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Differentiation of Spanish paprika from Protected Designation of Origin based on color measurements and pattern recognition

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A B S T R A C T

A method based on the measurement of color is proposed to differentiate paprika samples from different geographical origin. ASTA scale and coordinates in the CIELAB color space were obtained from UV–Vis spectra of acetone extracts of samples. Samples of sweet, hot/sweet and hot paprika from the two recognized Spanish Protected Designation of Origin, Murcia and Extremadura, were analyzed. Two strategies were considered with the aim of building classification models. The first used the computed color parameters as input data, whilst the second used the scores of the samples obtained after applying principal component analysis to reduce the dimensionality of the data matrix from the absorbance spectrum. The developed pattern recognition models were based on linear discriminant analysis, support vector machines and multilayer perceptron artificial neural networks. In both considered strategies, the best results were obtained in the case of artificial neural networks, with classification efficiencies ranging from 92% to 95% for the different varieties of paprika.

1. Introduction

Paprika is a red powder obtained from fruits of some varieties of *Capsicum annuum* L. that is used as spice and natural colorant. It is usually found in marinated meat products, soups, sauces, processed cheeses and snacks, as well as a common ingredient in some traditional cuisines. Paprika contains capsorubin and capsanthin and about 20 others carotenoids pigments that are related to its color. Depending on the variety, it could contain high levels of capsacinoids, compounds that are responsible of the pungency. Accordingly, the use of paprika as colorant is limited to products compatible with flavor (Francis, 2002). Spanish paprika is mainly produced in two growing areas, Murcia and La Vera, both recognized by the European Union under Protected Designation of Origin (PDO) (European Commission Agricultural and Rural Development). The products from both areas are made with raw materials from different varieties growing in different soils and being affected by different climate. The elaboration process is also different, especially in the drying of the fruit. Those factors may contribute to subsequent differences in the chemical composition of the final product (Almela, López-Roca, Candela, & Alcázar, 1991; Brunner, Katona, Stefánka, & Prohaska, 2010; Navarro, Flores, Garrido, & Martínez, 2006; Palacios-Morillo, Jurado, Alcázar, & Pablos, 2014) that can influence its properties, such as color and flavor (Jarén-Galán &. Minguez-Mosquera, 1999; Mateo, Aguirrezábal, Domínguez, & Zumalacarregui, 1997; Ordóñez-Santos, Pastur-García, Romero-Rodriguez, & Vázquez-Oderiz, 2014; Vidal-Aragón, Lozano, & Montero, 2005).

Color is one of the most important sensorial attributes of food as its appearance has influence in the decisions of the consumers and must convince them of potential properties. Food color has been usually related to the product quality and influences the perception of other attributes such as flavor, sweetness and saltiness, therefore in its acceptance (Clydesdale, 1991). Food industry is very interested in controlling and assuring stability of this property and the use of colorants dates back to antiquity. Nowadays, consumers pay special attention to all that refers to healthy and natural foods and the use of natural colorants in food industry plays a predominant role in marketing strategies. Color of paprika is usually determined, according to the American Spice Trade Association (ASTA, 1986), by measuring the absorbance at 460 nm of an acetone extract of the product. The ASTA parameter is considered by the European Union legislation to establish the minimum requirement of color for both Spanish PDO of paprika at the time of milling (European Union, 2000; European Union, 2006). This method has also been used by several authors to monitor the quality of paprika products with

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temperature, storage in controlled atmospheres or ripening stage (Gómez-Ladrón de Guevara, Pardo-González, Varón-Castellanos, & Navarro-Albadalejo, 1996; Jarén-Galán &. Minguez-Mosquera, 1999; Ordoñez et al., 2014; Pérez-Gálvez, Mínguez-Mosquera, Garrido-Fernández, Lozano-Ruiz, & Montero-de-Espinosa, 2004). On the other hand, color can be also evaluated in terms of the parameters L*, a* and b* to obtain the coordinates in the space defined by the Commission Internationale de L'Eclairage, called CIE 1976 (L*a*b*) color space or simply CIELAB color space. L* refers to clarity, whilst a* and b* are related to red/green and blue/yellow components, respectively. The parameters L*, a* and b* are obtained from tristimulus values XYZ, previously calculated from reflectance or absorbance spectra in the range 380 nm–780 nm according to CIE's Technical Report on Colorimetry (CIE, 2004).

CIELAB color coordinates obtained from reflectance spectra has been used by some authors to monitor color changes during storage or drying stage (Gómez-Ladrón de Guevara et al., 1996; Ordoñez et al., 2014; Park, Kim, & Moon, 2011). The absorbance UV–Vis spectrum has been also used in the study of color changes in beverages (García-Marino, Escudero-Gilete, Heredia, Escribano-Bailón, & Rivas-Gonzalo, 2013; Hernanz et al., 2009; Moyano, Meléndez-Martínez, Alba, & Heredia, 2008) or food and plants extracts (Fan, Han, Gu, & Gu, 2008; Gonnet, 1998) according to CIELAB coordinates. Absorbance spectra have also great importance in the characterization and classification of food by means of pattern recognition techniques. Some examples on the use of UV–Vis absorbance as input variables for developing classification method for food samples such as wine and other alcoholic beverages (Casale, Oliveri, Armanino, Lanteri, & Forina, 2010; Urbano, Luque de Castro, Pérez, García-Olmo, & Gomez-Nieto, 2006; Uríčková & Sádecká, 2015), coffee (Souto et al., 2010), tea (Diniz, Barbosa, Milanez, Pistonesi, & Araujo, 2016; Palacios-Morillo, Alcázar, Pablos, & Jurado, 2013) and olive oil (Lin, Chen, & He, 2012) can be found.

