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Original scientific paper

NEAR INFRARED SPECTROSCOPY AS A RAPID METHOD FOR DETECTING PAPRIKA POWDER ADULTERATION WITH CORN FLOUR

John-Lewis Z. Zaukuu[1]*, *Zsanett Bodor*[1], *Flora Vitalis*[1], *Victoria Zsom-Muha*[1], *Zoltan Kovacs*[1]

[1] Szent István University, Faculty of Food Science, Department of Physics and Control, Somlói str. 14-16.,
H-1118, Budapest, Hungary

Paprika powder is a spice of culinary importance in many homes but it's powdered form, has been targeted for fraudulent activities intended at consumer deception. Diverse methods have been used to investigate some of these adulterations but there is no report of paprika adulteration with corn flour, although it remains a suspicion. Technologies such as the near infrared spectroscopy (NIRS) possess non-invasive and rapid advantages that could be explored to monitor this type of adulteration. The study aimed to discriminate and quantify different levels of paprika powder adulterated with corn flour, using NIRS. Two authentic paprika types (DP and SP) were purchased from reputable sources in Hungary and artificially adulterated in the laboratory. Three repeats of each adulteration level (40%, 30%, 25%, 20%, 15%, 10%, 5%, 3%, 1%) were prepared and scanned with the Metri NIRS respectively, then, analysed with chemometrics: Linear discriminant analysis (LDA) and partial least squares regression (PLSR). LDA showed 100% recognition and prediction accuracies respectively when DP and SP were analyzed separately to discriminate different concentrations of paprika adulteration. LDA models with NIRS recognize corn flour adulteration with 95.55% and predict it with 95.02% accuracy irrespective of the paprika type used in this experiment. PLSR prediction of 40%, 30%, 25%, 20%, 15%, 10%, 5%, 3%, 1% corn flour adulteration yielded an R^2CV of 0.98 (high accuracy) and a low RMSECV of 1.71 g/100g (low error). Near infrared as a non-invasive technique exhibited good potentials for paprika powder authentication when corn flour is used as an adulterant.

Keywords: spices, herb, corn-flour, authentication, spectroscopy

INTRODUCTION

Herbs, as important spices have played vital roles in cuisines since the ancient times. They have been used for food fortification, aroma, taste, preservatives and to improve the appearance of food (1). From the 2010-2013, patronization of herbs and spices was pegged at an increasing rate of 1.7% per year across the European Union with major imports from developing countries accounting for 57% of total EU imports with 302 thousand tones (2). Important among the family of herbs is paprika, an affordable plant product that has increasingly become sorted for its flavor and spicy impact in food quality.

The supply chains of the paprika industry however, involves a matrix of lengthy sequences often involving a complex nature of the processes that avails several points of possible criminal adulteration activities. The U.S. Food and Drug Administration (FDA) defines adulteration (EMA) as "the fraudulent, intentional substitution or addition of a substance in a food product in order to increase the apparent value of the product or reducing the cost of its production, that is, for economic gain" (3). 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).

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* Corresponding author: John-Lewis Z. Zaukuu, Szent István University, Faculty of Food Science, Department of Physics and Control, Somlói str. 14-16., H-1118, Budapest, Hungary, e-mail: izaukuu@yahoo.com

The most targeted form of paprika for fraudulent activities is the powdered form. In this semi-processed form, many adulterants can easily go undetected depending on the technique of adulteration or the adulterant used. Common adulterants include food color (5), sudan IV dyes (6). The stages of the supply chain can include grower, collector, primary processor, local traders, secondary processor, exporter, importer, trader, processor/packager, food manufacturer/retailer/wholesaler, and finally the consumer. At any stage of this supply chain, a number of fraud opportunities can occur including misrepresentation and substitution (2).

