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Quantitative analysis of diclofenac sodium powder via near-infrared spectroscopy combined with artificial neural network

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ABSTRACT

A method for quantitative analysis of diclofenac sodium powder on the basis of near-infrared (NIR) spectroscopy is investigated by using of orthogonal projection to latent structures (O-PLS) combined with artificial neural network (ANN). 148 batches of different concentrations diclofenac sodium samples were divided into three groups: 80 training samples, 46 validation samples and 22 test samples. The average concentration of diclofenac sodium was 27.80%, and the concentration range of all the samples was 15.01–40.55%. O-PLS method was applied to remove systematic orthogonal variation from original NIR spectra of diclofenac sodium samples, and the filtered signal was used to establish ANN model. In this model, the concentration of diclofenac sodium was determined. The degree of approximation was employed as selective criterion of the optimum network parameters. In order to compare with O-PLS–ANN model, principal component artificial neural network (PC-ANN) model and calibration models that use different preprocessing methods (first derivative, standard normal variate (SNV) and multiplicative scatter correction (MSC)) of the original spectra were also designed. In addition, partial least squares regression (PLS) models were also established to compare with ANN models. Experimental results show that O-PLS–ANN model is the best.

1. Introduction

Near-infrared (NIR) spectroscopy has been proved to be a powerful analytical tool for analyzing a wide variety of samples that are used in agricultural, food, chemical and pharmaceutical industries [1–10], mainly due to its advantages over other analytical techniques, such as being expeditious, without destruction, low cost, being adaptable for almost all kinds of samples in all states and with little or no sample preparation. Frequently, the objective with this characterization is to determine the concentrations of different components in the samples. However, NIR spectra often contain serious systematic variation that is unrelated to the response data set, and the analyte of interest absorbs only in small parts of the spectral region. For solid samples this systematic variation is mainly caused by light scattering and differences in spectroscopic path length. Furthermore, the baseline and slope variations may often constitute the major part of the variation of the NIR spectra. The variation in X (a given data set) that is unrelated to y (the response set) may disturb the multivariate modeling and cause imprecise predictions for new samples. So the first step of a multivariate calibration based on NIR spectra is often to preprocess the original data.

For the preprocessing of NIR spectral data, conventional methods that are commonly used including smoothing, derivation, multiplicative scatter correction (MSC) and standard normal variate (SNV). These signal corrections are different cases of filtering, practical effect of the first derivative is that it removes an additive baseline. The second derivative removes also a multiplicative baseline. But the drawbacks of using derivatives are the inevitable change of the shape of the spectra and the noise is seriously enlarged. SNV and MSC remove both additive and multiplicative baseline variation without altering the shape of the spectra. Common for all these methods is that they do not require a response variable in the preprocessing step, which is a prerequisite when orthogonal projection to latent structures (O-PLS) method [11,12] is applied. Being a generally applicable preprocessing and filtering method, O-PLS provides a way to remove systematic orthogonal variation from a given data set X without disturbing the correlation between X and the response set y. Compared with the original data, because the orthogonal variation is removed by applying O-PLS method, the filtered data which is used as input data for the calibration model is simplified, thus the complexity of the calibration model is reduced and the predictive ability is preserved,

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effectively improved the interpretational ability of the model for both correlated and non-correlated variation in NIR spectra.

Artificial neural networks (ANNs) technique is considered one of the best approaches to non-linear calibration and fitting problem in every field of chemistry. The distinct characteristic of ANNs is their ability to learn from experience and examples and to get adapted with changing situations accordingly. In quantitative analysis, ANNs have been more and more widely applied during the past several years [13–20], mainly due to their anti-jamming, anti-noise and robust non-linear transfer ability. Generally, proper ANNs models result in lower mapping errors and prediction errors. They are an alternative for modeling non-linear data sets when the more classical multivariate calibration methods fail. ANNs also suffer from some drawbacks: the predictive properties of ANNs strongly depend on the learning parameters and the topology of the network, and ANNs models are complex and difficult to interpret.

2. Theory

2.1. Preprocessing methods

In order to simplify the interpretation of NIR spectral data, O-PLS uses the input data set X and the response set y to filter and remove variability in X that is orthogonal to y. The O-PLS preprocessing method with a single response set y is described as following:

1. Optional transformation, centering and scaling of the raw data to give the matrices X and y.

2. Calculation of the parameters w, t, p, u and c with the normal NIPALS method [21] for single y, where w represents the weight vector of X; t is the score vector of X; p is the loading vector of X; u is the score vector of y and c is the loading vector of y.

