

## Application of FT-IR spectroscopy to assess the olive oil adulteration

Mariana-Atena Poiana<sup>1\*</sup>, George Mousdis<sup>2</sup>, Ersilia Alexa<sup>1</sup>,  
Diana Moigradean<sup>1</sup>, Monica Negrea<sup>1</sup>, C. Mateescu<sup>1</sup>

<sup>1</sup>Banat's University of Agricultural Sciences and Veterinary Medicine, Faculty of Food Processing, Calea Aradului 119, 300645 Timisoara, Romania

<sup>2</sup>National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, 48 Vas. Constantinou Ave. 116-35 Athens Greece

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### Abstract

This study was focused to evaluate the use of FT-IR spectroscopy as an effective analytical tool in order to assess the olive oil (OO) adulteration with cheaper vegetable oil (sunflower oil - SFO). Taking a closer inspection to different regions of recorded IR spectra of both pure oil sample (OO, SFO) and their mixture it is noticed that a band shift identified at  $3011\text{ cm}^{-1}$  due to the C-H stretching vibration of the cis-double bond proved to be reliable index for assessing of OO adulteration by SFO addition. Also, the absorbance at  $1753\text{ cm}^{-1}$ , characteristic to the oils with a high saturated fatty acids content and short carbohydrate chain, recorded appreciable changes by increasing of SFO percent added in OO. Based on calibration curve (absorbance versus percent of SFO added in OO), it is possible to determine the degree of OO adulteration. A significant positive correlation ( $R>0.95$ ) were found in our study. Our data demonstrated that FT-IR spectroscopy prove to be a valuable tool to identify the differences recorded in oil samples spectra and finally, to appreciate the degree of OO adulteration.

**Keywords:** Fourier transform infrared (FT-IR) spectroscopy; olive oil; sunflower oil, adulteration

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### 1. Introduction

Consumer demands and their preoccupation for a rational and healthy diet determined a high consumption of vegetable oils rich in unsaturated fatty acids, leading to increased imports of expensive oil, which are not usually produced in Romania. This is the reason for which olive oil is one of the favourite products for Romanian consumers. Unfortunately, the current legislation does not require manufacturers and retailers to verify the authenticity of food and the analytical capabilities to detect adulteration are reduced. Major implications of counterfeiting on consumer health is the focus of interest required to detect the adulteration. Substitution of expensive vegetable oils or diet oils and replacing them with cheap oils

may have repercussions on consumers, revealing the theme importance [1-3].

Falsification of vegetable oils refers to two aspects: first - repeated reuse of vegetable oil collected from previous workings and second - replacement of some components by others, depending on the price level [4,5].

High prices of food oils (like olive oil), causes producers and traders to resort to partial or total substitution of these with other cheaper oils (sunflower oil, soybean oil and rapeseed oil). These falsifications is a major economic fraud that may have serious implications for consumer health. It is therefore important that the food control authorities have the ability to detect these adulterations.

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\* Corresponding author: e-mail: [atenapoiana@yahoo.com](mailto:atenapoiana@yahoo.com)

Although analytical methodologies used in commercial and government laboratories cover almost all olive oil adulterants, they are time consuming and require sample transportation to the lab. In our country there have been concerns for revealing adulteration of vegetable oils since 1970. Checking oil authenticity causes a permanent competition between analytical techniques and often involves complex chemical treatment and the use of sophisticated instruments. In the last 10 years, FT-IR spectroscopy has become a powerful analytical tool in the study of edible oils [6-8]. FT-IR is a fast analysis method, which is sensitive to the presence of chemical functional groups (structural fragments) in a molecule [9-10].

Based on these considerations, our work used the FT-IR spectroscopy in order to assess the olive oil adulteration by addition of sunflower oil. Finally, the problem we face right now is to extract correct information from the obtained FT-IR spectra which makes it possible to differentiate pure olive oil of the adulterated olive oil samples.

## 2. Materials and methods

*Oil samples.* The oils used in this work for spectral analysis had followed origin: olive OO (Olive Pomace Oil produced by Pietro Coricely, Italy) and sunflower oil - SFO (refined sunflower oil Bunica produced by S.C Cargill Oils S.A., Bucuresti). Samples for analysis were obtained by deliberate addition of SFO as adulteration agent in established proportions in the range 5 to 50% (v/v), from 5 to 5%, to samples of pure OO. The mixture was shaken manually to ensure total homogenization.

*FT-IR spectra acquisition.* A FTIR-8400S Fourier Transform Infrared Spectrophotometer (Shimadzu, Japan) equipped with attenuated total reflectance (ATR) accessory was used to obtain the infra-red spectra of oil samples.

