NON-DESTRUCTIVE ANALYSIS OF KRAFT PULP BY NIR SPECTROSCOPY

MÁRIA FIŠEROVÁ, ANNA ILLA and MARTA MAHOLÁNYIOVÁ

*Pulp and Paper Research Institute, Lamačská cesta **3**, 84104 Bratislava, Slovak Republic*

A fast and convenient analytical technique is needed for quality assessment and precision management in pulp production. The main objective of this study was to evaluate the ability of NIR spectroscopy to predict diverse pulp properties. Near-infrared reflectance spectra of handsheets, prepared from unbleached beech kraft pulps obtained under different pre-extraction and pulping conditions were evaluated. The pulp characteristics were modelled using the first derivatives of optical density [log(1/R)] and the application of the partial least squares (PLS) method. The models were verified by using cross-validation and validation methodology. Kappa number, tensile index, burst index, tear index and brightness were successfully predicted by NIR spectroscopy (R > 0.90). The results indicate that NIR spectroscopy can be used as a rapid analytical technique to simultaneously estimate several characteristics with acceptable accuracy and can reduce time in conventional methods, so it could be suitable for direct applications, where "real time" data are needed.

Keywords: NIR spectroscopy, multivariate calibration, validation, unbleached beech kraft pulp, kappa number, tensile index, burst index, tear index, brightness

INTRODUCTION

In recent years, NIR spectroscopy has rapidly developed into an important and extremely useful method of analysis and has become very widespread in process analysis and within paper industry for raw material testing, product quality control and process monitoring as a non-destructive analytical technique.[1,2]

Infrared spectrum is an important record, which gives sufficient information about the structure of a compound. NIR range of spectrum at 780-2500 nm (4000-10000 cm^{-1}) covers several important bands that are characteristic for cellulose and other compounds commonly associated with wood.[3,4]

The NIR spectrum contains physical and chemical information of the analysed product. The spectral information has its origin in the different vibrational modes of the molecules caused by their interaction with the electromagnetic radiation absorbed.

The NIR spectroscopy is a technique, usually requiring tandem chemometric statistics, with a wide and varied use in chemical, physical and process analysis. This includes identification, qualification and assay of starting materials, intermediates and finished products and verification of chemical and physical properties. NIR spectroscopy has a wide range of qualitative and quantitative applications and its use requires a sound understanding of the physicochemical basis on which its measurements rely and of the instrumental and chemometric principles involved. The NIR spectroscopy signal may be directly attributed to the analyte of interest or may be an indirect measurement correlated with light scattering effects.

The use of chemometrics allows extracting the relevant information contained in the NIR spectra and develops calibration models that permit the prediction of the composition of unknown samples. The technique is rapid and, in contrast to standard techniques of analysis, it can be performed at a low cost analysis without using chemicals. In addition, the error sources related with laboratory analysis are avoided. The control of these sources of error specific to the NIR analysis leads to equations of high accuracy and precision.[5]

NIR spectroscopy requires reference techniques to build up calibration routines and to guarantee the proper maintenance of an established calibration with reference to outlier detection and troubleshooting. The conventional methods of determining pulp mechanical properties are time-consuming and require tedious or destructive sample preparation.[6]

One of the most popular techniques in use for relating spectral data to physical and chemical data is Partial Least Squares (PLS) regression. The PLS calibration technique is tailor-made for pulp and paper applications, since only knowledge of the constituent of interest is required for the calibration. In addition, PLS can be used for prediction of unknown samples, even in the presence of contaminants, which are not present in the original calibration samples. The PLS naturally lends itself to the accurate determination of pulp constituents.[7] This technique takes a set of spectral data derived from samples with known properties and builds a regression model, which can be used with spectra from unknown samples to predict the chemical/physical properties of the unknown sample.[8] NIR spectrometry and multivariate data analysis were used for determination of mechanical and optical properties of kraft pulps.[9]

Near-infrared spectroscopy is a fast, accurate, easy and non-destructive technique that can be used as an alternative to time-consuming methods. NIR can be used as a quick and effective means of determining kappa number of pulp.[10]

The main objective of this study was to evaluate the ability of near-infrared spectroscopy to predict diverse pulp properties, such as kappa number, tensile index, burst index, tear index and brightness.

