Transfer of a calibration model for the prediction of lignin in pulpwood among four portable near infrared spectrometers

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Abstract

In order to reduce the time and cost for near infrared (NIR) model development and maintenance, the transfer of NIR spectra measured on four different portable spectrometers (one master and three target instruments) for predicting the lignin content of pulp wood is investigated in this work. Eighty-two wood samples were prepared by chipping and grinding, and their NIR spectra were recorded with four spectrometers. Calibration models for the determination of lignin in pulp wood have been developed by partial least squares (PLS) regression, while average Mahalanobis distances (AMD) and average differences of spectra (ADS) were used to quantify the spectral differences. Then piecewise direct standardization (PDS) has been applied, and compared to direct standardization (DS), slope/bias correction (SBC) and canonical correlation analysis (CCA). The accuracy of the models has been evaluated by comparing their prediction performance. The results indicated that the prediction performances of the three target instruments are greatly improved by using the three algorithms. The advantage of the PDS algorithm is that fewer samples are required for the transfer sets, which means lower model maintenance cost for practical applications. When it comes to window size setting procedure, it was found that if there are large spectral differences between the master and the target spectrometer, a large window size should be used and if the spectral difference is a significant lateral shift, an asymmetric window with appropriate window size is necessary to ensure a good transfer performance for the PDS algorithm.

Introduction

As the second most abundant natural product and one of the main components of wood,[1] lignin is closely related to the properties of wood and its processing and utilization performance. For example in pulp and paper production, the content of residual lignin directly determines the dosage of bleach,[2] which would affect the quality and quantity of pulp as well as the burden of chemical recovery in black liquor. Conventional chemical wet laboratory methods are time-consuming, costly, and not convenient for handling a large amount of wood samples.[3] Near infrared (NIR) spectroscopy on the other hand is rapid, non-destructive, has low operational technical requirements, and is widely used in the petroleum, pharmaceutical, chemical, food, forestry and other industries.[4–7] Many literature references that report the application of NIR spectroscopy for the rapid detection of wood content have been published.[8–11]

Portable near infrared spectrometers, which are small in size and light in weight and have a wider range of adaption to ambient temperature, humidity and vibration resistance, are gradually being promoted for the on-site analysis of various dispersed objects.[12,13] However, in practice, it often happens that a calibration model developed with the spectra of one instrument cannot be used for the spectra recorded by other instruments. This contributes to two main scenarios: (1) using the same calibration model for other instruments with different hardware of light sources, optical paths or detectors; or (2) using the same calibration model to adapt to new measuring conditions or different instrument performances, such as temperature and humidity change, sample morphology change, instrument aging and accessory replacement.[14–16] Since building a suitable calibration model for NIR spectroscopy analysis requires a lot of time

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and material resources, it is necessary to choose a suitable method for sharing models among portable spectrometers, which is referred to as calibration model transfer.[17]

Many model transfer methods have been proposed.[18–21] Among all the transfer methods, direct standardization (DS) and piecewise direct standardization (PDS) algorithms are the most commonly used methods.[22] PDS is similar to the DS algorithm, but the standardization of the PDS algorithm is calculated by selecting different window sizes rather than directly using the entire spectrum. Therefore the superiority of PDS algorithm is attributed to its local character and multivariate nature which enable simultaneously correction of intensity differences, wavelength shifts and peak broadening.[23] In recent years, a calibration method based on canonical correlation analysis (CCA) has also been widely used.[24] Compared to other model transfer methods, owing to the ability of CCA to exploit the correlation between the spectra of the master and the target instruments, it has shown good performance and is therefore adopted for model transfer in this work. In addition, the algorithm of slope/bias correction (SBC) is also used for comparing and validating the possible existence of an offset deviation.

All of the algorithms used in this study are model transfer strategies that require standard samples. In practice, if fewer standard samples are required in the algorithm, the detection cost can be greatly reduced. Therefore, the number of the transfer set could be an indicator for the evaluation of the different algorithms.

When the PDS algorithm is used, choosing an appropriate window size plays an important role in model transfer. If the window size is too small, the differences between instruments might not be contained in the selected spectrum, resulting in poor transfer performance. If the window size is chosen too large, the selected spectral data will involve some irrelevant information, which not only requires too much computation, but leads to the phenomenon of overcorrection, which eventually also leads to poor performance of the model transfer.[25]

In practice it often occurs, that the instruments used have different design of detectors or light sources. Four different portable instruments were used for the investigations in the present work. With the aim to share the calibration model of lignin in pulp wood among the four portable instruments, DS, CCA, SBC and PDS algorithms were used to transfer the master calibration model to three different target instruments. The selection of window size for the PDS algorithm was also an issue in the present investigation.

Materials and methods

Samples and reference measurements

A set of 82 pulp wood samples from five species of common pulp wood (*Pinus massoniana, Cunninghamia lanceolate, Acacia, Eucalyptus* and *Poplar*), was provided by the Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry. All those samples are prepared by chipping and grinding pre-treatment, and the chips that passed the 40 mesh sieve and were retained on the 60 mesh sieves were collected for chemical analysis

and spectral acquisition. Then the wood powder were put under environment condition with constant temperature and humidity. When the moisture content of wood powder is stabilized at about 12% and the difference of moisture content does not exceed 0.1% in 24 h interval, the equilibrium moisture content of wood powder is considered to be fully reached. The content of acid insoluble lignin was measured according to the People's Republic of China national standard method (GB/T 2677.8-1994). In this method, 1g of sample extracted with benzene/ethanol is first treated with 72% H_2SO_4 for 2 h at 20°C. Subsequently, the sample is diluted with water to reduce the concentration of H_2SO_4 to 3% and boiled for 4 h to hydrolyse the polysaccharides to soluble monosaccharides. Finally, the solid residue (acid insoluble lignin) is collected and weighed. The measurement result and distribution of lignin content are shown in Table 1.

