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Short communication

Multivariate detection limits of on-line NIR model for extraction process of chlorogenic acid from *Lonicera japonica*

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ABSTRACT

A methodology is proposed to estimate the multivariate detection limits (MDL) of on-line near-infrared (NIR) model in Chinese Herbal Medicines (CHM) system. In this paper, *Lonicera japonica* was used as an example, and its extraction process was monitored by on-line NIR spectroscopy. Spectra of on-line NIR could be collected by two fiber optic probes designed to transmit NIR radiation by a 2 mm-flange. High performance liquid chromatography (HPLC) was used as a reference method to determine the content of chlorogenic acid in the extract solution. Multivariate calibration models were carried out including partial least squares regression (PLS) and interval partial least-squares (iPLS). The result showed improvement of model performance: compared with PLS model, the root mean square errors of prediction (RMSEP) of iPLS model decreased from 0.111 mg to 0.068 mg, and the R^2 parameter increased from 0.9434 to 0.9801. Furthermore, MDL values were determined by a multivariate method using the type of errors and concentration ranges. The MDL of iPLS model was about 14 ppm, which confirmed that on-line NIR spectroscopy had the ability to detect trace amounts of chlorogenic acid in *L. japonica*. As a result, the application of on-line NIR spectroscopy for monitoring extraction process in CHM could be very encouraging and reliable.

1. Introduction

With the issuing of the Process Analytical Technology (PAT) guidance for industry in September 2004, the FDA is encouraging pharmaceutical manufacturers to adopt new technologies during drug manufacturing process, mainly for timely assessment of critical products and their production process attributes [1]. In recent years, near-infrared (NIR) has been regarded as an excellent PAT tool for process monitoring in Chinese herbal medicine (CHM) [2–6]. It could provide rapid, non-destructive information collection with minimal or no sample preparation, and has been widely applied in the quantitative and qualitative analysis of CHM.

However, like each technique, NIR also has drawbacks. When used in CHM with complex chemical composition, overlapping absorption bands and low molar absorbance of signals may occur, leading to high detection limit and low sensitivity [7–10]. Admittedly, with the improvement upon the precision and sensitivity of equipment, it is now able for NIR spectroscopy to detect substance in low concentrations. However, it should be noted that the amount of active pharmaceutical ingredients (API) in most CHM is below 0.1%. Thus, an analysis method capable of determining the multivariate detection limits (MDL) will be beneficial for NIR applications in CHM.

The limit of detection (LOD) is one of the most significant values to assess an analytical method. A single equation is used to calculate LOD for a classical univariate calibration [11]. However, this LOD estimator is not generally accepted for multivariate calibration methods [12]. Among the proposals made so far, none has received general approval. This has become a point of interest and a review on the MDL of multivariate calibration methods has recently appeared.

Several approaches have been used to estimate MDL estimator using chemometrics [11,13,14]. Lorber was one of the first to calculate a MDL, starting from the definition of net analyte signal [15]. Subsequently, Lorber and Kowalski defined MDL estimator as a function of the confidence intervals associated with the predicted concentration [16]. Bauer et al. obtained an estimator that is a function of the error in the predicted concentration with the theory of error propagation [17]. Finally, for multivariate inverse calibration models, Boque et al. proposed a method for calculating MDL in the concentration domain of calibration model [18].

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Nevertheless, presently, there is no study to report the prediction performance of on-line NIR model with MDL parameter. At the same time, no literature has investigated the MDL of NIR analysis when complex herbal medicine system is involved. This article deals with the on-line NIR application in extraction process of *Lonicera japonica*. NIR spectroscopy, using a flange and two fiber optic probes, was applied to monitor the concentration of chlorogenic acid during the extraction process.

Calibrations of NIR data are often made by the partial least squares regression (PLS). Due to the fact that some variables, which are not related to the concentration of chlorogenic acid, might also be contained in PLS mode, the reliability of prediction results could be questionable. With theoretical and experimental evidence, spectral region selection has been recognized to have significant influence on model performance. Selection methods include some classical approaches [19], e.g. manual approach (knowledge based selection); sophisticated methods, e.g. uninformative variable elimination (UVE); elaborate search-based strategies, e.g. artificial neural networks (ANN) and genetic algorithms (GAs); and interval base algorithms, e.g. interval partial least squares (iPLS) [20], windows PLS and iterative PLS.