The classification of food samples is of great interest for identification of the product's geographical origin and authenticity, or for establishing characteristics of products. In the case of paprika some classification studies has been carried out based on atomic spectroscopy measurements (Brunner et al., 2010; Palacios-Morillo et al., 2014), but these methods are tedious and expensive. The main objective of this work is to propose a simple and cheap methodology to differentiate Spanish PDO paprika. By considering the hypothesis that some differences can occur between colors of samples from different origins (Navarro et al., 2006), models based on ASTA and CIELAB coordinates of paprika extracts has been developed. The absorbance in the spectral interval used to obtain the above mentioned parameters (380–780 nm) was also considered as input data to develop classification models. Pattern recognition techniques such as principal component analysis (PCA), linear discriminant analysis (LDA), support vector machines (SVM) and multilayer perceptrons artificial neural networks (MLP-ANN) were considered to obtain the classification models.

2. Materials and methods

2.1. Samples and reagents

Samples of paprika belonging to La Vera (Extremadura) ($n = 62$) and Murcia ($n = 48$) have been obtained from local stores. Within these classes there are three types of paprika: sweet, hot/sweet and hot. In the case of Extremadura there are 20, 18 and 24 samples of sweet, hot/sweet and hot paprika, respectively. Samples from Murcia were 14 sweet, 14 hot-sweet and 20 hot.

Acetone used as extraction solvent was purchased from Merck (Darmstadt, Germany). Ammonium cobalt (II) sulfate hexahydrate (99%) and potassium dichromate (99%), both from Sigma–Aldrich (Steinheim, Germany), and 98% sulfuric acid (Merck) were used to prepare the standard for ASTA measurement. This ASTA standard consist of 34.96 g $L^{-1}$of ammonium cobalt (II) sulfate hexahydrate and 0.3005 g $L^{-1}$of potassium dichromate in sulfuric acid1.8 M.

2.2. Color measurements

A mass (m_{sample}) between 0.035 and 0.05 g of paprika sample, weighted with precision of 0.1 mg, was extracted with 100 mL of acetone in a beaker with magnetic stirring at 300 r.p.m. Samples were filtered using an 0.45 μm nylon filter and absorbance spectra from 380 nm to 780 nm were registered in a Thermo Spectronic UNICAM UV 500 spectrometer using a standard quartz cuvette.

For ASTA measurement (ASTA, 1986) the absorbance of this solution (A_{sample}) at 460 nm was used. The absorbance of the ASTA standard was also measured at 460 nm. ASTA units were calculated as:

$$ASTA\ units = \frac{A_{sample} \cdot 16.4 \cdot I_f}{m_{sample}} \tag{1}$$

Being I_f the ratio between the expected absorbance for the ASTA standard, 0.6 absorbance units, and the experimental value.

The transformation of absorbance spectral data of the acetone extract into CIELAB coordinates was carried out by means of a Microsoft Excel spreadsheet prepared according to equations and data for 10° observer and D65 standard illuminant from CIE's Technical Report on Colorimetry (CIE, 2004).

2.3. Data analysis

Multivariate data analysis was performed by using Statistica 8.0 (StatSoft, 2007) software package. PCA was applied in order to reduce the dimensionality of absorbance data matrix and visualize data trends. LDA, SVM and MLP-ANN were applied to obtain adequate classification models to perform geographical characterization of paprika.

LDA computes discriminant functions as a linear combination of the original variables in order to differentiate the considered classes by minimizing the within-class and between-class ratio. The distance between a case and the centroid of each class is obtained and this sample is classified according to the shortest distance to the centroid of the class (Brereton, 2003). In the case of SVM, a decision boundary (optimal hyperplane) is computed to best separate the groups by maximizing the distance between classes. Test cases are classified as belonging to a class when they fall within its computed margin (Brereton & Lloyd, 2010). In this study, three-layered MLP-ANNs were applied. The input layer reads the values of the variables used in the model. Each neuron in the hidden layer performs a weighted sum of their inputs and transforms it with an activation function to produce their output. In the output layer, the probability of pertaining at each class is computed (Sarle, 1994).

Classification models were validated by applying a stratified delete-a-group jackknifing (SDAGJK) procedure previously described by Palacios-Morillo et al. (2013). Considering a set of data consisting of various classes, cases belonging to each class are randomly divided in a training set (2/3 of the samples) and a test set (1/3 of the samples). The training cases are used to build the model and its classification efficiency is computed for each class according to the classification results for test cases. This procedure is applied in nine replicates and the mean classification efficiency of the model is computed. In this paper, two classes, Extremadura and Murcia, are considered. In the case of sweet paprika, 14 samples from Extremadura and 9 from Murcia were