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Detection of Corn and Whole Wheat Adulteration in White Pepper Powder by Near Infrared Spectroscopy

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Abstract White pepper is a high-value commodity that is a target for adulteration, leading to loss of quality and encroachment on the rights and interests of consumers. Therefore, it is imperative to develop fast and reliable methods for detecting white pepper powder adulteration. The present paper investigated the feasibility of using near infrared (NIR) spectroscopy for quantifying adulteration (including whole wheat flour and corn flour) in white pepper powder. Partial least squares (PLS) calibration models were developed. Results showed that the standard error of calibration (SEC) and prediction (SEP) were 0.788% and 0.920%, respectively.

Keywords: *white pepper powder adulteration, NIR spectroscopy, PLS calibration models, whole-wheat flour, corn flour*

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1. Introduction

Pepper is a member of the spice family. In addition to the main component of pepper piperine, it also contains of aromatic oils, starch, crude protein and soluble nitrogen [1,2,3]. Since being introduced to China in 1947, pepper has become one of the most popular spices in China, and is widely planted in the southeast provinces of Hainan (over 80% of the total output), Guangdong, Yunnan and Guangxi [2,3]. In recent years, a wide number of varieties of pepper are available in the market, and white pepper takes a large part of the market. White pepper powder is made of nearly mature pepper plant by peeling, soaking and blanching. It is one kind of spice that has high nutritional and medical values [4,5,6] (such as having certain curative effect on vitiligo and myocardial ischemia), therefore, white pepper powder owns a broad market prospect.

Nowadays, food adulteration has become a common and serious problem in many countries, and adulteration of white pepper powder with lower value materials such as corn and wheat being used as adulterants. Because adulteration of white pepper powder in these forms may be difficult to distinguish by sense due to the similar colour and small particle size, it has become a problem that affects both the quality and potentially the safety of the product, as well as encroaching on the rights and interests of consumers. Besides, there are no relevant national standards for the rank of pepper in China [3], a real-time, low-cost and convenient detection method is in need.

Currently, chemical methods such as supercritical fluid extraction can be used to detect the adulteration of peppers [7,8,9,10]. However, these analytical methods may not be convenient for routine sample analysis or require a certain degree of expertise. In some cases, chemical standards may be rare or expensive or lack identifiable markers. Thus, there is still a need to develop a fast, chemical-free, and cost-effective method for the detection of adulteration of white pepper powder. Near infrared (NIR) spectroscopy primarily reflects absorption of overtones and combination of vibrations of X-H functional groups (such as C-H, O-H, and N-H). Because of weak absorption strength, most of samples can be measured directly without pre-processing, moreover, NIR analysis has the advantage of rapid determination, non-pollution, low cost and being non-destructive, and is commonly used in many areas, including agriculture, food, environment, bio-medicine and pharmaceuticals [11-22]. It was shown that satisfactory results were achieved in food adulteration detection carried out by NIR spectroscopy in such foods as milk, oil, onion [11,17,19]. However, white pepper powder adulteration detection using NIR is a novel application.

The aim of this study was to show the possibility to apply NIR to determine the adulteration in white pepper powder. Whole wheat flour and corn flour were used as adulterants according to the actual situation. Partial least squares (PLS) regression combined with NIR spectroscopy was employed for the quantitative detection of white pepper powder adulteration.

2. Materials and Methods

2.1. Instrument

A laboratory NIR spectrometer (NIR B603, Boer instrument (Tianjin) CO., LTD, China) was employed throughout. The instrument operates in the 1300-2600nm range, with a spectral resolution of 8nm. The instrument uses tungstem radiation source to illuminate samples for diffuse reflectance measurements, and adopts an InGaAs sensor for detection. The lamp was allowed to warm up for 30min before use. A rotary sample cell with 6.5cm diameter was used for sample presentation. Self-calibration was undertaken before measurements, and spectral data acquisition was an average of 30 scans.

2.2. Samples

As this paper was a confirmatory study of using NIR to detect the adulteration percentage of white pepper powder, only one sample of pure white pepper powder was used to obtain adulterated samples. The pepper powder was produced in Lingshui Li Autonomous County, Hainan, China. And the adulterants including whole wheat flour and corn flour were produced in Shandong, China.

In order to present the diversity of pepper adulteration in the market, adulterants were made in five categories, respectively: corn flour, whole-wheat flour and the mixture of corn flour and whole-wheat flour in three kinds of proportions (1:1, 1:2 and 2:1). Then adulterated samples were obtained with pure white pepper and each adulterant, and the adulteration concentration ranged from 1% to 50% with step size 1%. Finally, a total of 250 adulterated samples were used for this study, as shown in Table 1.