For iPLS model, an interval base algorithm for variables selection, Chen et al. investigated the total flavone content in snow lotus using NIR [21]; Shi et al. established a quantitative method for total flavonoids content in fresh Ginkgo biloba leaf with different colors using NIR [22]. In this work, the optimal iPLS model was also employed to predict the concentration of chlorogenic acid in real-time analysis. Furthermore, to highlight the accuracy of chemical information, the spectral region provided by iPLS model was validated by the assignment of band using deuterated solvent method. Finally, MDL result was obtained based on the on-line PLS and iPLS model to assess the detection capability of substances in low concentrations.

2. Materials and methods

2.1. Materials

L. japonica was purchased from Yabao Beizhongda Pharmaceutical Co., Ltd. (Beijing, China), and deposited in the Key Laboratory of TCM-information Engineering of State Administration of Traditional Chinese Medicine (No. 120322, No. 120401). Chlorogenic acid reference standard (lot number: 110777-201005) was supplied by the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). HPLC grade methanol was purchased from Tedia (USA). Deionized water was purified by Milli-Q water system (Millipore Corp., Bedford, MA, USA).

2.2. Extraction process and sampling

Extraction of *L. japonica* was carried out in a 100 L extractor, which was located at a pilot-scale lab (Pharmaceutical Engineering and New Drug Development of TCM of Ministry of Education, China). 3 kg of the *L. japonica* was soaked in 30 kg of water at room temperature for 30 min, and then heated to 100 °C for 30 min. The whole extraction process took about 1 h to complete. During the whole extraction process, stirring paddle was kept running at a speed of 50 rpm.

During the extraction process, NIR spectra of extracts were collected on-line. 5 mL samples were also taken by a sample cup at regular intervals, and analyzed with the same parameters by HPLC assays. In order to obtain similar prediction accuracy and trend of various concentrations, it was necessary to ensure uniform distribution of samples. Hence, samples were collected at 5 min interval in the soaking process, and at 3 min interval in the heating process. In this study, 60 samples were obtained in whole extraction process (Batch A), which were used as a calibration set for the model development. New data provided by the second extraction process were performed for the external validation of the models (Batch B).

2.3. NIR equipment and software

The on-line NIR spectra were collected by two fiber optic probes, which were designed to transmit NIR radiation by a 2 mm optical path flange that was connected to a XDS process analyzer (Foss NIR Systems, Silver Spring, MD, USA). Each spectrum was the average of 32 scans with a wavelength increment of 0.5 nm. The range of spectra was from 800 nm to 2200 nm. On-line NIR spectra have been found to be susceptible to air bubble, solid impurities, temperature, etc. [23,24]. To avoid the influence of solid impurities, the liquids need to pass through a 100 μm strainer before entering the optical path flange.

Data analysis was performed with the VISION software (Foss NIR Systems, Silver Spring, MD, USA) and home-made routines programmed in MATLAB code (MATLAB v 7.0, The MathWorks, MA). The toolbox of iPLS model used to select the most informative variables was downloaded from http://www.models.kvl.dk/.

2.4. HPLC methods

Chromatographic analysis was primarily performed by an SHIMADZU HPLC apparatus, which was comprised of a LC-20AT system, an auto-sampler, a column temperature controller and a diode-array detector (DAD) (SHIMADZU Corporation, Japan). Samples were primarily separated on a Sunfire-C18 column (150 mm × 4.6 mm; 5 μm particles, Waters Columns, USA) at 30 °C using acetonitrile and water containing 0.4% phosphoric acid (13: 87, v/v) as mobile phase. The detection wavelength was set to 327 nm.

3. MDL theory

The theory of MDL used in this article is briefly described as below. A more detailed description and the process used to derive the mathematical equations can be found in the references [11,25,26]. This section consists of four subsections: (1) calibration models; (2) detection limits for linear calibration (against type I error); (3) detection limits for linear calibration (against both type I and type II error); (4) MDL for multivariate calibration model (against both type I and type II error).

3.1. Calibration models

A model of observed response Y is necessary to formulate the detection capability and its behavior in repeated applications based on the analyte concentration X. Here we assume that when $X = x$

$$Y_x = a + bx + \varepsilon \quad (1)$$

where ε is normally distributed with mean zero and variance σ^2 for all x. Observational errors in determinations of Y_x are assumed to be independent.

