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Quantification of sterols and fatty acids of extra virgin olive oils by FT-NIR spectroscopy and multivariate statistical analyses

İbrahim Sani Özdemir[a,*], Çağdaş Dağ[a], Gizem Özinanç[c], Öznur Suçsoran[a], Erdal Ertaş[a], Somer Bekiroğlu[b]

[a] TUBITAK Marmara Research Center, Food Institute, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey
[b] TUBITAK Marmara Research Center, Chemical Technology Institute, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey
[c] Yıldız Teknik University, İstanbul, Turkey

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ABSTRACT

In this study FT-NIR spectra of 73 extra virgin olive oil (EVOO) samples obtained from 21 different cultivars and 4 geographic regions were used to develop partial least squares regression (PLS-R) models for the rapid quantification of sterols for the first time in the literature. The results of the model validation showed that the total sterol content of the EVOO samples could be predicted with good prediction ability (R_p^2 = 0.839, RMSEP = 192 mg/kg, RPD = 2.64). However, the prediction models for the individual sterol forms performed poorly. Except for heptadecanoic and eicosenic acids, models with good prediction ability could be established for the quantification of the major fatty acids found in EVOOs with R_p^2 and RPD values ranging between 0.716-0.997 and 2.02–17.6, respectively. Even better model performances were obtained when fatty acids were grouped according to their unsaturation degree as SFA (R_p^2 = 0.998, RMSEP = 0.102%, RPD = 21.8), MUFA (R_p^2 = 0.997, RMSEP = 0.255%, RPD = 18.7) and PUFA (R_p^2 = 0.998, RMSEP = 0.147%, RPD = 25.1).

1. Introduction

Olive oil is the flagship food product of the Mediterranean basin countries. Due to its superior organoleptic and nutritional quality virgin olive oils are the most valued type of olive oils compared to refined and riviera olive oils. The virgin label assures that the oil was extracted through a chemical-free process without heating and was not mixed with oils of different characteristics. Virgin olive oils are further classified as extra virgin olive oil (EVOO), virgin olive oil (VOO) and ordinary virgin olive oil (OVOO) on the basis of their free acidity values expressed as oleic acid which should be less than 0.8%, 2% and 3.3%, respectively (International Olive Oil Council, 2003).

The superiority of the EVOO over other oils is also attributed to the content and composition of the several health promoting substances found in the unsaponifiable fraction of the oil such as phenolic compounds, tocopherols, chlorophylls, carotenoids, and sterols (Covas et al., 2006). Although they constitute 1–2% of the olive oil, these minor constituents are regarded as the important quality indicators. Apart from their nutritional values the content and composition of these compounds can also be used in the authentication of olive oils on the basis of geographical origin and cultivar (Dag, Demirtas, Ozdemir, Bekiroglu, & Ertas, 2015; Krichene et al., 2007; Temime et al., 2008). However, analyses of these compounds are rather tedious and require skilled personnel and expensive laboratory equipment's. Therefore, most of the olive oil producers cannot routinely analyse these compounds by their own means and they summon the help of specialised laboratories which generates extra costs for producers to bear.

In this respect, Fourier transform near-infrared spectroscopy (FT-NIRS) coupled with appropriate chemometric techniques can be regarded as a practical solution for the rapid and simultaneous analyses of the minor constituents found in olive oil (Nenadis & Tsimidou, 2017; Wang, Sun, Zhang, & Liu, 2016). The results of the studies carried out so far showed that the content of the major fatty acids can be measured precisely with the FT-NIRS (Azizian & Kramer, 2005; Inarejos-García, Gómez-Alonso, Fregapane, & Salvador, 2013; Mailer, 2004). Similarly, good results were also reported for the measurement of phenolic compounds, tocopherols, chlorophylls, and carotenoids (Dupuy, Galtier, Ollivier, Vanloot, & Artaud, 2010; Inarejos-García et al., 2013; Mailer, 2004). FT-NIRS was also successful in predicting the sensorial quality of the EVOOs (Sinelli, Cerretani, Di Egidio, Bendini, & Casiraghi, 2010). However, up to our knowledge, feasibility of using FT-NIRS for the measurement of the content of total and individual sterol forms in olive oil has not been studied yet.

Therefore, the major objective of this study was to investigate the

* Corresponding author.
E-mail address: ibrahim.ozdemir@tubitak.gov.tr (İ.S. Özdemir).

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potential of using FT-NIRS and chemometrics for the rapid analysis of the total and individual sterol forms found in extra virgin olive oils. In addition, partial least squares regression (PLS-R) models were also developed for the prediction of the major fatty acids found in EVOOs.

