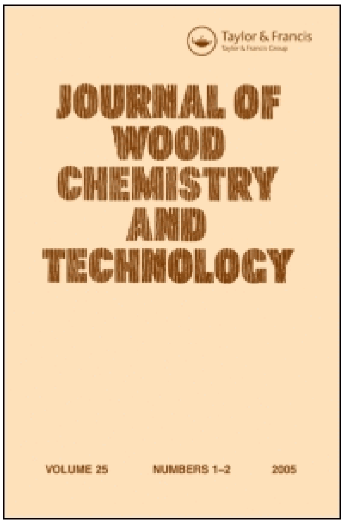

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MULTIVARIATE CALIBRATION FOR QUANTITATIVE ANALYSIS OF EUCALYPT KRAFT PULP BY NIR SPECTROMETRY

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ABSTRACT

Near infrared spectrometry and multivariate data analysis were applied to predict the chemical composition and physico–chemical characteristics of eucalypt unbleached kraft pulps obtained at different laboratory pulping conditions. Viscosity, degree of polymerization (DP), kappa, brightness and contents of glucan, xylan, uronic acids, and lignin were the modeled variables using diffuse reflectance near infrared

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spectra obtained on pulp handsheets and the partial least squares (PLS) method. Models with two to four PLS components and good predictive ability were established after first derivative spectra pre-processing and application of cross-validation methodology. The predictive models can reduce the time consuming traditional analyses in the pulping industry laboratories, and also lead to a better process monitoring for suitable applications.

Key Words: Kraft pulp; Carbohydrates; Automation; Multivariate calibration; NIR spectrometry

INTRODUCTION

The interest in monitoring chemical processes by spectrometric techniques and multivariate data analysis has increased remarkably. Advantages of low cost, fast and reliable data and the possibility to obtain ‘‘on-line’’ or ‘‘at-line’’ information are attractive considerations in recent investigations.[1,2] These terms are related with the analysis automation; if it is fully automated it is termed ‘‘on-line’’, whereas if conducted in a laboratory instrument located in the manufacturing area after manual sampling it is termed ‘‘at-line’’. The term ‘‘on-line’’ has been also subdivided into on-line, in-line and non-evasive analysis.[3,4] Traditionally, process control has been performed using ‘‘off-line’’ analysis involving manual sampling and transportation to a specialized laboratory where complex sample preparation and considerable time is necessary. The use of spectrometric methods can provide rapid determination of many production parameters and if a spectrometer is located close to the manufacturing it may be possible to make rapid changes to optimize the process, thus improving efficiency for industry.[5]

In the pulping process, traditional ‘‘on-line’’ process measurements are limited to pressure, temperature and pH, while other physico–chemical and composition parameters are usually determined in the laboratory, resulting in a delay of a few hours that sometimes can be difficult to manage, especially in large scale integrated mills. Once the pulp is made, brightness and consistency are also some pulp properties that can be determined ‘‘on-line’’, but pulping and bleaching are complex processes requiring many simultaneous controlled parameters.

The implementation of ‘‘on-line’’ and ‘‘at-line’’ measurements requires not only instrumentation, but also reliable calibration. Applications of spectrometric methods combined with multivariate data analysis have shown to be useful for investigation of pulping kinetics[6] and beating effects on pulp.[7]

Of the various spectrometric methods, near-infrared (NIR) applications have been most often reported for several industrial materials including solids, liquids, and melts,[8–10] with a recent growth seen in many wood based applications. NIR has advantages such as non-destructive analysis, a fast and simple procedure, minimal sample pre-treatment and the possibility of employment in process monitoring using fiber optic technology. The drawbacks are sensitivity to matrix effects caused by light scattering and physical dimensions, spectral complexity due to overlapping peaks and non-linearity between apparent absorbance and concentration, and specificity of the calibrations. Applications of an integrating sphere for diffuse spectrum acquisitions, preparation of pulp sheets and chemometric tools combining linearizing transform and multivariate calibration can reduce the drawbacks improving the technique performance. Linear transforms such as the Kubelka-Munk (KM) transform, multiplicative scatter correction (MSC), orthogonal signal correction (OSC), and derivatives have been described elsewhere.[11–13]

