Food Chemistry 202 (2016) 432–437

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Chemometric analysis for discrimination of extra virgin olive oils from whole and stoned olive pastes

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ARTICLE INFO

Article history:
Received 12 April 2015
Received in revised form 29 September 2015
Accepted 1 February 2016
Available online 2 February 2016

Keywords:
Virgin olive oil
Chemometrics
Partial least square discriminant analysis
Principal component analysis
Fourier transform infrared
Stoned olive pastes

ABSTRACT

Chemometric discrimination of extra virgin olive oils (EVOO) from whole and stoned olive pastes was carried out by using Fourier transform infrared (FTIR) data and partial least squares-discriminant analysis (PLS1-DA) approach. Four Italian commercial EVOO brands, all in both whole and stoned version, were considered in this study. The adopted chemometric methodologies were able to describe the different chemical features in phenolic and volatile compounds contained in the two types of oil by using unspecific IR spectral information. Principal component analysis (PCA) was employed in cluster analysis to capture data patterns and to highlight differences between technological processes and EVOO brands. The PLS1-DA algorithm was used as supervised discriminant analysis to identify the different oil extraction procedures. Discriminant analysis was extended to the evaluation of possible adulteration by addition of aliquots of oil from whole paste to the most valuable oil from stoned olives. The statistical parameters from external validation of all the PLS models were very satisfactory, with low root mean square error of prediction (RMSEP) and relative error (RE%).

1. Introduction

A large increase in demand for high-quality virgin olive oil during the last years can be attributed not only to its particular organoleptic properties but also to its potential health benefits (Clodoveo, Camposeo, De Gennaro, Pascuzzi, & Roselli, 2014). Usually, the quality of an EVOO is strictly related with the quality of fruits, with the harvesting systems and above all with the oil extraction process. In this regard, the improvement of the quality standards for EVOO is continuously stimulating the search for new extraction technologies. In particular, it has been reported that the type of crusher is critical in determining the quantity and the quality of EVOO (Clodoveo, 2012; Clodoveo, 2013; Clodoveo, Durante, & La Notte, 2013; Clodoveo & Hbaieb, 2013).

Currently, the de-stoner technique is the only mechanical system that allows a selective crushing of the fruits excluding the stone from the paste. The stone exclusion has the undoubted advantages to increase both nutritional quality of the product and sustainability of the process. When the olive paste is made exclusively from the mesocarp, the bio-phenol content is protected from oxidation because most of the oxidative enzymes, as polyphenol oxidase and peroxidase, mainly localized in the stone, is removed (Amirante, Clodoveo, Dugo, Leone, & Tamborrino, 2006; Clodoveo, Dipalmo, Schiano, La Notte, & Pati, 2014; Restuccia et al., 2011; Servili et al., 2007). On the contrary, when the "integral crushing" is applied, the presence of olive kernel reduces the work capacity of the whole mill plant. Moreover, the crushing of the kernel requires a large dissipation of mechanical energy partially converted into thermal energy which heats the olive paste before the triggering of thermolabile enzymes, such as lipoxygenase and hydroperoxide lyase (Clodoveo, Hbaieb, Kotti, Mugnozza, & Gargouri, 2014). The heating of the fragments constitutes again a by-product, absorbing in vain thermal energy, with the burden of a heavy economic and energetic cost. Secondary advantages derive from the olive seed that can be source of valuable compounds for the cosmetics and pharmaceutical industries. The de-stoned pomace is easier to use as an animal feed, while the kernel can be employed for the production of coal for food industries (Spizzirri et al., 2011). Despite these benefits, this technology is not widespread and the main reason lies in the fact that the de-stoning process produces higher quality EVOO but in lower yield. At the time, the commercial market does not acknowledge in EVOO stoned an extra charge sufficient to compensate for the loss of yield. The justification for a higher price should also be supported by security on product quality. Therefore, it seems necessary to

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http://dx.doi.org/10.1016/j.foodchem.2016.02.018
0308-8146/

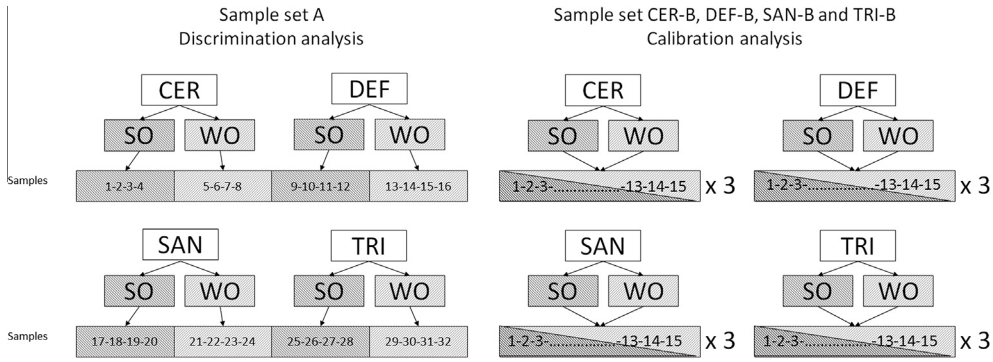

Fig. 1. Sample set scheme.

have analytical techniques able to ascertain that the oil from olives pitted is intact and not adulterated with oil of different origin.