2. Materials and methods

2.1. Chemicals

All chemical reagents were obtained from Sigma-Aldrich-Fluka Co. Ltd. (Steinheim, Germany), unless otherwise stated. Potassium hydroxide and anhydrous sodium sulphate were purchased from Carlo Erba (Milano, Italy). Tri-methyl chlorosilane, 5α-cholastene-3-β-ol and fatty acid methyl esters (FAMEs) standard mixture were purchased from Merck (Darmstadt, Germany) and Supelco (Bellefonte, U.S.A).

2.2. EVOO samples

In total, 73 monocultivar EVOO samples were prepared from the olive drupes which were harvested manually. Samples were collected between October and November. The list of olive cultivars used in this study was given in Table 1. For all the olive cultivars, fruits having maturity level of 3–4 were harvested according to the Maturity Index (MI) described by Guzmán, Baeten, Pierna, and García-Mesa (2015) which classifies olives in 7 distinct maturity levels according to the color of the skin and flesh of the fruit.

Each EVOO sample was prepared from 4 kg of olives. Olive samples were processed for oil production as follows; upon arrival to the laboratory, olive samples were stored at 4 °C and processed within 1 day after harvesting. EVOOs were prepared by using lab-scale equipment. As the first stage of the processing, leaves and other debris were removed from the olive samples by washing. Then, olives were crushed by using a grinding mill of screw conveyor type. Crushed olives were then moved to malaxation step where they were mixed for 25 min at 30 °C. Finally, extracted oil was collected by a centrifugal separation system. The olive oil samples obtained were flash frozen in liquid nitrogen and kept at −26 °C in freezers until further analyses.

Table 1
The geographic location of harvest and the number of samples of the olive cultivars used for the EVOO production.

Geographic Region	Cultivar	Number of Sample
Ege	Akhisar Uslu	3
	Arbekina	1
	Domat	1
	Edremit yağlık	10
	Gemlik	4
	Karamürsel su	1
	Manzalina	1
	Memecik	12
Akdeniz	Ascolana	1
	Beylik	2
	Edincik su	1
	Erkence	1
	Gemlik	1
	Kilis yağlık	2
	Manzalina	1
	Memecik	1
	Meski	1
	Nizip yağlık	1
	Samanlı	1
	Sarıulak	11
	Saurani	2
	Silifke yağlık	1
	Tavşan yüreği	2
Güneydoğu	Gemlik	2
	Halhalı	2
	Nizip yağlık	3
Marmara	Gemlik	2
Total		*73*

2.3. Spectral measurements

Prior to spectral acquisition the samples were thawed at 7 °C and placed in glass vials with 8 mm path length and let for temperature equilibration at 40 °C for 20 min in a climatic cabinet. Then the vials

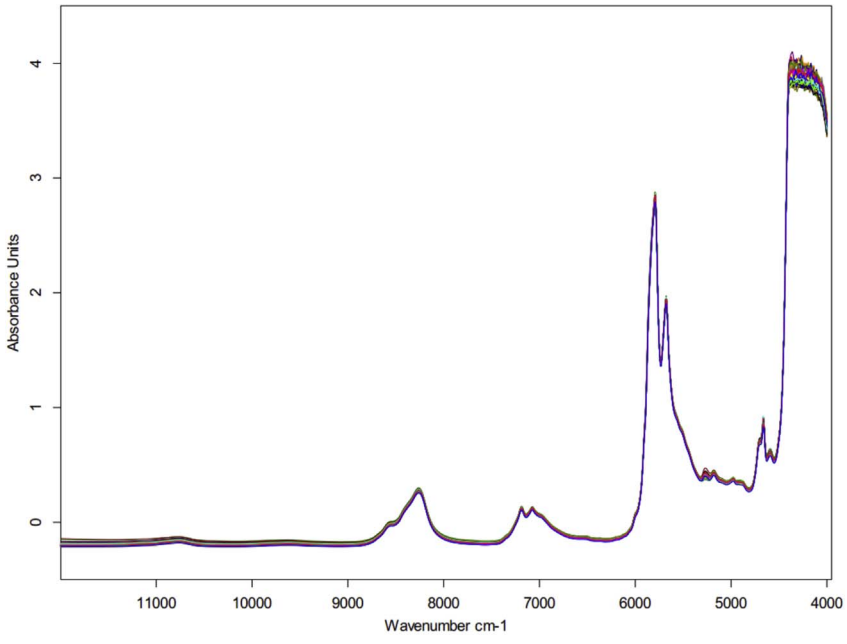

Fig. 1. Raw FT-NIR spectra (12000–4000 cm^{-1}) of the 73 monovarietal EVOO samples.