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SPECTROSCOPY AS A RAPID METHOD FOR DETECTING PAPRIKA POWDER ADULTERATION

Author(s):
JLZ. Zaukuu[1], Z. Bodor[1], D. Laryea[2], F. Wireko-Manu[2], F. Vitalis[1], V. Zsomné Muha[1] Z. Gillay[1], and Z. Kovacs[1]

Affiliation:

[1]Department of Physics and Process Control, Szent István University, Páter K. u. 1., Gödöllő, H-2103, Hungary
[2]Department of Food Science and Technology, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

Email address:
izaukuu@yahoo.com

Abstract

Paprika powder, a spice known for imparting flavour, colour and aroma in foods has recently become compromised by fraudulent activities involving diverse adulterants such as corn flour and has prompted quality assurance (QA) measures. Near infrared spectroscopy (NIRS) is a non-destructive method gaining grounds in QA applications. The study applied NIRS to detect paprika powder adulterated with corn flour. Chemometric evaluation spectra showed that NIRS could discriminate corn-flour adulteration with 100% classification accuracy. Adulteration was also predicted with high accuracies coefficient of determination (R2CV) between 0.97 and 0.99 and low errors (0.72 g/100g), proving the future QA applications of NIRS.

Keywords

Spectroscopy, adulteration, quality, chemometrics, authentication

Introduction

Urbanization and increasing population has resulted in surge in demand for products and services associated to fast-paced city living, especially, convenient or semi processed food products that mostly in the ready-to-eat state and are therefore time saving [1]. More importantly, convenient food products such as powdered food products are made available in hypermarkets and supermarkets near to the consumers. Thus, it replaces the traditional ways of cooking food with those that are less involving, fast and provides the equal desired features in the food. The fast growth of disposable income among consumers in urban area has enabled them to have more opportunities to consider a wider array of products and services compared to those in rural area but this has equally triggered greed and fraudulent activities in the food chain. Capsicum annuum is a group of vegetable spices widely consumed for their nutritional benefits such as vitamin C, red pigments and carotenoids. Frequent consumption of red pepper or its products has been acknowledged to promote glucose and lipid metabolism while stimulating the immune system to delay the aging or even prevent cancer [2]. Its powdered form has recently become a preferred option as a spice for imparting flavour, color and aroma in diverse cuisines. However, its quality is often compromised. The supply chains of the paprika industry involve a matrix of lengthy sequences often involving a complex nature of the processes that avails several points of possible criminal adulteration activities. It's bright red color, mostly attributed to the presence of Capsanthin and capsorubin antioxidants [3] is, sometimes manipulated for selfish gains by producers who use diverse types of adulterants. One of such adulterants that has recently come under suspicion is corn flour. It is often done with the intention of deceiving the consumer even though consumers have the right to know that the food they eat is safe and suitable for consumption. Food fraud is disagreeable at best and at worst sometimes presents serious health concerns [4]. In view of authentication and quality assurance (QA) in this fast-moving industry, rapid, non-destructive methods are promising for future QA applications. Near infrared spectroscopy (NIRS) is one of such methods gaining grounds for its sensitivity, ease of application and cost efficiency. It operates with a light absorption pattern at wavelengths between 700 nm (13,300 cm^{-1}) and 2500 nm (4,000 cm^{-1}) and is performed in combination with chemometrics for chemical fingerprints of foods. NIRS has been used for the determination of Sudan I-II-II-IV dye adulteration in spices [5], identification of papaya seeds in black pepper [6], paprika adulteration with lead chromate, 3% (w/w) lead oxide 5% (w/w) silicon dioxide, 10% (w/w) polyvinyl chloride, and 10% (w/w) gum Arabic [7]. The aim of this study was to test the feasibility of two different NIRS instruments in detecting adulteration of paprika powder with corn flour through chemometric data evaluations.