EXPERIMENTAL
Materials

To assess the properties of handsheets made from unbleached beech kraft pulps, using FT NIR spectroscopy and chemometrics, unbeaten and beaten beech kraft pulps, prepared from original and pre-extracted beech chips with dilute oxalic acid (0.0825% and 0.165%), hot water and green liquor (1%, 2%, 3% and 4% charge as Na_2O) were used. Wood weight losses in the pre-extraction process were of 4-13%. The hemicelluloses pre-extraction experiments were performed at a maximum temperature of 160 °C, the H-factor of pre-extraction ranging from 55 to 287 h. The kraft pulping experiments were performed at a maximum temperature of 170 °C, while H-factors varied from 432 to 1122 h and effective alkali charges

– from 12% to 15% Na_2O. To determine the properties of beech kraft pulps, laboratory handsheets (80 g/m^2) were prepared. The kappa numbers were in the range from 13 to 32.

Methods

The beech kraft pulps were beaten in a Jokro pulp mill (ISO 5264-3) to beating degrees of 20, 30, 40 or 50 °SR. The beating degree was determined according to ISO 5267-1. Laboratory handsheets (80 g/m^2) were prepared in a Rapid-Köhten laboratory sheet former, according to ISO 5269-2. Mechanical and optical properties of the handsheets were determined by following conventional destructive methods: tensile index (ISO 1924-2), burst index (ISO 2758), tear index (ISO 1974) and brightness (ISO 3688). The kappa number was determined according to ISO 302:2004.

Spectrometric measurements of handsheet surface in the near infrared spectrum (10000-4000 cm^{-1}) were carried out using the Drift FTIR spectrometer Nicolet IS10 with an IR integrator. For each sample (total of 100 handsheets), 6 measurements were made (3 measurements on one side, 3 measurements on the other side of the handsheet), at a resolution of 2 cm^{-1}. For further evaluation, the average spectra were used. Spectral data were collected using an Omnic ver. 8.0 (Thermo Scientific) software and further analyzed and evaluated using the TQ Analyst at ver. 8.0 (Thermo Scientific) software. Each calibration model was constructed by the PLS method.

RESULTS AND DISCUSSION
NIR spectra

For prediction of pulp characteristics (kappa number, tensile index, burst index, tear index, brightness), FT NIR spectra of handsheets from unbeaten and beaten beech kraft pulps, prepared from original and pre-extracted beech chips with dilute oxalic acid, hot water and green liquor solutions, were obtained by measuring the spectra of the tested handsheets in order to construct the calibration models. Figure 1 shows the average spectrum of the unbleached beech kraft pulp.

Calibration model

Based on FTIR spectroscopy and chemometric methods, calibration models were obtained for a series of (100) samples of unbleached beech kraft pulps and were evaluated for appropriateness of quantitative determination of the characteristics listed above.

Based on the calculated/predicted values of the unbleached beech kraft pulp samples obtained from the NIR spectra and the values obtained by conventional methods, the calibration models were constructed (dependence of NIR predicted