Mathematical modeling using data obtained with chemical methods and spectral information can be performed using classical least squares (CLS),[14] multiple linear regression (MLR), principal component regression (PCR) and partial least squares (PLS).[15] The latter has the versatility to predict more than one variable, because a non-iterative PLS (NIPALS) algorithm is used to calculate model parameters.[16,17] This advantage has made PLS used extensively for NIR applications in wood, pulp and paper samples.[18–23] In this study, we present a multivariate calibration model for eight chemical and physico-chemical variables developed for eucalypt kraft pulp that can be applied as ‘‘at-line’’ in a routine pulp mill laboratory close to the digestor.

MATERIAL AND METHODS

Materials

Wood and Chips

Wood of *Eucalyptus grandis*, eight years old, was used to obtain chips employing an industrial chipper. Chip fractions in the width range of 2–5 mm and length range of 16–45 mm were selected for pulping using a bar and hole chip classifier.

Pulps

The process for pulping was conventional kraft using NaOH and Na_2S as liquor components and a REGMED laboratory reactor of 20 l equipped with automatic temperature and heating rate control. The wood content for pulping was 1000 g.

Nine kraft pulp samples were obtained using active alkali of 15.5, 18.1, 19.4, 20.7, 22.0, 23.3, 25.9, 28.5 and 31.1% as NaOH, respectively. The pulping temperature of $165 \pm 2^\circ C$, heating rate of $2.8 \pm 0.1^\circ C/min$, sulfidity $27.2 \pm 0.1\%$ as NaOH, and a liquor-wood ratio of 4 : 1 were used in all experiments.

Pulp Handsheets

Pulp handsheets with a grammage of 75 g/m^2 were prepared in a Rapid Köthen apparatus using deionized water.

Methods

Carbohydrates and Uronic Acids

Glucose, xylose, mannose, arabinose, galactose, and rhamnose were determined in acidic pulp hydrolyzates using HPLC-PAD.[24] Uronic acids were determined according to the Scott method.[25]

Lignin

Acid insoluble and soluble lignin were determined according to a modified method[26] and ultra-violet spectrometry at 205 nm (TAPPI useful method T 259, 1975), respectively.

Kappa, Relative Viscosity and DP

Kappa, relative viscosity and DP were determined using standard methods (TAPPI method T 236, 1985; TAPPI method T 230, 1994; SCAN method C15-16, 1962), respectively.

ISO Brightness

Brightness was determined using a DATACOLOR 3300 spectrophotometer and standard method ISO 3688.

Diffuse Reflectance Near Infrared Spectrometry

Diffuse reflectance NIR spectra was obtained using PERKIN ELMER Lambda 19 spectrometer equipped with a 60 mm integrating sphere, coated with $BaSO_4$. A scanning rate of 120 nm/s was used in a range of 900-2200 nm for pulp handsheets. NIR spectra were converted to Kubelka-Munk, first and second derivative modes using the software PERKIN ELMER UV WinLab 1.51.

Data Analysis

Calibration

Calibration is a procedure of modeling that describes the relationship between two groups of variables, often called dependent (Y) and independent (X) variables. Univariate calibration is applied elsewhere for chemical analyses using instrumental methods. In this procedure a relationship $Y=f(X)$ is established using an instrumental variable, e.g., spectral absorbance at one wavelength, for different concentration standards. The model parameters called regression or sensitivities are used for prediction of new samples. Multivariate calibration is based on the same principle, but the model or relationship is obtained employing data from the whole spectrum, e.g., spectral absorbance at several wavelengths, and more than one dependent variable can be used simultaneously.