Materials and methods

Sample preparation

Authentic paprika powder was purchased from reputable sources in two Hungarian paprika growing regions and coded: DP and SP (Fig. 1). Each paprika type (DP and SP) was artificially adulterated in the laboratory at nine concentrations of corn flour: 40%, 30%, 25%, 20%, 15%, 10%, 5%, 3%, 1%. Each adulteration concentration was prepared in three repeats (3 grams each) and homogenized by shaking for two mins in plastic containers, before NIRS measurements. Pure paprika powder (non-adulterated) and pure corn flour (non-adulterated) was also included in the NIRS measurements.

Figure 1. Paprika powder samples and corn flour sample used for the experiment

NIRS measurements and data evaluation

Two types of spectrometers (Fig. 2): The metri analyzer (benchtop) with wavelength range of 740-1700nm and Nirscan nano NIRS (handheld) with wavelength range 900- 1700nm were used to collect diffuse reflectance spectra. Spectra was collected using a cuvette providing 0.4mm layer thickness of the tested paprika powder samples in a spectral step of 3nm. The samples were prepared in three replicates each and randomly scanned with both devices by taking three consecutive scans each, at room temperature. The collected spectra were pretreated with Savitzky-Golay smoothing filter using 2nd order polynomial and XY number of points and multiplicative scatter correction (MSC).

A) B)

Figure 2. Spectrometers used for scanning the experimental samples; Metri NIRS (A) and Nirscan NIRS (B)

Linear discriminant analysis (LDA) was used for multi-class classification of the different corn flour concentrations. LDA is a supervised method; the class membership has to be known for the analysis [8]. Partial least squares regression (PLSR) was used to derive the models to predict paprika powder adulteration with corn flour, first in DP and SP paprika powder separately, and then in the whole dataset to see the influence of varietal differences on our model. Three-fold cross-validation (CV) was used to test the predictive significance of the results in LDA and also in PLSR to test the predictive significance of the regression. The statistical parameters used to evaluate the performance of the PLSR models were the Root Mean Square Error and the coefficient of determination both in calibration (RMSEC and R2C) and cross-validation (RMSECV and R2CV), respectively. The optimum number of latent variables was determined based on the minimum RMSECV value. All data evaluations were done in R project at a wavelength range of 950-1650nm.

Results and discussion

Discriminant analysis of paprika powder samples

The plots in Fig. 3 shows the visual classifications for corn flour adulteration in paprika powder using the Metri analyzer (A) and Nirscan nano (B). An increasing pattern of adulteration from 0% to 40% corn flour adulteration could be noticed from the left to right in both plots. Corn flour at 40% adulteration was the most discriminated. In Fig. 3A, all the other concentrations were classified separately from each even the lower concentrations of 1% 3% and 5% corn flour. There was some overlapping between 0% and 1% corn flour concentration in the case both instruments. Generally, better separation patterns were observed with the Metri NIRS (Fig. 3A) than with the Nirscan nano (Fig. 3B) and the plot confirms the prediction accuracies in Table 1 and Table 2.