This spectrophotometer uses a DLATGS (L-alanine-doped deuterated triglycerine sulphate) sensitive pyroelectric detector that provides a good signal-to-noise ratio and allows reduction of analysis time was used to collect FT-IR spectra. For FT-IR spectra recording a small quantity of the oil sample in a thin film was used [11].

BKG scan and samples were sequentially measured at  $4\text{ cm}^{-1}$  resolution, and 2.8 mm/s mirror speed with 45 accumulations (1 minute scan). All spectra, both for pure oils and their mixtures, were recorded from 4000 to  $500\text{ cm}^{-1}$  and processed with the computer software program Spectrum for Windows XP Professional (Shimadzu).

## 3. Results and Discussion

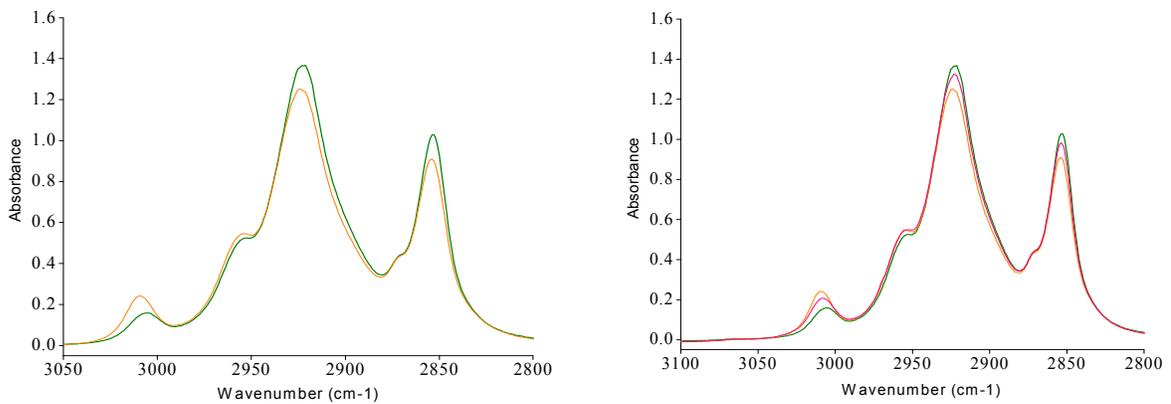
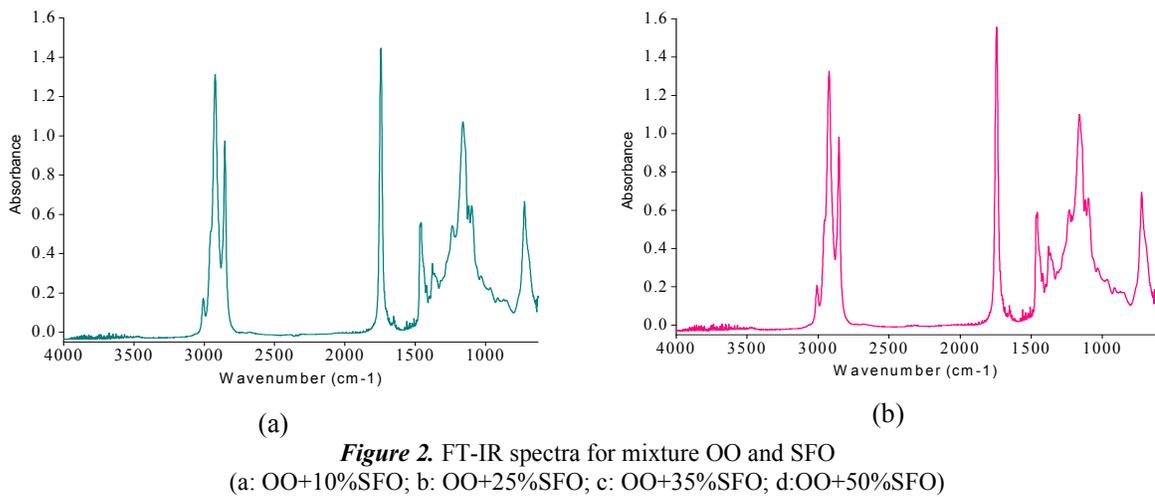
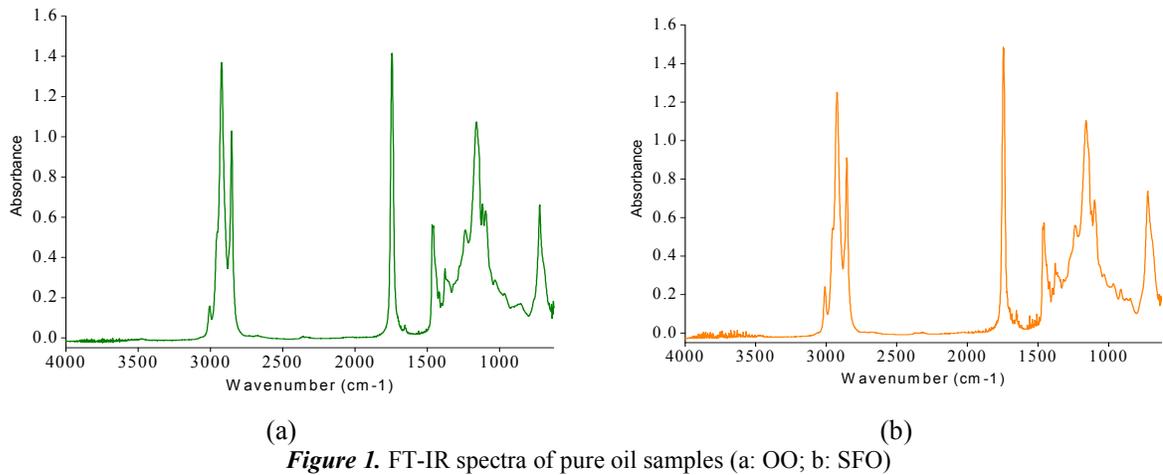
The typical FT-IR spectra for pure OO and SFO are shown in Figure 1. Also, the FT-IR spectra of their mixture in different percents are presented in Figure 2. It can be observed that it is difficult to find differences between these oils only by visual examination of their whole spectrum.

