Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 143 (2015) 298–303

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Thermal oxidation process accelerates degradation of the olive oil mixed with sunflower oil and enables its discrimination using synchronous fluorescence spectroscopy and chemometric analysis

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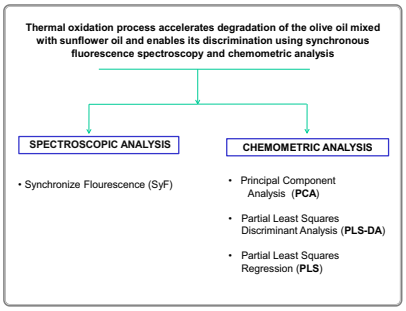
HIGHLIGHTS

- To develop synchronize fluorescence spectroscopic method.
- To analyze sunflower adulteration in extra virgin olive oil.
- To build Partial least-squares discriminant analysis (PLS-DA) models.
- To check the effect of thermal treatment on the enhancement of discrimination.
- To build PLS regression models to quantify the unknown level of adulteration in extra virgin olive.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 October 2014
Received in revised form 15 December 2014
Accepted 31 January 2015
Available online 18 February 2015

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

ABSTRACT

We have investigated the effect of thermal treatment on the discrimination of pure extra virgin olive oil (EVOO) samples from EVOO samples adulterated with sunflower oil. 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 samples were then measured with synchronous fluorescence spectroscopy. Fluorescence spectra were acquired by varying the excitation wavelength in the region from 250 to 720 nm. In order to optimize the differences between excitation and emission wavelengths, four constant differential wavelengths, i.e., 20 nm, 40 nm, 60 nm and 80 nm, were tried. Partial least-squares discriminant analysis (PLS-DA) was used to discriminate between pure and adulterated oils. It was found that the 20 nm difference was the optimal, at which the discrimination models showed the best results. The best PLS-DA models were those built with the difference spectra (75–25 °C), which were able to discriminate pure from adulterated oils at a 2% level of adulteration. Furthermore, PLS regression models were built to quantify the level of adulteration. Again, the best model was the one built with the difference spectra, with a prediction error of 1.75% of adulteration.

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Introduction

Extra virgin olive oil (EVOO) due to its high price, fine aroma, pleasant taste and health benefits is a target for adulteration with low price/quality oils such as sunflower, rapeseed, soybean and

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http://dx.doi.org/10.1016/j.saa.2015.01.119
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walnut oils as well as low quality olive oils, such as olive-pomace oils [20,19]. Adulteration is a major issue in the olive oil market and its detection is important for the protection of wealth and health of consumers. Consumer, buying such a product is not only buying the product of lower quality for higher price but also a product with a shorter shelf-life.

Various methods like spanning from classic wet chemistry [7] to chromatographic methods relying on quantification of fatty acids, triglycerols, sterols and hydrocarbons [1,2] were used. More recently, spectroscopic techniques, combined with multivariate analysis, have also been used to detect adulteration [9–11]. Amongst these spectroscopic techniques are nuclear magnetic resonance (NMR) [6,12] and vibrational techniques [3–5]. Molecular fluorescence spectroscopy is a highly sensitive technique, used for the characterization of edible oils. Very early work pointed out good prospects for characterization of edible oils through fluorimetry [22,8]. However, molecular fluorescence 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 prove 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 [13–15,21]. Synchronous fluorescence (SyF) spectra are obtained by plotting fluorescence intensity as a combined function of the excitation wavelength and the wavelength interval [23]. In this way, spectra selectivity is increased. Recently, a SyF method was described for the classification of edible and lampante olive oils [16–18,25].

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 canola oil) still have relatively low smoke points and cannot withstand a large amount of heat. Unless these high-MUFA oils have been refined or conditioned in a way that increases their smoke point, they typically cannot withstand heats of much greater than 200–250 °F (93–121 °C) without incurring damage (the temperature of stove-top frying is 375–525 °F, or 191–274 °C). So even though the high-MUFA composition of extra virgin olive oil increases its chemical stability, it does not protect it from most stovetop or oven cooking temperatures [24]. The presence of other vegetable oils in EVOO as adulterants also may change this stability against temperature.

In this study the effect of temperature and oxidation on monounsaturated and polysaturated fatty acids has been used to enable a better discrimination between EVOOs and EVOOs adulterated with sunflower oil, using SyF spectroscopy and PLS-DA and PLS regression.

Materials and methods

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. The 11 EVOOs samples were then adulterated with two types of sunflower oil at four different percentage levels: 2%, 5%, 10% and 20%. The total number of samples used was 99: 11 pure, 44 adulterated with SF1 and 44 adulterated with SF2. 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.

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 × 10 × 45 mm were used. Right-angle geometry was used for spectral acquisition.

SyF spectra were collected by simultaneously scanning the excitation and emission monochromator in the excitation wavelength range from 250 to 720 nm. SyF spectra were obtained by measuring the excitation wavelength in the same spectral region and varying the wavelength interval from 20 to 80 nm keeping 20 nm difference of wavelength interval.

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 four different wavelength intervals i.e., 20 nm, 40 nm, 60 nm and 80. For some models spectral pretreatments, such as baseline correction, Savitzky–Golay smoothing and normalization, were carried. Leave-one-out cross validation was used to validate the PLS-DA models. For PLS regression all the samples (both adulterated with SF1 and SF2) 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. RMSECV is calculated using Eq. (1):

$$\mathrm{RMSECV} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n}} \quad (1)$$

where y_i is the measured value (actual % of adulteration), $\hat{y}_i$ 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 of samples of the training set. Smaller values of RMSECV are indicative of a better prediction ability of the model.

The RMSEP is a statistical measure how well the model predicts new samples (not used when building the model). It is calculated using Eq. (2):

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n_t}(y_{t,i} - \hat{y}_{t,i})^2}{n_t}} \quad (2)$$

where $y_{t,i}$ is the measured value (actual % of adulteration), $\hat{y}_{t,i}$ is the % of adulteration predicted by the model, and n_t is the number of samples in the test set. RMSEP expresses the average error to be

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