3. Calculation of weight vector of the orthogonal variation.

$$w_{ortho} = p - \left[\frac{w^T p}{w^T w}\right] w \tag{1}$$

Then make normalization of w_{ortho}, where w_{ortho} represents the weight vector of orthogonal variation.

4. Calculation of score vector and loading vector of the orthogonal variation and saving of found parameters.

$$t_{ortho} = \frac{X w_{ortho}}{w_{ortho}^T w_{ortho}} \tag{2}$$

$$p_o = \frac{X^T t_{ortho}}{t_{ortho}^T t_{ortho}} \tag{3}$$

t_{ortho} is the score vector of orthogonal variation and p_{ortho} is the loading vector of orthogonal variation.

5. Removal of orthogonal variation from X.

$$E_{\text{O-PLS}} = X - t_{ortho} p_{ortho}^T \tag{4}$$

$t_{ortho} p_{ortho}^T$ represents the matrix of orthogonal components, $E_{\text{O-PLS}}$ represents the residual matrix, for additional orthogonal components, return to step 2 and set, run the circle till the orthogonal variation $X = E_{\text{O-PLS}}$ does not exist in X.

After preprocessing with O-PLS method, the filtered data $E_{\text{O-PLS}}$ does not contain any variation that is orthogonal to y, so the stability of the calibration model is greatly improved.

SNV is a mathematical transformation method used to remove slope variation and to correct for scatter effects, and MSC corrects for difference in light scatter between samples before calibration. The SNV theory and MSC theory are described in Refs. [22–26] in detail.

2.2. Artificial neural networks

The current interest in artificial neural networks is largely due to their ability to mimic natural intelligence in its learning from experience [27]. They learn from examples by constructing an input–output mapping without explicit derivation of the model equation. Artificial neural networks are parallel computational devices consisting of groups of highly interconnected processing elements called neurons. Traditional neural networks have neurons arranged in a series of layers: input, hidden(s), and output layers. The layers work parallel in time, taking input from the previous layer and passing their output to the next layer in a synchronous manner at every time step. The number of neurons in the input layer and the output layer are determined by the number of input and output parameters, respectively. In order to find the optimal architecture, number of neurons in the hidden layer has to be determined (this number will be determined based on the ANN during the training process by taking into consideration the convergence rate, mapping accuracy, etc.). In each neuron, the sum of the weighted signals is calculated and when it overcomes a certain value, or threshold, it is processed by a so-called transfer function and sent to all neurons in the next layer, and during training, the weight coefficients and threshold values are adjusted to fit the training data. Of all the ANNs, the most widely used network type is multilayered feed-forward network [28,29] trained with the back-propagation (BP) learning algorithm [30–32]. The BP algorithm is based on the selection of a suitable error function, whose values are determined by the actual and predicted outputs of the network. The model with lowest prediction error is being used as the final and optimal model. Generally, the root mean squared error (RMSE) is used as the error function for finalizing the training and testing process [29].

2.3. Evaluation of artificial neural networks

The present criterion of optimization of the network is to minimize the performance error measured on the training set. However, it is very easy to choose an overfitting model, namely, the error of testing set is not at the minimum. This kind of network is unsteady when it is used to predict an unknown sample. To avoid this kind of situations, a new evaluation criterion of the network, the degree of approximation, is employed [33–35]. The definition of this criterion is given by Eqs. (5) and (6):

$$e_a = \left(\frac{n_1}{n}\right) e_1 + \left(\frac{n_c}{n}\right) e_c + |e_1 - e_c| \tag{5}$$

where e_a is the error of the approximation; e_1 and e_c are the relative standard errors of training set and validation set, n_1 and n_c are the numbers of samples in the training set and validation set, n is the number of all known samples, and n_1/n and n_c/n are the weights contributed to the error of approximation (e_a) by training set and validation set:

$$D_a = \frac{c}{e_a} \tag{6}$$

where D_a represents the degree of approximation and c is a constant number by which D_a is adjusted to get a good chart, here the value of c is set with 0.08. It is very obvious that the smaller e_a, the larger D_a can obtain the better ANN models. Therefore, the effects of both training set and validation set are considered in this evaluation criterion.