Model building in multivariate calibration can be performed using the PLS method that can use the NIPALS algorithm to calculate model parameters. Firstly, dependent variables, e.g., concentration values, are grouped in the **Y** block and independent variables, e.g., spectral data, are grouped in the **X** block. The **Y** and **X** blocks are decomposed using NIPALS to a sum of outer products of vectors called scores (t) and loadings (p). An additional set of vectors termed weights (w) is also calculated in order to improve the relation between the two blocks. NIPALS uses t, p, and w to calculate a vector of "inner-relationship" coefficients which relate **X** and **Y** block scores. Residuals for **X** and **Y** blocks and regression coefficients (b) are also calculated for each PLS component.[16,17]

Prediction

Prediction in PLS is performed by decomposing the independent block **X** and building up a new dependent **Y** block. For such a purpose, t, p, w, and b calculated during the calibration step are saved for each PLS component. The number of PLS components for a model is determined by using cross validation methodology, which calculates the lack of prediction accuracy, called prediction residual error sum of squares (PRESS). A number of PLS components that yields the lowest PRESS is usually chosen to establish a model.[16]

Multivariate calibration and prediction were performed using the PLS Toolbox with MATLAB 4.0 software.

RESULTS AND DISCUSSION

Pulping Experiments

The change in the active alkali in pulping experiments affected both pulp chemical composition and physical chemistry parameters as presented in Table 1. The series of pulp obtained covered the different properties usually required for production of tissue and printing and writing papers.

Pulp Characterization Is Time Consuming

Determination of carbohydrates and the lignin content in pulp samples are time consuming procedures and are generally not performed in the pulping industry. In order to have information about pulp degradation by the process, parameters such as viscosity and kappa are measured due to their relative simplicity. Kappa was developed as a parameter associated with lignin content in pulp, and it is traditionally employed to estimate the extent of delignification in pulping, in spite of the interference from hexenuronic acid.[27] Viscosity is another process parameter generally used to indicate the damage in the carbohydrate portion in pulping. Despite their simplicity to perform, a skilful worker requires at least 90 min for both results. Brightness is also a time consuming and costly determination requiring specific instruments and proper sample preparation.

Table 1. Active Alkali Applied in Pulping, Pulp Properties and Chemical Composition (% Dry Pulp). Laboratory Errors Are Given in Parentheses

Active Alkali (% NaOH)	Kappa	Visc.[1] (mPa.s)	Bright.[2] (% ISO)	D.P.[3]	Glucan (%)	Xylan (%)	UA[4] (%)	L[5] (%)
15.5	23.7	58.2	29.3	1757	78.1	14.4	3.4	3.2
	(0.5)	(2.0)	(0.1)	(60)	(0.2)	(0.3)	(0.2)	(0.3)
18.1	21.9	46.1	31.0	1705	79.6	13.8	3.0	2.8
	(0.5)	(1.6)	(0.1)	(58)	(0.2)	(0.3)	(0.2)	(0.3)
19.4	18.3	35.0	32.4	1481	81.2	13.5	2.6	2.2
	(0.4)	(1.2)	(0.1)	(50)	(0.2)	(0.3)	(0.2)	(0.2)
20.7	17.2	30.2	33.8	1463	82.8	13.8	2.4	2.2
	(0.4)	(1.0)	(0.1)	(49)	(0.3)	(0.3)	(0.1)	(0.2)
22.0	16.2	27.8	34.5	1428	83.3	13.3	2.3	2.0
	(0.4)	(0.7)	(0.1)	(48)	(0.3)	(0.3)	(0.1)	(0.2)
23.3	15.5	26.9	36.0	1362	82.7	12.3	2.0	2.3
	(0.3)	(0.7)	(0.1)	(46)	(0.3)	(0.3)	(0.1)	(0.2)
25.9	14.6	20.5	38.0	1223	82.2	11.1	1.8	1.8
	(0.3)	(0.6)	(0.1)	(42)	(0.3)	(0.2)	(0.1)	(0.2)
28.5	11.9	15.9	38.4	988	82.3	10.6	1.6	1.6
	(0.2)	(0.5)	(0.1)	(33)	(0.3)	(0.2)	(0.1)	(0.2)
31.1	11.6	14.9	38.6	943	84.6	9.7	1.6	1.6
	(0.2)	(0.5)	(0.1)	(32)	(0.3)	(0.2)	(0.1)	(0.2)

(1) Relative Viscosity; (2) ISO Brightness; (3) Degree of Polymerization; (4) Uronic Acids; (5) Total Lignin.