values (y-axis) on values measured by conventional methods (x-axis)). The calibration models for kappa number, tensile index, burst index, tear index and brightness of unbleached beech kraft pulps are shown in Figures 2 to 6.
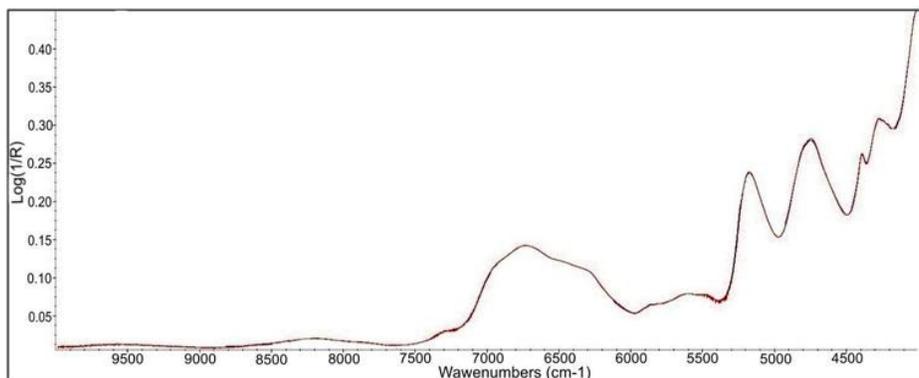

Figure 1: Average spectrum of unbleached beech kraft pulp
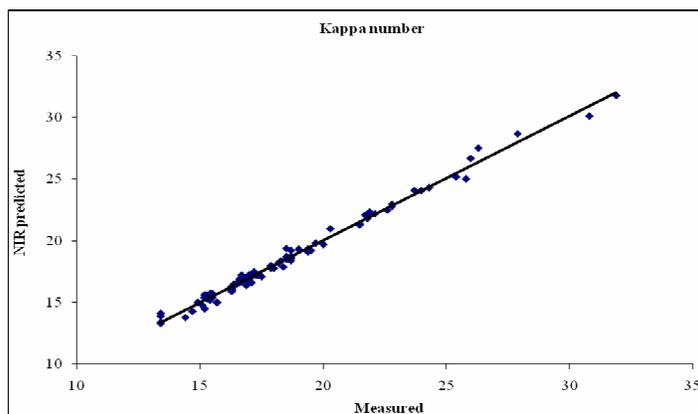

Figure 2: Calibration model for kappa number of unbleached beech kraft pulps (R = 0.9957)
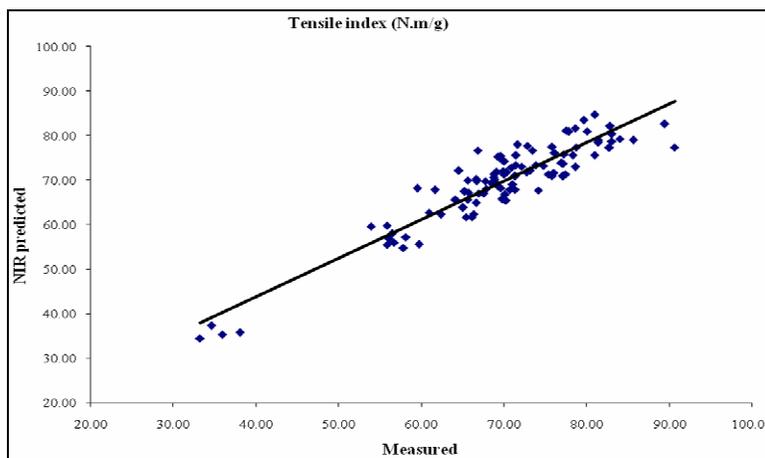

