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RAPID DETERMINATION OF AVERAGE FIBER LENGTH OF WOOD PULP BY VISIBLE SPECTROSCOPY COUPLED WITH MULTIVARIATE ANALYSIS

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This paper reports on a new method for the rapid determination of the average fiber length of wood pulp, based on multivariate analysis assisted visible spectroscopy. Using selected data preprocessing techniques, *i.e.*, Savitzky-Golay and multiple scattering corrections, for the spectra (400-780 nm) of fiber suspensions and partial least square regression (PLSR), a predictive model for determining the average fiber length of pulp was established. The results show that the model has good precision and robustness, in which the square of the regression coefficient (R2) was 0.984, the root mean square error of cross-validation (RMSECV) was 0.046, and the relative prediction error (RPE) was 4.15%. The new method can be used as an efficient tool for the rapid determination of the average fiber length of wood pulps in the paper industry.

Keywords: wood pulp, average fiber length, visible spectroscopy, multivariate analysis

INTRODUCTION

Fiber length is an important parameter used when evaluating the quality of plant fibers extracted from lignocellulosic materials for the purpose of producing paper with desired strengths: *e.g.*, tensile, tear, and folding strength.[1] Therefore, an efficient and accurate method that is able to provide fiber length information is very important in mill operations.

There are several methods available for measuring this fiber information, including image analysis, the raster method, and polarized and un-polarized light methods.[2-9] With the assistance of computer technology, image-based methods can also analyze fiber morphology.[3] Although most of these techniques have good measurement reproducibility, the instruments are usually very expensive and thus have limited utilities in many mills. Currently, the average fiber length is the only parameter commonly used to assess fiber quality in mill practice. The traditional method for determining the average fiber length is the so-called "frame method", which involves passing a pulp slurry through a metal frame, collecting the long fibers retained by the frame, weighing them and calculating the weight percentage of the retained (and presumably long) fibers in the original pulp.[10] Although the information is very helpful for the adjustment and control for the process parameters and conditions, there is a significant uncertainty in the measurement because the amount of fibers retained on the frame depends not only on the fiber length, but also on other factors, such as the degree of hydration of fiber swelling.[10,11]

It is well-known that light is partially scattered when it passes through a solution containing suspended solids, and the degree of light scattering at a single wavelength and over a given wavelength range is related to the size and size distribution of the solids in the suspension.[12-14] Therefore, the size information can affect the transmittance (or absorbance) signal of the spectral measurement of a fiber suspension, and thus can be determined by spectroscopic methods.

In this paper, we propose a simple method, the visible spectroscopic method, for the determination of the average fiber length in wood pulps based on multivariate analysis assisted visible spectroscopy. The effect of conditions, such as the pulp consistency and the timing of the measurement, are also described.

EXPERIMENTAL

Materials

Deionized water was used in all solution preparation and washing processes. Twenty-four different types of wood pulps from seven manufacturers in China were collected. The fiber morphological information of these samples is listed in Table 1.

Apparatus

The fiber morphological information of the original pulps was determined by a fiber length analyzer (FS-300, Kajaani Company, Finland). All spectral measurements were conducted with a UV-visible spectrophotometer (Model 8453, Agilent Company, USA).

Sample preparation and measurement

A 0.030±0.001 g sample of oven-dried pulp was placed in a 100-mL beaker. 50-mL of distilled water in the beaker were added and stirred until the fibers were uniformly dispersed. The resulting fiber suspension was transferred to a 100-mL volumetric flask and filled to the mark with distilled water. Under mild agitation, a 10 mL sample of fiber suspension was transferred by pipet to a 2-cm (optical path-length) cuvette. The visible spectrum of the fiber suspension solution was immediately recorded over the range of 400-780 nm. Distilled water was used as the blank in the spectroscopic measurement.

Spectral data preprocessing and multivariate regression analysis

To minimize baseline shifts, improve the spectral resolution of the broad bands, and increase the spectral difference between the samples, the spectra were subjected to data pretreatment by Savitzky-Golay (S-G) smoothing, first derivative calculation (FDC) and multiplicative scattering correction (MSC), in which both S-G smoothing and FDC were performed using a second-order polynomial fitting algorithm with a moving window (9-point).[15,17] FDC and MSC were performed after the smoothing of the spectra.

