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Rapid authentication of starch adulterations in ultrafine granular powder of Shanyao by near-infrared spectroscopy coupled with chemometric methods

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ABSTRACT

Near-infrared reflectance (NIR) spectroscopy combined with chemometric techniques was developed for classification and quantification of cheaper starches (corn and wheat starch) in ultrafine granular powder of Shanyao (UGPSY). By performing orthogonal partial least squares discrimination analysis (OPLS-DA), NIR could efficiently distinguish among authentic UGPSY and UGPSY adulterated with cornstarch and wheat starch. In addition, the starch content in adulterated UGPSY was determined by NIR coupled with an appropriate multivariate calibration method. Partial least squares (PLS), interval PLS (iPLS) and synergy interval PLS (siPLS) algorithms were performed comparatively to calibrate the regression model. Experimental results showed that the performance of the siPLS model is the best compared to PLS and iPLS. These results show that the combination of NIR spectroscopy and chemometric methods offers a simple, fast and reliable method for the classification and quantification of the ultrafine granular powder of the herb.

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1. Introduction

Shanyao (the Chinese name) is the rhizome of *Dioscorea opposite* Thunb., which is a Chinese yam that is rich in many chemical components such as mannan, allantoin, dopamine, ergosterol, phytic acid, amino acids, glucoprotein, choline, saponins, starch and non-starch polysaccharides (Ma et al., 2005; Mishra & Gaikar, 2004; Yang, Lu, & Hwang, 2003). Shanyao not only is a familiar edible vegetable in China that exhibits multiple nutritional properties but also has been used as a traditional Chinese medicine for the treatment of diabetes, diarrhoea, asthma and other ailments (Pharmacopoeia Commission of PRC, 2015).

Ultrafine granular powder of the herb (UGPH) is the latest category of food and Chinese medicines in recent years. UGPH is popular with people because of its advantages of better absorption and convenient intake by breaking the plant cell wall. The determination of food and drug authenticity and the detection of adulteration are major issues in the food and drug industry, and the safety and quality parameters of UGPH are important because this herb is widely used for health and commercial purposes. Consumption of the ultrafine granular powder of Shanyao (UGPSY) is very extensive due to its nutritious and therapeutic properties, and Shanyao is prone to adulteration with other cheaper materials such as cornstarch and wheat starch. Adulteration of UGPSY results in degradation of its nutritional, physiochemical and medicinal properties and creates not only economical loss but also health hazards. Consequently, the discrimination of authentic and adulterated UGPSY becomes a very important issue for producers, retailers, consumers and regulatory authorities. Many analytical techniques such as microscopic identification of the characteristics of Shanyao (Cheng et al., 2014), HPLC-PAD analysis (Kwon et al., 2013), structural analysis combined with mass spectrometry (Tsai et al., 2013) and several DNA-based marker systems (Mignouna, Abang, & Fagbemi, 2003) have been used to detect adulteration and the origin of the Shanyao or yam. However, most of the analysis methods mentioned above are laborious, expensive, destructive, time consuming and environmentally unfriendly. Thus, it is imperative to develop a simple, rapid, inexpensive and highly effective method for authentication and detection of UGPSY products.

Trends in analytical chemistry are towards simpler and less time-consuming analytical methods. Near-infrared (NIR) spectroscopy has been shown to be a rapid, simple, non-destructive and effective analytical tool and has been widely used for qualitative and quantitative analyses of food (Zhang et al., 2014) and pharmaceutical commodities (Woo, Kim, Ze, & Chung, 2005). NIR spectroscopy records the spectral bands that mainly correspond

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to C—H, O—H and N—H vibrations, which are overtone and combination bands, and an NIR method was constructed to identify the origin of the yam (Gong, Bai, Song, & Chen, 2010).

Chemometrics offers greater possibilities to analyse a very large amount of data obtained by different analytical techniques (De Luca et al., 2011). With the evolution of chemometrics, NIR is gaining strong acceptance in the area of food science and technology. To reveal the relevant information in the data obtained using the multivariate spectroscopic techniques, different chemometric methods need to be applied. Orthogonal partial least squares discrimination analysis (OPLS-DA) was introduced as an improvement of the PLS-DA method to discriminate between two or more groups (classes) using multivariate data (Bylesjo et al., 2006). The advantage of OPLS-DA compared to PLS-DA is that a single component is used as a predictor for the class, while the other components describe the variation orthogonal to the first predictive component (Westerhuis, van Velzen, Hoefsloot, & Smilde, 2010). In addition, partial least square (PLS) regression is the most popular multivariate calibration technique to build prediction models using spectroscopic signals. NIR combined with chemometric tools in food and pharmaceutical science has been used to identify adulteration such as lotus root powder adulterated with cheaper starches (Xu, Shi, Ye, Yan, & Yu, 2013), Soya bean products adulterated with melamine (Haughey, Graham, Cancouet, & Elliott, 2013), the adulteration of extra virgin olive oil (Mignani et al., 2011), pure onion powder and starch adulteration (Lohumi et al., 2014) and notoginseng powder and its adulterants (Nie et al., 2013). However, to the best of our knowledge, there is no information available on the use of NIR combined with chemometrics for determination and quantification of adulterants in UGPSY.