Spectral acquisition

Spectra were collected with four different portable instruments: a micro optical fibre NIR spectrometer from Insion (Insion Gmbh, Heilbronn, Germany) equipped with a 10 W halogen lamp while the other instruments were all from the same company (Wuxi Intelligent Analysis Service Co. Ltd, Wuxi, China) consisting of a IAS-2000 spectrometer equipped with a 10 W tungsten halogen lamp and two IAS-5000 spectrometers of IAS-5000 equipped with a 5 W tungsten halogen lamp, where one was identified as 5000A and the other was identified as 5000B. The light source irradiation direction of IAS-5000 is bottom-up while it is top-down for the IAS-2000. The two irradiation modes are shown in Figure 1.

The wavelength of the IAS instruments range from 900-1700 nm with a spectral resolution of 16 nm, a wavelength interval of 1 nm, a signal-to-noise ratio of 10000:1. An integration time of 10 ms was set for acquisition. The Insion spectrometer's wavelength range extends from 844-1894 nm with a resolution of 16 nm, a wavelength interval of 8 nm and an integration time of 20 ms was used for acquisition. Although all the instruments have a stationary diffraction grating, the Insion uses a linear array detector and is designed monolithically so that optical and electronic devices are integrated in one small unit with no moving parts, while the IAS instruments are MEMS-based and employ only a single-pixel detector coupled with a digital mirror device (DMD).

Each sample was measured six times in different positions by accumulating 50 scans, and the average spectrum was used for further processing. The IAS-5000B as denoted as the master instrument while the IAS-5000A, IAS-2000 and Insion were considered as target instruments.

Model transfer techniques

In this study, the techniques of direct standardization (DS), slope/bias correction (SBC), piecewise direct standardization (PDS) and canonical correlation analysis (CCA) were employed to transfer the calibration models from the master to the target instruments.

Table 1. The distribution of lignin in samples.

Species	Number of samples	Range (%w/w)	Mean (%w/w)	Standard deviation
Eucalyptus	24	21.49–27.56	23.73	1.2
Cunninghamia lanceolata	23	32.55–34.20	33.43	0.4
Poplar	13	14.81–20.50	17.99	2.1
Acacia	12	24.62–27.15	25.69	0.9
Pinus massoniana	10	28.47–28.95	28.63	0.2
Total	82	14.81–34.20	26.43	5.4
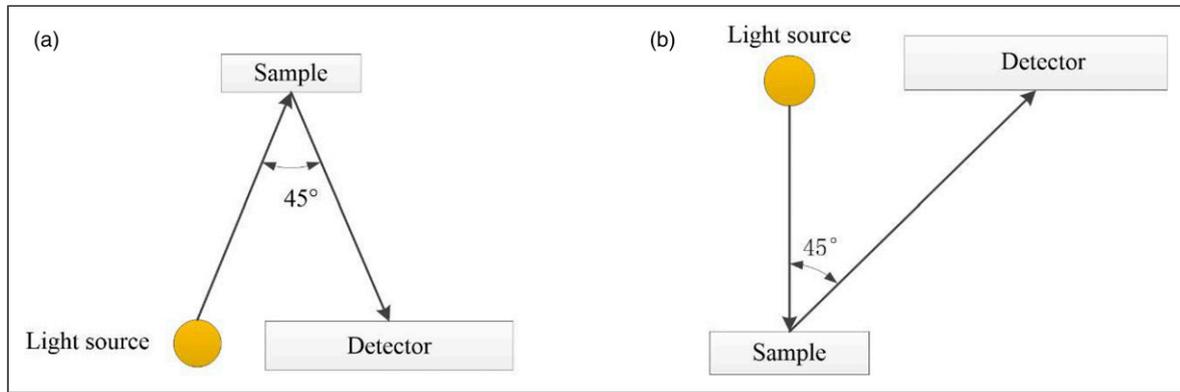
Figure 1. The diagram of two irradiation modes, (a) bottom-up irradiation (b) top-down irradiation.

Direct standardization (DS). An important development in multivariate model transfer is direct standardization (DS),[22] which relates the spectra A_m measured on the master instrument to the spectra A_t measured on the target instrument by the transformation matrix F

$$A_t = A_m F \qquad (1)$$

The transformation matrix F is estimated as

$$F = A_t^+ A_m \qquad (2)$$

Where A_t^+ is the generalized or pseudo-inverse of A_t.

Once F is calculated, the spectrum of a new, unknown sample ($X_{unknown}$), measured on the target instrument can be projected to the master instrument space, and then the property values can be predicted by the old model.

$$X_{std} = X_{unknown} F \qquad (3)$$

Slope/Bias Correction (SBC). The SBC algorithm is a model transfer method based on the correction of the predicted results between the master and the target instruments.[26] Firstly, n samples are selected as the transfer sets from the master and target instruments, respectively. Then, the predicted results y_m and y_t of the transfer sets are calculated by the model of master instruments. The corresponding slope and bias are then assumed as follows

$$Slope = \frac{\sum (y_{s,i} - \bar{y}_s)(y_{t,i} - \bar{y}_t)}{\sum (y_{s,i} - \bar{y}_s)^2} \qquad (4)$$

$$Bias = \bar{y}_t - Slope \cdot \bar{y}_s \qquad (5)$$

Finally, the predicted results Y_t of the target instrument can be corrected as follows

$$Y_{t,corr} = Slope \cdot Y_t + Bias \qquad (6)$$

where $Y_{t,corr}$ is the prediction value matrix of the target instrument after correction.

Piecewise direct standardization (PDS). In direct standardization, each wavelength of the master spectra is simultaneously related to all wavelengths of the target spectra.[22] However, in the actual spectra, the variations of the spectroscopic data may be limited to small wavelength regions only. Thus, piecewise direct standardization was proposed in which each spectral data point $A_{m,i}$ measured on the master instrument is related to the wavelengths in a small window around the wavelength i measured on the target instrument. The subset spectra $A_{t,i}$, which are measured on the target instrument at nearby wavelengths window from index i-k to i+w, are chosen and then the regression vector bi is calculated by the PLS method. In addition, the window can be symmetric (k = w) or asymmetric (k ≠ w) which is decided by the extent of wavelength shift. Normally an asymmetric window can improve the model transfer result if there exist obvious spectral shifts between the master and target instrument. The regression vectors calculated for each window in the data are assembled to form a banded diagonal matrix F. Then the transformation matrix F is calculated by setting the off-diagonal elements to zero as follows

$$F = diag\left(b_1^T, b_2^T, \dots b_i^T, \dots b_n^T\right) \qquad (7)$$

where n is the number of wavelengths.

