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Evaluation of olive oils from the Mediterranean region by UV–Vis spectroscopy and Independent Component Analysis

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ABSTRACT

Extra-virgin olive oil (EVOO) from Mediterranean were analyzed by Ultraviolet–Visible (UV–Vis) spectroscopy and Independent Component Analysis (ICA). The use of ICA resolution provided information over dienes (primary oxidation compound), polyphenolic compounds, tocopherol, carotenoids and chlorophylls when EVOO was evaluated by UV–Vis spectroscopy. Based on these data, ICA could be used to determine the contribution of chemical compounds to the composition of EVOO produced in different regions from Mediterranean. The results suggest that the combination of UV–Vis measurements and ICA makes possible the EVOO evaluation, and can contribute to suggesting that a foodstuff comes from an alleged origin. The proposed methodology is a low cost, fast and sample preparation free methodology to highlights the EVOO characteristics produced in the Mediterranean region.

1. Introduction

Extra-virgin olive oil (EVOO) has nutritional and sensory characteristics that make it unique and a basic component of the Mediterranean diet. EVOO is obtained exclusively by mechanical and physical processes including collecting, washing, and crushing olives, malaxation of olive paste, centrifugation, storage, and filtration (Calabriso, Scoditti, Pellegrino, & Carluccio, 2015).

It is known that EVOO present high monounsaturated fatty acids composition (55–85%), low polyunsaturated fatty acids (2–21%) and, the presence of highly antioxidative phenolic compounds (Tena, García-González, & Aparicio, 2009). EVOO is a rich source of α-tocopherol, a compound belonging to the group generic named as Vitamin E (α-, β-, γ-, δ-tocopherol and tocotrienols) (Guinazi, Milagres, Pinheiro-Sant'Ana, & Chaves, 2009). Furthermore, α-tocopherol is suggested as presenting highest antioxidant activity among the tocopherols (Yoshida, Niki, & Noguchi, 2003).

The EVOO production is a very important industry for the Mediterranean countries, both in terms of wealth, health, and tradition (Souilem et al., 2017). Foods with certificates of quality are gaining more and more relevance in people's diets. For example, in Andalusia (southern Spain) there are companies on the olive-oil gastronomic route and their designations of origin involved in the development of the tourism product of "olive oil tourism" (de la Torre, Arjona-Fuentes, & Amador-Hidalgo, 2017). In this sense, is mandatory the development of analytical methodologies that contribute to highlights the characteristics of the EVOO produced in the Mediterranean region and that can contribute to the evaluation, certification, and designation.

EVOO samples from Mediterranean region have been analyzed using spectroscopy techniques such as photoluminescence (Sena, Isnaeni, & Juliastuti, 2017), fluorescence (Tena et al., 2009), and infrared (Tena, Aparicio-Ruiz, & García-González, 2013). The coupling of the spectroscopy techniques with resolution methods in oil analysis made it possible to resolve the signals corresponding to the various oil constituents without resorting to physical separation methods (Gonçalves, Março, & Valderrama, 2014). In this sense, the Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) was coupled with ultraviolet–visible (UV–Vis) spectroscopy in order to verify the modifications that occur in oil samples when heated from ambient to high temperatures such as happens during frying (Gonçalves et al., 2014). Infrared spectroscopy and MCR-ALS was employed in the evaluation of the aging of edible oils (Le Dréau, Dupuy, Artaud, Ollivier, & Kister, 2009).

MCR-ALS is based on a bilinear model which assumes that the observed spectra are a linear combination of the spectra of the pure components in the system (Jaumot, de Juan, & Tauler, 2015). The algorithm steps include the determination of the number of components by rank analysis methods and an initial estimation of concentration and/or spectra with as many profiles as the number of components estimated from the rank analysis. Once the initial estimate is generated, the iterative optimization step is started (Valderrama, Gonçalves, Março, Rutledge, & Valderrama, 2016). However, sometimes, suitable

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results may not be achieved when MCR-ALS is applied. The main reason for this is the initial estimates step that reaches a local minimum resulting in insufficient curve resolution due to a problem of local minimum instead of the global minimum. There is a large possibility of occurrence of this by using the UV–Vis spectroscopy technique due to the high degree of band overlapping and the lack of selectivity in this technique (Valderrama et al., 2016). In this sense, other curve resolution tools can be investigated in order to evaluate UV–Vis spectra data set, since it is a fast and low-cost technique.

In this paper, EVOO samples from Mediterranean region were evaluated by UV–Vis spectroscopy coupled with the resolution method of Independent Component Analysis (ICA). ICA searches for the decomposition of signals from the mixture into a more statistically independent component. There are several different algorithms to performer ICA resolution (Bell & Sejnowski, 1995; Hyvärinen & Oja, 1997) however the Joint Approximate Diagonalization of Eigenmatrices (JADE) (Cardoso & Souloumiac, 1993) present an advantage over the others. The JADE algorithm is based on matrix computation, involving matrix diagonalization to calculate Independent Components (ICs). Other algorithms rely on an optimization procedure and hence may yield variable results depending on the starting point and on the optimization path followed by the search algorithm (Rutledge & Bouveresse, 2013). Moreover, some ICA algorithms allow applications of constraints such as non-negativity (for concentration and spectra) which drastically reduces the independence between ICs (Parastar, Jalali-Heravi, & Tauler, 2012).

Here it is employed ICA with JADE algorithm in order to avoid the problem of local minimum instead of the global minimum of the MCR-ALS and, break away from the problem reported with other algorithms in the computation of the ICs. So, the main objective is to verify similarities between EVOO samples from Mediterranean region due to its constituents from UV–Vis spectra and contribute to the proposal of a methodology to assist in the highlights the EVOO characteristics produced in the Mediterranean region.