Under the distributional hypothesis that has been assumed, the estimated $\hat{y}$, at a concentration x of analyte, is a Student's t-distribution with $(n-2)$ degrees of freedom, whose mean and variance are

$$E(\hat{y}) = \hat{a} + \hat{b}x \quad \text{and} \quad \mathrm{Var}(\hat{y}) = \omega_x^2 \hat{\sigma}^2 \quad (2)$$

The ω_x is defined as:

$$\omega_x^2 = \frac{1}{r} + \frac{1}{n} + \frac{(x-\bar{x})^2}{\sum_{i=1}^{n}(x_i-\bar{x})^2} \quad (3)$$

where r is the number of measurements on a calibration sample, and $\hat{\sigma}$ is the standard deviation of regression.

$$\hat{\sigma}^2 = \frac{\sum_{I=1}^{I}(y_i-\hat{y})^2}{I-2} \quad (4)$$

3.2. Detection limits for linear calibration (against type I error)

For mathematical Eq. (1), traditional techniques for determining detection limits have only been concerned with providing protection against type I errors or false positive conclusions.

$$\alpha = \mathrm{pr}\left\{Y > y_p/x = 0\right\} \quad (5)$$

where y_p is a threshold value of the response variable.

With the hypothesis of Eq. (1) it follows that the distribution of a false positive is a Student t, with $(n-2)$ degrees of freedom, mean $\hat{y}_0 = \hat{a}$, and variance $\omega_0^2\hat{\sigma}^2$. Thus, Eq. (4) allows one to determine y_p for the significance level α

$$y_p = \hat{a} + \omega_0\hat{\sigma}t_\alpha \quad (6)$$

where t_α is the one-sided threshold value of a Student's t with $n-2$ degrees of freedom at level α.

3.3. Detection limits for linear calibration (against both type I and type II error)

Furthermore, it is apparent that the false negative rate can be computed by any $x > 0$.

$$\beta = \mathrm{pr}\left\{Y \le y_p/x > 0\right\} \quad (7)$$

β is a function of x, that is, it depends on how much the true concentration x differs from the null concentration (y_0).

$$\beta = \mathrm{pr}\left\{Y - \hat{a} > \omega_0\hat{\sigma}t_\alpha/x = 0\right\} = \mathrm{pr}\left\{\frac{Y-\hat{y}_0}{\omega_0\hat{\sigma}} > t_\alpha\right\}$$
$$= \mathrm{pr}\left\{t_{(\Delta)} > t_\alpha\right\} \quad (8)$$

where $t(\Delta)$ is a non-central Student's t-distribution with $(n-2)$ degrees of freedom, an estimated mean $\hat{y}_0$ and a parameter of non-centrality Δ which is a function of α and β

$$\Delta_{(\alpha,\beta)} = \frac{Y-\hat{y}_0}{\omega_0\hat{\sigma}} \quad (9)$$

3.4. MDL for multivariate calibration model (against both type I and type II error)

The MDL can be calculated easily from Eqs. (1) and (9).

$$x_d = \frac{\Delta_{(\alpha,\beta)}\omega_0\hat{\sigma}}{\hat{b}} \quad (10)$$

When applying a multi-way calibration model (principal components regression (PCR), PLS), MDL is defined as a function of the variance of the concentration predicted by the model [27]:

$$\mathrm{MDL}_K = \Delta_{(\alpha,\beta)}\,\mathrm{Var}\,(x_0, k)^{1/2} \quad (11)$$

where $\mathrm{Var}(x_0, k)$ is defined as estimated variance at 'zero concentration level':

$$\left[(1+h)\,\mathrm{MSEC} - \sigma_c^2\right] \quad (12)$$

h is the leverage of the sample in the calibration space; $\sigma_c{}^2$ is the variance of the concentrations in the reference method; MSEC is the mean square error of calibration.

Therefore, when we consider the false positive and false negative errors, the MDL of on-line NIR model can be obtained.

4. Results and discussion

4.1. Quantitative analysis of chlorogenic acid by HPLC method

HPLC method adopted to determine chlorogenic acid content in *L. japonica* was carried out as guided in Chinese Pharmacopoeia (ChP) [28]. Supplementary data show typical HPLC chromatograms of extration solution. The retention time of the chlorogenic acid in the sample solution was the same as reference standard solution. The calibration curve of the HPLC method was drawn before actual sample analysis. The calibration curve exhibited good linearity (Y = 115418.46 X–6984.37, R^2 = 0.9999) within the content range (7.92×10^{-2} μg–0.792 μg).

4.2. Comparison of different spectral pretreatment methods

The raw NIR spectra of sample solutions were also shown in supplementary data. As we can see in the raw spectra, large fluctuations appeared in the region of combinations and first combination overtone for NIR spectra. Furthermore, the result of spectral preprocessing treatments showed that noise significantly affected the region of combinations (Supplementary data). Therefore, to improve the accuracy of PLS model, the spectral region of 800–1900 nm was selected in follow analysis.