Figure 3: Calibration model for tensile index of unbleached beech kraft pulps (R = 0.9226)
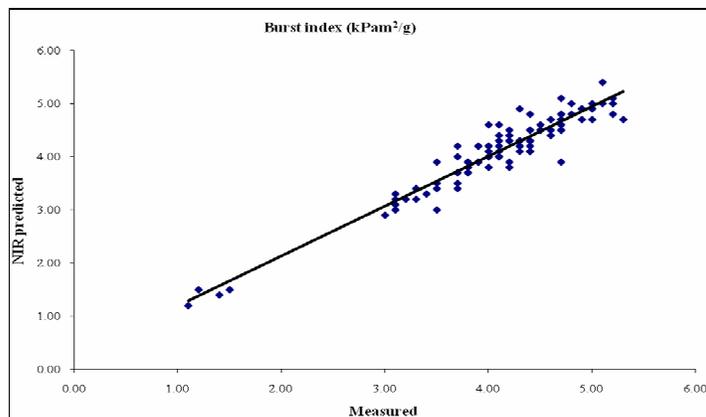
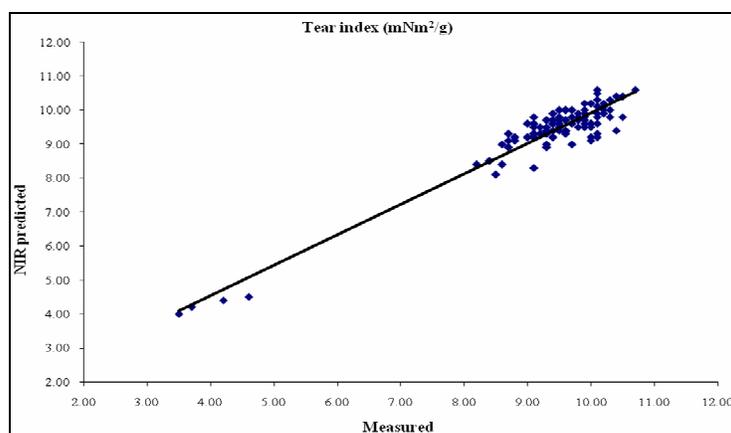Figure 4: Calibration model for burst index of unbleached beech kraft pulps (R = 0.9580)

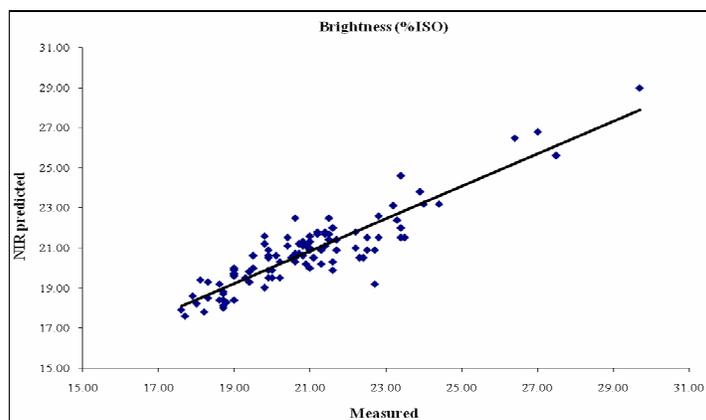Figure 5: Calibration model for tear index of unbleached beech kraft pulps (R = 0.9515)

Figure 6: Calibration model for brightness of unbleached beech kraft pulps (R = 0.9377)

Calibration models determine how exactly it is possible to determine the characteristics, indirectly, by NIR spectroscopy. The accuracy of the calibration model is characterized mainly by the linear regression correlation coefficient (R), which should be as close as possible to the value of one. Another characteristic of the calibration model is the calibration error RMSEC (Root

Mean Square Error of Calibration – a statistic measuring the difference between the NIR spectroscopy procedure and the reference method quantitative analyte values of the calibration set), which should be as low as possible.

The results of the validation standards analysis are used to calculate the prediction error RMSEP (Root Mean Square Error of Prediction), which characterizes the ability of the calibration model to predict the properties of the samples, which were not part of the calibration set.

In order to determine the accuracy of the calibration model, and thus diagnose the accuracy of the calibration models, it is necessary to perform cross-validation of the data obtained from the calibration. The cross-validation is an internal sub-setting stability assessment vehicle and speaks only about the robustness of a particular

model as gauged by internal sub-setting of a training data set.[11]

The accuracy of the calibration model is also considered by the value of the correlation coefficient of cross-validation and cross-validation error RMSECV (Root Mean Square Error of Cross Validation – a statistic method determining the difference between the NIR spectroscopy procedure and reference method quantitative analyte values of the calibration set using a cross-validation method). According to Workman[12], RMSEC, RMSECV and RMSEP values should be as low as possible (near 0), while R should be as high as possible (near 1).