Then the spectrum X_{unkown} measured on the target instrument can be modified to match the spectrum measured on the master instrument.

Canonical correlation analysis (CCA). The primary idea of CCA is to calculate the correlation between two batches of spectra.[24] Owing to its ability, it has been widely used in recent years. The detailed calculation procedures are as follows:

Firstly, the transfer set measured on the master and target instrument are assumed as A_m and A_t, respectively. A_m and A_t can be executed by CCA

$$L_m = A_m W_m \tag{8}$$

$$L_t = A_t W_t \tag{9}$$

where W_m and W_t denote the canonical weights, and L_m and L_t stand for canonical scores of the master and target instruments, respectively.

Then, the transformation matrix F can be calculated as follows

$$F_1 = L_t^+ L_m \tag{10}$$

$$F_2 = L_m^+ A_m \tag{11}$$

$$F = W_t F_1 F_2 \tag{12}$$

where L_m^+ and L_t^+ are the pseudo-inverse of L_m and L_t, respectively.

Next, the new samples $X_{unknown}$ measured on the target instrument can be converted to the master instrument space by the transformation matrix F, and then the property values can be predicted by the old model.

Spectral difference evaluation

The spectral differences between the master and the target instruments were evaluated by the average difference of spectra (ADS) and average Mahalanobis distance (AMD). The ADS is used for evaluating the overall difference between instruments. Low ADS values mean the spectral difference between two instruments is small. The AMD is used to evaluate the model transfer performance. The transfer performance is evaluated by comparing the AMD before and after transferring. A lower AMD value means that the spectral difference between two instruments becomes smaller.

$$ADS = \frac{1}{n} \sum_{i=1}^{n} \sqrt{\frac{1}{M} \sum_{k=1}^{M} \left| A_{t,k}^i - A_{m,k}^i \right|} \tag{13}$$

Here, n stand for the number of samples, M stands for the number of wavelengths. $A_{t,k}^i$, $A_{m,k}^i$ denote the absorbance of the k-th wavelength of the i-th sample of master and target instrument, respectively.

$$AMD = \frac{1}{m} \sum_{i=1}^{m} \sqrt{(x_i - \mu)^T \Sigma^{-1} (x_i - \mu)} \tag{14}$$

Here, m denotes the number of samples in the prediction set, x_i denotes the i-th sample, and μ denotes the mean of the calibration set. $\sum$ is the covariance matrix of the calibration set.

Model evaluation

The performance of the prediction model was evaluated by the correlation coefficient between the predicted value and

the standard value (R_p), root mean square error of prediction (RMSEP) and ratio of performance to standard deviation (RPD) (Equations. (15)–(18)).

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{i,predicted} - y_{i,actual} \right)^2}{n}} \tag{15}$$

$$R_p = \frac{\sum_{i=1}^{n} \left(y_{i,actual} - \overline{y}_{actual} \right) \left(y_{i,predicted} - \overline{y}_{predicted} \right)}{\sqrt{\sum_{i=1}^{n} \left(y_{i,actual} - \overline{y}_{actual} \right)^2} \sqrt{\sum_{i=1}^{n} \left(y_{i,predicted} - \overline{y}_{predicted} \right)^2}}$$
$$\tag{16}$$

$$RPD = \frac{1}{\sqrt{1 - R^2}} \tag{17}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left(y_{i,predicted} - y_{i,actual} \right)^2}{\sum_{i=1}^{n} \left(y_{i,actual} - \overline{y}_{actual} \right)^2} \tag{18}$$

where n denotes the number of samples in prediction set, $y_{i,predicted}$ is the predicted value of i-th sample, $y_{i,actual}$ is the measured value of the i-th sample, $\overline{y}_{actual}$ and $\overline{y}_{predicted}$ are the mean of the measured and predicted value of the samples in the prediction set. NOTE: It is possible that R^2 calculated in this way can be negative, because the prediction formula can perform worse than using the mean of the set being predicted.

To establish an optimal model, higher RPD and R_p values, along with lower RMSEP should be achieved. A model with an RPD value exceeding 8.0 is excellent and can be used in any analytical situation, values above five are appropriate for quality control analysis, values of 3.0 and upward are regarded as satisfactory for screening, and values of 2.0–3.0 can be used for rough screening, whereas a model is not suitable for prediction if the values are less than 2.0.[27,28]

Software

The software package NIRSA (Chinese version 5.3) which is a self-developed chemometrics tool based on Delphi 7.0 (Borland Software Corporation, Austin, USA) and MATLAB 2018a (The MathWorks Inc, Natick, MA, USA) were used in this study. The results provided by NIRSA are akin to that of the Unscrambler software (CAMO AS, Oslo, Norway), which has been reported in the literature.[29] NIRSA was applied to pre-process the spectra, partition calibration and prediction subsets and develop PLS models. The other algorithms were calculated by using MATLAB 2018a.