The application of NIR spectrometry combined with multivariate calibration can address sample preparation and analyses in 9 min, reducing the time by 90%.

Near Infrared Spectrometry

The NIR spectra for the different pulp samples are presented in Figure 1a. Characteristic bands of OH of water (1930 nm), OH of alcohol (2100 nm) and OH of phenol (1490 nm) and other overlapping peaks are

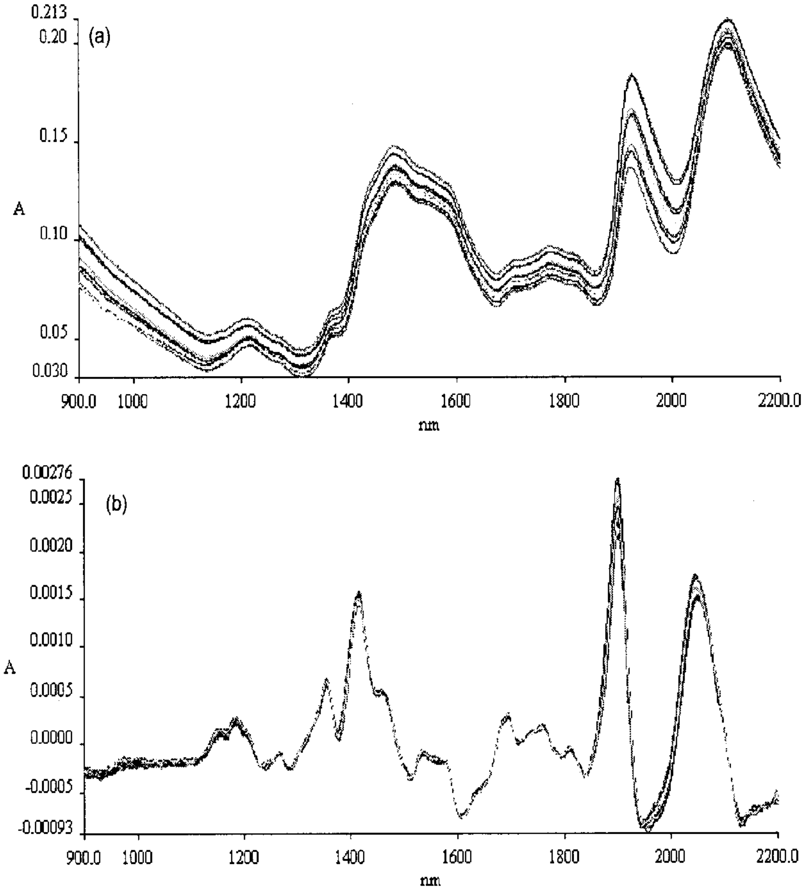

Figure 1. NIR spectra for kraft pulp samples obtained with different active alkali dosage; (a) Original diffuse reflectance spectra; (b) First-derivative treated spectra.

observed at different intensities, but the complex nature of the pulp chemical composition address difficult spectral interpretation if a conventional approach is used. In order to linearize the spectral information with the investigated variables, methods of mathematical pre-processing were used. The first derivative transform was applied and the obtained spectra are presented in Figure 1b. Other pre-processing methods such as second derivative and Kubelka-Munk were also tested, but first derivative gave calibration models with better correlations.

