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Quantifying binary and ternary mixtures of monovarietal extra virgin olive oils with UV–vis absorption and chemometrics

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ABSTRACT

The pigment profile of three monovarietal extra virgin olive oils (EVOOs) (Cornicabra, Picual, and Hojiblanca varietals) and their binary and ternary mixtures have been analyzed through visible spectroscopy. The information extracted from the registered spectra was treated and then modeled following two different chemometric approaches: a linear one based on multiple linear regression models, and a non-linear one based on the employment of artificial neural networks. All the designed models were validated using a k-fold cross-validation, and the largest mean absolute errors (MAEs) obtained for the varietal quantifications were 10% for the linear model and 2.8% for the non-linear one. These results let us prove the efficient generalization capability of these mathematical tools, as they are able to accurately quantify olive oil varietals in mixtures through their pigment profile only requiring visible spectroscopy data.

1. Introduction

Olive oil, and especially extra virgin olive oil (EVOO), is the main source of fat in the Mediterranean diet [1]. It is obtained directly from the olive fruit through mechanical processes, and its popularity rate has been on the increasing side due to, among other reasons, the numerous scientific studies concerning its organoleptic properties and proving its beneficial effects on human health [2–4]. The composition of EVOO has been traditionally divided in two different fractions: the major one, the saponifiable fraction, mainly composed of fatty acids and triacylglycerides (TAGs), and the minor one, the insaponifiable fraction, which is formed by a wide-ranging amount of compounds such as polyphenols, sterols, and pigments, like carotenoids and chlorophylls (mainly lutein and phephitin-a, respectively) [3,5]. Its rich and complex composition, makes EVOO economically and nutritionally highly-valuable. Due to the relevance of EVOO in the market, it is necessary to legally protect such a high-quality product. This is achieved by doing several procedures to chemically determine and guarantee the quality and denomination of origin of the EVOO and also to avoid adulterations or illegal mixtures with other low-quality vegetal oils [6–8].

In this sense, monovarietal EVOOs, which are obtained from a single variety of olive fruit, have been deeply looked into and analyzed, thus maintaining the organoleptic properties intrinsically linked to the fruit variety selected, such as flavor, odor, phenolic profile, and so on [9]. These single-composition oils have been analyzed and characterized in diverse studies. The results have led to a better comprehension of the existent dependency between the organoleptic profile and the composition of a specific EVOO, and even with the health benefits their consumption might imply [6,10,11]. Determining the chemical differences between two different monovarietal EVOOs can lead to the development of methods and techniques able to determine the quality of EVOOs.

Among all the chemical components that experiment fluctuations when considering different monovarietal EVOOs, pigments are one of the most relevant groups [12]. These compounds (mainly pheophytin-a and lutein for the chlorophyll and carotenoid fraction, respectively) are not only responsible of the visual properties of EVOOs, but also play an essential role regarding oil ripening and various oxidative processes which take place within them [4,12]. Because of this, monovarietal EVOOs have been analyzed and studied to assess quality, following different methodologies among which various spectroscopic methods and HPLC are worth mentioning [13,14]. One of the most promising approaches is visible absorption spectroscopy, as it is a non-expensive and relatively quick technique that can be implemented for real-time analysis.

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It can be used to quantify the concentration of chemical species following the Lambert-Beer law without consuming the sample or requiring any chemical treatment or derivatization [15]. The existence of the multiple mentioned pigments in olive oil enables employing such technique for the differentiation between monovarietal EVOOs and to control their quality. It could even facilitate or permit the evaluation of EVOO storage conditions, ripeness, or adulteration presence [12,16].

Due to the high quantity of data obtained through these experimental procedures, statistical and mathematical tools should be employed to correctly interpret such data. Traditionally, linear statistical approaches (such as multiple linear regressions (MLRs), principal components analysis, and so on) have been used to complete these kinds of tasks [15]. Nevertheless, the use of more intricate non-linear models, such as artificial neural networks (ANNs), which have the ability of finding non-linear relations between analyzed parameters, is required in many cases. They have been used in the past to achieve relevant results in food technology research and, specifically, in the olive oil field to, for instance, discriminate varietals, estimate its degradation, or detect adulterants [16–20].

The main goal of this work is to assess the efficiency of both linear and non-linear mathematical models in estimating the composition of three monovarietal EVOOs from the South of Spain (Cornicabra, Picual, and Hojiblanca) in binary and ternary mixtures. The data used to test these models were obtained from the absorption spectra of the pigment profile of the EVOOs. This information was acquired using visible absorption spectroscopy and then modeled through MLRs (linear mathematical tool) and ANNs (non-linear mathematical tool). Both types of models were optimized and validated and then compared for this specific case, in terms of applicability, reliability, and accuracy.