The predictive ability of calibration model for training set, validation set and test set are evaluated in terms of the relative standard error (RSE) [36,37], defined as:

$$\text{RSE} = \sqrt{\frac{\sum_{i=1}^{n} (C_{NIR_i} - C_{REF_i})^2}{\sum_{i=1}^{n} C_{REF_i}^2}} \tag{7}$$

where n is the number of samples, C_{REF} and C_{NIR} are concentrations of samples provided by the State Drug Standard method and the method of prediction from NIR spectra, respectively.

3. Experimental

3.1. Apparatus and software

All of the NIR diffuse reflectance spectra were measured with a Shimadzu® UV–VIS-NIR-3100 spectrophotometer (Tokyo, Japan) equipped with ISR-3101 integrating sphere. Data were transferred to a microcomputer through a RS-232C interface. Commercial available NIR spectral analysis software package (UVPC Personal Spectroscopy Software) enabled the recording of spectra and their mathematical processing of derivation. The extended deltabar-delta back-propagation training routines contained in Neural Works Explorer (NeuralWare, America) software package were used. The scores of principal component analysis of the response data and PLS algorithms were performed by using of TQ6.1.1 (Thermo Nicolet, America) software package. Other mathematical pretreated methods (O-PLS, SNV and MSC) were designed in Matlab 7.0 (MathWorks Inc.) by our laboratory.

3.2. Preparation of samples

All of the pharmaceutical raw materials, including diclofenac sodium as active component, and starch as main excipient were supplied by Pharmaceutical Factory of Norman Bethune University of Medical Science (Changchun, China). The average concentration of diclofenac sodium in the laboratory prepared samples was 27.80%, and the concentration range of all the samples was 15.01–40.55%. 148 batches laboratory prepared powder samples with different concentrations of diclofenac sodium were divided into three groups stochastically: the training set including 80 samples, the validation set including 46 samples and the test set including 22 samples. The standard reference concentrations of diclofenac sodium were measured according to the Chinese Pharmacopoeia [38].

3.3. Reference method

Ultraviolet (UV) spectrophotometry was used as the stated reference method for quantitative determination of diclofenac sodium powder drug. Diclofenac sodium powder was homogenized, an amount of the powder was weighed accurately, and the weighted powder was dissolved in ethanol. After the solution was diluted to 0.5 mg/ml with ethanol, it was filtrated. Put 20 ml of the filtrate into a 100 ml measuring cylinder, after diluted it to 0.1 mg/ml with ethanol, its absorbency was determined at wavelength of 284 nm by ultraviolet spectrophotometric method according to the Chinese Pharmacopoeia. Finally, accurate weighed 50 mg of dry diclofenac sodium as reference substance, it was determined with the same method, and then calculated the concentration of diclofenac sodium in diclofenac sodium powder.

As we can see, the reference method need to dissolve samples and separate active components to measure their proportions, and compared with the proposed NIR method, this method is time-consuming, laborious, destroying drugs and even causing a certain amount of chemical pollution.

3.4. Recording of NIR spectra

All measurements were obtained in reflectance mode, using six scans performed at 1 nm intervals over the wavelength range of 1100–2500 nm. The collected entrance slit of NIR spectrophotometer was 12 nm. Fig. 1 shows the NIR spectra of the main components in diclofenac sodium power (diclofenac sodium as the active ingredient and starch as main excipient) and the samples with different concentrations of diclofenac sodium.

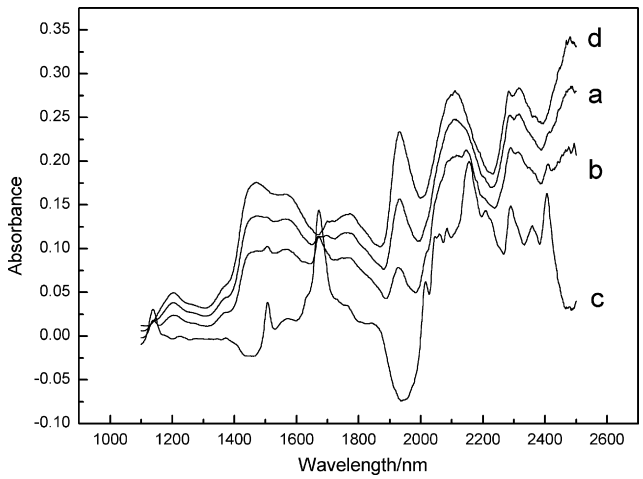

Fig. 1. NIR original spectra of (a) sample in training set (the concentration of diclofenac sodium is 15.01%); (b) sample in test set (the concentration of diclofenac sodium is 39.97%); (c) diclofenac sodium; (d) starch.