Authentication of food thus, has become critical and crucial for consumer safety. Food authentication, by legal definition is the distinctive characteristics of a "genuine food product, being its uniqueness, quality, safety, and traceability guaranteed by a certification regulatory framework" (7). This process often involves the use of scientific instruments. Chromatography (GC-MS, LC-q-TOF-MS, HPLC) (4,6,8), and spectrophotometry (5), are some of the most often reported analytical instruments used for qualitative and quantitative food authentication of spices. In recent times however is a paradigm shift for more rapid but relatively cheap methods such as spectroscopy (9-11). Spectroscopy is a science of light interaction (absorbance/reflectance) with an analyte across the electromagnetic spectrum. It is reported to give a non-invasive complete overview of the investigated food product. Gaining grounds in this field is the near infrared spectroscopy (NIRS).

NIRS is a non-destructive analytical method that operates with the light absorption pattern at wavelengths between 750 nm (13,300 cm^{-1}) and 2500 nm (4,000 cm^{-1}) (12) and is performed in combination with chemometrics for chemical fingerprints of foods. NIRS is routinely employed to give a compositional, functional and sensory analysis overview of food raw materials, process intermediates and final products. An outstanding advantage of NIRS is that little or no sample preparation is necessary, so the analysis is very rapid (from less than a second to some minutes), free of danger (to both the user and the analyte) and can be carried out on-line (17). One of its major strength is the possibility to measure several constituents concurrently. It has been used for the determination of Sudan I-II-II-IV dye adulteration in spices (13), identification of papaya seeds in black pepper (14), 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 (15), fingerprinting to detect adulteration in black pepper (16), etc. It can there be inferred from literature that, NIRS is a good tool for qualitative and quantitative investigation of foods. This study aimed to apply near NIRS and chemometrics for the authentication of paprika powder with decreasing concentrations of corn flour as an adulterant.

EXPERIMENTAL

Materials

Authentic paprika powder was purchased from reputable sources in two Hungarian paprika growing regions: DP and SP. 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 (Figure 1), before NIRS measurements. Pure paprika powder (non-adulterated) and pure corn flour (non-adulterated) was also included in the NIRS measurements.

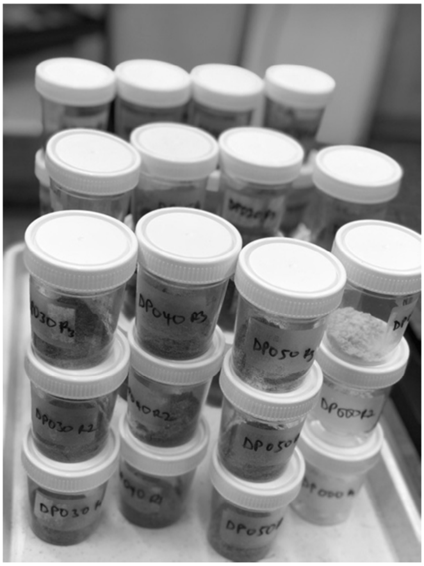

Figure 1. Artificial adulteration of paprika powder samples in the laboratory at nine different concentrations of corn flour

Methods

The metri analyzer (benchtop spectrometer) with wavelength range of 700-1700 nm was used to collect transflectance spectra, 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 the Metri NIRS by taking three consecutive scans each, at room temperature. The collected spectra were pretreated with Savitzky-Golay smoothing filter using 2nd order polynomial and multiplicative scatter correction (MSC). 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 (18). Partial least squares (PLS) regression was used to derive the models to predict paprika powder adulteration with corn flour first of all in DP and SP paprika powder respectively 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 R^2C) and cross-validation (RMSECV and R^2CV), 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

Classification models built separately for SP and DP paprika types resulted in 100% recognition and prediction accuracy respectively. Classification models built for the whole datasets was capable of discriminating and predicting corn flour adulteration in paprika irrespective of the type of paprika. This is shown in Figure 2.

