Quality determination of *Coptis chinensis* (Franch. 1897) by Fourier transform near infrared spectroscopy

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Introduction

Coptis chinensis (Franch. 1897) has a range of pharmacological activities including antibacterial, antitumor and antiarrhythmic effects and it has been used widely in clinics to inhibit influenza. Furthermore, *Coptis chinensis* is used to treat gastrointestinal and upper respiratory infections, hypertension, bone-joint tuberculosis and anal fissure.[1] The main active component of *Coptis chinensis* is berberine, an isoquinoline alkaloid $[C_{20}H_{18}NO_4]^{+5}$. Traditional methods for determining berberine concentration are destructive, i.e. high-performance liquid chromatography (HPLC), atomic emission spectrometry (AES) and polarographic catalytic wave (PCW).[2-4] The standard method for determining the moisture content of *Coptis chinensis* is also destructive. These factors emphasise the need for a reliable technique to quickly and non-destructively analyse *Coptis chinensis*.

Previous near infrared (NIR) spectroscopic studies of berberine in *Coptis chinensis*[6,7] did not determine moisture content which is an important quality index of traditional Chinese medicine. Here, we assess the quality of *Coptic chinensis* with regard to both berberine and moisture content according to the traditional Chinese medicine standard.

Materials and methods

Sample preparation

Samples (n = 108) of *Coptis chinensis* and a related species were studied, including *Coptis chinensis* and *Coptis deltoidea* (C. Y. Cheng et Hsiao) from Chongqing ShiZhu and *Coptis chinensis* from HuBei, China. According to the distinctness of their taxonomy and geography, samples were classified into three levels. All samples were crushed into a suitable particle size and their NIR spectra were collected. One sample was randomly-selected and crushed with five sieves of different mesh sizes (16, 40, 70, 100 and 120 mesh). Their NIR spectra were collected and it is demonstrated that the absorbance of samples reduced gradually with the decrease of the particle size and the effects of particle size through a 100 or 120 mesh sieve on the absorption spectra were almost uniform.Therefore according to principal component analysis, the *Coptis chinensis* processed through the 100 mesh sieve were fit for the experiment. The calibration set contained 78 samples and the prediction set contained 30 samples.

Laboratory reference method

Berberine: 2.0 g were removed from each crushed sample and immersed in 100 ml deionised water for 1 hour. Samples were ultrasonically extracted (SB-5200D, Ningbo Xinzhi biological Polytron Technologies Inc, Zhejiang, China) for 1 hour, centrifuged at 12000 rpm for 40 min (Z323K, HERMLE, Germany, Beijing, LABSUN CHINA) and filtered. Berberine concentrations in samples were determined spectrophotometrically from the absorption at 336 nm in berberine standards (U-3010, Hitachi, Japan)[1]. Moisture: 2.0 g removed from each crushed sample were weighed. Samples were then dried in 100°C for 3 hours with a thermostatic drying chamber (101, Shangyu Hunan Electric Factory, Zhejiang, China), cooled,

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and reweighed.[1] Mass difference was considered as moisture loss.

NIR spectra collection

NIR spectra were collected in transmission mode using an FT-NIR spectrometer (VECTOR 22/ N, Bruker Optics, Ettlingen, Germany). Spectra were collected between 4000 and 10000 cm^{-1} at 4 cm^{-1} intervals and each spectrum was obtained by averaging 64 scans.

Software analysis

The calibration model for determining berberine and moisture in *Coptis chinensis* was built with OPUS 5.5 (Bruker Optics, Ettlingen, Germany). The spectral pre-treatment method and number of principal components (PCs) were chosen based on the highest determination coefficient (R^2) of the calibration model and the lowest root mean square of cross-validation (RMSECV) calculated by the software. The overall predictability of each calibration model was expressed in terms of root mean square error of cross-validation (RMSECV) and root mean square error of prediction (RMSEP).[8-10]

Results and discussion

NIR spectra of calibration set samples

The most informative spectral region for quantitative analysis was between 7000 and 4000 cm^{-1} (Figure 1). The information contained in this spectral region included stretching vibrations for C-H in $–CH_3$, C-H in $–CH_2$, C-H in $CH_a=CH_b$ and O-H in H_2O[11].

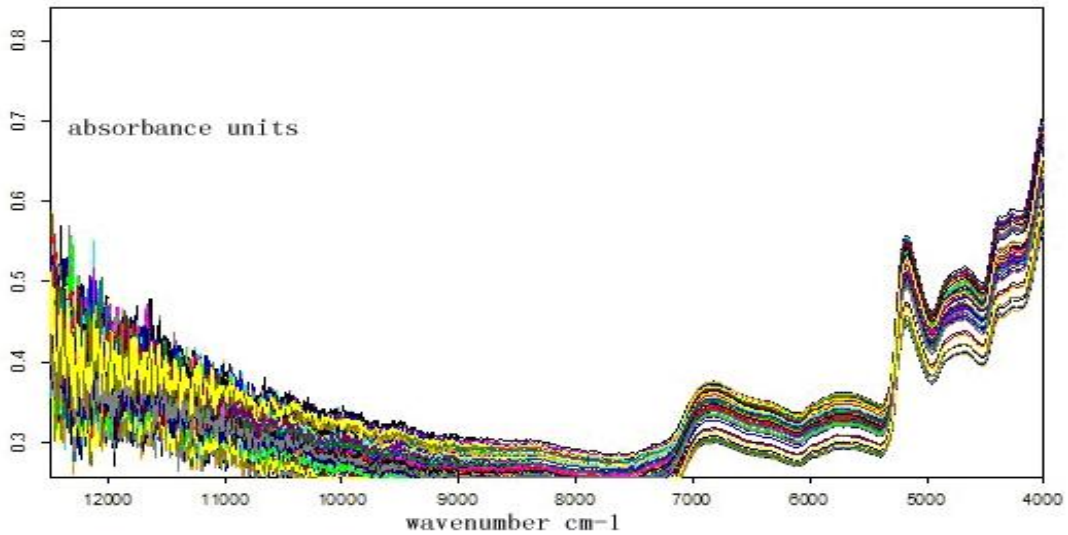

Figure 1. NIR spectra of the calibration set samples.

