Rapid determination of methoxyl groups in plant fibrous material by near infrared spectroscopy

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Introduction

The methoxyl group, a typical group in the lignin of plant cell wall, has significant effects on pulping characteristics of plants and their utilisation as bio-resource. To determine the content of methoxyl groups quantitatively, the traditional method involving destructive cleavage reaction with hydroiodic acid (HI) is applied. However, HI is not stable under normal conditions. The reaction and the following purification must be carefully controlled. The precision of data depends mostly on operator skillfulness.

Near-infrared (NIR) spectroscopy has the advantages of nondestructive, good precision and minimal operative errors.[1] Moreover, in cooperation with the diffuse reflectance technique, good quality spectra can be easily obtained in the NIR region. The NIR method is very convenient and offers a rapid quantification method of analysis for samples from living plants.[1] NIR spectroscopy has been applied in wood chemistry and pulping chemistry, for example, for on-line measurement of the Kappa number of pulps during batch cooking,[2] and the contents of cellulose and lignin[3–7].

The objective of this research is to develop a rapid and efficient method to determine methoxyl group content by NIR, combined with models using the chemometrics tools of partial least squares (PLS) regression, back propagation network (BP) and support vector machine (SVM). In order to reduce the background noise of the spectra, a corrective wavelet transform was also applied. This work will contribute to the understanding of cell wall composition of plant fibrous material and its efficient utilisation.

Materials and methods

Sample preparation

Twenty six plant samples suitable for pulping and papermaking industry including aspen, pine, eucalyptus and reed were collected and divided into two groups assigned as "calibration set" (No. 1–20) and prediction set (No. 21–26) respectively. The air-dried samples were milled and screened to be 40–60 mesh size.

Methoxyl group determination by a chemical method

The content of methoxyl group was analysed according to the modified *Virböck* method.[7]

NIR spectroscopic determination

The spectra were determined with a UV3101 PC UV-VIS-NIR spectrometer at 2 nm intervals over the range 800–2500 nm. The diffuse reflectance technique was applied. A total of 30 scans were accumulated and averaged for each sample.

Data pretreatment and establishment of models

The NIR spectral data were pretreated with wavelet transform.[8] The PLS, BP and SVM models were then established. The models were evaluated by the standard error of prediction (*SEP*) with the following formula:

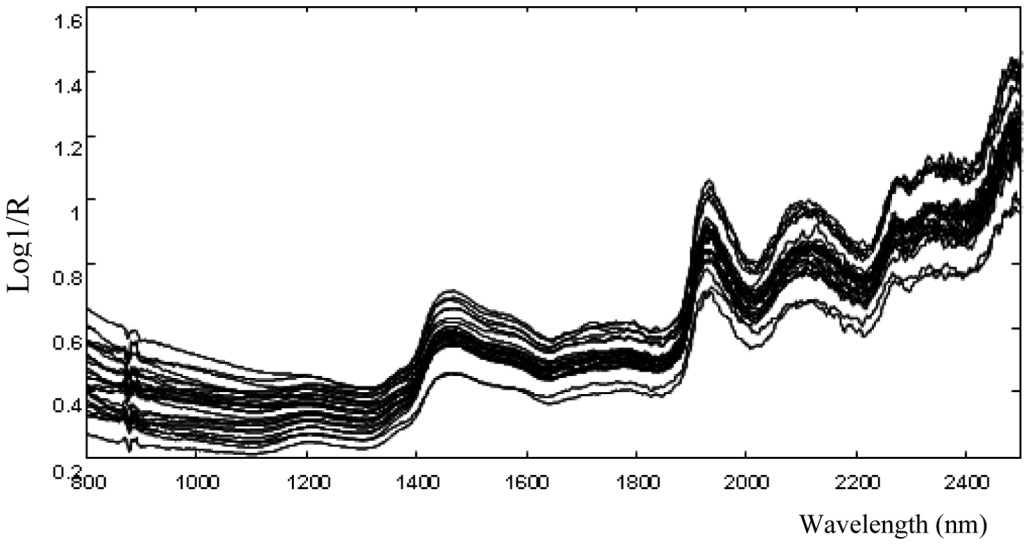

Figure 1. NIR spectra of plant fibrous materials.

$$SEP = \sqrt{\frac{\sum_{i=1}^{m} (y_i - \hat{y}_i)^2}{m-1}}$$

where y_i = value determined by chemical analysis, $\hat{y}_i$ = value predicted by a model, m = the number of samples in the prediction set.

Results and discussion

NIR spectra of fibrous materials

Because they contain lignin, polysaccharides and extractives, the fibrous materials are complex. Figure 1 demonstrates the NIR diffuse reflectance spectra of the 26 fibre samples.

The absorption intensities are different because of the different composition and structure of the fibres. This is the basis of qualitative and quantitative determination of the characteristics of fibrous materials by NIR spectroscopy.

Establishment of prediction models

The results of chemical analysis and those from NIR-PLS calculation are plotted. It was found that the methoxyl content was in agreement between the two methods. The PLS model developed was tested on the 6 samples of the prediction set. Good fits were obtained as shown in Table 1.

The *SEP* was 0.75, 0.71 respectively. Due to elimination of high frequency background noise through wavelet transform, the precision of the PLS model is better than that without this

Table 1. Comparison of OCH_3 contents calculated by NIR-PLS models with that determined by chemical analysis.

Sample No.	Methoxyl content (%) (chemical analysis)	Methoxyl content (%) by PLS models			
		Without pretreatment		Wavelet transform pretreatment	
		Calculated value (%)	Error	Calculated value (%)	Error
21	4.69	4.76	–0.07	4.71	–0.02
22	4.40	4.34	0.06	3.74	0.66
23	5.63	4.40	1.23	4.55	1.09
24	4.40	3.97	0.43	4.05	0.35
25	4.01	5.05	–1.04	4.84	–0.83
26	4.27	4.18	0.09	3.96	0.31
SEP		0.75		0.71	

Table 2. Methoxyl contents predicted by NIR-BP and NIR-SVM modeling and that from chemical analysis.

Sample No.	Methoxyl content (%) (chemical analysis)	Methoxyl content (%) by BP model		Methoxyl content (%) by SVM model	
		Predicted value (%)	Error	Predicted value (%)	Error
21	4.69	5.01	–0.32	4.69	–0.00
22	4.40	4.67	–0.27	4.40	–0.00
23	5.63	5.53	0.10	5.01	0.62
24	4.40	4.43	–0.03	4.40	–0.00
25	4.01	4.88	–0.88	4.67	–0.66
26	4.27	4.19	0.08	4.61	–0.34
SEP		0.44		0.43	

pretreatment. The regression coefficient increased from 0.986 to 0.995, meanwhile *SEP* decreased from 0.75 to 0.71.

The BP and SVM models were developed by a similar procedure as the PLS model with the data treated by wavelet transform. As shown in Table 2, the *SEP* was 0.44, 0.43 respectively.

It was found that BP network model had the best training precision and SVM model had the best predicting precision. That is believed to be because the BP network can better accommodate the non-linear character of near-infrared spectra. The SVM model appeared to have the best abilities for generalisation and prediction.

Conclusions

1. A method for the prediction of methoxyl groups in plant fibres has been developed, using NIR spectroscopy, combined with PLS, BP and SVM for data processing.
2. Data pretreatment with wavelet transform, combined with PLS regression improved the prediction statistics.
3. The back-propagation model appeared to have the best training ability, but the SVM model gave the best statistics for prediction.

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