Table 1 shows an overview of the achieved correlation coefficients of calibration, calibration errors RMSEC, correlation coefficients of cross-validation and error of cross-validation RMSECV for individual characteristics.

Table 1
Summary values of correlation coefficients and errors, cross-validation correlation coefficients and errors

Property	Calibration			Cross-validation		RMSEC and RMSECV difference
	Correlation coefficient	RMSEC	RMSEP	Correlation coefficient	RMSECV	
Kappa number	0.9957	0.313	0.530	0.9889	0.503	0.190
Tensile index	0.9226	3.880	3.740	0.9109	4.150	0.270
Burst index	0.9580	0.235	0.175	0.9508	0.254	0.019
Tear index	0.9515	0.354	0.425	0.8624	0.587	0.233
Brightness	0.9377	0.708	1.62o	0.8553	1.060	0.352

As shown in Table 1, the values of the correlation coefficients for the calibration decreased in the sequence of values for kappa number (0.9957), burst index (0.9580), tear index (0.9515), brightness (0.9377) and tensile index (0.9226), respectively.

The highest values of the cross-validation correlation coefficients were achieved for kappa number (0.9889) and burst index (0.9508). Lower calibration model accuracy was obtained for tensile index (0.9109), tear index (0.8624) and brightness (0.8553).

The accuracy of the calibration model is also characterized by a small difference between the error of calibration (RMSEC) and cross-validation (RMSECV). The summary (Table 1) indicated high calibration model accuracy for burst index (RMSEC 0.235, RMSECV 0.254, difference 0.019), tensile index (RMSEC 3.880, RMSECV

4.150, difference 0.270), followed by kappa (RMSEC 0.313, RMSECV 0.503, difference 0.190) and tear index (RMSEC 0.354, RMSECV 0.587, difference 0.233). Lower calibration model accuracy was obtained for brightness (RMSEC 0.708, RMSECV 1.060, difference 0.352).

According to these results (Table 1), all calibration models had a very good predictive ability. Higher RMSECV values, in comparison with the RMSEC values, indicate that the prediction ability for new samples tends to be poorer than for the calibration set. To verify this role, 25 samples obtained in different extraction, pulping and refining experiments were selected (validation set) and analysed by conventional methods for determining their characteristics. After that, the results obtained were compared with the characteristics determined using NIR

spectra and the calibration models of the same samples.

Determination of "unknown" pulp samples

To determine the characteristics of the "unknown" samples of unbleached beech kraft pulps, calibration models constructed for kappa number, tensile index, burst index, tear index and brightness were used. A validation set (25 selected samples) was used for an independent assessment of the accuracy and preciseness of the calibration model. Validation incorporates information for the future use of the particular data model. Validation, in the exemplar multivariate calibration context, means assessing or substantiating that the prediction performance is valid, i.e. the objective of validation is to confirm that a particular prediction model will work according to its purpose.[11]

The spectra of selected pulp handsheets were measured under the same conditions as the spectra of the calibration samples. NIR predicted values, the values calculated from NIR spectra, using the calibration model were compared with those obtained by conventional methods. From the dependences of the measured values by conventional methods (x-axis) and NIR predicted values from the calibration model of the characteristics of the "unknown samples" (y-axis), correlation coefficients of validation were obtained and compared with the correlation coefficients of the calibration.

The possibility to combine information about the chemical and physical properties gives an overview of the overall suitability of the material for the process and the ability to predict the degree of certainty with which the material will meet the required specification. Table 2 presents an overview of the correlation coefficients of calibration and validation for individual characteristics.