Multivariate Calibration

The first derivative NIR spectra were grouped in a matrix **X** (9,1300) and data of viscosity, kappa, brightness, degree of polymerization and contents of glucan, xylan, uronic acid and total lignin were organized in individual matrices named **Y** (9,1). The matrices **X** and **Y** were mean-centered.

The PLS method was applied and the **X** matrix attributed as predictor or independent variables and **Y** matrices as predicted or dependent variables. The leaving-one-out cross-validation method was used to calculate the (PRESS) and to establish the number of PLS components for each model. The obtained models were evaluated through the root-mean-square error of cross-validation (RMSECV), root-mean-square error of calibration (RMSEC), root-mean-square-error of prediction (RMSEP), and plots of actual versus predicted values and leverage versus studentized residuals. The PLS models and their root-mean-squares errors are presented in Table 2.

Table 2. PLS Models for Kraft Pulp Chemical Composition and Physical Chemistry Properties

Model	PLS Components	RMSECV$^{(1)}$	RMSEC$^{(2)}$	RMSEP$^{(3)}$
Kappa	02	1.56	0.814	1.87
Viscosity	04	7.20	0.352	8.16
Brightness	03	1.07	0.266	1.28
DP	02	77.92	33.990	96.32
Glucan	04	1.69	0.082	2.03
Xylan	03	0.70	0.165	0.87
Uronic acids	03	0.24	0.048	0.32
Total lignin	03	0.30	0.049	0.39

Root-Mean-Square-Error of: (1) Cross-validation; (2) Calibration; (3) Prediction.

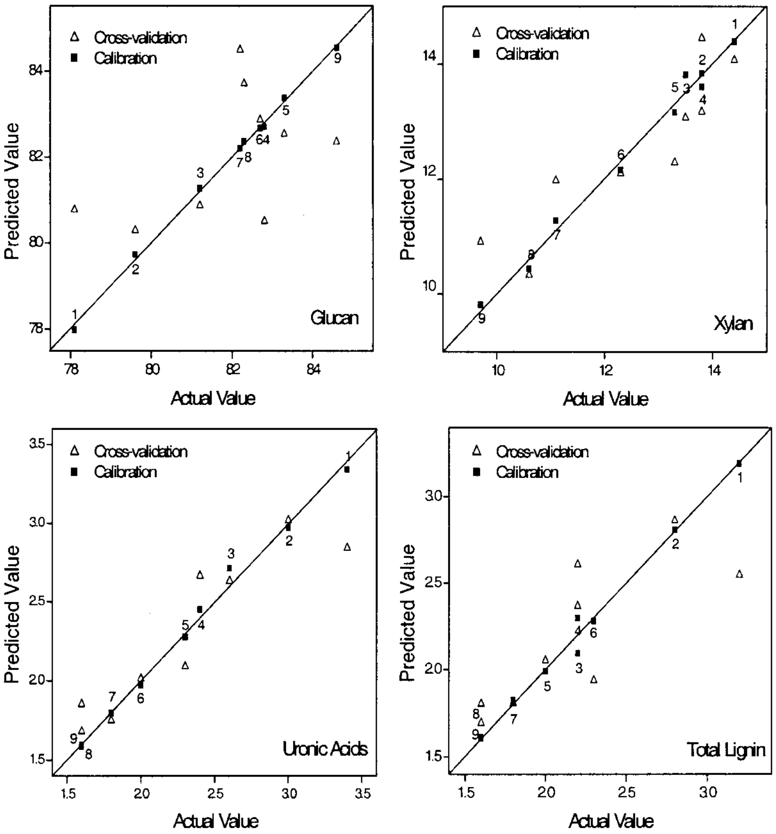

Figure 2. Actual versus predicted values for models to estimate contents of glucan, xylan, uronic acid and total lignin.