The partial least squares regression (PLSR), an important approach in multivariate analysis, was used to quantify the length of fiber. In PLS analysis, the covariance between the spectral data and the known fiber length data is maximized to obtain as much information as possible, while unrelated data are neglected, and the optimal number of latent variables (Lvs) is obtained by cross-validation.[18,19]

The quality of the model was evaluated by the square root of correlation coefficient (R2), the cross-validation root mean square error (RMSECV), and the relative prediction error (RPE).[20,21] The formulas used in these calculations are expressed as follows:

$$R^2 = \frac{\sum_{i=1}^{n} (\hat{y}_i - \overline{y}_i)^2}{\sum_{i=1}^{n} (y_i - \overline{y}_i)^2} \tag{1}$$

$$RMSECV = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{n}} \tag{2}$$

$$RPE,\% = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{\sum_{i=1}^{n} (y_i)^2}} \times 100 \tag{3}$$

where n is the total number of samples, y_i is the measured value of sample i, $\hat{y}_i$ is the predicted value of sample i, and $\overline{y}_i$ is the average of the measured values in the total samples.

All calculations were performed using SIMCA-P multivariate data analysis software (Umetrics AB, Umea, Sweden).

RESULTS AND DISCUSSION

Visible spectroscopy of fiber suspension solution

Figure 1 shows the visible spectra of fiber suspensions from two different pulp samples, indicating that there are significant differences between the spectra. In general, the solutions containing fibers with shorter average lengths show relatively higher absorbance in the longer wavelength range than that in the shorter wavelength range.[12,13]

Table 1
Type of pulps and their average fiber length and width*

Sample no	Number average fiber length (L_n, mm)	Length-weight average fiber length (L_l, mm)	Quality-weight average fiber length (L_w, mm)	Number average fiber width (W_n, um)	Length-weight average fiber width (W_l, um)	Quality-weight average fiber length (W_w, um)
1	0.63	0.88	1.01	14.76	15.46	20.07
2	0.38	0.58	0.74	19.63	19.98	21.30
3	0.54	0.69	0.78	12.21	12.75	18.20
4	0.46	0.84	1.04	15.04	15.55	17.47
5	0.60	0.86	1.02	14.93	15.65	19.54
6	0.55	0.70	0.78	12.61	12.89	15.38
7	0.48	0.63	0.71	13.22	13.77	19.19
8	0.52	0.74	0.88	14.79	15.44	20.15
9	0.34	0.51	0.65	19.44	20.23	26.44
10	0.44	0.58	0.66	12.16	12.46	15.91
11	0.45	0.58	0.65	12.52	12.76	16.69
12	0.31	0.89	1.52	13.14	14.88	20.43
13	0.67	1.81	2.59	22.62	25.01	26.65
14	0.63	1.77	2.56	22.42	24.65	26.45
15	0.94	2.13	2.78	24.99	27.31	29.08
16	0.56	1.73	2.64	20.45	23.47	26.16
17	0.55	1.60	2.71	22.89	25.41	27.35
18	0.72	1.69	2.26	19.87	21.06	22.20
19	0.36	0.96	1.42	12.80	13.59	16.05
20	0.63	1.53	2.16	20.79	22.72	23.94
21	0.32	0.94	1.54	13.96	14.62	17.39
22	0.30	0.86	1.37	12.10	13.06	15.65
23	0.29	0.95	1.62	12.81	14.23	18.35
24	0.59	1.59	2.32	22.88	25.07	26.71

*The data were obtained by a fiber length analyzer. Hardwoods: Samples 1-12; Softwoods: Samples 13-24

Therefore, the spectrum of a fiber suspension solution carries the information about the fiber length. However, a correlation is often difficult to establish if it is based on the spectral absorbance measured at any single wavelength.

Effect of fiber consistency in the suspension

It is important to fix the fiber consistency (*i.e.*, fiber content) in the suspension solutions, so that a comparison can be made between the spectra of different pulp samples. Moreover, a suitable fiber consistency in the solution is also important for improving the precision in the spectral measurement 14.