Results and discussion

Multivariate calibration models

For the determination of the lignin content 82 sample spectra were measured on the master instrument, using a sample set partitioning based on the x-y distance (SPXY)

algorithm to choose 62 samples for calibration, and 20 samples for validation. Then, PLS calibration models were developed, which is the most common method for linear regression of NIR spectral data. To eliminate irrelevant information and noise, this research adopts several spectral pre-processing methods which are commonly used, including the first derivative, moving average filtering (MAF), multiplicative scatter correction (MSC) and standard normal variate transformation (SNV). The merits of the pre-processing methods are evaluated by the prediction performance of the corresponding PLS analysis model. According to many comparative studies, five points MAF and MSC are used for pre-treatment since their modelling performance was the best. The reason is based on the fact, that MAF can improve the signal-to-noise ratio of the original spectrum by spectral smoothing, while MSC can eliminate the influence of different scattering coefficients caused by uneven distribution of wood powder particles and different particle sizes of the measured spectrum.[30] After selecting the appropriate pre-treatment method, the prediction model for lignin was built by PLS. In this study, the number of latent variables was set in the range of 2–14, and
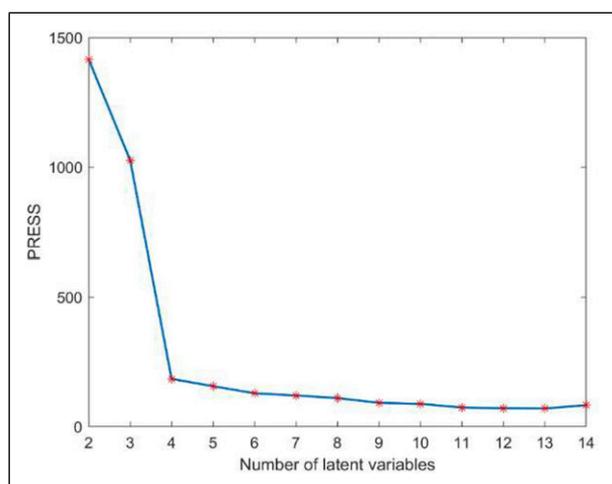
determined by leave-one-out cross validation. Figure 2 shows the change of PRESS value of the lignin calibration model with the number of latent variables. As can be seen from Figure 2, the PRESS value is the smallest when the number of latent variables is 13. At this point, the R_c and RMSEC values were 0.98 and 0.54% (w/w), and the RMSECV value was 1.07% w/w) indicating that the model had a good correlation and accuracy.

Spectral difference

Figure 3 shows the average spectra of 82 wood samples acquired on two spectrometers of the IAS-5000 type (5000A and 5000B), on the IAS-2000 spectrometer and the Insion spectrometer. Figure 3(a) shows that the wavelength range of the Insion spectrometer (844–1894 nm) is larger than the one of the other instruments. However, its spectral resolution is lower than the spectral resolution of the IAS instruments. The sampling interval of the IAS instrument is 1 nm, but the corresponding interval of the Insion instrument is 8 nm, which means there are fewer wavelength points across the same spectral range. Therefore, it is essential to align the wavelength of the target and master instruments first. To match the data point interval of the Insion instrument to the master instrument, piecewise linear interpolation was adopted. Then, the wavelength range was truncated to 900nm–1640 nm in order to match the master instrument. Figure 3(b) shows the average spectra of the four instruments after alignment. It can be seen from the figure that apart from the common strong absorption peaks of water near 1200 nm and 1450 nm there are only minor spectral differences among the three instruments.

To compare the instrument difference between the three target instruments and the master instrument, the average spectral difference diagram is shown in Figure 4. As can be seen from this figure, there is a larger difference between the Insion and the master instrument. The largest difference can be found in the range of 1400–1600 nm where the absorption band of the first overtone of the $\nu(OH)$ band is located. Since the IAS-5000A instrument is the same type as the master instrument regarding the optical components, electronic components and assembly process, the spectral difference for
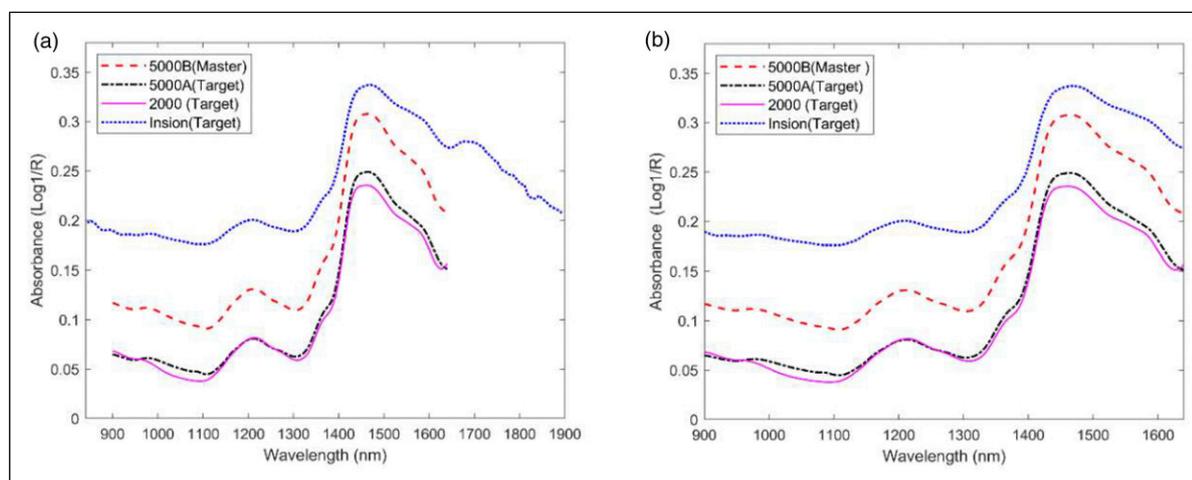

Figure 2. The trend of prediction residual of error sum of squares (PRESS) with the number of latent variables in partial least squares.

Figure 3. (a) The average of the raw spectra acquired by four spectrometers. (b) The average spectra of the four instruments after alignment.

the corresponding sample is small. In contrast, the master and the IAS-2000 instrument have different irradiation directions of the light source, different light source power and a different assembly process, which cause larger differences in the spectra. Because the detector and light source of the Insion instrument are entirely different from the master instrument, the spectral difference is the most obvious. The light transmitting medium of the Insion spectrometer is an optical fiber which leads to less background interference and energy loss. Therefore, the absorbance of the average spectral difference shows an apparent discrepancy.

The model established by the master instrument was used to predict the validation sets measured by the master and target instruments, and the prediction results of the four instruments are shown in Table 2. Additionally, the ADS and AMD used for quantifying the spectral difference are also included in Table 2.