4. Results and discussion

In this work, a method for expeditious, non-destructive analysis of diclofenac sodium as active component in diclofenac sodium powder is developed by using of O-PLS method combined with artificial neural network. After NIR spectra were acquired, O-PLS was applied to remove the non-correlated systematic variation. The filtered signal was used as input data for artificial neural network. With the aid of degree of approximation, the parameters that affected the network were studied and the optimal ANN model was established, in this model, the concentration of diclofenac sodium was determined.

4.1. Selection of the number of orthogonal components with O-PLS method

Here eigenvalue criterion is employed to estimate the number of orthogonal components, the eigenvalue approach is to analyze the ratio of $||p - [w^T p/(w^T w)]w||/||p||$, which becomes zero for correlated O-PLS components if no orthogonal variation exist in X. A plot of the ratio $||p - [w^T p/(w^T w)]w||/||p||$ gives a good indication of the number of orthogonal components to extract. In Fig. 2 this ratio for each O-PLS component is shown, and three orthogonal components were removed from X, because after three components the amplitude of the other components is negligible. After the removal of these orthogonal components from X, the residual matrix was used as input data of artificial neural network.

4.2. Training and optimization of ANN models

In this paper, a three layers back-propagation network was used. The properties of the training set determined the number of input and output neurons. The pretreated NIR spectral data were regarded as input nodes. The number of input nodes (interval of wavelength) was changed in order to scan the data. Because there was only one kind of active ingredient in diclofenac sodium powder samples, the output layer contained one neuron. ANN model was trained with different numbers of hidden neurons and training cycles. At the start of a training run, both momentum and learning coefficient were initialized with random values. During

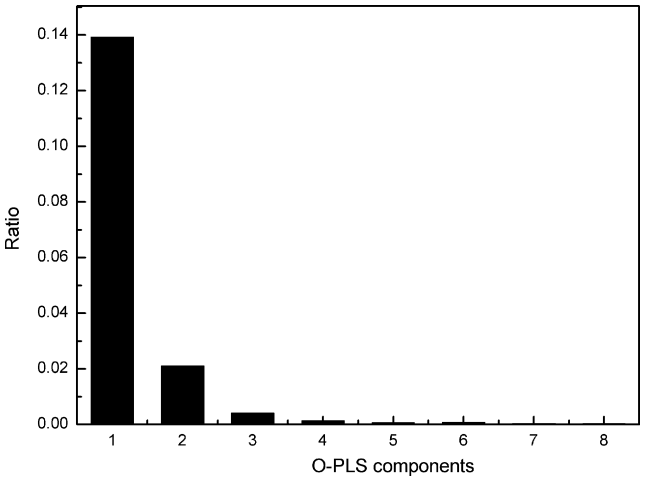

Fig. 2. Selection of number of orthogonal components.

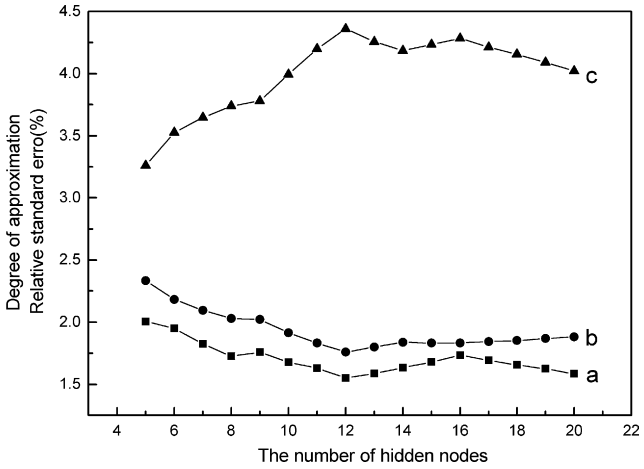

Fig. 4. Effect of hidden nodes: (a) relative standard error of training set; (b) relative standard error of validation set; (c) degree of approximation.

training, the modifications of the network input nodes (10–90), hidden nodes (5–20), momentum (0.05–0.60), learning coefficient (0.05–0.60) and iteration numbers (500–6000) were made by back-propagation on the basis of relative standard errors (RSEs) and degree of approximation. The training set was used to train the network, the validation set was used to avoid over-fitting and the maximal degree of approximation was used to determine the network topology parameters (number of input, hidden, iterations, momentum and learning coefficient). While the network was optimized, the testing data were fed into the network to evaluate the trained network.

