Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 161 (2016) 83–87

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

The effect of thermal treatment on the enhancement of detection of adulteration in extra virgin olive oils by synchronous fluorescence spectroscopy and chemometric analysis

F. Mabood [a], R. Boqué [b], R. Folcarelli [c], O. Busto [b], F. Jabeen [d], Ahmed Al-Harrasi [e], J. Hussain [a]

[a] Department of Biological Sciences & Chemistry, College of Arts and Sciences, University of Nizwa, Oman
[b] Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Tarragona, Spain
[c] Department of Chemistry, University of Rome "Sapienza", P.e Aldo Moro 5, I-00185 Rome, Italy
[d] Department of Chemistry, University of Malakand, KPK, Pakistan
[e] UoN Chair of Oman Medicinal Plants and Marine Products, University of Nizwa, Sultanate of Oman

ARTICLE INFO

Article history:
Received 5 July 2015
Received in revised form 25 January 2016
Accepted 28 February 2016
Available online 2 March 2016

Keywords:
Thermal treatment
Extra virgin olive oil (EVOO)
Refined olive oil
Synchronous fluorescence spectroscopy
Adulteration
PLS-DA
PLS regression

ABSTRACT

In this study the effect of thermal treatment on the enhancement of synchronous fluorescence spectroscopic method for discrimination and quantification of pure extra virgin olive oil (EVOO) samples from EVOO samples adulterated with refined oil was investigated. Two groups of samples were used. One group was analyzed at room temperature (25 °C) and the other group was thermally treated in a thermostatic water bath at 75 °C for 8 h, in contact with air and with light exposure, to favor oxidation. All the samples were then measured with synchronous fluorescence spectroscopy. Synchronous fluorescence spectra were acquired by varying the wavelength in the region from 250 to 720 nm at 20 nm wavelength differential interval of excitation and emission. Pure and adulterated olive oils were discriminated by using partial least-squares discriminant analysis (PLS-DA). It was found that the best PLS-DA models were those built with the difference spectra (75 °C–25 °C), which were able to discriminate pure from adulterated oils at a 2% level of adulteration of refined olive oils. Furthermore, PLS regression models were also built to quantify the level of adulteration. Again, the best model was the one built with the difference spectra, with a prediction error of 3.18% of adulteration.
© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The detection of olive oil adulteration with olive oils of lower quality as well cheaper seed oil with the use of fluorescence spectroscopy is already well investigated [1,2]. Very early work pointed out good prospects for characterization of edible oils through fluorimetry [3,4]. However molecular fluorescence spectroscopy may not be suitable for the analysis of complex multi-component samples without prior separation, due to severe overlaps of excitation and emission bands. In such cases, synchronous fluorescence (SyF) could be proved beneficial as both the excitation and emission monochromators are scanned simultaneously in such a manner that a constant wavelength interval is kept between emission and excitation wavelengths ($\Delta\lambda$). Using suitable $\Delta\lambda$, SyF reduces spectral overlaps by narrowing spectral bands and simplifies the spectra [5–8]. In this way, spectra selectivity is increased. Recently, a SyF method was described for the classification of edible and lampante olive oils [9–20].

All types of olive oil (including extra virgin) contain a large amount of monounsaturated fat. In fact, 70–80% of the total fat found in olive oil is monounsaturated. This monounsaturated fat comes from oleic oil, a monounsaturated fatty acid (MUFA). Olive oil is fairly unique in its high MUFA content. Canola oil comes close (60–70% MUFA), but many of the other common vegetable oils, including sunflower, corn and soybean oils, naturally contain less than half MUFA than olive oil. In general, monounsaturated fat increases the stability of a vegetable oil in comparison to polyunsaturated fat. This increased stability is related to the chemical structure of monounsaturated fat. MUFAs have fewer "reactive spots" than PUFAs (polyunsaturated fatty acids) and it is more difficult for oxygen radicals to interact with them. However, despite this lower reactivity, olive oil and other vegetable oils containing a high amount of MUFAs (like sunflower oil) still have relatively low smoke points and cannot withstand a large amount of heat. So the presence of other vegetable oils like sunflower in EVOO as adulterants also changes this stability against temperature [20–25].

So the novelty of this study is to check the effect of thermal treatment and exposure to air to favor detection and discrimination of adulteration of extra virgin olive oils from EVOOs adulterated with refined olive oil, using SyF spectroscopy and PLS-DA and PLS regression.

E-mail addresses: mehboob@unizwa.edu.om, mehboob86@yahoo.com (F. Mabood).

http://dx.doi.org/10.1016/j.saa.2016.02.032
1386-1425/© 2016 Elsevier B.V. All rights reserved.

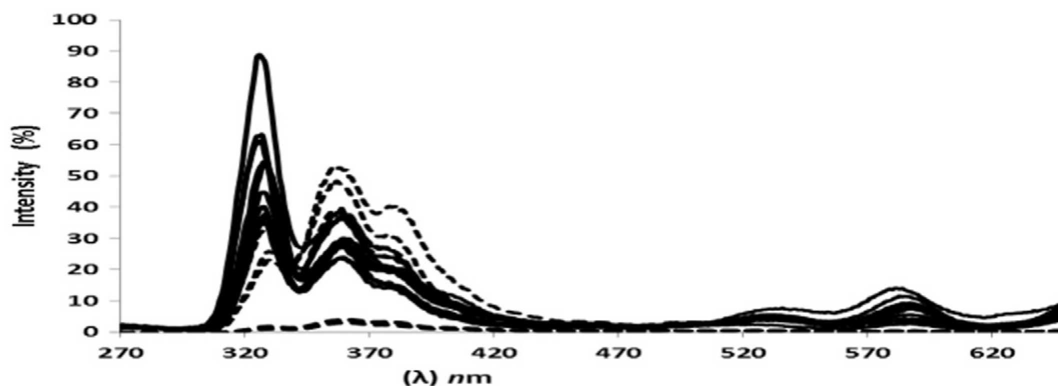

Fig. 1. SyF spectra at 20 nm difference for EVOO samples, both pure (solid line spectra) and adulterated with 10% RF1(point spectra) at 25 °C.