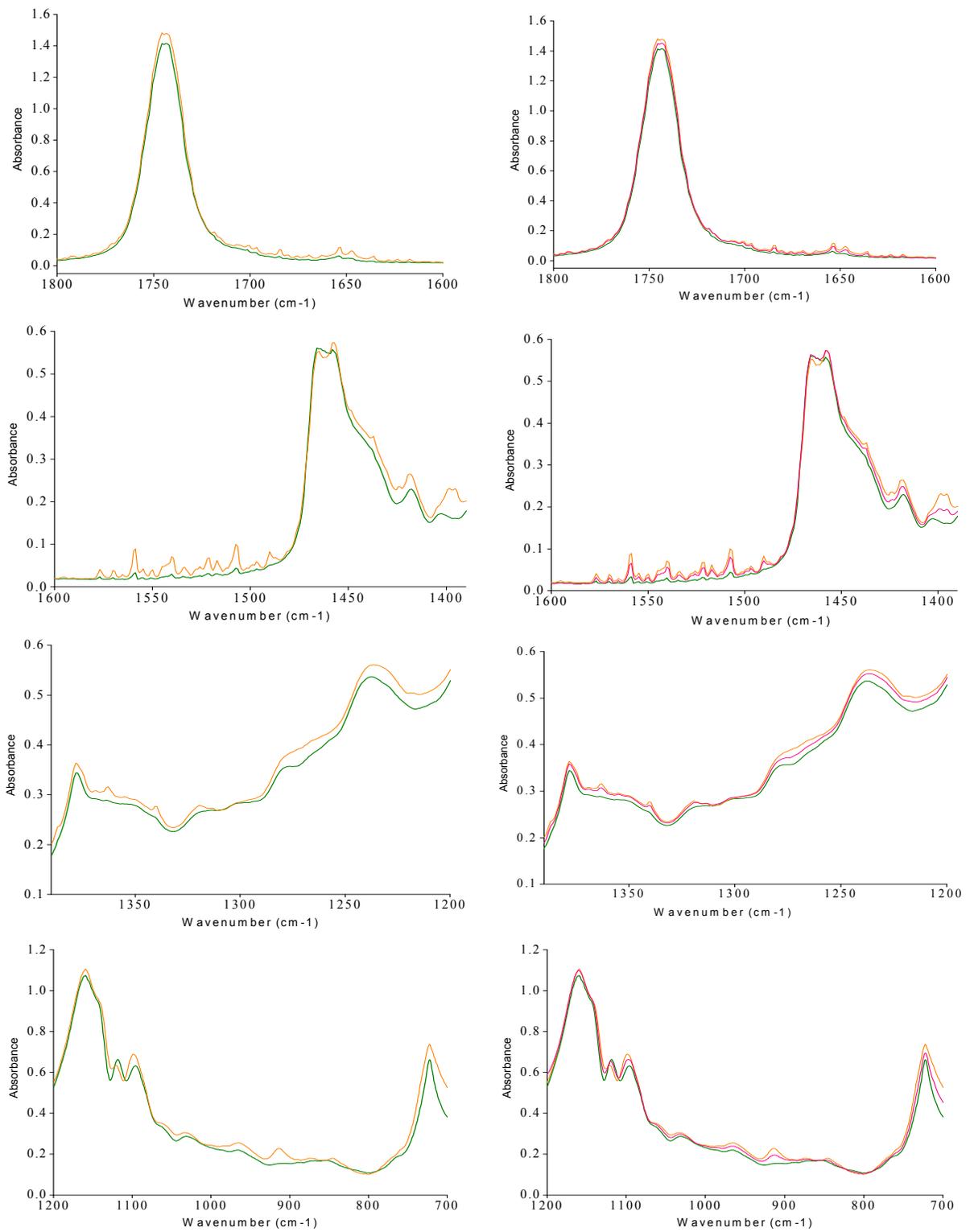
Taking a closer inspection to the Figure 1 it is noticed that there are visual differences in the absorption intensity registered for pure OO and SFO samples. In order to discuss the recorded spectra collection we compared our spectra with a series of preliminary data available in on this topic. Thus, FT-IR spectra of investigated oil sample present a lot of bands with different intensities and forms. According to absorbance recorded at different wavenumber we divided the recorded FT-IR spectra in six regions in the range  $4000\text{ to }500\text{ cm}^{-1}$  [1].