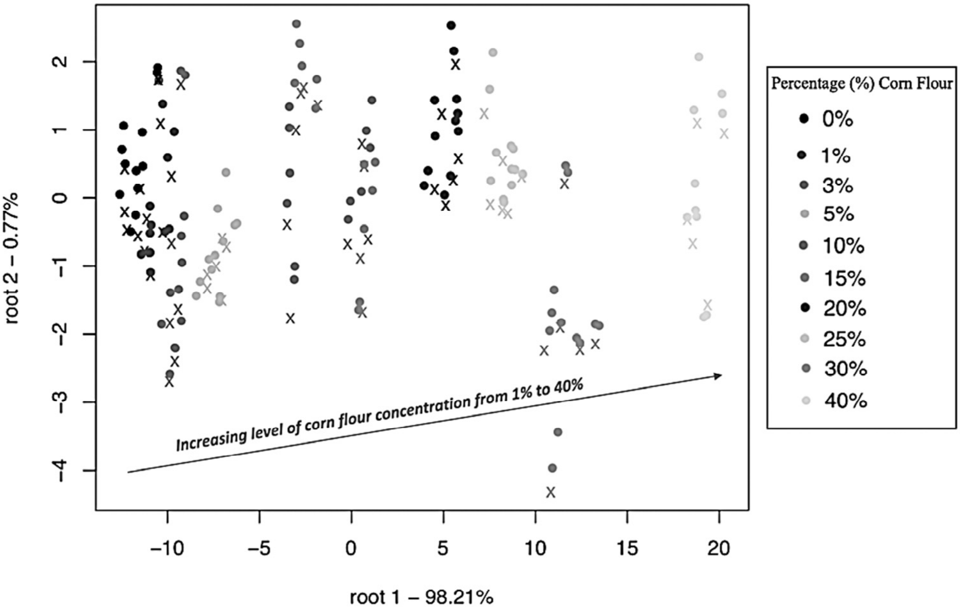

Figure 2. Discrimination of Adulterated DP and SP paprika powder at nine different concentrations of corn flour after spectral pretreatment (smoothing and MSC) and cross-validation at wavelength of 950-1650nm (n = 177)

Figure 2 shows a separation pattern in an increasing order of corn flour adulteration, from 0% to 40%. There was an average recognition accuracy of 100% and prediction of 98.23%. Each different corn flour concentration could be predicted in LDA with an accuracy of 100%, except 0% and 1% corn flour concentration. Paprika powder with 1% corn flour concentration showed 5.5% misclassification as 0% (pure paprika powder) and pure paprika powder (0%) showed also showed misclassification of 5.5% as paprika powder with 1% corn concentration. This shows the potential of low corn flour concentrations (1%) to go undetected. Similar results were reported for the detection of black pepper with papaya seeds using NIRS (16).

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

	0%	1%	3%	5%	10%	15%	20%	25%	30%	40%
0%	**94.50**	5.50	0	0	0	0	0	0	0	0
1%	5.5	**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**

PLSR prediction of paprika adulteration with corn flour after spectral pretreatment and cross validation

Table 2. PLSR prediction of corn flour adulteration after spectral pretreatment and cross-validation at wavelength of 950-1650 nm

Model type	Data points	Components	R^2C	RMSEC	R^2CV	RMSECV
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

The PLSR model for the experiment was capable predicting corn flour adulteration in both DP and SP paprika powder with an R^2CV of 0.99 and 0.977 respectively. An R^2CV 0.98 was achieved when a model was built for the whole dataset, the model had an RMSECV of 1.71 g/100g after three-fold cross validation. An R^2 close to 1 is a necessary condition for a good model [19]. This means our model was capable of predicting 40%, 30%, 25%, 20%, 15%, 10%, 5%, 3%, 1% corn flour adulteration in DP and SP paprika powder adulteration with a high accuracy and low error.

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 after pretreatment. LDA models could also classify corn flour adulteration when models were built for both paprika powders (whole data) with a recognition accuracy of 100% and prediction accuracy of 98.23% irrespective of the paprika type. PLSR models could also predict paprika powder adulteration with corn flour in an accuracy range of 0.97 to 0.99, with errors between 0.71 and 2.81 g/100g. Near infrared as a non-invasive technique exhibited good potentials for paprika powder authentication when corn flour is used as an adulterant.

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