Provided the same concentration range is considered, the closer the correlation coefficient R_p between the measured value and the predicted value is to 1, the better is the model performance. It can be seen from Table 2 that the R_p values of all IAS instruments (the master and two target instruments) are greater than 0.94, and the prediction result of the master instrument is the best with a RPD value greater than 5. Therefore, the NIR calibration model established on the master instrument IAS-5000B can be applied to rapidly determine the chemical compositions of pulp woods if their spectrum is also recorded on the same device. In contrast, the two target instruments show a poor performance based on their RMSEP and RPD values.
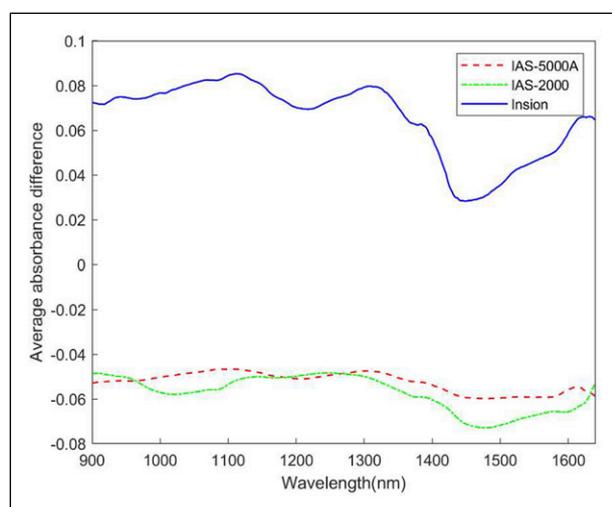

Figure 4. The diagram of spectral differences for the target and master instruments.

The relatively high positive values of R_p with large RMSEP and low RPD values of the three target instruments mean that the predicted values tend to move in line with the measured values but with a larger bias error which lead to a lower R^2 or even a negative value that can be derived from Table 2 and Figure 5. There are parallel trends between three instruments from the same manufacturer which are similar to the contour line for predicted and measured values (Y = X). The predicted scatter diagram of the master instrument basically coincides with the contour line and there are upward and downward offsets of the two target instruments relative to this line. However, the poor performance on all the evaluation indicators for the Insion instrument (Table 2) was also obvious from Figure 5. The low Rp of the Insion instrument manifests an inconsistent trend with the other instruments in the scatter plot. This prediction performance is due to the differences between the light sources and detectors of the Insion and the master instruments. It can also be concluded that the performance of the model cannot be independently evaluated by R_p, because RMSEP, R^2 and RPD metrics play a better role in measuring the systematic errors in model transfer. Therefore, the value Rp was not considered further in the model transfer evaluation.

According to the prediction results above, the model established on the master instrument cannot be directly used or shared among the three target instruments before employing an appropriate method of model transfer.

In order to analyse the spectral differences, the average difference of spectra (ADS) between the validation sets of the master and the three target instruments was calculated. The ADS of the master instrument and the 5000A, 2000 and Insion instruments are 0.2186, 0.2371 and 0.2628, respectively (Table 2). After comparing the values, it can be concluded that there is a larger ADS between the master instrument and the Insion instrument. The average Mahalanobis distances (AMD) of spectra between the calibration set and all validation sets were calculated and presented in the final column in Table 2. It can be seen from Table 2 that compared to the IAS-5000A instrument, there are relatively large distance values for the three target instruments. Among the target instruments, the value of the IAS-5000A instrument is the lowest owing to it being an identical model to the master instrument.

Comparison of model transfer methods

All of the algorithms used in this study are model transfer strategies that require standard samples, and the number of samples selected for the transfer set has a large influence on

Table 2. Prediction results of lignin content and the spectral difference for the validation sets measured with the four instruments before model transfer.

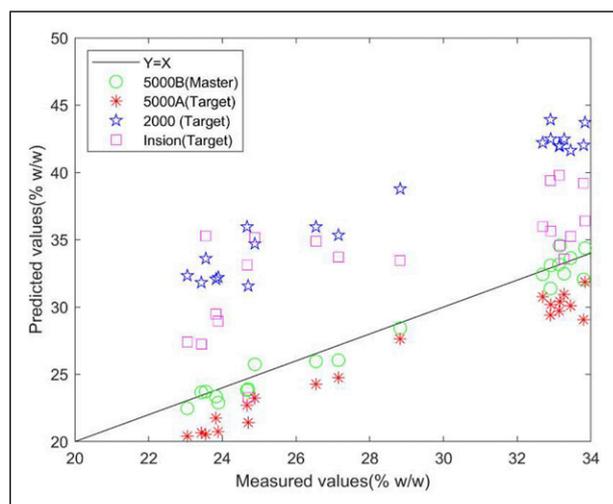|	Instrument	R_p	R^2	Root mean square error of prediction	Ratio of performance to standard deviation	Average differences of spectra	Average Mahalanobis distances
Master	IAS-5000B	0.990	0.96	0.84	5.2		0.195
Target	IAS-5000A	0.98	0.59	2.77	1.6	0.219	1.6
Target	IAS-2000	0.97	−3.5	9.21	0.5	0.237	13.9
Target	Insion	0.72	−0.84	5.86	0.7	0.263	7.9

Figure 5. Predicted scatter diagram for lignin of master model for master and target instruments before model transfer。.

the model transfer performance. In this study the Kennard-Stone (KS) algorithm was adopted to select 5, 10, 15, 20, 30 samples from all the samples measured on the master instrument and two target instruments, respectively, as the transfer set. DS, PDS and CCA algorithms were then used to transfer the model built on the IAS-5000B master instrument to the target instruments, IAS-5000B, IAS-2000 and Insion. The performance of the four algorithms is summarized in Table 3, Figure 6 and 7.