In Figure 3 are separately treated the spectral region where the oil samples have infrared absorption for a better highlighting of changes registered in FT-IR spectra of OO by its substituting in proportion of 50% with SFO. We have seen that in the interval  $4000\text{-}3100\text{ cm}^{-1}$  corresponding to the first region, the investigated oil samples showed no infrared absorption.

In the second spectral region,  $3100\text{-}2800\text{ cm}^{-1}$  can be noticed that presents absorption both OO and SFO. In this region occur bands close to the wavenumbers 2965, 2935, 2895 and  $2855\text{ cm}^{-1}$ . These absorptions are assigned to the symmetrical and asymmetrical C-H stretching vibration of the CH<sub>2</sub> and CH<sub>3</sub> aliphatic groups from the alkyl rest of the triglycerides, which are found in large quantities in vegetable oils [1].

Absorption close to  $3010\text{ cm}^{-1}$  proved to be reliable index for evaluation the unsaturated oil degree and can be used to assess the degree of OO falsification.





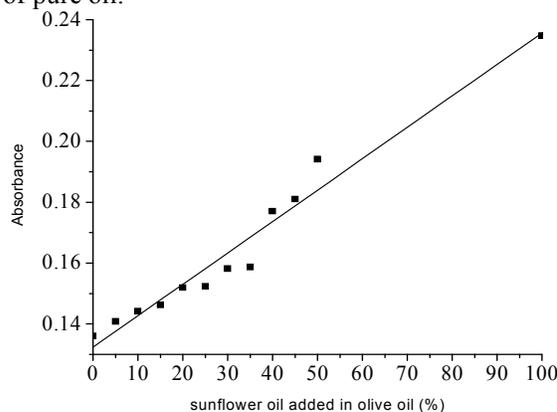
(a) (b)  
**Figure 3.** Comparativ FT-IR spectra of pure OO, SFO and their mixture  
 (a: pure OO, SFO; b: pure OO, FSO and mixture OO+50% SFO)

For pure OO (Figure 3) we can see that the absorbance at  $3011\text{ cm}^{-1}$ , specific frequency of the methyl-linoleate, is lower (0.1360) than the value recorded at  $3006\text{ cm}^{-1}$ , specific to the methyloleate (0.1585). These results reveal that the increasing of SFO proportion in OO induced an increase of absorbance at  $3011\text{ cm}^{-1}$  as effect of increasing of linoleic acid content in triglycerides composition.

Based on calibration curve - absorbance at  $3011\text{ cm}^{-1}$  versus SFO (%) added to OO - it is possible to determine the degree of OO adulteration by SFO addition. A significant positive correlation was found ( $R=0.9823$ ) – Figure 4.

Obtained FT-IR spectra for pure OO, SFO and their mixture show that there exist notable differences in the band around  $3006\text{ cm}^{-1}$  assigned to the C-H stretching vibration of the cis-double bond ( $=\text{CH}$ ). According to the spectral data, for  $3006\text{ cm}^{-1}$  there was recorded a good correlation ( $R=0.95460$ ) between absorbance and percent of SFO added to OO. This means that the absorption at this wavenumber is also used as a criterion in order to assess OO adulteration by SFO addition.