4.3. The establishment of O-PLS–ANN model

4.3.1. Selection of the optimal number of input nodes and hidden nodes

After the removal of orthogonal components from NIR spectra with O-PLS method, the filtered data were regarded as input data for ANN model. The effect of different number of input nodes is shown in Fig. 3. As can be seen, the network had the highest degree of approximation when the number of input nodes was 50 (the interval of wavelength was about 28 nm), beyond 50 the degree of approximation reduced evidently, so the optimum number of input neurons was 50.

The number of hidden nodes had great effect on predictive ability of ANN model. Fig. 4 shows the effect of hidden nodes. Both curves a and b jumped obviously, and it was difficult to determine the optimum number of hidden nodes from them, but we could determine the optimum number of hidden neurons was 12 according to the largest degree of approximation.

4.3.2. Selection of the optimal momentum and learning coefficient

The learning coefficient and momentum terms appeared to influence the prediction too. Appropriate learning behavior was only found with low learning coefficient and momentum. Too high coefficient and momentum lead to the network instability. Figs. 5 and 6 show the effect of learning coefficient and momentum. In Figs. 5 and 6, the relative standard errors of both training set and validation set did not change obviously. But according to the degree of approximation curve we could draw a conclusion easily, when both momentum and learning coefficient reached at 0.10, the network had the highest degree of approximation.

4.3.3. Selection of the optimal number of iterations

ANN model was trained with different number of training cycles. The optimum topology parameters (number of input nodes and hidden nodes, learning coefficient and momentum) were kept constant during the determination of the optimal number of iterations.

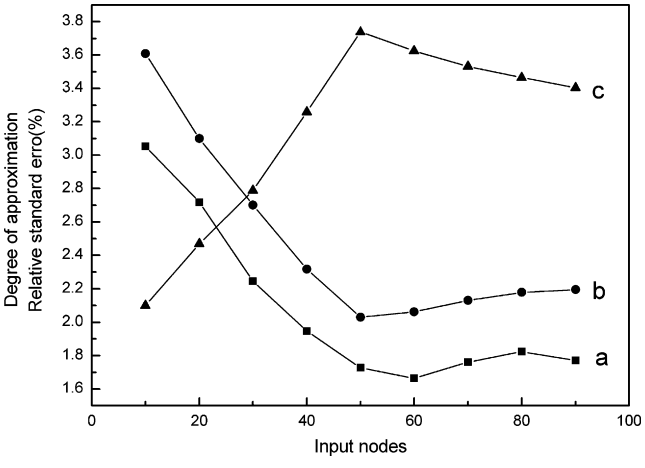

Fig. 3. Effect of input nodes: (a) relative standard error of training set; (b) relative standard error of validation set; (c) degree of approximation.

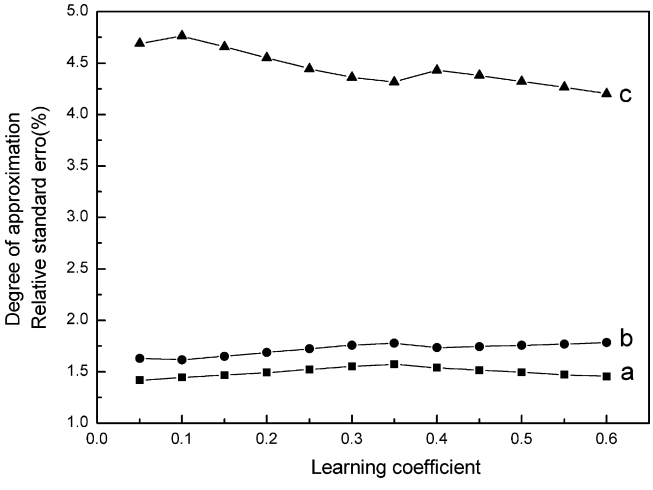

Fig. 5. Effect of learning coefficient: (a) relative standard error of training set; (b) relative standard error of validation set; (c) degree of approximation.