Figure 2 shows the relationship between the absorbance (at 600 nm) of a particular fiber suspension and its consistency. Here, there is a strong linear correlation between the absorbance and the fiber consistency of the pulp samples. Although a higher fiber consistency can improve the detection sensitivity of the method, it also increases the risk of fiber agglomeration, which affects the stability of the spectral measurement. As a compromise, we chose 0.3 g/L of fiber consistency in the rest of the study.

Effect of time on fiber precipitation in the solution

Because of the relatively large fiber size, the fiber precipitation in the solution is inevitable. As shown in Figure 3, the absorbance (at 600 nm) of a fiber suspension solution in the cuvette decreases rapidly in the first 60 s and more slowly after that. We believe that this behavior is caused by fiber agglomeration and precipitation. As a result, the non-uniform fiber dispersion in the solution leads to the observed decrease of absorbance in the spectral measurement. However, it is also noticed that absorbance at very beginning (within 10 s) is relatively stable. To minimize the time effect, throughout this study we chose 5 seconds as the maximum to record the spectral data after the cuvette containing the fiber solution was placed in the spectrophotometer.

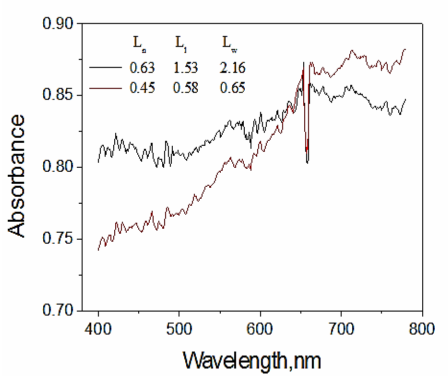

Figure 1: Visible spectra of fiber suspensions

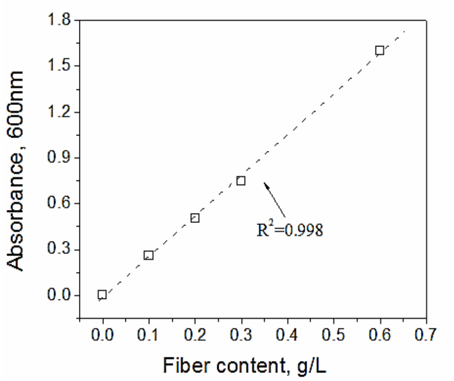

Figure 2: Change of absorbance at 600 nm as a function of fiber content in the solution

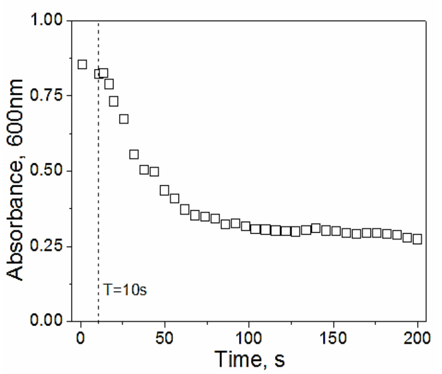

Figure 3: Absorbance at 600 nm *vs.* time for the fiber suspension measurement

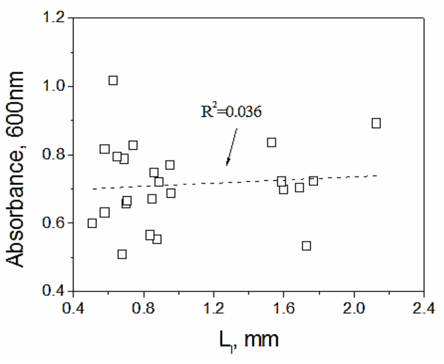

Figure 4: Relationship between absorbance at 600 nm from fiber suspension and average fiber length

Correlation between absorbance at a single wavelength and average fiber length

The fiber suspension solutions from 24 wood pulp samples were prepared and their absorbances at the visible wavelength range were measured. Figure 4 shows the relationship between the absorbance at 600 nm and the length-weight average fiber length (Ll, commonly used in mill practice) of these samples. There was essentially no correlation between them. Further study indicated that it is impossible to find a meaningful correlation between the absorbance and the average fiber length at any single wavelength because of the changes of the pulp types. Therefore, the absorbances collected from multiple wavelength measurements of the fiber suspension solutions must be used in the establishment of such a correlation.