Our results are consistent with those reported by Vlahos et al. (2006) [3] and Alexa et al. (2009) [1] which revealed that based on absorption registered close to  $3010\text{ cm}^{-1}$ , can be possible the assessment of falsification by addition of foreign oil to a sample of pure oil.



**Figure 4.** Linear correlation absorbance versus (%) SFO added to OO

The third region corresponds to the interval  $1800\text{--}1600\text{ cm}^{-1}$ . In this region occurs two major bands close to  $1750$  and  $1660\text{ cm}^{-1}$ . The absorbance at  $1753\text{ cm}^{-1}$ , significant characteristic to the oils with a high saturated fatty acids content and short

carbohydrate chain, recorded appreciable changes by increasing of SFO percent added in OO sample. Thus, the absorbance increases with the percentage of SFO added in OO sample. This can be explained by the fact that SFO have a higher content of saturated acids in their composition than OO.

The second band that brings the important information on the oil occurs at  $1665\text{ cm}^{-1}$ . It can be noticed that the signal intensity increases with increasing the SFO percent added in OO. This spectral band close to  $1665\text{ cm}^{-1}$  corresponds to the double  $\text{C}=\text{C}$  bond and can be correlated with the content of polyunsaturated fatty acids from oil samples. Based on recorded data at this wavenumber it is possible to identify the addition of SFO in pure OO sample.

In the interval  $1600\text{--}1390\text{ cm}^{-1}$ , the fourth spectral region, occurs only a single spectral band close to  $1440\text{--}1445\text{ cm}^{-1}$  assigned to the vibrations of deformation  $\delta(\text{C-H})$ . This band can be used to determine the total unsaturation. In our study, in this region, for IR spectra of SFO it was recorded a maximum at  $1457\text{ cm}^{-1}$  and for OO spectra at  $1466\text{ cm}^{-1}$ . There was not recorded a linear dependence between these absorbances and the percent of SFO added in OO sample. Therefore, this region isn't used for OO adulteration by SFO addition.

In the fifth spectral region,  $1390\text{--}1200\text{ cm}^{-1}$ , it can be observed two bands close to  $1303\text{ cm}^{-1}$  (assigned to deformation vibration of methylene group) and at  $1270\text{ cm}^{-1}$  (specific to deformation vibration in the plan of  $=\text{CH}$  from the unconjugated *cis* double bonds). In this study we can identify two maximums at  $1378\text{ cm}^{-1}$  and  $1236\text{ cm}^{-1}$ . The absorbances at these wavenumbers were higher for SFO than pure OO sample and could be used in order to evaluate the OO falsification by SFO addition. The last investigated interval was  $1200\text{--}700\text{ cm}^{-1}$ , the sixth region. In order to quantify further the OO adulteration, the maximum absorbance of the two bands was also used.

The bands recorded at  $1100\text{--}1000\text{ cm}^{-1}$  and  $900\text{--}800\text{ cm}^{-1}$  are assigned to vibration of C-C bonds of carbohydrate chain from oil composition, while those to  $1150\text{--}1060$  and  $970\text{--}800\text{ cm}^{-1}$  are characteristic to vibration of  $\text{C}=\text{O}$  bonds. Our data reveal that the absorbance at these wavenumbers were higher for SFO than pure OO sample and could be used, after a proper calibration, to assess the OO falsification by SFO addition.

#### 4. Conclusion

The results of this paper indicates that specific FT-IR spectral regions prove to be very useful for determination the OO adulteration by SFO addition even through the differences in the FT-IR spectra are small, because most of vegetable oils contain the same fatty and triglyceride content is similar. A band shift identified at  $3011\text{ cm}^{-1}$  due to the C-H stretching vibration of the cis-double bond has been used in order to determine OO adulteration by addition of SFO. Also, the absorbance at  $1753\text{ cm}^{-1}$  as an important characteristic to the oils with a high saturated fatty acids content and short carbohydrate chain, recorded appreciable changes by increasing of SFO percent added in OO. Furthermore, the bands observed close to  $1303\text{ cm}^{-1}$ ,  $1270\text{ cm}^{-1}$  and those recorded in the range  $1100\text{-}1000\text{ cm}^{-1}$  and  $900\text{-}800\text{ cm}^{-1}$  could be very used in order to obtain information about degree of OO falsification by SFO addition. The absorbance at these wavenumbers could be used, after a proper calibration, to assess the OO falsification by SFO addition. Our data highlight that FT-IR spectroscopy is a rapid, non-destructive technique, with minimum sample preparation which can be used as an effective analytical tool in order to determine OO adulteration with cheaper vegetable oil as SFO.

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