For PLS model, it is generally known that the number of latent factors is a critical parameter. The optimum number of latent factors is determined by the lowest RMSECV (root mean squared error of cross-validation, a segment size of five) and RMSEP (root mean square errors of prediction). Table 1 shows the model performance for determining chlorogenic acid contents vs. different spectral preprocessing methods. The results indicated that the calibration model constructed with raw spectra exhibited the best performance. The calibration gave RMSECV and R^2 value of 0.048 mg/mL and 0.9313, respectively. In the validation process, the RMSEP and R^2 were 0.101 mg/mL and 0.9431, respectively.

4.3. Variable selection using iPLS model

Variable selection emerges as a critical step to improve model performance, as it allows interactive improvement of data quality during the calibration procedure. The goal of variable selection is to identify a subset of spectral frequencies which produce the smallest possible errors in quantitative determinations. The iPLS model was developed on spectral subintervals of equal width, and the prediction performance of these local models was compared with the global (full-spectrum) model. The comparison was mainly based on the RMSECV parameter [29].

The data set of full-spectrum was splited into different intervals. The optimal interval numbers were selected according to the lowest RMSECV. The results showed that 10 equidistant subintervals were the best choice. The bar plots of Fig. 1 indicated that interval number 7 (1640–1779.5 nm) with 6 latent variables produced models with better performance than the full-spectrum model with 8 latent variables.

The characteristic second derivative spectra of chlorogenic acid were assigned by deuterated DMSO solutions. According to Fig. 2, the characteristic absorbance of 1650–1800 nm was assigned for the chlorogenic acid. This band was consistent with the interval number 7 from iPLS model. The result demonstrated that variable

Table 1
The result for PLS model with different pre-processing methods.

Pretreatment	Latent factors	Calibration set		Validation set		Prediction set	
		R^2	RMSEC	R^2	RMSECV	R^2	RMSEP
Raw	6	0.9861	0.048	0.9313	0.048	0.9431	0.101
1D	4	0.9624	0.079	0.2674	0.364	0.3171	0.466
2D	3	0.9215	0.115	0.3318	0.341	0.4222	0.325
SG	3	0.8555	0.156	0.3254	0.325	0.3023	0.350
SNV	5	0.9835	0.053	0.9255	0.115	0.9423	0.101
Mean center	6	0.9861	0.048	0.9294	0.048	0.9398	0.107

[a]Raw: raw spectra, 1D: first derivative, 2D: second derivative, SG: Savitzky–Golay, SNV: standardizing normalization vector

Table 2
MDL obtained from PLS model and iPLS model for different error types (mg/mL).

Method	$\Delta_{0.1,0.1}$	$\Delta_{0.1,0.05}$	$\Delta_{0.1,0.01}$	$\Delta_{0.05,0.1}$	$\Delta_{0.05,0.05}$	$\Delta_{0.05,0.01}$	$\Delta_{0.01,0.1}$	$\Delta_{0.01,0.05}$	$\Delta_{0.01,0.01}$
PLS	0.028	0.032	0.039	0.032	0.036	0.044	0.040	0.044	0.052
iPLS	0.011	0.013	0.015	0.013	0.014	0.017	0.016	0.017	0.020

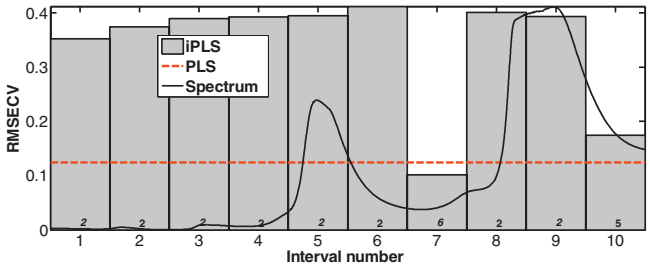

Fig. 1. Cross-validated prediction errors (RMSECV) for 10 interval models (bars) and full-spectrum model (red dotted line) versus interval number for 1–6 latent variables of the localized models and 8 latent variables of the global model. The interval represents different wavelength ranges ("1", 800–939.5 nm; "2", 940–1079.5 nm; "3", 1080–1219.5 nm; "4", 1220–1359.5 nm; "5", 1360–1499.5 nm; "6", 1500–1639.5 nm, "7", 1640–1779.5 nm, "8", 1780–1919.5 nm, "9", 1920–2059.5 nm and "10", 2060–2199.5 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

selection using iPLS model was accurate, and could be used for extracting chemical information of chlorogenic acid.