The best prediction results for the three target instruments as a function of the three transfer methods, the size of transfer set and the window of the PDS, are shown in Table 3. As can be seen from the last two columns of this table, the ADS and AMD has been largely reduced after the transfer process. This means, that after spectral transfer, the spectra of target and master instrument are very similar. For the IAS-5000A and IAS-2000 instruments, the prediction results are improved by DS, PDS and CCA algorithms. For the IAS-5000A spectrometer, the best performance can be obtained if 30 samples were selected as the transfer set while using the CCA algorithm. The values of R_p, RMSEP and RPD are 0.97, 1.29 and 3.4, respectively, which are slightly better than those of DS. For the IAS-2000 instrument, the application of the CCA algorithm leads to a considerable improvement in the prediction of lignin as illustrated by the significant decrease in RMSEP (0.90) and improvement in RPD (4.8). For the Insion spectrometer, the best prediction performance (R_p = 0.90 RMSEP = 1.97 RPD = 2.2) is found when DS is used for the transfer procedure. This is due to the fact that most of the data points of the Insion spectra are obtained by interpolation and the differences between the Insion and the master instrument are mainly a systematic bias. The method of SBC normally can be applied when the instrumental difference is small.[26] Although the master IAS-5000B and target IAS-5000A belong to one product of the same series, the differences between them are not compensated well by the SBC method, not to mention the other two target instruments. Therefore, SBC is not discussed further.

In practice, the number of standard samples also affects the time consumption of model transfer. Thus, the number of the standard samples is also worth careful consideration. The

change of the RMSEP value with the number of standard samples for the three target instruments using the three model transfer algorithms is shown in Figure 6. Since there are only 62 samples for calibration, a maximum of 50% of the samples in the calibration set is selected for the transfer set to obtain representative results. It can be seen from Figure 6(a) that, as the number of samples in the transfer set increases, the useful information in the transfer set also increases, and the RMSEP of the three instruments shows an overall trend of decreasing. Therefore, the lowest RMSEP is found when the number of samples in the transfer set is 30 for all target instruments. Figure 6(b) shows the trend of the RMSEP value for two target instruments when the PDS algorithm is adopted. As can be observed in Figure 6(b), the minimum RMSEP was observed when the number of samples in the transfer set for the two IAS instruments is 10. For the Insion spectrometer, the minimum RMSEP (4.8) occurs when the number of samples in the transfer set is 5, and as the number of samples in the transfer set increases, the RMSEP value also increases. This is clear evidence, that the PDS algorithm is not suitable for this model transfer. Figure 6(c) shows the RMSEP trend for the three target instruments when the CCA algorithm is used. Thus, it can be concluded, that the trend for the three instruments is similar to the application of the DS algorithm. The lowest RMSEP is found when the number of samples in the transfer set is 30 for all target instruments.

Since the selection of an appropriate window size is required for the PDS algorithm, a variety of different windows sizes have been tried based on the prior knowledge of the lowest RMSEP with 10 samples in the transfer set. The relationship between RMSEP and window size for the IAS-5000A spectrometer is shown in Figure 7(b). The best transfer performance (RMSEP = 1.34) is found when the window size is set to 8. For the IAS-2000 instrument, the best performance (RMSEP = 0.97, RPD = 4.4) is found when setting the window size to 30. Comparing the two instruments, it is necessary to select a larger window size for the PDS model transfer of the IAS-2000 to include the inter-instrumental differences to the master instrument.

Comparing the three model transfer algorithms, contrary to the DS and CCA algorithms the PDS algorithm requires a complex window size selecting procedure. Nevertheless, the PDS method can transfer the spectral data of the two target instruments successfully with only 10 samples in the transfer set and obtain a good prediction performance, whereas the DS and CCA algorithms require a minimum of 30 samples. In conclusion, the DS and CCA algorithms are simpler and do not require a complex parameter selection procedure. With the PDS algorithm a better model transfer performance can be achieved with a smaller number of samples in the transfer set. Therefore, in practical applications, the PDS algorithm is the better choice as model transfer method compared to DS and CCA, because of the fewer samples needed for the transfer set, which means model maintenance cost is lower. However, if there are significant systematic differences among the master and the target instrument, it can occur that no acceptable result can be obtained by PDS but the simple DS algorithm can be a good alternative.

Table 3. The prediction results of transferring the lignin calibration model of the IAS-5000B instrument to the three target instruments by direct standardization, piecewise direct standardization and canonical correlation analysis. (k: number of wavelengths on the left side of the center wavelength, w: number of wavelengths on the right side of the center wavelength, window size=1+k+w).

Instrument	Method	Number of standard samples	Window size		Partial least squares number	R^2	Root mean square error of prediction	Ratio of performance to standard deviation	Average differences of spectra	Average Mahalanobis distances
IAS-5000A	DS	30				0.91	1.32	3.3	0.1189	0.211
	SBC	5				0.37	3.45	1.3		1.6
	CCA	30				0.91	1.29	3.6	0.1175	0.209
	PDS	10	8	k3w4	1	0.90	1.34	3.2	0.1014	0.322
IAS-2000	DS	30				0.95	0.93	4.6	0.1297	0.253
	SBC	10				−11.8	15.5	0.3		13.9
	CCA	30				0.96	0.90	4.8	0.1276	0.239
	PDS	10	30	k14w15	1	0.95	0.97	4.5	0.1300	1.4
Insion	DS	30				0.79	1.97	2.2	0.1607	0.210
	SBC	30				−4.1	9.75	0.4		7.9
	CCA	30				0.79	1.99	2.2	0.1608	0.214
	PDS	5	8	k7w0	1	−0.22	4.77	0.9	0.1683	1.160

