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Qualitative and quantitative analysis of peanut adulteration in almond powder samples using multi-elemental fingerprinting combined with multivariate data analysis methods

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ABSTRACT

In this study, adulteration of almond powder samples with peanut was analyzed using multi-elemental fingerprinting based on inductively coupled plasma optical emission measurements (ICP-OES) combined with chemometric methods. The ability of multivariate data analysis approaches, such as principal component analysis (PCA) and principal component analysis-linear discriminant analysis (PCA-LDA), to achieve differentiation of samples and as partial least squares (PLS) and least squares support vector machine (LS-SVM), to quantify the adulteration based on the elemental contents has been investigated. Ten variables i.e. the contents of B, Na, Mg, K, Ca, Fe, Cu, Cu, Zn and Sr at μg g^{-1} level, determined by ICP-OES were used. Different almond and peanut samples were then mixed at various ratios to obtain mixtures ranging from 95/5 to 5/95 w/w and PCA-LDA was applied to classify the almonds, peanuts and adulterated samples. This method was able to differentiate peanut and almond samples from the adulterated samples. PLS and LS-SVM models were developed to quantify the adulteration ratios of almond using a training set and the constructed models were evaluated using a validation set. The root mean squared error of prediction (RMSEP) and the coefficient of determination (R^2) of the validation set for PLS and LS-SVM were 3.81, 0.986 and 1.66, 0.997, respectively, which demonstrates the superiority of the LS-SVM model. The results show that the combination of multi-elemental fingerprinting with multivariate data analysis methods can be applied as an effective and feasible method for testing almond adulteration.

1. Introduction

The authentication of food products has been recognized as a worldwide topic of interest covering many different aspects, from adulteration to mislabeling and misleading origin. Economically motivated adulteration for economic gain of the seller is a process by which the quality of a substance is reduced through the addition, substitution or removal of food ingredients without the consumer's knowledge (Moore, Spink, & Lipp, 2012). Most food products susceptible for fraud are high commercial cost products, often produced worldwide on a large scale (Cordella, Moussa, Martel, Sbirrazzouli, & Lizzani-Cuvelier, 2002). Therefore, the ability of the industry, governments, and standards-setting organizations to authenticate, to control food constituents and to check for food fraud is increasingly important (Ellis et al., 2012; Gupta & Panchal, 2009; Zhang, Zhang, Dediu, & Victor, 2011).

Several methods have been proposed for the detection of the adulteration in food products, such as PCR assay for meat adulteration (Ali et al., 2014; Karabasanavar, Singh, Kumar, & Shebannavar, 2014), visible and near infrared hyperspectral imaging for meat adulteration (Kamruzzaman, Makino, Oshita, & Liu, 2015), high performance liquid chromatography with mass spectrometric detection for lemon juice adulteration (Wang & Jablonski, 2016), solid-phase micro extraction, gas chromatography with mass spectrometry detection (SPME-GC-MS) for cognac and brandy adulteration (Mozhayeva, Zhakupbekova, Kenessov, & Akmoldayeva, 2014), electrospray ionization mass spectrometry for

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meat adulteration (Ruiz Orduna, Husby, Yang, Ghosh, & Beaudry, 2015), two-dimensional gas chromatography for medicinal herb adulteration (Welke et al., 2015), an electronic nose for saffron adulteration (Heidarbeigi et al., 2015), Fourier transform infrared attenuated total reflectance (Jiménez-Sotelo et al., 2016) and Raman spectroscopy for milk powder characterization (Karunathilaka, Farris, Mossoba, Moore, & Yakes, 2016). Most methods are time consuming, use large volumes of solvents and are not readily adaptable for rapid monitoring through portable instrumentation. Meanwhile, spectroscopic techniques combined with multivariate data analysis methods form a promising strategies to overcome the drawbacks and can effectively be used to detect adulteration of different food products (López, Trullols, Callao, & Ruisánchez, 2014).

Almond (*Prunus amygdalus*) with several unique features is one of the most popular nuts worldwide. It is highly nutritious and classified as a drupe in which the edible seed is a commercial product (Alonso, Kodad, & Gradziel, 2012). Almond powder is generally used in a variety of processed foods, particularly in bakery and confectionery products (Dourado, Barros, Mota, Coimbra, & Gama, 2004). Because of its high price, almond powder is a target of illegal practices, such as mixing with cheaper nuts. One of the most common adulterations consists of using peanut as an adulterant with very similar chemical composition and much lower prices. To the best of our knowledge, adulteration studies for this kind of nut are not extended in the literature. Thus, it is important to develop analytical procedures to verify the quality of almond powder, identifying peanut fraud, motivated primarily by economic gain.