Table 2
Comparison of correlation coefficients obtained for calibration and validation of the characteristics of unbleached beech kraft pulps using "unknown" samples

Characteristic	Correlation coefficient	
	Calibration	Validation
Kappa number	0.9957	0.9872
Tensile index	0.9226	0.9189
Burst index	0.9580	0.9492
Tear index	0.9515	0.9417
Brightness	0.9377	0.9287

A comparison of the correlation coefficients of calibration and validation shows that all observed characteristics (kappa number, tensile index, burst index, tear index and brightness) can be quickly determined by measuring the NIR spectra of laboratory handsheets of unbleached beech kraft pulp with a high precision, as opposed to conventional methods, which require much more time. Calibration models will be used to determine the characteristics of unbleached beech kraft pulps prepared from the original and pre-extracted chips, with a wide range of kappa numbers.

CONCLUSION

Based on the obtained calibration models for kappa number, tensile index, tear index, burst index and brightness, it can be concluded that the calibration models are useful for fast determination of the characteristics of unbleached beech kraft pulps, using NIR spectroscopy and chemometrics. The correlation coefficient values for calibration were in the range 0.9957-0.9226, and for cross-validation values in the range 0.9889-0.8553. The highest correlation coefficients for calibration and cross-validation were obtained for kappa number, thus the accuracy of determination using NIR spectra measurements of laboratory handsheets is the highest from the observed characteristics. High correlation coefficients of calibration and cross-validation were achieved despite the fact that for constructing calibration models, pulp samples prepared from original and pre-extracted beech chips with kappa numbers in the range from 13 to 32 were used. Kappa number significantly influences the mechanical and optical properties of the pulps.

The models developed had an excellent predictive ability of all properties, including measurements of new different samples. Their utilization is recommended for immediate applications in "on-line" conditions. With very low investment, NIR spectrometry can be an attractive alternative to substitute the routine control testing methods in pulp and paper mills and improve process monitoring and product quality. NIR spectroscopy is a fast and relatively simple method for performing compositional analysis of the pulp.

REFERENCES
[1] G. Reich, *Adv. Drug Deliv. Rev.*, **57**, 1109 (2005).
[2] C. Sandorfy, R. Buchet and G. Lachenal, "Near-Infrared Spectroscopy in Food Science and Technology", John Willey & Sons, Inc., Hoboken, New Jersey, 2007, pp. 424-468.
[3] H. P. R. Aenugu, D. S. Kumar, Srisudharson, N. Parthiban, S. S. Ghosh and D. Banji, *Int. J. ChemTech. Res.*, **3**, 825 (2011).
[4] J. S. Shenk, J. J. Workman Jr. and M. O. Westerhaus, in "Handbook of Near-Infrared Analysis", edited by D. A. Burns and E. W. Ciurczak, Marcel Dekker Inc., 1992, pp. 383-431.
[5] R. Font, M. Del Rio-Calestino and A. De Haro-Bailón, *Methods Biotechnol.*, **23**, 205 (2007).
[6] H. W. Siesler, Y. Ozaki, S. Kawata and H. M. Heise, "Near-Infrared Spectroscopy: Principles, Instruments, Applications", Wiley-WCH, Weinheim, 2008, pp. 248-259.
[7] D. F. Leclerc, in "Encyclopedia of Analytical Chemistry", John Wiley & Sons Ltd, 2000, pp. 8361-8388.
[8] R. Hodges, H. Cullinan and G. A. Krishnagopalan, *Tappi J.*, **5**, 3 (2006).
[9] P. Fardim, M.M.C. Ferreira and N. Durán, *J. Wood Chem. Technol.*, **25**, 267 (2005).
[10] W. Shen and H. Liu, Y. Xie, in *Procs. Tappi Technology Summit*, Atlanta, March 3-7, 2002, pp. 16-21.
[11] K. H. Esbensen and P. Geladi, *J. Chemom.*, **24**, 168 (2010).
[12] J. J. Workman, in "Handbook of Near Infrared Analysis", edited by D. A. Burns and E. W. Ciurczak, 3rd ed., CRC Press, 2008, pp. 123-150.