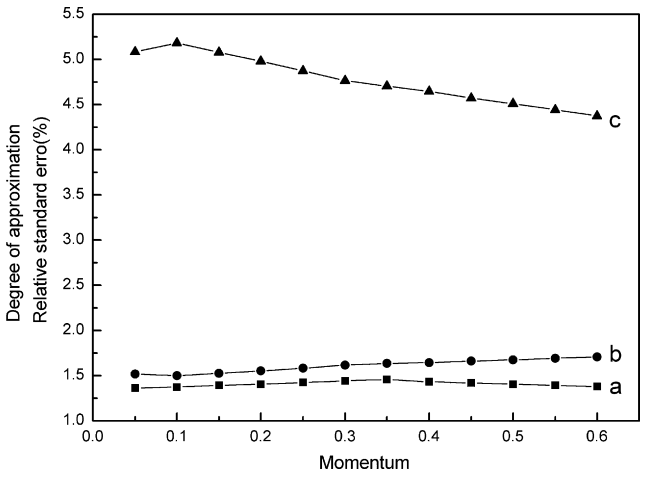

Fig. 6. Effect of momentum: (a) relative standard error of training set; (b) relative standard error of validation set; (c) degree of approximation.

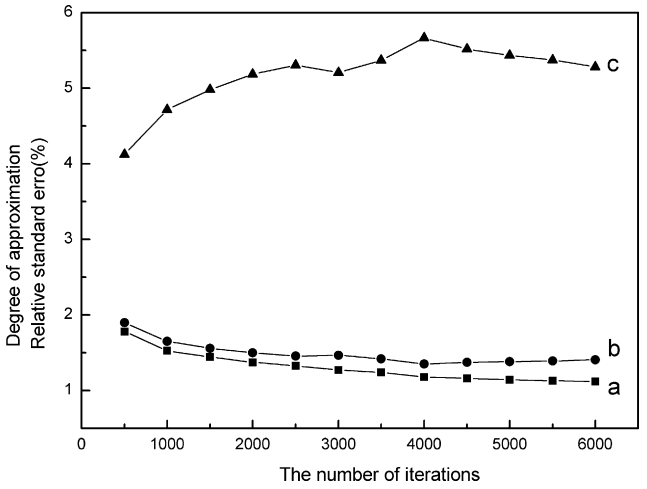

Fig. 7. Effect of number of iterations: (a) relative standard error of training set; (b) relative standard error of validation set; (c) degree of approximation.

The selection of training cycles by error curves and degree of approximation is shown in Fig. 7. As can be seen, the degree of approximation was largest at 4000 iterations, beyond 4000 the relative standard errors of training set decreased and that of validation set increased. Thus the degree of approximation reduced evidently. This result demonstrates that the network appears to have an overfitting phenomenon.

4.4. Comparison of the ANN models designed with different preprocessing methods

In order to evaluate the O-PLS–ANN model, the principal component artificial neural network (PC-ANN) model and calibration models that use different preprocessing methods (first derivative, SNV and MSC) of the original spectra were designed. Furthermore, the optimal ANN models were established separately. The optimal parameters are shown in Table 1. In PC-ANN model, original NIR spectral data were initially analyzed by principal component analysis, and then the scores of the principal components were chosen as input nodes for the input layer instead of the spectral data, so input nodes of the model was greatly reduced, and the training time was shortened, that can be seen in Table 1.

When all network parameters were optimized, the artificial network had a high ability for prediction. To evaluate the optimal ANN models, the linear regression equations between concentration values provided by the reference method and NIR method were established. The intercept and slope represented the linearity degree between the concentrations gained from the above two methods. The intercept, slope of regression equation and *R* (correlation coefficient) which are shown in Table 2 show a good linearity. The RSE of training set and validation set are also shown in Table 2. We can see the O-PLS–ANN model has the smallest RSE and the best *R*, and in PC-ANN model, these are a little worse than that of O-PLS–ANN model.

The optimal models were used to predict the concentrations of diclofenac sodium in the 22 test samples. The results are listed in Table 2, too. Because the testing set did not join in training networks, it had the highest RSE and the lowest *R* compared with that of training set and validation set.