2. Materials and methods

2.1. Samples

Eleven extra virgin olive oil (EVOO) samples from PDO Siurana (Tarragona, Catalonia) were used. The EVOOs were purchased at the cooperatives to guarantee their traceability and quality. Those eleven EVOO samples were then adulterated with two types of refined olive oil at four different percentage levels: 2, 5, 10 and 20%. The total number of samples used was 99: 11 pure, 44 adulterated with RF1 and 44 adulterated with RF2. The samples were prepared by duplicate. One group of 99 samples was kept at room temperature (25 °C) and the other group of 99 samples was kept in a water bath at 75 °C for 8 h, in contact with air and with light exposure, to favor oxidation.

2.2. Fluorescence measurements

Fluorescence spectra were acquired with an AMINCO-Bowman Series 2 Luminescence Spectrometer (Thermo Electron Scientific Instrument Corporation) including the AB2 Series2 software. This is a fully computer controlled instrument using a double-grating monochromator for excitation and a single-grating emission monochromator. Excitation and emission slit widths were set at 2 nm. The acquisition interval and integration time were maintained at 1 nm and 60 s, respectively. A xenon lamp 950 W and a quartz cell $1 \times 10 \times 45$ mm were used. Right-angle geometry was used for spectral acquisition. SyF spectra were collected by simultaneously scanning the excitation and emission monochromator wavelengths with 20 nm difference of wavelength interval between excitation and emission wavelengths in the range from 250 to 720 nm.

2.3. Statistical analysis

Microsoft Excel 2010 and The Unscrambler version 9.0 by Camo were used for statistical analysis. The PLS-DA and PLS regression models were built at 20 nm difference of wavelength interval between excitation and emission wavelengths. For some models spectral pretreatments, such as baseline correction, and 1st derivative with Savitzky–Golay smoothing were carried. Leave-one-out cross validation was used to validate the PLS-DA models. PLS-DA using one partial least squares (PLS) component provides equivalent classification results to Euclidean distance to centroids, and by using all nonzero components to linear discriminant analysis. PLS-DA can provide good insight into the causes of discrimination via weights and loadings, which gives it a unique role in exploratory data analysis. For PLS regression all the samples (both adulterated with RF1 and RF2) were joined together and split into two sets, a training set (70% of the samples) and a test set for validation (30% of the samples). Leave-one-out cross validation was used to validate the PLS regression models built with the training set. The Root Mean Square Error of Cross Validation (RMSECV) was used as an internal indicator of the predictive ability of the models. Smaller values of RMSECV are indicative of a better prediction ability of the model. RMSECV is calculated using Eq. (1):

$$\mathrm{RMSECV} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - y_i)^2}{n}} \tag{1}$$

where y_i is the measured value (actual % of adulteration), y_i is the % of adulteration predicted by the model, and n is the number of segments left-out in the cross-validation procedure, which is equal to the number

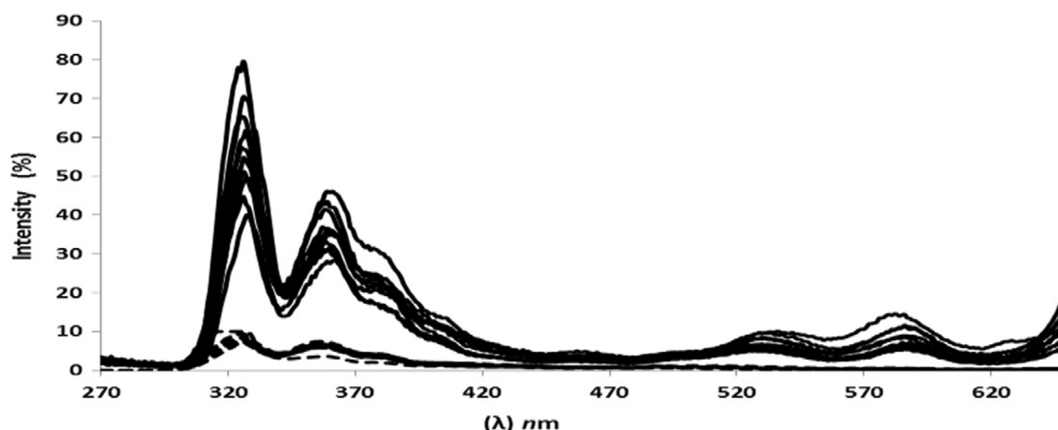

Fig. 2. SyF spectra at 20 nm difference for EVOO samples, both pure (solid line spectra) and adulterated with 10% RF1 (point spectra) at 75 °C.

Download English Version:

https://daneshyari.com/en/article/1228851

Download Persian Version:

https://daneshyari.com/article/1228851

Daneshyari.com