2. Materials and methods

In the following subsections, the different EVOOs, materials, and methods employed are detailed.

2.1. Commercial olive oils

A total of three commercial monovarietal EVOOs within their expiration date, were purchased and utilized to prepare the binary and ternary mixtures. The oils used were Hojiblanca (Aceites Borges Pont SAU), Cornicabra (Aceites Toledo S.A.) and Picual (Aceites Borges Pont SAU) varietals.

2.2. Sample preparation

Samples with a final volume of 5 mL were prepared in different v/v composition ranges. The binary mixtures were prepared in order to contemplate the whole range of composition, with increments of 5% (v/v). This rate was increased to 10% in the case of the ternary mixtures (Fig. 1). All the samples were stored in a dry and dark location at room temperature before the measurements.

2.3. Absorption measurements

The absorption spectra of the EVOO mixtures were registered in the visible region, between 470 and 720 nm, where the relevant and varietal discriminating information is found, using a UV–vis spectrophotometer (Varian Cary 50 Conc). The EVOO samples were measured in a transparent cell of 1 cm length path. Each studied spectrum consists of the average of three independent measurements of the considered mixture, and was characterized by the area under the curve (AUC) of the four major absorption bands found [21]. These four AUCs were used as independent variables

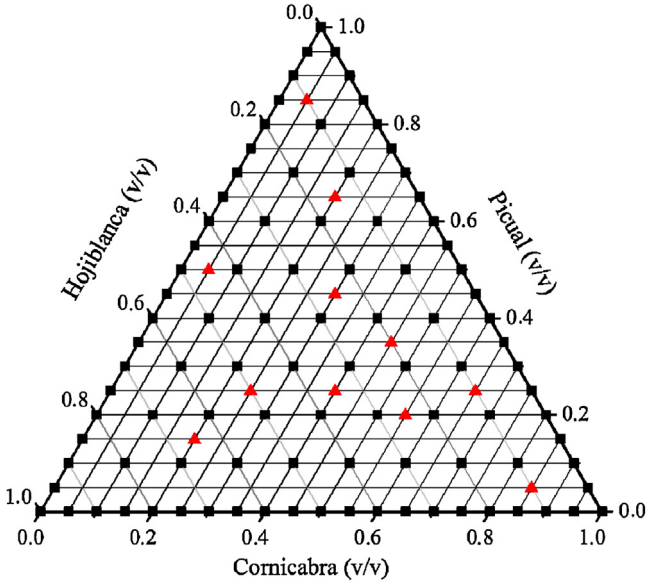

Fig. 1. Ternary system concerning the three monovarietal EVOOs studied. Each unit represents a prepared sample with a unique composition of the three varietals employed. ■, Correspond to the different blends used to design and train the mathematical models. ▲, Correspond to the samples used for the internal validation of the models (data not used to build the mathematical tools).

in the modeling phase of this research, and two different sets were employed (4-AUC and 2-AUC) and the results compared to determine if the less intense absorption bands provided relevant information to characterize the EVOO mixtures.

The analysis of the spectra was carried out using OriginPro v8.0724 (B724) and Matlab 2013b software packages.

2.4. Database

The final database consists of 96 data points (Fig. 1) containing spectroscopic and compositional information of the analyzed mixtures (the AUC of the different bands observed, and the v/v percentage of each EVOO varietal, respectively, *vide infra*). Also, an additional set of 11 samples was prepared and measured to carry out an internal validation in order to test the applicability of the models (Fig. 1). Their composition can be seen in Table SI. 1 of the Supplementary material.

2.5. Mathematical tools employed

Two different types of models have been employed to face this chemical problem and, additionally, their performance was compared: a MLR and an ANN-based model. Both mathematical approaches are explained in the following subsections.

2.5.1. Multiple linear regression models

Multiple linear regression models (MLRs) are widely used modeling methods, as they do not require an advanced mathematical knowledge, and are easy to apply and understand, being described by relatively simple algorithms [22,23]. They describe the importance of a series of quantitative factors or independent variables for a dependent variable, thus obtaining a linear equation containing all these variables (Eq. (1)). The goodness of the linear fit provided by this linear equation is given by the residuals and the adjusted correlation coefficient (R^2_a) [24]. Usually, as there is more than one single independent variable, the regression line cannot be described in a two-dimensional space.

$$Y = C + a_1 \times X_1 + a_2 \times X_2 + a_3 \times X_3 + \ldots + a_n \times X_n + \varepsilon \quad (1)$$