Currently, the main problem of NIR spectroscopy with multivariate analysis is to select target wavelengths, especially when the spectra display unresolved peaks or fail to identify important features. To remove irrelevant spectral variables and to improve model performance, various approaches have been investigated to select the optimal variables for multivariate calibration. One of these methods is called interval partial least squares (iPLS) (Leardi & Nørgaard, 2004; Nørgaard et al., 2000). Interval partial least squares can provide an overall picture of the relevant information in different spectral subdivisions, thereby focusing on important spectral regions and removing interference from other regions. However, the exclusion of interference from other regions would lose useful information. Thus, another method called synergy interval partial least square (siPLS) has been proposed by Nørgaard to select the combination of several intervals of spectral data and then develop a PLS model (Abrahamsson, Johansson, Sparén, & Lindgren, 2003).

Given the limited effort devoted to the investigation of rapid techniques for the determination of UGPSY with adulterants, the major objective of this study was to establish a qualitative and quantitative analysis of UGPSY adulterated with cornstarch and wheat starch by using NIR spectroscopy and chemometric tools. The specific aims of this paper were to (1) establish a classification model with the OPLS-DA method to classify adulterated and authentic UGPSY samples, (2) develop an NIR calibration model with the PLS method to accomplish the adulterant analysis and (3) select which spectral wavelengths may be best suited for the adulterant quantification using the iPLS and siPLS methods.

2. Material and methods

2.1. Pure and adulterated UGPSY samples

Two batches of 40 pure and authentic UGPSY samples and intermediate ultrafine powder of Shanyao were produced by Zhongshan Zhongzhi Pharmaceutical Group Co., Ltd., and the cornstarch and wheat starch were obtained from a local market in Zhongshan. Cornstarch and wheat starch were used as the adulterant in UGPSY because of their cheap prices, similar physical properties and lack of significant effects on human health. All samples including pure intermediate ultrafine powder of Shaoyao, cornstarch and wheat starch were dried in an oven at 45 °C overnight. After drying, 192 adulterated ultrafine powders of Shanyao were prepared by mixing the above cornstarch and wheat starch with pure intermediate ultrafine powder of Shaoyao to final concentrations (w/w) of 10%, 20%, 25%, 30%, 40%, 50%, 55%, 60%, 70%, 75%, 80% and 95%, with eight samples for each level, and then each mixture was manufactured into different adulterated UGPSY samples according to the manufacturing process of UGPSY. All authentic UGPSY samples and different adulterated UGPSY samples were powdered to a homogeneous size by a mill and sieved through a No. 80 mesh, and sample quantities of approximately 50 mg were prepared for the NIR study.

2.2. Collection of NIR spectra and pre-processing

NIR reflectance spectra of pure and adulterated UF powder samples were recorded with a Luminar 5030 AOTF-NIR spectrometer (Brimrose, USA). The samples containing approximately 25 mg were loaded on a circular sample cup and pressed slightly to obtain a similar packing density. A total of 32 successive scans for both the reference and each sample were collected over the wavelength range of 1100–2300 nm at 2-nm intervals. Averaged spectra were used for analysis.

Raw spectra acquired from the NIR spectrometer contained background information and noise in addition to sample information. Different data pre-processing techniques were studied to obtain reliable, accurate and stable models, including smoothing, derivative, standard normal variate (SNV) transformation, mean centring (MC) and multiplicative scatter correction (MSC). Both smoothing and derivatives were computed by MSC to obtain reliable qualitative classification and quantitative calibration models.

2.3. Chemometric analysis

2.3.1. Classification with OPLS-DA

After pre-processing, the exploratory principal component analysis (PCA) was performed to acquire general insight and visualize the trends and outliers among all samples.

Then, classification analysis was applied with OPLS-DA. OPLS-DA is an extension of the supervised partial least squares (PLS) regression method that manages to increase the quality of the classification model by separating the systematic variation in X into two parts, one that is linearly related to Y (predictive information) and one that is unrelated to Y (orthogonal information) (Trygg, Holmes, & Lundstedt, 2007). The Kennard-Stone algorithm (Daszykowski, Walczak, & Massart, 2002; Grasel & Ferrão, 2016; Kennard & Stone, 1969) was applied for the selection of training and test samples separately in three classes. Thus, the samples were split into 157 (29 pure samples, 64 samples adulterated with cornstarch and 64 samples adulterated with wheat starch) for the training subset and 75 (11 pure samples, 32 samples adulterated with cornstarch and 32 samples adulterated with wheat starch) for the test subset. In the case of the two subsets studied (adulterated and unadulterated samples), a dummy matrix (Y block) was created containing the value 0 for the unadulterated samples, 1 for the samples adulterated with cornstarch and 2 for the samples adulterated with wheat starch. The regression models have been validated using cross validation-analysis of variance (CV-ANOVA), with a P-value < 0.05. Permutation testing was applied (100 permutations) to check the validity and the degree of overfit for the

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