Table 1. Sample

Adulterant		Adulteration concentration	Sample number
Corn flour		(1,2,…,50)%	50
Whole-wheat flour		(1,2,…,50)%	50
Corn flour, whole-wheat flour	1:1	(1,2,…,50)%	50
	1:2	(1,2,…,50)%	50
	2:1	(1,2,…,50)%	50

All samples were sealed in sample bottles and allowed to stabilise to room temperature (22°C±2°C) before NIR spectra were recorded.

2.3. Data Analysis

The raw spectra data were imported into the MATLAB software (version R2014a) for data treatment and modelling. In order to achieve high instrument performance, both edges of wavelength band were discarded, and the 1400-2500nm range was used to build PLS models. Leave-one-out cross validation method was used to find out singular points, and 6 outliers were removed from sample set. The Kennard-Stone (K-S) algorithm was used and samples were divided into calibration (163 samples) and validation (81 samples). The statistics of samples involved in modelling was shown in Table 2. Detrending was used and several other mathematical pretreatments were tested to improve the PLS models. Correlation coefficient method was tested to select appropriate wavelength combinations. And this method calculated the correlation between spectral absorbance at each wavelengths and adulteration concentration, and picked up characteristic wavelengths by a proper threshold of correlation coefficient. The calculation formula of correlation coefficient was shown in Eqn. (1), where X is the spectral absorbance matrix, Y is the concentration matrix, Cov(X,Y) is the covariance between X and Y, D(X) is the variance of X, and D(Y) is the variance of Y. The correlation between actual and predicted constituent values (R2), standard error of both calibration (SEC) and validation (SEP), average of difference between actual and NIR predicted values (bias) and ratio of standard deviation to SEP (RPD) were used to test the performance of calibrations.

Table 2. Calibration and validation sample sets of white pepper powder adulteration

Adulteration	N	Range	Mean	SD
Calibration set	163	1-50%	23.91%	0.1423
Validation set	81	1-50%	28.02%	0.1384

N: number of samples; SD: standard deviation.

$$\rho_{XY} = \frac{Cov(X,Y)}{\sqrt{D(X)}\sqrt{D(Y)}}. \tag{1}$$

3. Results and Discussion

The detrending spectral data of three pure materials including whole wheat flour, corn flour and white pepper powder were recorded and shown in Fig 1. It can be seen that the spectra of three materials were closely, and they shared similar trends and peaks. The main absorbance peaks can be found at 1457nm, 1705nm, 1927nm, 2077nm, 2296nm and 2466nm.

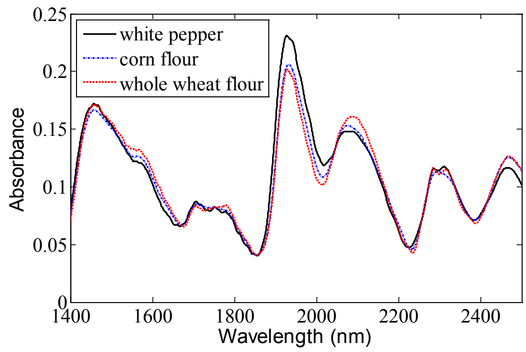

Figure 1. The detrending spectral data of pure corn, wheat and white pepper powder

Several spectral pretreatment methods such as multiple scatter correction, derivative, standard normal variable and Savitzky-Golay convolutions were tested, and it was indicated that none of the mathematical pretreatments tested improved the prediction accuracy of the PLS models. Similar results had been reported in models developed for the prediction of chemical components in food such as olive fruits 23.

Table 3. Calibration and validation results of white pepper powder adulteration

Adopted range	Calibration			Validation		
	F	R2	SEC	SEP	Bias	RPD
Full	8	0.996	0.824%	1.03%	0.671%	13.5
Th=0.19	8	0.996	0.788%	0.920%	0.645%	15.2
Th=0.85	8	0.994	1.134%	1.142%	0.858%	12.1