Food products are also usually tested for metal contents for a variety of reasons. Determination of the mineral composition is an important approach reflecting the nutritional value and its relationship with food quality. In fact, some elements are essential for numerous bodily functions and have a metabolic role (Co, Cu, Fe, Se, Zn), while others have potentially toxic characteristics (As, Cd, Pb). Therefore, trace metal profiling can be used to authenticate food Chen et al., 2014; D'Archivio, Giannitto, Incani, & Nisi, 2014; Drivelos, Higgins, Kalivas, Haroutounian, & Georgiou, 2014; Laursen, Schjoerring, Kelly, & Husted, 2014) and it is also expected that food adulteration could change the elemental profile of a particular sample, such as almond.

Fingerprinting based on chemical composition and multivariate data analysis have become one of the most powerful systematic approaches to determine authenticity (Coetzee, Van Jaarsveld, & Vanhaecke, 2014). A fingerprint is a characteristic profile of a sample, which can be established through common techniques such as chromatography and spectroscopy to characterize food products based on their quality or origin (Gan et al., 2015). The most common procedures used for pattern recognition purposes include: (i) principal component analysis (PCA) as an unsupervised technique, which provides uncorrelated objective latent variables (principal components) capable of extracting valuable information from the experimental data, exploring the relationship between objects in addition to the relationship between variables, and between objects and variables, (ii) linear discriminant analysis (LDA) as a supervised pattern recognition technique which is based on the determination of linear discriminant functions through maximizing the variance between classes and minimizing the variance within the classes.

In this paper, multi-element fingerprints of almond and peanut samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and subsequently two methodologies were proposed for multivariate classification. First, PCA was used to investigate the ability of elemental fingerprinting to discriminate the samples and then LDA was applied to detection of pure and adulterated almond samples. The second main objective of this study was to build a reliable model using elemental fingerprinting coupled with multivariate calibration methods for the quantification of peanut adulteration in almond powder samples. In this context, we have focused on the development and validation of calibration models using PLS and LS-SVM for the quantitative determination of adulteration in binary mixtures of peanut/almond powder samples in the concentration range of 5–95% (w/w).

2. Materials and method

2.1. Reagents and samples

Analytical reagent-grade materials were used for all experiments. All solutions were prepared using high-purity deionized water (>18 MΩ) (TKASmart2pure Water Purification Systems, Niederelbert, Germany). Nitric acid 65% w.v^{-1} and reference solutions of Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Se, Te and Zn at 1000 mg L^{-1} were obtained from Merck (Darmstadt, Germany).

Due to the large variation in available almonds and peanuts as a result of flavoring and processing, only raw, unflavored samples were used to minimize the sample variability. Almond samples were collected from Shahr-e-kord, which is the main producer of almonds with the highest quality in Iran. Peanut sampling was performed from Astaneh-ye-ashrafiyeh orchards. This region covers more than 80% of the peanut production in Iran. All samples were collected during the harvesting periods of 2013–2014. The adulterated samples were prepared as different ratios of almond-peanut mixtures. Almonds and peanuts were oven dried at 30 °C for at least 5 days. Afterwards, the samples were stored in a refrigerator at 4 °C till the preparation process.

2.2. Sample preparation and digestion

The raw unshelled samples were powdered using a mortar and pestle and were used for the preparation of the pure and the adulterated samples (ranging from 95/5 to 5/95 w/w). A total of 150 samples was measured, including 25 pure almond samples, 25 pure peanut samples and 100 adulterated almond samples. Almond powder was adulterated with peanut powder at a variety of levels from 5 to 95%, w/w. The finely ground kernels (1.0 g) (pure or adulterated with specific weight fraction of peanut) were introduced into a 50-mL PTFE (polytetrafluoroethylene) closed vessel. A volume of 20.0 mL concentrated nitric acid and 5 mL of concentrated hydrogen peroxide were added to the vessel. The bomb was sealed and put in a furnace set at 180 ± 10 °C and remained at this temperature during 2 h. The addition of H_2O_2 to the nitric acid was necessary to increase the oxidation efficiency. After cooling down to room temperature, solutions were quantitatively transferred to glass volumetric flasks and volumes were made up to 50.0 mL with deionized water.

2.3. Analysis by ICP-OES

An ICP-OES (Perkin Elmer, Optima 7300 DV, Shelton, USA) was used for the Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Se, Te and Zn determination. The sample introduction system was composed of a Scott spray chamber and a Gem-cone nebulizer. The operational parameters are tabulated in Table 1. A multi-element calibration curve was prepared by diluting standard solutions at 100 mg L^{-1} of each metal (CertiPur, Merck). The instrument is operated with computer software WinLab32. All