DS: direct standardization; SBC: slope/bias correction; CCA: canonical correlation analysis; PDS: piecewise direct standardization.
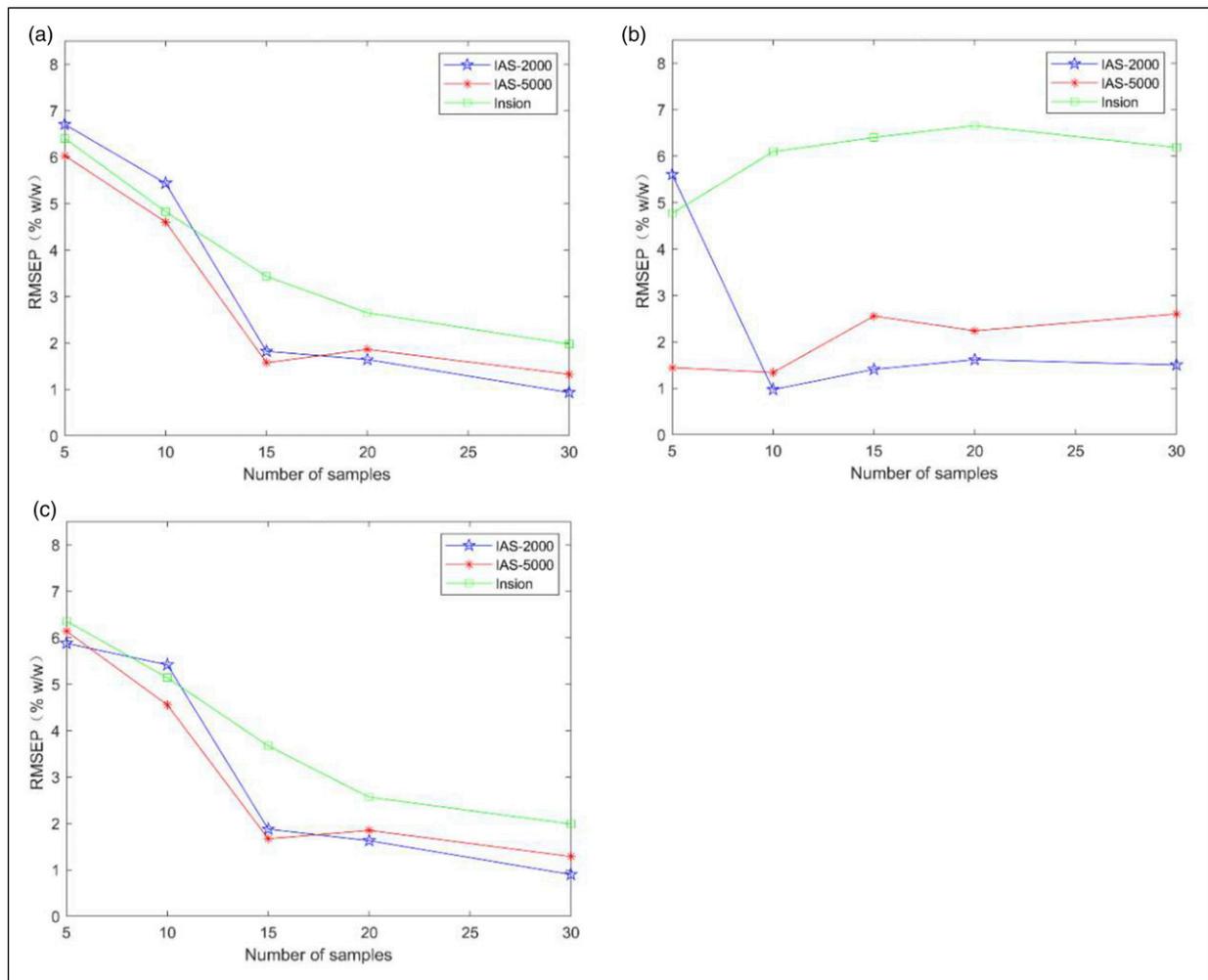

