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Prediction of various chemical parameters of olive oils with Fourier transform infrared spectroscopy

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ABSTRACT

Vibrational spectroscopic techniques offer advantages such as rapid and accurate measurements with minimum sample preparation and waste generation. In this study, it was aimed at determining some important quality parameters (oxidative stability, colour pigments, fatty acid profile and phenolic composition) of olive oils by Fourier transform infrared spectroscopy as one of the vibrational spectroscopic methods. Partial least square calibration models were constructed in order to reveal any correlation between quality parameters and spectral data. Regression coefficients for developed models showed that oxidative stability (0.99), chlorophyll content (0.98), some major fatty acids (palmitic (0.87), oleic (0.94), and linoleic acids (0.97), saturated (0.91), monounsaturated (0.94) and polyunsaturated fatty acids (0.97)), hydroxytyrosol as a phenolic compound (0.97) and total phenolic content (0.99) were predicted successfully. Variable influence on the projection values indicated that palmitic, vanillic and cinnamic acids and hydroxytyrosol are the most significant contributors to oxidative stability of olive oils.

1. Introduction

Olive oil, extracted from the fruit of olive tree, is known for its precious nutritional, functional and sensorial qualities. Olive oil consumption has been increasing in recent years due to its positive health effects that are attributed to its balanced unsaturated fatty acid content and the presence of other functional compounds such as phenolics, tocopherols and chlorophyll (Matos et al., 2007; Temime et al., 2008). Extra virgin olive oil is defined as the oil which is produced only by mechanical processes like crushing, malaxation and centrifugation without any further chemical treatment. Since no refinement process is involved in its production, organoleptic and nutritional values of olive oils are well preserved as well as its defense mechanism against oxidative stress (Perona, Cabello-Moruno, & Ruiz-Gutierrez, 2006). There are many quality parameters of olive oils that need to be monitored in order to assure organoleptic and sensorial properties of the final product. One of these parameters is oxidative stability which can provide an idea about the storage history of olive oil. Furthermore, major components like fatty acid profile and minor components such as polyphenol content and chlorophyll level are also considered as important contributors to organoleptic and quality properties of olive oil (Mailer, 2004). Therefore, it is important to determine these parameters in a fast and a reliable way. For this purpose, spectroscopic methods like near infrared (NIR), mid-infrared (MIR), Raman and NMR have been used in several studies and they have advantages compared to time-consuming and expensive traditional methods since several analyses could be performed simultaneously with minimum waste generation (Moros, Garrigues, & de la Guardia, 2010). For instance, high-resolution ^{13}C NMR was used to predict oxidative stabilities of different oils including olive oil successfully (Hidalgo, Gómez, Navarro, & Zamora, 2002). Acidity and peroxide index of different types of edible oils were evaluated by NIR spectroscopy in another study (Armenta, Garrigues, & de la Guardia, 2007). Oxidized fatty acid concentration under different oxidative status was determined with FTIR (Fourier transform infrared) spectroscopy in a study by Lerma-García, Simó-Alfonso, Bendini, and Cerretani (2011). Also, Raman spectroscopy has been recently used in monitoring fatty acid composition of different vegetable oils with promising results (Dong, Zhang, Zhang, & Wang, 2013).

In the literature, FTIR spectroscopy has been mainly used in classification studies. Moreover, it has also gained popularity on the quantitative analysis due to the fact that the emitted IR energy is directly proportional to the concentration of compounds that are present in a tested sample (Ismail, van de Voort, & Sedman, 1997).

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FTIR spectroscopy has already been used in peroxide value determination for different vegetable oils (Allendorf, Subramanian, & Rodriguez-Saona, 2012) and in the quantification of fatty acids and triacylglycerols of olive oils (Galtier et al., 2008).

The aim of the present study is to investigate the ability of FTIR spectroscopy as a fast and a reliable method in the prediction of some important quality parameters of olive oils, oxidative stability, colour pigments (chlorophyll and carotenoid), fatty acid profile and phenolic compounds. Moreover, the effect of each measured chemical constituent on oxidative stability is evaluated.

2. Materials and methods

2.1. Olive oil samples

Sixty four olive oil samples were obtained from the various parts of Karaburun Peninsula of Izmir. Oils were extracted with an industrial scale two phase decanter system (Polat Machinery, Turkey) capable of processing 1.66 tonnes olive/h and located in Izmir Institute of Technology Campus and Eglenhoca village of Izmir. Samples in glass containers were kept in the dark at refrigeration temperature (8 °C) after their head spaces were flushed with nitrogen.

2.2. Chemical reagents

All reagents used in the experiments were of analytical grade and they were obtained from Riedel-de Haën (Germany), Sigma–Aldrich (Germany) and Merck (Germany). Phenolic acids (vanillic, syringic, caffeic, p-coumaric, o-coumaric, cinnamic, 4-hydroxyphenyl acetic, 3-hydroxyphenyl acetic and 2, 3-dihydroxybenzoic acids), flavonoids (apigenin, luteolin and vanillin) and phenolic alcohols (tyrosol and hydroxytyrosol) for HPLC analysis were the commercial phenolic standards (Fluka and Extrasynthase). Fatty acid methyl ester (FAME) mixture containing C4–C24 (2–4% relative concentration) was used as a reference standard (Supelco # 47885-U) for GC analysis.