4.4. Model performance and MDL

Fig. 3 illustrates the calibration and prediction regressions for PLS model and iPLS model. Implementation of variable selection showed the improvement of model performance, for the RMSEP of iPLS model (0.068 mg/mL) turned out to be smaller than that of PLS model (0.111 mg/mL), while the R^2 parameter of iPLS model (0.9801) was higher than that of PLS model (0.9434).

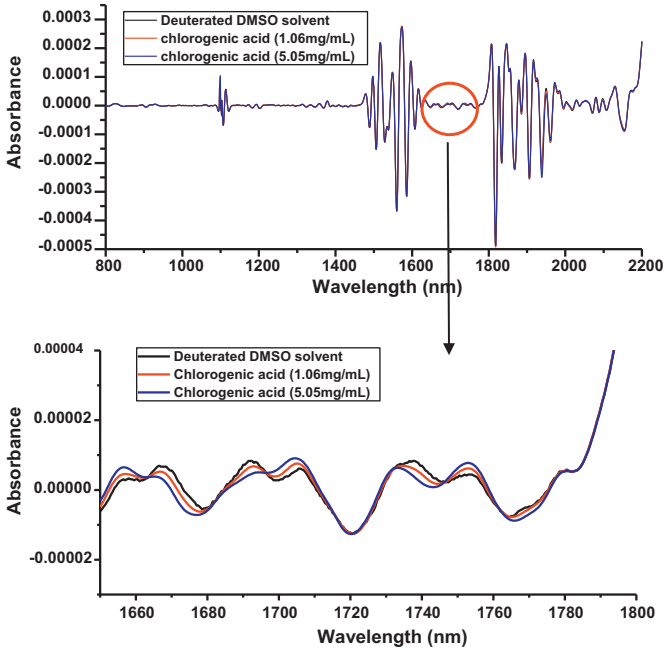

Fig. 2. NIR band assignments of chlorogenic acid compound in deuterated solution.

Once each on-line model was obtained from Fig. 3, MDL was calculated using Eq. (11). Besides investigating whether or not the chlorogenic acid can be detected, measures should also be taken to prevent false positive (probability of type I error, α) and false

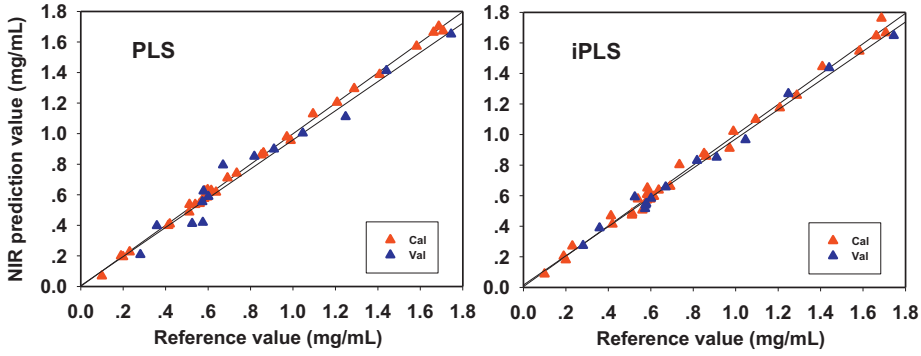

Fig. 3. Chlorogenic acid NIR predictions versus the reference method results. *X* axis represents the result of reference method; *Y* axis represents NIR prediction value. (a) PLS model and (b) iPLS model.

negative (probability of type II error, β) errors. Table 2 shows that MDL result depended on the range of concentration and the type of errors, and iPLS model enjoyed better accuracy performance than PLS model. Secondly, for a calibration set ranging from 0.2 mg/mL to 2 mg/mL (w/w), its MDL of on-line iPLS model was 14 ppm when taking into account both error α (0.05) and error β (0.05) (target acceptance criteria, 2% (bulk drug), 5% (dosage form) and 15% (bio-analysis)). The results showed that liquids with chlorogenic acid content of 14 ppm could be reliably detected by NIR (with proper quality prediction parameters).

5. Conclusion

According to the MDL result, on-line NIR spectroscppy is a promising technology for detection of low-concentration analyte and it should be highly recommended. The fiber optic probes allowed on-line process monitoring of the extracts passing through the flange. The on-line NIR calibration models developed were successfully applied to monitor the extraction process of *L. japonica* in real-time. According to the results obtained in this work, NIR spectroscopy allowed detection of minor analytes (MDL around 14 ppm) and can be applied, with success, to the quality control of *L. japonica*.

Given the promising results reported herein, further work should be carried out to adopt on-line NIRS technology in manufacturing processes and develop sound methods for rapid detecting of API in CHM.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jpba.2012.12.026.

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