The PLS models for kappa and DP showed highest prediction performances while the glucan and viscosity models showed the lowest performances, according to RMSECV/RMSEC and RMSEP/RMSEC ratios, respectively. In general, models showed good predictive ability as can be observed in Figures 2 and 3 where actual versus predicted data were respectively plotted for models of chemical composition and physical chemistry properties. Despite of it, the model errors are higher than the laboratory errors presented in Table 1, which can be expected once the traditional laboratory results were used as primary standards for NIR calibration.

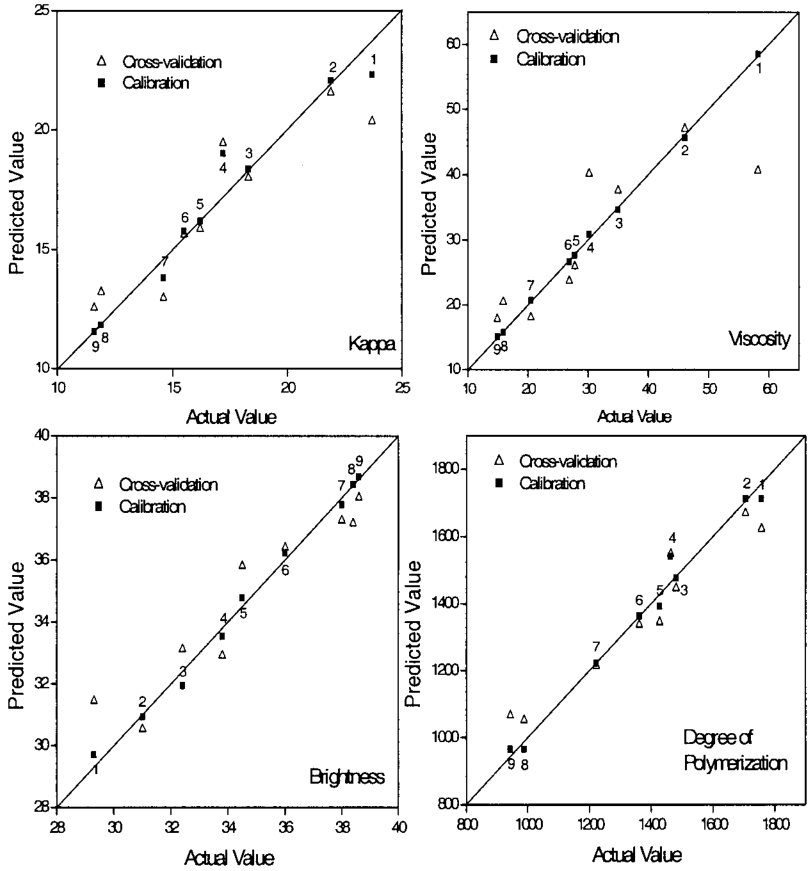

Figure 3. Actual versus predicted values for models to estimate kappa, viscosity, brightness and DP.

Perspectives for Application of Multivariate Calibration Models in Pulping

The application of multivariate calibration models in pulping as a process analytical chemistry tool, using "on-line" measurements, is dependent up on development of a proper sensor and sampling devices to acquire spectra under specific conditions. Fibers are often in water and effects of scattering, turbulence, temperature oscillations, and other interference sources can occur. The solution of these drawbacks has a promising future for a new era in the pulp mill process monitoring.

Water is another component that can affect both the fiber structure and the NIR measurement, but can be compensated by the linearizing transform tools. Many of the NIR applications reported previously were done on dried pulp or wood material to avoid the water effect. Despite the actual limitations for a direct process application for fiber analyses in pulp mills, models have a good perspective to be used in routine laboratories where tedious and time consuming procedures can be replaced by handsheet preparation and subsequent NIR measurement. This new procedure requires a strict experimental condition both for calibration and measurements, but will reduce analysis time and costs, improving the laboratory productivity and process monitoring.

CONCLUSION

Diffuse near infrared spectrometry and partial least squares method were applied to perform multivariate calibration models for kraft pulp chemical composition and physical chemistry properties. The obtained models showed good predictive ability for contents of glucan, xylan, uronic acids, and total lignin, as well as for kappa, viscosity, brightness, and degree of polymerization in a practical range used in eucalypt kraft pulping. Application of this procedure for performance improving in a routine pulp mill laboratory and better process monitoring is recommended.