2.3. Chemical analyses

2.3.1. Oxidative stability (OS)

Oxidative stability was determined with Rancimat equipment (873 Biodiesel, Metrohm, Switzerland) in terms of hour. Temperature range of this equipment is 50–220 °C and temperature stability is less than 0.1 °C. 3 g of olive oil was placed inside the glass reaction vessel for the measurement. Carrier medium was selected as deionized water. Reaction temperature was set to a constant value of 120 °C for both columns of Rancimat apparatus with a constant 20 L/h air flow.

2.3.2. Total phenol content (TPC)

Folin–Ciocalteu spectrophotometric method was used to determine the total amount of phenolic compounds in the olive oil samples (Montedoro, Servili, Baldioli, & Miniati, 1992). All the results were calculated in terms of gallic acid (GA) as mg GA/kg oil using gallic acid standard curve. The measurements were repeated for two times for the extracted samples.

2.3.3. High performance liquid chromatography (HPLC) analysis of phenolic compounds

The procedure from Brenes, García, García, Rios, and Garrido (1999) was used to extract phenolic compounds from olive oil samples. The extract having gallic acid as an internal standard was immediately injected to HPLC.

Amounts of individual phenolic compounds in olive oil were determined by an HPLC (Agilent 1200 HPLC, USA) equipped with refractive index (RI) and photodiode array (DAD) detectors, an auto sampler (ALS G1329A) and a column oven. A C18 column (250*4 mm, 5 μm, SGE 8211, Australia) was used in analyses. Column temperature was kept at 35 °C and injection volume was 20 μL. Flow rate was adjusted to 1 mL/min. Two different mobile phases were used as water/acetic acid (99.8:0.2 v/v) and methanol. Initial concentrations of mobile phases were 90% for water/acetic acid and 10% for methanol. Concentration of mobile phases was adjusted over time by the following procedure; firstly, the concentration of methanol was increased to 30% in 10 min and kept there for 20 min and at the same time water/acetic acid concentration was decreased to 70%. Then, methanol percentage was increased to 40% in 10 min, kept for another 5 min, followed by rising up to 50% in 5 min, and kept for 5 min. At last, methanol was increased to 60, 70, and 100% in 5 min periods. Finally, initial conditions were attained at the end of 85 min.

Internal standard method was used in order to compensate any loss of phenolic compounds during the experimental procedures. Gallic acid was chosen as the internal standard. Major phenolic compounds found in olive oil were determined by using their commercial standard forms at two different wavelengths of 280 and 320 nm. 5-point calibration curves for each standard were plotted and the results were expressed in terms of mg/kg.

2.3.4. Chlorophyll & carotenoid measurement

Chlorophyll and carotenoid contents of olive oils were determined according to a procedure in literature (Mínguez-Mosquera, Rejano-Navarro, Gandul-Rojas, Sánchez Gómez, & Garrido-Fernandez, 1991). 7.5 g of an olive oil sample was weighted into a test tube and filled up to 25 mL with cyclohexane. The absorbance corresponding to chlorophyll and carotenoid fractions were measured by a UV spectrophotometer (Shimadzu UV-2450 Spectrophotometer, Japan) at 670 nm and 470 nm, respectively.

2.3.5. Fatty acid profile determination

In order to determine fatty acid profile of the olive oil samples, firstly methyl esterification reaction was carried out according to European Official Methods of Analysis (European Union Commission, 1991). After esterification reaction, the solution was vortexed and centrifuged in order to collect supernatant and then filtered into dark brown vials. Immediately after filtration, supernatant was injected into the gas chromatography (GC) device.

Fatty acid profiles of olive oil samples were examined by a GC (Agilent 6890, Agilent Technologies, USA) equipped with an autosampler (Agilent 7863 & FID) and a split/splitless (1:50) injector. HP 88 capillary column (Agilent, USA) with dimensions of 100 m*0.25 mm ID*0.2 μm was used and helium with 2 mL/min constant flow rate was selected as a carrier medium. Injection volume was 1 mL with the injection temperature of 250 °C while the detector temperature was kept at 280 °C. Oven temperature was set to 120 °C initially and was maintained there for 10 min then increased with a rate of 3 °C/min until reaching to 220 °C which was kept at this temperature for another 5 min. FAME standard peaks were compared with sample chromatogram and the results were expressed as percentage of FAME.

2.4. Fourier-transform infrared (FTIR) spectroscopy analysis

All infrared spectra were recorded in mid-IR (4000–650 cm^{-1} wavenumber) range by a Perkin Elmer Spectrum 100 FTIR spectrometer (Perkin Elmer Inc., USA) having a deuterated tri-glycine sulphate (DTGS) detector. The instrument was equipped with a horizontal attenuated total reflectance (HATR) accessory with ZnSe