Partial least squares regression analysis

Figure 5a and b shows the original spectra and the spectra pretreated by S-G smoothing, respectively. Figure 5c and d shows the prediction results by the PLSR models based on the original spectra and the S-G smoothed spectra, respectively. It is clear that the correlation between the predicted Ll values and the reference Ll values in both cases is poor.

Figure 6a and b presents the spectra treated by FDC and MSC methods, respectively, after the S-G smoothed spectral processing (Fig. 5b). It is noticed that these pretreatments improve the spectral resolution of the broad bands.

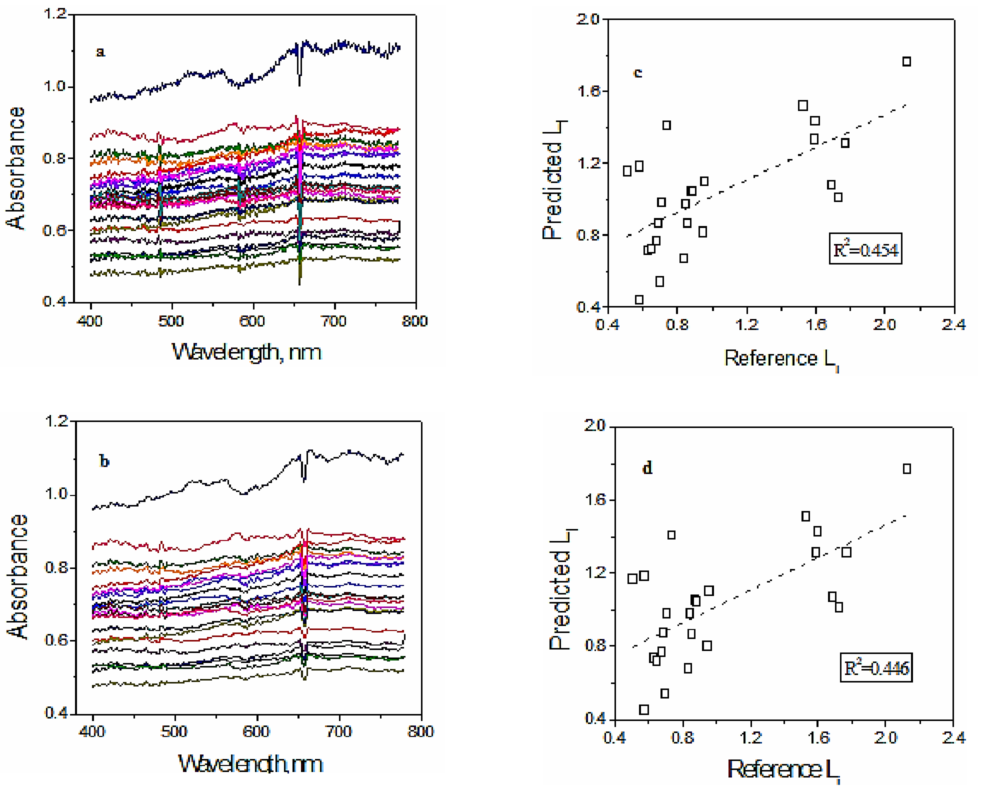

Figure 5: (a) Original spectra; and (b) S-G smoothed spectra; (c) and (d) the PLSR model predictions based on (a) and (b), respectively