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REFERENCES

1. Workman Jr, J.; Veltkamp, D.J.; Doherty, S.; Anderson, B.B.; Creasy, K.E.; Koch, M.; Tatera, J.F.; Robinson, A.C.; Bond, L.; Burgers, L.W.; Bokerman, G.N.; Ullman, A.H.; Darsey, G.P.; Mozayemi, F.; Bamberger, J.A.; Greenwood, M.S. Process Analytical Chemistry. Anal. Chem. **1999**, *71*(12), 121R–180R.

2. Andersson, M.; Folestad, S.; Gottfries, J; Johansson, M.O.; Josefson, M.; Wahlund, K.G. Quantitative Analysis of Film Coating in a Fluidized Bed Process by In-Line NIR Spectrometry and Multivariate Batch Calibration. Anal. Chem. **2000**, *72*(9), 2099–2108.
3. Callis, J.B.; Illman, D.L.; Kowalski, B.R. Process Analytical Chemistry. Anal. Chem. **1987**, *59*(9), 624A–635A.
4. McLennan, F. Process Analytical Chemistry in Perspective. In *Process Analytical Chemistry*; McLennan, F.; Kowalski, B.R., Eds.; Blackie Academic and Professional: Glasgow, 1995; 01–13.
5. Ozaki, Y.; Amari, T. Near-infrared Spectroscopy in Chemical Process Analysis. In *Espectroscopy in Process Analysis*; Chalmers, J.M., Ed.; Sheffield Analytical Chemistry; Chalmers, J.M.; Ibbett, R.N., Eds.; Sheffield Academic Press: Cleveland, 2000; 53–95.
6. Wallbäcks, L.; Edlund, U.; Nordén, B. Multivariate Data Analysis of In Situ Pulp Kinetics Using ^{13}C CP/MAS NMR. J. Wood Chem. Technol. **1989**, *9*(2), 235–249.
7. Wallbäcks, L.; Edlund, U.; Nordén, B.; Iversen, T. Multivariate Characterization of Pulp. Part 1. Spectroscopic Characterization of Physical and Chemical Differences Between Pulps Using ^{13}C CP/MAS NMR, FT-IR, NIR and Multivariate Data Analysis. Nord. Pulp Pap. Res. J. **1991**, *6*(2), 74–80, 94.
8. Sekulic, S.S.; Ward, H.W.; Brannegan, D.R.; Stanley, E.D.; Evans, C.L.; Sciavolino, S.T.; Hailey, P.A.; Aldrige, P.K. On-Line Monitoring of Powder Blend Homogeneity by Near-Infrared Spectroscopy. Anal. Chem. **1996**, *68*(3), 509–513.
9. Broad, N.W.; Jee, R.D.; Moffat, A.C.; Eaves, M.J.; Mann, W.C.; Dziki, W. Non-invasive Determination of Ethanol, Propylene Glycol and Water in a Multi-component Pharmaceutical Oral Liquid by Direct Measureament Through Amber Plastic Bottles Using Fourrier Transform Near-Infrared Spectroscopy. Analyst **2000**, *125*(11), 2054–2058.
10. Aldrige, P.K.; Kelly, J.J.; Callis, J.B.; Burns, D.H. Non-invasive Monitoring of Bulk Polymerization Using Short-Wavelength Near-Infrared Spectroscopy. Anal. Chem. **1993**, *65*(24), 3581–3585.
11. Geladi, P.; McDougall, D.; Martens, H. Linearization and Scatter-Correction for Near-Infrared Reflectance Spectra of Meat. Appl. Spectrosc. **1985**, *39*(3), 491–500.
12. Isaksson, T.; Naes, T. The Effect of Multiplicative Scatter Correction (MSC) and Linearity Improvement in NIR Spectroscopy. Appl. Spectrosc. **1988**, *42*(7), 1273–1284.