4.5. Determination by partial least squares (PLS) regression

In the previous sections, ANN models successfully determined and predicted the concentrations of diclofenac sodium as active component in diclofenac sodium powder samples. Partial least squares regression (PLS) is a usual method for analyzing multicomponent mixtures, which has been systematically applied in pharmaceutical analysis. Here the PLS models were also established to compare with ANN models. In order to use an amount of data similar to that employed for training ANN models, PLS models were trained with both the training and the validation sets (126 samples) of ANN. The 22 test samples of ANN were used as the test set of PLS. The cross-validation procedure was applied for the selection of the number of factors. Each training data was used as validation set for the prediction, and the remaining data were employed for the training of PLS model. The optimal PLS factors of PLS models that established with O-PLS, SNV, first derivative, MSC preprocessed spectra and the original spectra were 1, 4, 4, 6 and 7, respectively, we could know that the number of PLS components in the O-PLS model was reduced to a single component, making the calibration model much easier. The RSE and *R* (correlation coefficient) of calibration and test sets were shown in Table 2. As can be seen, the RSE and *R* of both training set and test set of O-PLS model were the best, which was the same result as ANN models. Furthermore, the results of ANN models were much better than that of PLS models. The present results strongly validate the advantage of ANN approach to the problems in determination of pharmacological active compounds.

Table 1
Optimum parameters used for construction of PC-ANN and ANN models.

Model	Spectra	Input/output neurons	Hidden neurons	Momentum	Learning coefficient	Number of iterations
PC-ANN	Original spectra	7/1	16	0.200	0.150	3500
ANN	O-PLS pretreated spectra	50/1	12	0.100	0.100	4000
	First-derivative spectra	70/1	16	0.100	0.150	4500
	SNV pretreated spectra	70/1	14	0.200	0.100	4500
	MSC pretreated spectra	60/1	15	0.200	0.150	4000

Table 2
Linear regression parameters and RSE values of the optimal calibration models.

Model	Spectra	Set	Intercept	Slope	*R*	RSE (%)
PC-ANN	Original spectra	Training set	0.0055	0.9871	0.9990	1.3305
		Validation set	0.0055	0.9867	0.9986	1.4656
		Test set	0.0027	0.9918	0.9973	1.6354
ANN	O-PLS pretreated spectra	Training set	0.0054	0.9825	0.9992	1.1818
		Validation set	0.0037	0.9897	0.9988	1.3500
		Test set	0.0015	0.9951	0.9978	1.4827
	First-derivative spectra	Training set	−0.0001	0.9981	0.9986	1.4883
		Validation set	−0.0040	1.0050	0.9984	1.6356
		Test set	0.0022	0.9860	0.9971	1.7834
	SNV pretreated spectra	Training set	−0.0006	0.9983	0.9983	1.5568
		Validation set	−0.0014	1.0025	0.9976	1.6947
		Test set	0.0119	0.9614	0.9970	1.8920
	MSC pretreated spectra	Training set	0.0004	1.0007	0.9980	1.7268
		Validation set	0.0007	1.0062	0.9976	1.8779
		Test set	0.0127	0.9614	0.9967	2.0222
PLS	Original spectra	Training set	0.0094	0.9971	0.9962	2.3034
		Test set	−0.0191	1.0585	0.9918	3.4125
	O-PLS pretreated spectra	Training set	0.0109	0.9730	0.9983	1.8889
		Test set	−0.0074	1.0083	0.9967	2.5298
	First-derivative spectra	Training set	0.0107	0.9719	0.9980	2.0518
		Test set	−0.0049	1.0006	0.9954	2.7102
	SNV pretreated spectra	Training set	0.0057	0.9871	0.9970	2.1379
		Test set	0.0045	0.9661	0.9944	2.9677
	MSC pretreated spectra	Training set	0.0091	0.9747	0.9969	2.2282
		Test set	0.0161	0.9306	0.9928	3.1579

5. Conclusions

In conclusion, a new method that combines O-PLS with artificial neural network is introduced for non-destructive quantitative analysis of diclofenac sodium powder samples on the basis of NIR spectroscopy. The application of O-PLS greatly improved the stability of ANN model, and very satisfactory results were obtained with the proposed method. In addition, according to the results in Table 2, both the ANN model and the PLS model that based on O-PLS preprocessing have the smallest RSE and the best *R*, and compared with PLS models, ANN models can obtain much better results. Therefore, of all the optimal models, the O-PLS–ANN model is the best. Although the result of PC-ANN model is a little worse than that of O-PLS–ANN model, in PC-ANN model the scores of the principal components are chosen as input nodes instead of the original spectral data, thus the complexity of the model is greatly reduced and the training time is shortened, so the PC-ANN model is also an effective analytical tool.

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