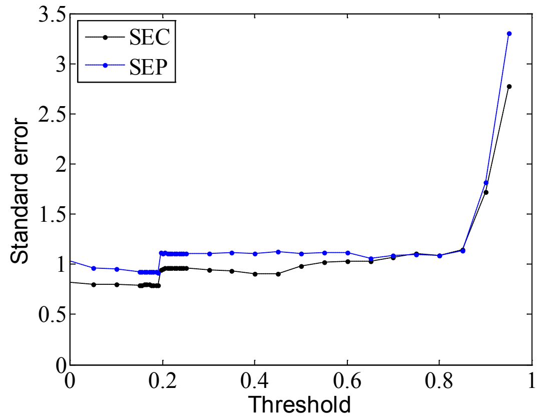

Figure 2. The relationship between standard error and threshold

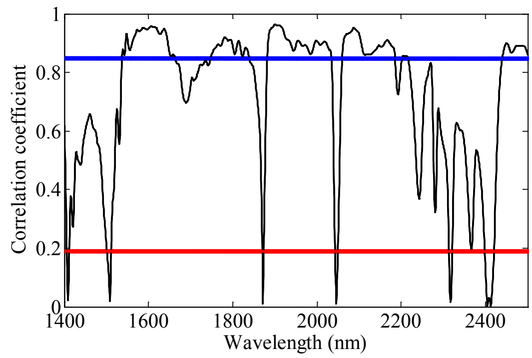

Figure 3. The relationship between correlation coefficient and wavelength

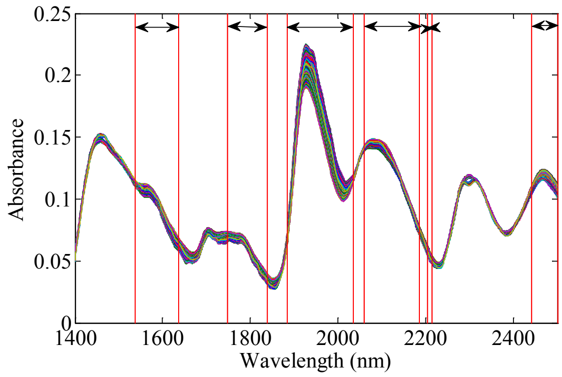

Figure 4. The selected wavelength points when Th equalled to 0.85

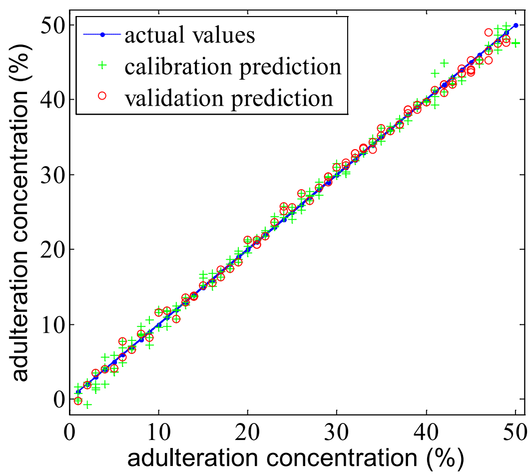

Figure 5. Relationship between the predicted and actual concentrations of adulteration with Th equaling to 0.19

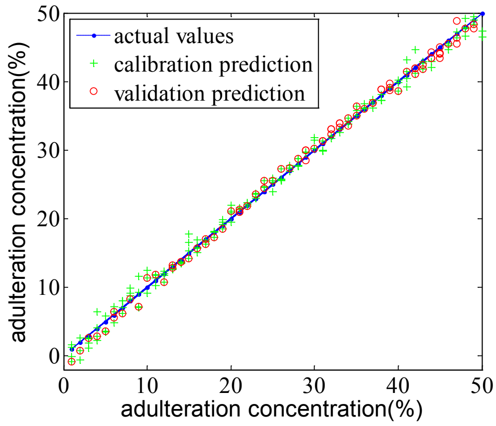

Figure 6. Relationship between the predicted and actual concentrations of adulteration with Th equaling to 0.85

Correlation coefficient method was tested to select characteristic wavelengths. The threshold of correlation coefficient was optimized based on SEC and SEP, as shown in Figure 2, and the correlation coefficient at each wavelength points was shown in Figure 3. It was indicated that the accuracy of PLS models barely changed when threshold of correlation coefficient (Th) was below 0.85, and it decreased rapidly in other range. The lowest values of SEC and SEP occurred when threshold equalled to 0.19, as shown in Table 3, where F was the number of factors. It can be obtained that when threshold equalled to 0.19, a total of 1046 wavelength points were selected, including [1400, 1406] ∪ [1413,1501]∪[1512,1869]∪[1874,2043] ∪[2050,2313]∪[2321,2397]∪[2420,2500]nm, and the prediction of corresponding PLS model was shown in Figure 5. When threshold equalled to 0.85 (Figure 4), a total of 569 wavelength points were selected, including [1537,1636]∪[1748,1838]∪[1883,2034]∪[2060,2185] ∪ [2203,2215]∪[2441,2500]nm, and the prediction of corresponding PLS model was shown in Fig 6. In comparation, the PLS model was good enough for practical application when threshold was 0.85, meanwhile, its compute was reduced largely.

4. Conclusion

White pepper powder is one of the most popular flavorings, and owns a broad market prospect in China. The identification of adulteration is of great significance for white pepper powder food safety and the interests of consumers. In the present study, a fast-screening approach for detecting adulteration such as whole wheat flour and corn flour in white pepper powder with NIR spectroscopy was developed. Quantitative PLS models were constructed and showed satisfactory performance with a RPD of 15.2. More samples of pure white pepper and adulterants will be used to build quantitative model combined with handheld NIR spectroscopy, which will be the direction of the future researches.

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