ICA is a blind source separation method that extracts the pure underlying signals from a signals data set where they are mixed in unknown proportions. The ICA general model is (Stone, 2004):

$$\mathbf{X} = \mathbf{A}.\ \mathbf{S}$$

where **X** is the matrix of observed signals (UV–Vis spectra in our case). **S** is the matrix of unknown pure source signals. **A** is the mixing matrix of unknown coefficients, related to the corresponding proportions. ICA aims to maximize the non-gaussianity of the extracted signals. Then, ICA assumes that statistically independent source signals have intensity distributions that are less Gaussian than are their mixtures (Ammari, Jouan-Rimbaud-Bouveresse, Boughanmi, & Rutledge, 2012). Recent researches have shown the ICA with JADE algorithm employed to unsupervised pattern recognition applications (Ammari, Redjdal, & Rutledge, 2015; Kassouf, Maalouly, Rutledge, Chebib, & Ducruet, 2014; Mishra et al., 2016).

2. Experimental

2.1. Samples

EVOO samples from France (Languedoc Roussillon 0.5%, Marseille 0.5%), Spain (Catalonia 0.2% and Andalusia 0.1%), Italy (Tuscany 0.33%, Sicily 0.35%, Puglia 0.22%), Greece (Crete 0.4 and 0.5%), Morocco (Atlasgebergte 0.15%) were purchased in the Leiden Holland marketplace.

2.2. Experimental parameters and software

Samples from each EVOO were analyzed in triplicate. The spectra were taken at the room temperature (25 °C). UV–Vis spectra were acquired in an Ocean Optics equipment (model USB-650-UV–VIS) in the range 200–750 nm (steps of 1 nm) in a 1 mm quartz cuvette. Data were analyzed using MATLAB version R2007b (The Mathworks Inc., MA, USA) where curve resolution was performed by ICA with JADE algorithm (Cardoso & Souloumiac, 1993). The mathematical steps for ICA method are described by Rutledge and Bouveresse (2013) and Rutledge and Bouveresse (2015), while the Matlab code for JADE algorithm can be found on the website < http://perso.telecom-paristech.fr/~cardoso/Algo/Jade/jadeR.m > .

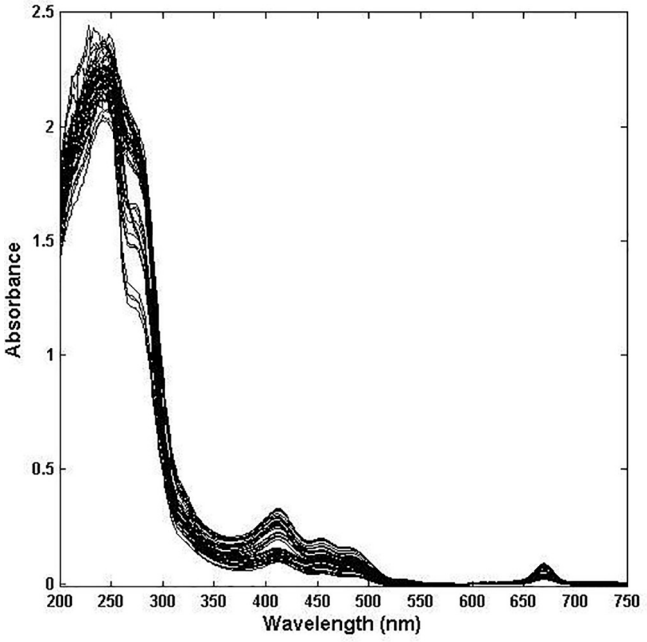

Fig. 1. UV–Vis spectra to extra-virgin olive oil from different Mediterranean regions.

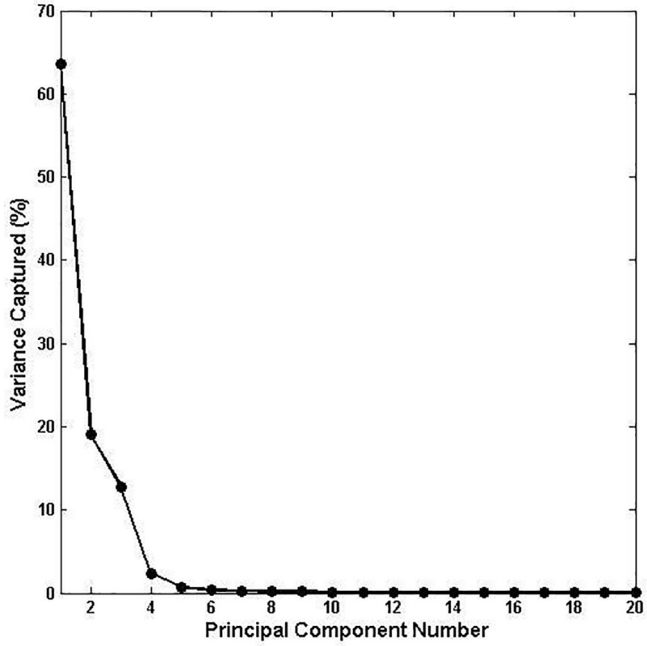

Fig. 2. Percentage of variance captured by PCA.

3. Results and discussion

The UV–Vis spectra of the samples after spectral baseline adjustment made by the first-order polynomial and smoothed through Savitsky-Golay algorithm (Savitzky & Golay, 1964) (13 points and first