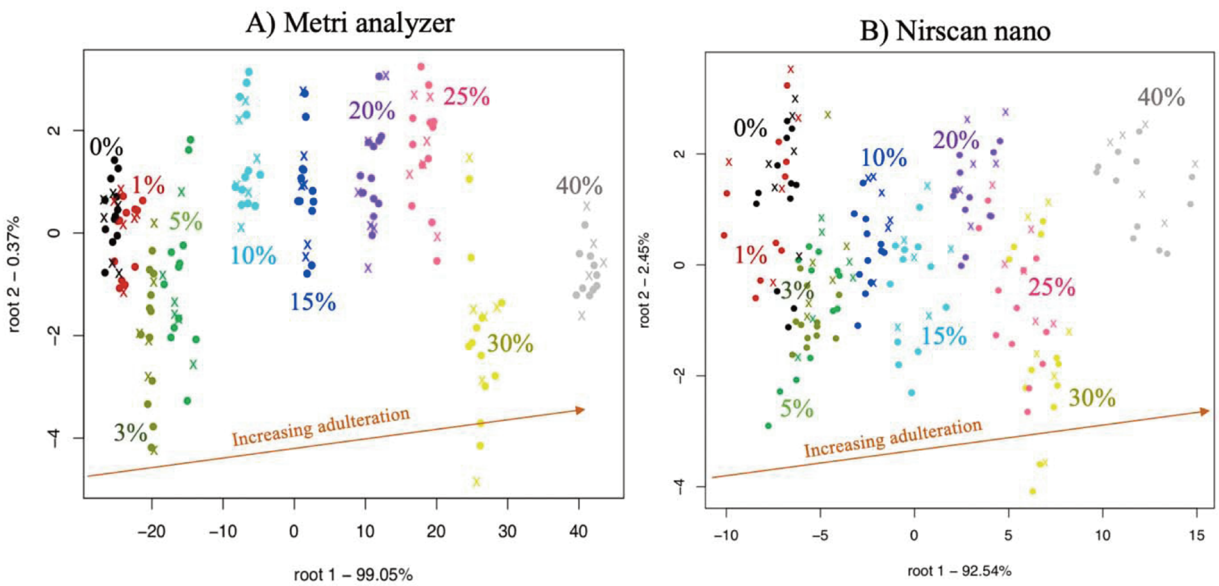

Figure 3. Discriminant analysis plot of paprika powder adulterated with corn flour at nine different concentrations and after spectral pre-treatment (smoothing and MSC) and cross-validation at wavelength of 950-1650nm (n = 177). A) Nirscan nano nirs, B) Metri nirs

Classification models built separately for SP and DP paprika types resulted in 100% average recognition and prediction accuracy for corn flour adulteration when, Metri NIRS used. An average recognition and prediction of 100% was also achieved when the Nirscan nano was used to separately classify DP and SP paprika type adulteration with corn flour. Classification models built for the whole datasets was capable of discriminating and predicting each different concentration of corn flour in paprika powder with a high accuracy, irrespective of the type of paprika. This is shown in Table 1 for Metri NIRS and in Table 2 for Nirscan NIRS.

Table 1. LDA classification results of paprika adulteration with corn flour after spectral pre-treatment and cross validation at wavelength of 950-1650nm with Metri NIRS

	0%	1%	3%	5%	10%	15%	20%	25%	30%	40%
0%	**77.83**	5.50	0	0	0	0	0	0	0	0
1%	22.17	**94.50**	0	0	0	0	0	0	0	0
3%	0	0	**100**	0	0	0	0	0	0	0
5%	0	0	0	**100**	0	0	0	0	0	0
10%	0	0	0	0	**100**	0	0	0	0	0
15%	0	0	0	0	0	**100**	0	0	0	0
20%	0	0	0	0	0	0	**100**	0	0	0
25%	0	0	0	0	0	0	0	**100**	0	0
30%	0	0	0	0	0	0	0	0	**100**	0
40%	0	0	0	0	0	0	0	0	0	**100**

Irrespective of the paprika type, all the different corn flour concentrations could be predicted in LDA with 100% recognition and 97.23% prediction accuracy when Metri NIRS was used (Table 1). With the exception of 0% and 1% corn flour concentrations, there was no misclassification (100% correct classification) in all the other different corn flour concentration levels after cross-validation. Similar results were reported for the detection of black pepper with papaya seeds using NIRS [9].

Table 2. LDA classification results of paprika adulteration with corn flour after spectral pre-treatment and cross validation at wavelength of 950-1650nm with Nirscan NIRS

	0%	1%	3%	5%	10%	15%	20%	25%	30%	40%
0%	**77.70**	46.60	0	0	0	0	0	0	0	0
1%	11.15	**53.40**	0	0	0	0	0	0	0	0
3%	0	0	**83.33**	0	0	0	0	0	0	0
5%	11.15	0	16.67	**100**	0	5.5	0	0	0	0
10%	0	0	0	0	**83.33**	16.67	0	0	0	0
15%	0	0	0	0	16.67	**77.83**	0	0	0	0
20%	0	0	0	0	0	0	**100**	16.67	0	0
25%	0	0	0	0	0	0	0	**77.83**	0	0
30%	0	0	0	0	0	0	0	5.50	**100**	0
40%	0	0	0	0	0	0	0	0	0	**100**