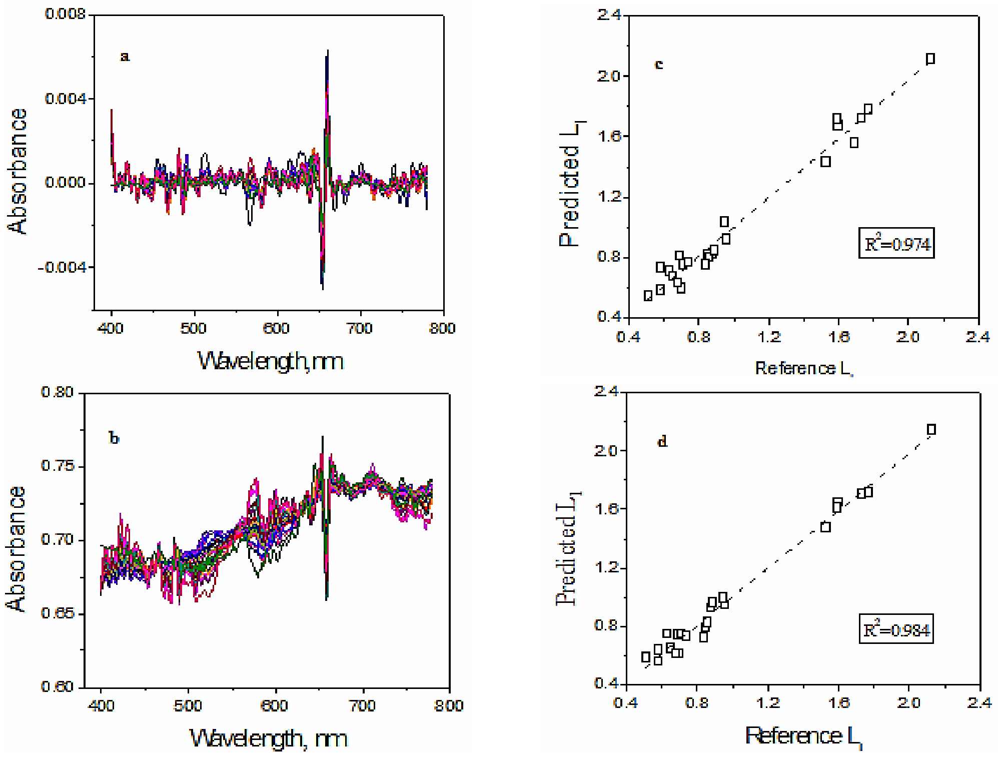

Figure 6: (a) FDC spectra; (b) MSC spectra; (c) and (d) prediction results of the PLSR model based on (a) and (b), respectively

Table 3
Method comparisons

Sample no.	Average fiber length (mm)		Relative difference (%)
	Polarized method	PSLR method	
1	0.86	0.89	-3.43
2	0.58	0.56	3.51
3	0.95	0.95	0
4	0.94	0.90	4.35
5	1.81	1.80	0.55

Table 2
Evaluation of the prediction PLSR model based on different spectral data pretreatments

Preprocessing approach	RMSECV	R^2	RPE (%)
Original spectrum	0.348	0.454	30.72
S-G smooth processing	0.345	0.446	30.49
S-G smooth processing + FDC	0.071	0.974	6.26
S-G smooth processing + MSC	0.046	0.984	4.15

Figure 6c and d illustrate the predictions from the PLSR models based on the FDC and MSC treated spectra, respectively. Clearly, the predictions of the PLSR with the treated spectra are significantly improved; *cf.*, the correlation coefficient of 0.984 based on the MSC transformed spectra. Table 2 shows the performance of the PLSR models in predicting the average fiber length of the pulp samples based on the different spectral transformation methods. Clearly, the PLSR model with the MSC transformed spectra provides the best prediction, in which the relative prediction error (RPE) and the root mean square error (RMSECV) from the cross-validation are 4.15 and 0.046, respectively, indicating that this method has good precision and robustness.

Method validation

The above PLSR model based on spectral S-G smooth and MSC pretreatment was also evaluated by the data from an external set of the pulp samples. The comparison results are listed in Table 3. It can be seen that the results predicted by our new PLSR model for these external samples are in excellent agreement with the data measured by the reference method; *i.e.*, the polarized light method (using FS-300 fiber analyzer). The relative difference of the results from the two methods are within 5%, indicating that this new method is validated and can be an efficient tool in the determination of average fiber length of wood pulps in mill practice.

CONCLUSION

A new method for the determination of average fiber length in wood pulp by visible spectroscopy assisted by multivariate analysis has been developed. The model based on Savitzky-Golay smoothing, combined with multiple scattering corrections pretreatment of the spectra of the original fiber suspensions, provides the best results. The method has been shown to meet the needs in mill practice for rapid determination of the average fiber length in a wide variety of pulp samples.

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