Choice of spectrum pre-treatment method

Spectra contain signal and noise. Noise may be introduced from scattered or stray light and instrument errors,which lead to baseline drift and irreproducible spectra. Calculating a derivative can mitigate baseline drift and discriminate overlapping peaks but may adversely amplify spectral noise. The selction of a pre-treatment method should be carefully considered; several methods were compared in this experiment (Table 1). First derivative and vector normalisation produced the best models in this experiment (Table 1).

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Table 1. Comparison of model effect with different pre-treatment method.

	Berberine			H_2O		
	R^2	RMSECV	PCs	R^2	RMSECV	PCs
First derivative and vector normalisation	0.9298	0.239%	6	0.8898	0.302%	8
Multivariate scattering correction	0.9125	0.241%	8	0.8201	0.480%	8
Min-max normalisation	0.8909	0.239%	7	0.8421	0.902%	8

Determination of loadings in model development

The number of loadings in the PLS model was very important; using too few would generate an underfitted model and using too many would incorporate noise into the model.

External verification of model

A prediction set containing 30 *Coptis chinensis* samples was used to test the model.. The standard error of prediction (SEP) for berberine and H_2O were 0.104% and 0.330%, respectively and the R^2 of berberine and H_2O were 93.47% and 91.46%, respectively (Figures 2 and 3). The experimental results were credible.

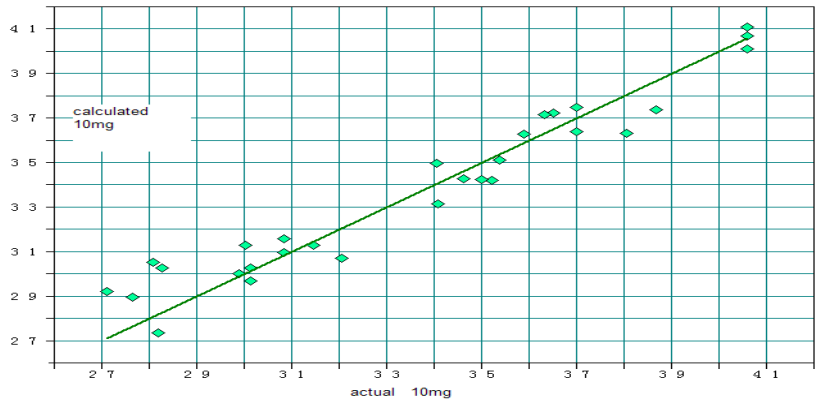

Figure 2. Correlation of predicted and actual berberine concentrations in samples.

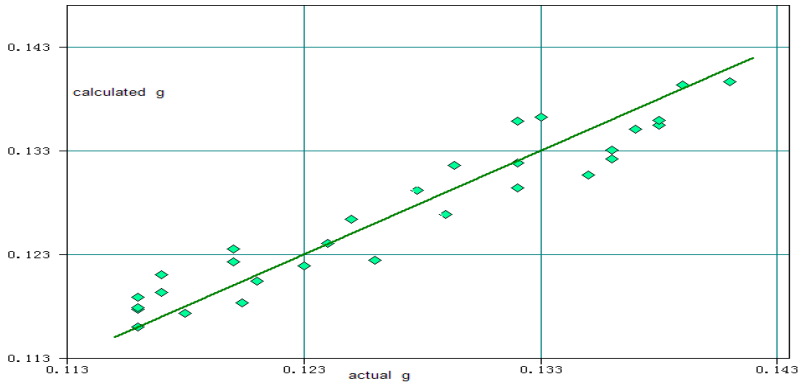

Figure 3. Correlation of predicted and actual moisture content in samples.

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Test results of major constituents in *Coptis chinensis*

Berberine concentrations varied taxonomically such that *Coptis chinensis* had higher concentrations than *Coptis deltoidea* (Table 2). Berberine concentration also varied geographically, with *Coptis chinensis* from ShiZhu featuring higher amounts than *Coptis chinensis* from HuBei. Furthermore, the grade of *Coptis chinensis* was independent of berberine content. The medical value of *Coptis chinensis*, defining different grades, was not linked to berberine content.

Table 2. Test results of major constituent in different kinds of *Coptis chinensis*.

	berberine（%）	H_2O（%）
Coptis chinensis (ShiZhu)	4.971–5.916	6.0–7.1
Coptis deltoidea (ShiZhu)	3.807–4.578	5.3–6.3
Coptis chinensis (HuBei)	4.564–5.311	6.6–7.1

Conclusions

Near infrared spectroscopy can be used to quantify berberine and moisture in *Coptis chinensis*. In particular, NIR dramatically reduced the time and cost of chemical assessment, and removed the need for chemical reagents inherent to traditional HPLC analyses. The NIR method described here would be suitable for on-line detection in pharmaceutical companies.

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