Irrespective of the paprika type, all the different corn flour concentrations could be predicted in LDA with an average accuracy of 85.34% when the Nirscan nano NIRS was used (Table 2). This was less than the 95.02% observed with the Metri NIRS (Table 1). There was no misclassification for 5%, 20%, 30% and 40% respectively. This was also observed with the Metri NIRS. In comparison with the Metri NIRS, there was lower classification accuracy for 0% and 1% corn flour adulteration. Generally, there was lower classification accuracies compared to the Metri NIRS. This may be due to the difference in sensitivity as benchtop instruments are often reported to be more sensitive compared to handheld devices.

PLSR prediction of corn flour adulteration after pre-treatment and cross-validation

The PLSR model for the Metri NIRS was capable of predicting corn flour adulteration in both DP and SP paprika powder with an R^2CV of 0.99 and 0.98 respectively. An R^2CV 0.99 was also achieved when a model was built for the whole dataset, with an RMSECV of 1.72 g/100g after cross validation. An R^2 close to 1 is a necessary condition for a good model [10]. This means that the Metri NIRS was capable of predicting 40%, 30%, 25%, 20%, 15%, 10%, 5%, 3%, 1% corn flour adulteration in both DP and SP paprika powder adulteration with a high accuracy and low error but the best model was the DP paprika with five latent variables.

Table 3. PLSR prediction of corn flour adulteration after spectral pre-treatment and cross-validation at wavelength of 950-1650nm using the Metri NIRS and Nirscan nano NIRS

	Model type	Data points	Components	R^2C	RMSEC	R^2CV	RMSECV
Metri NIRS	DP Paprika	87	5	0.999	0.439	0.997	0.719
	SP Paprika	90	6	0.977	1.945	0.972	2.180
	Whole dataset	177	10	0.986	1.508	0.981	1.715
Nirscan Nano NIRS	DP Paprika	90	10	0.992	1.175	0.988	1.412
	SP Paprika	87	10	0.988	1.394	0.980	1.823
	Whole dataset	177	10	0.971	2.205	0.964	2.436

The PLSR model for the Nirscan nano also capable of predicting corn flour adulteration in both DP and SP paprika powder with an R^2CV of 0.99 and 0.98, respectively. An R2CV 0.96 was achieved when a model was built for the whole dataset, the model had an RMSECV of 2.44 g/100g after three-fold cross validation. NIRS was capable of predicting 40%, 30%, 25%, 20%, 15%, 10%, 5%, 3%, 1% corn flour adulteration in both DP and SP paprika powder adulteration with a high accuracy and low error but the best model was the DP paprika with 10 components. The Nirscan nano had a better prediction accuracy for SP paprika in comparison with the Metri NIRS but Metri NIRS had an overall higher prediction accuracy when the whole dataset was analysed.

Conclusions

Two types of paprika powder samples artificially adulterated in the laboratory were classified and predicted with 100% accuracy in separate LDA models built with NIRS spectra scans from both Metri NIRS (Benchtop) and Nirscan nano NIRS (Handheld) respectively after pretreatment. Irrespective of the paprika type, LDA models could also classify corn flour adulteration when models were built for both paprika powders (whole data) with a prediction accuracy of 95.55% and 85.34% for Metri NIRS and Nirscan nano NIRS respectively. Metri NIRS was generally more effective in LDA classification compared to Nirscan nano. PLSR models could predict paprika powder adulteration with corn flour in an accuracy range of 0.97 to 0.99 for both Metri NIRS and Nirscan nano NIRS with errors less than 2.44 g/100g. Generally, the Metri NIRS could predict adulteration in SP adulterated samples better than Nirscan nano. The best PLSR model was found for DP paprika with five components using the Metri NIRS. Near infrared spectroscopy, as a non-invasive technique exhibited good potentials for paprika powder authentication when corn flour was used as an adulterant.

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