In recent years, numerous analytical studies using physical–chemical techniques combined with chemometric methodologies have been proposed for the characterization of food genuineness (Arvanitoyannis & Vlachos, 2007; Bassbasi, De Luca, Ioele, Ragno, & Oussama, 2014). Clustering of the samples (objects) can be performed by unsupervised methods, which identify the natural pattern, and group samples based on similarities among the samples. Information stored in the experimental data elaborated in models, used to predict new unknown samples. Application of spectroscopic techniques in the study of the origin and differentiation of food products has considerably developed in the recent years (Bassbasi, De Luca, Ioele et al., 2014; Bassbasi et al., 2014; De Luca, Terouzi, Bolli et al., 2011; De Luca, Terouzi, Ioele et al., 2011; Forina, Oliveri, Lanteri, & Casale, 2008; Poulli, Mousdis, & Georgiou, 2005). In particular, FTIR has been successfully used to characterize many olive oil parameters (Tapp, Defernez, & Kemsley, 2003). This technique is simple to perform, not expensive in terms of time and money and usually does not require sample pre-treatment (Lerma-García, Ramis-Ramos, Herrero-Martínez, & Simó-Alfonso, 2010; Ozen & Mauer, 2002). FTIR has been proposed to authenticate extra virgin olive oils or to detect adulteration and some attempts in using FTIR to distinguish olive oils from different geographical origin and different genetic varieties have been published (De Luca, Terouzi, Bolli et al., 2011; De Luca et al., 2012; Gurdeniz, Tokatli, & Ozen, 2007; Sinelli, Cerretani, Di Egidio, Bendini, & Casiraghi, 2010; Tapp et al., 2003).

Multivariate analysis provides a series of tools for handling a very large number of data and variables from different analytical methods.

The aim of this paper is to develop a multivariate analytical method able to certify that an olive oil has been extracted solely from stoned olives in order to offer the maximum guarantee to consumers and a proper profit for producers. In addition, a further PLS modeling on the ATR-FTIR data has been defined, allowing to assess any adulteration due to the addition of oil from whole paste to oil from stoned olives.

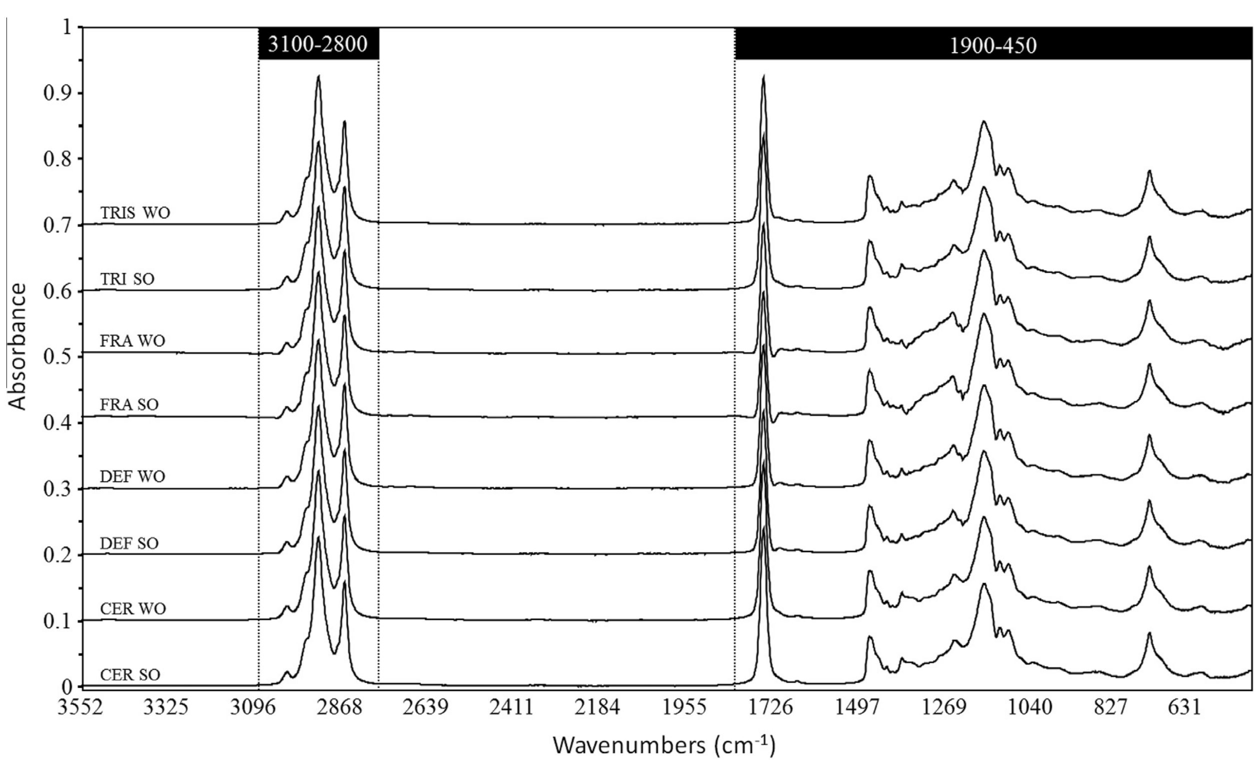

Fig. 2. Average FT-IR spectra calculated for each oil brand in both SO and WO versions.