13. Wold, S; Anti, H.; Lindgren, F.; Öhman, J. Orthogonal Signal Correction of NIR Spectra. Chemometr. Intell. Lab. **1998**, *44*(1,2), 175–185.
14. Erickson, C.L.; Lysaght, M.J.; Callis, J.B. Relationship Between Digital Filtering and Multivariate Regression in Quantitative Analysis. Anal. Chem. **1992**, *64*(24), 1155A–1163A.
15. Kowalski, B.; Gerlach, R.; Wold, H. Chemical Systems Under Indirect Observation. In *System Under Indirect Observation*; Jöreskog, K., Wold, H., Eds.; Noeter-Holland: Amsterdam, 1982; 191–209.
16. Geladi, P.; Kowalski, B.R. Partial Least-Squares Regression: A Tutorial. Anal. Chim. Acta **1986**, *185*, 1–17.
17. Geladi, P.; Kowalski, B.R. An Example of 2-Block Predictive Partial Least-Squares Regression with Simulated Data. Anal. Chim. Acta **1986**, *185*, 19–32.
18. Olsson, R.J.; Tomani, P.; Karlsson, M.; Joseffson, T.; Sjöberg, K.; Björklund, C. Multivariate Characterization of Chemical and Physical Descriptors in Pulp Using NIRR. Tappi J. **1995**, *78*(10), 158–165.
19. Marklund, A.; Hauksson, J.B.; Edlund, U.; Sjöström, M. Multivariate Data Analysis Based on Orthogonal Signal Correction and Near-Infrared Spectroscopy. Nord. Pulp Pap. Res. J. **1999**, *14*(2), 140–148.
20. Schimleck, L.R.; Wright, P.J.; Michell, A.J.; Wallis, A.F.A. Near-Infrared Spectra and Chemical Compositions of E. globulus and E. nitens Plantation Woods. Appita J. **1997**, *50*(1), 40–46.
21. Antti, H.; Alexandersson, D.; Sjöström, M.; Wallbäcks, L. Detection of Kappa Number Distributions in Kraft Pulps Using NIR Spectroscopy and Multivariate Calibration. Tappi J. **2000**, *83*(3), 102–108.
22. Easty, D.B.; Berben, S.A.; DeThomas, F.A.; Brimmer, P.J. Near-infrared Spectroscopy for the Analysis of Wood Pulp: Quantifying Hardwood-Softwood Mixtures and Estimating Lignin Content. Tappi J. **1990**, *73*(10), 257–261.
23. Elg-Christofferson, K.; Hanksson, J.; Edlund, U.; Sjöström, M.; Dolki, M. Characterization of Dissolving Pulp Using Designed Process Variables, NIR and NMR Spectroscopy, and Multivariate Data Analysis. Cellulose **1999**, *6*(3), 233–249.
24. Fardim, P.; Durán, N. Wood and Pulp Carbohydrate Analysis Using HPLC and Electrochemical Detection. Proceedings of the 6th Brazilian Symposium on the Chemistry of Lignins and Other Wood Components, Guaratinguetá, SP, Brazil, Oct 25–28, 1999; Silva, F.T., Ferraz, A., Paiva, T.C.B.; Eds.; Faculdade de Engenharia Química de Lorena: Lorena, Brazil, 2001; 167–172.

25. Scott, R.W. Colorimetric Determination of Hexuronic Acids in Plant Materials. Anal. Chem. **1979**, *51*(7), 936–941.
26. Effland, M. Modified Procedure to Determine Acid-Insoluble Lignin in Wood and Pulp. Tappi J. **1977**, *60*(10), 143–144.
27. Li, J.; Gellerstedt, G. On the Structural Significance of the Kappa Number Determination. Nord. Pulp and Pap. Res. J. **1998**, *13*(2), 147–152.

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