Figure 6. The trend of root mean square error of prediction with the number of transfer samples when using (a) the direct standardization algorithm, (b) the piecewise direct standardization algorithm, and (c) the canonical correlation analysis algorithm.
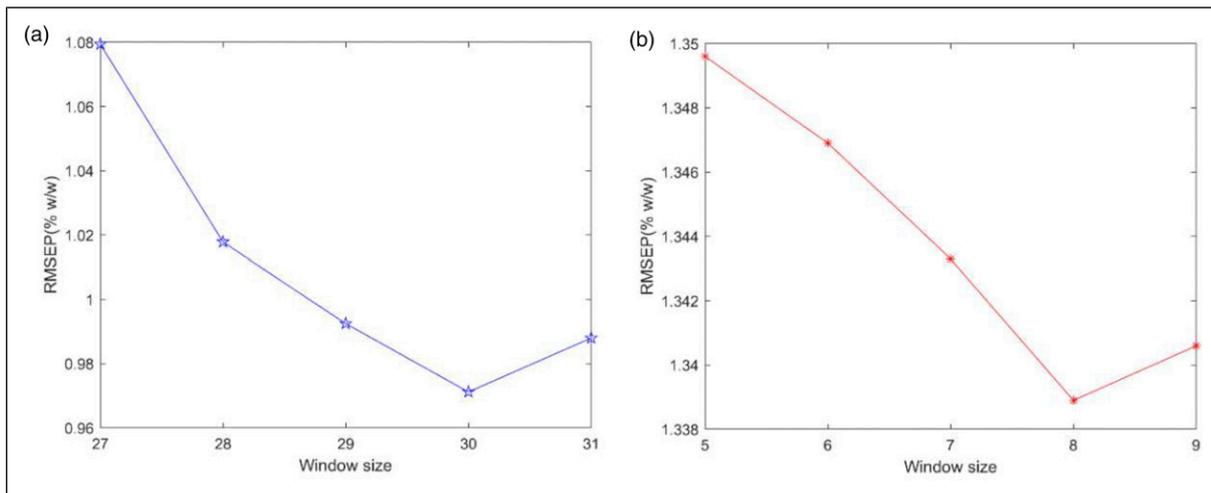
Figure 7. The trend of root mean square error of prediction with different window sizes for the piecewise direct standardization transfer to the (a) IAS-2000 and (b) IAS-5000A instruments.
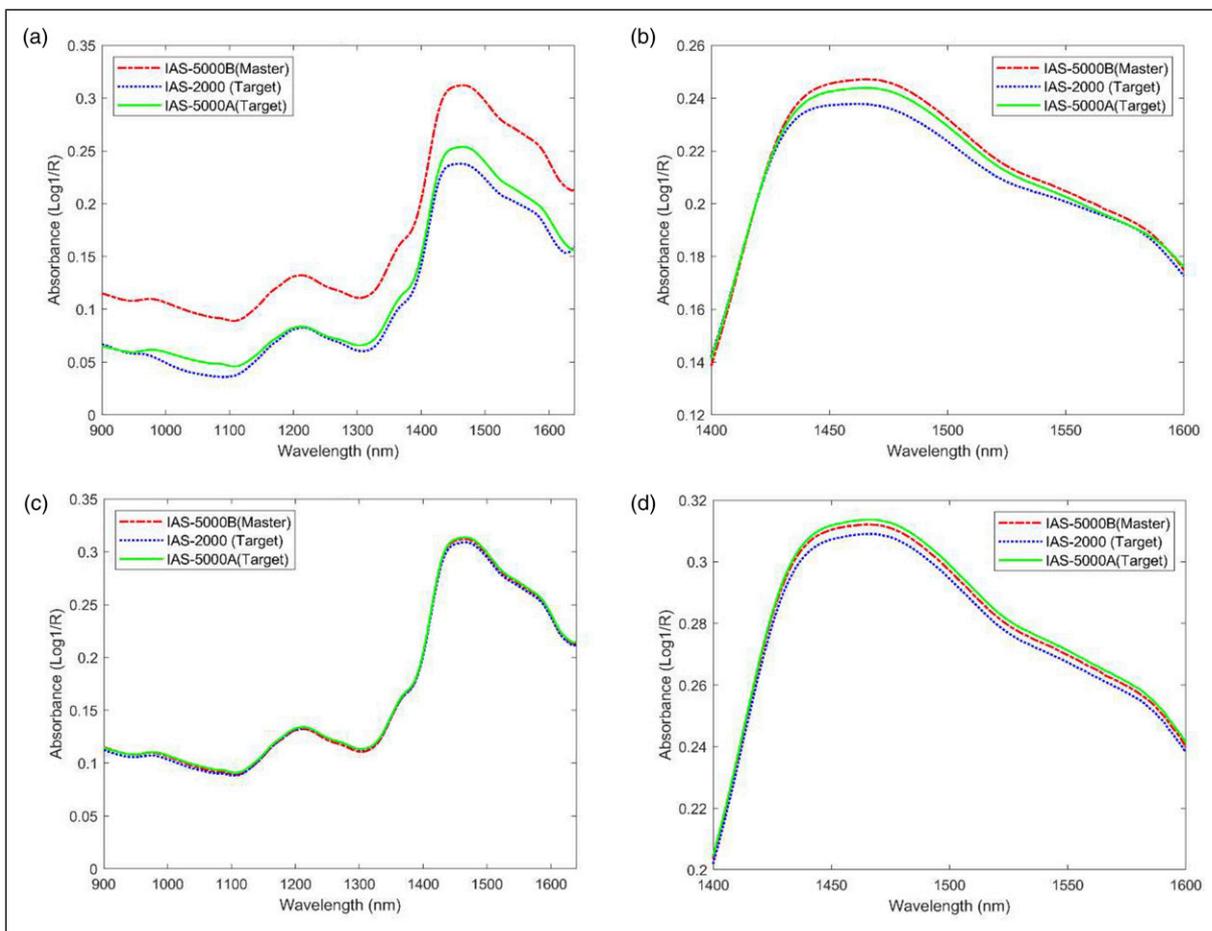

Figure 8. The average spectra of the prediction set measured on the three spectrometers (a) before spectra transfer (b) after longitudinal translation and truncation (c) after spectra transfer and (d) after truncation.

Once PDS is used for the model transfer, it is mandatory to determine the window size. It can be either symmetrical (k = w) or asymmetrical (k ≠ w) centered on each calibrated wavelength. When wavelength shifts can be ignored, a symmetric window can be used; if wavelength shifts are obvious, the transfer performance can be improved by choosing an asymmetric window. As it can be seen from Table 3, good results can be obtained when an asymmetric

window size was selected. This illustrates that there are wavelength shifts between the master instrument and the target instruments which can also be observed in Figure 8(a), where the average spectra of the prediction set of the three instruments are illustrated. As can be seen from this figure, there are lateral shifts between the three instruments and vertical offsets between the IAS-2000 and IAS-5000 instruments. For the accentuation of the lateral

shift, the spectra along the y-axis were truncated to the 1400–1600 nm wavelength range in Figure 8(b).

To demonstrate the transfer performance in more detail, the average spectra of the three instruments after transfer are plotted in Figure 8(c). This figure demonstrates, that although the spectra of the three instruments are essentially coincident, there are still small discrepancies that can be further accentuated by truncation (Figure 8(d)). Nevertheless, comparison of the figures before and after transfer demonstrates, that the vertical offset and the lateral shift are largely eliminated by the PDS algorithm.

Conclusion

The main purpose of this study is to share the master calibration models for lignin determination of pulp wood with three different target instruments. Due to the differences hardware, optical design and structure designs of the four instruments, the impact of their spectral differences on the DS, SBC, PDS and CCA model transfer algorithms was comparatively evaluated. In what follows the results of these investigations are summarized:

(1) The ADS and AMD parameters were used to evaluate the differences between the master and target spectrometers. Both of them were significantly decreased by the transfer process, viz. the spectra of the target instruments became more similar to the spectra measured by the master instrument. Furthermore, ADS is a more sensitive criterion to measure the differences among instruments since the largest ADS was observed practically between the master and the Insion instrument.

(2) All three target instruments can be successfully transferred by CCA. For the Insion spectrometer, the transfer performance of DS is slightly better than CCA. This means if there are significant systematic differences, a simple algorithm like DS might be a good choice. For the IAS-2000 and the IAS-5000A instruments, good model transfer effects can be obtained by the PDS algorithm with only a few standard samples, which is a great advantage of the PDS algorithm.

(3) When using a PDS for model transfer, a proper choice of window size is very important. A large window should be chosen if there are significant differences between instruments. If wavelength shifts cannot be ignored between the master and the target instruments, an asymmetric window of appropriate size has to be selected to ensure a good PDS algorithm transfer performance.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

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