



## The use of FT-IR spectroscopy in the identification of vegetable oils adulteration

Ersilia Alexa <sup>1\*</sup>, Anca Dragomirescu <sup>2</sup>, Georgeta Pop <sup>1</sup>, Călin Jianu <sup>1</sup> and Dan Dragoș <sup>2</sup>

<sup>1</sup>Banat University of Agricultural Sciences and Veterinary Medicine, Calea Aradului 119, 300645 - Timisoara, Romania.

<sup>2</sup>University of Medicine and Pharmacy of Timisoara, Faculty of Pharmacy, P-ta Eftimie Murgu 2, Timisoara, Romania.

\*e-mail: ersilia\_alex@yahoo.com

Received 2 January 2009, accepted 13 April 2009.

### Abstract

Expensive high quality vegetable oils and animal fats are susceptible to adulteration. Substitution of high quality and expensive oils and fats with cheaper and inferior quality oils or fats and labeling of those products as pure products are often used by producers to obtain a maximum profit. Such falsification in the oils and fats domain as well as the other food products represents a major economic fraud, and it may have serious implications for public health. The present work intends to identify the adulteration of some olive, peanut, corn germ and pumpkin oils with sunflower oil, the most common oil in Romania, using FT-IR spectroscopy. Experimental results showed that even if the spectral differences in the middle infrared spectral region are very small, because most vegetable oils contain the same type of fatty acids (especially those with C16 and C18) and triglyceride content is similar (C50, C52, C54), nevertheless, there are subtle spectral differences in the spectrum of various types of vegetable oils. This enables us to identify the addition of foreign oil in an oil sample using calibration curves established for certain characteristic frequencies in known mixed oils.

**Key words:** Olive oil, sunflower oil, peanut oil, corn germ oil, pumpkin oil, FT-IR spectra, adulteration.

### Introduction

The domain of food fraud is very broad, comprising a huge number of food products included in the falsification process. These processes can range from minor falsification to complex technologies, involving earlier stages of sophisticate pretreatment, which show a great interest for the forgery <sup>1,2</sup>.

Classical methods based on liquid or gas chromatography analysis are typically used to classify oils and fats. Chromatographic methods for the dosage of fatty acids or triglycerides fraction are the main methods to identify the forgery in vegetable oils <sup>3-5</sup>. Many non-chromatographic methods have been proposed for determining adulteration in vegetable oils and animal fats as UV spectroscopy, excitation-emission fluorescence spectroscopy for the main components, the principal component analysis (PCA) and parallel factor analysis (PARAFAC), mass spectrometry or ultrasonic attenuation <sup>6-8</sup>. Fourier transform infrared spectroscopy (FT-IR) was also used to detect the adulteration of oils and have the potential to complement the classical methodologies for oils adulteration control <sup>9-14</sup>. These studies were conducted to identify the adulteration of olive, peanut, corn germ and pumpkin oils with sunflower oil, the most common oil in Romania, using FT-IR spectroscopy.

### Materials and Methods

The oils used for determinations had the following origin: corn germ oil (Mazola oil, Bestfoods Markenartikel GmbH), olive oil (Extra Virgin Olive Oil Minerva - Aceites Borges Pont, Spain), sunflower oil (Ulcom International SA Slobozia), peanut oil (Brande oil, Brande GmbH) and pumpkin oil obtained by pressing. Samples

for analysis were obtained by the deliberate addition of adulteration agent in known proportions (5, 10, 25 and 50%) to samples of pure oil.

IR spectra were obtained using a spectrometer Nicolet 510 (Nicolet Analytical Instruments, Madison, WI) equipped with DTGS KBr detector that provides a good signal-to-noise ratio and allows reduction of analysis time. The IR spectra were made in the field of 500-4000  $\text{cm}^{-1}$  both for pure oils and their mixtures. The IR spectral characteristics are as follows: number of sample scans 32, number of background scans 32, resolution 4000, sample gain 1, mirror velocity 1.5825 and aperture 65.00.

### Results and Discussion

Fig. 1 shows the typical FT-IR spectra for pure edible oil and for their mixture. As shown from this figure it is difficult to differentiate between these oils by just visual examination of their whole spectrum. However, a careful investigation of the fingerprint region revealed that there are visual differences in the absorption intensity (Figs 2-4). The spectrum interpretation was done by comparing the obtained spectra with a series of preliminary data presented in the control lists.

The FT-IR spectra of vegetable oils present a series of bands with different intensities and forms. Some regions of the spectra present a very good signal/noise ratio, which corresponds to various types of vibration ( $\nu$ ,  $\delta$ ) characteristic to different types of atoms. Based on the intensity of absorption at different wavelengths we divided the spectra from 4000 to 500  $\text{cm}^{-1}$  in 6 regions.

**Region A** corresponds to the 4000-3100  $\text{cm}^{-1}$  interval where the vegetable oils do not have infrared absorption.

Maximum absorption frequency of the major molecules of vegetable oils is presented in Table 1. The results obtained by measuring the intensity of absorption at different frequency for the analyzed vegetable oils are presented in Tables 2–5.

**Region B** in the interval of 3100-2800  $\text{cm}^{-1}$  from the IR spectra presents the absorption bands in the vicinity of frequencies 2965, 2935, 2895 and 2855  $\text{cm}^{-1}$ . These absorptions are characteristic to the symmetrical and asymmetrical vibrations  $\nu(\text{C-H})$  of the  $\text{CH}_2$  and  $\text{CH}_3$  aliphatic groups from the alkyl rest of the triglycerides, which are found in large quantities in vegetable oils. Absorption near 3010  $\text{cm}^{-1}$  represents a significant index of the degree of unsaturated oil and it can be used in the identification of vegetable oils forgery. By measuring the absorption intensity near 3010  $\text{cm}^{-1}$ , one can make a classification of vegetable oils and also identify the addition of foreign oil in a sample of pure oil.

For pure olive oil (Table 2, Fig. 2) one observes that the absorption intensity at 3011  $\text{cm}^{-1}$ , specific frequency of the methyl-linoleate, is less than the absorption at 3006  $\text{cm}^{-1}$ , specific to the methyl-oleate, and that is 2.71. The increased content of sunflower oil in olive oil leads to an increased intensity of absorption at 3011  $\text{cm}^{-1}$  due to the increased content of linoleic acid in the composition of triglycerides. Instead, the sunflower oil presents a higher absorption at 3011  $\text{cm}^{-1}$  and a lower one at 3006  $\text{cm}^{-1}$ , due to its high content of linoleic acid. By drawing up a calibration scale at 3011  $\text{cm}^{-1}$  absorbance versus the content of sunflower oil in the sample, one can determine the degree of olive oil counterfeit with sunflower oil. Correlation coefficients were found to be good ( $R = 0.97101$ ,  $SD = 0.09376$ ), and the result was reproducible.

At a 3006  $\text{cm}^{-1}$  frequency, which, according to spectral data, is appropriate to the absorption of methyl-oleate, a linear dependence between the increased content of sunflower oil in the sample and the decrease of the absorbance does not exist. Therefore, one cannot use the absorption intensity at this wavelength as a criterion for identifying olive oil counterfeit with sunflower oil.

In the 3006-3011  $\text{cm}^{-1}$  interval there are not differences in the intensity of the absorption of samples of sunflower oil and corn germ oil, because of a similar content in unsaturated fatty acids, mainly linoleic acid, in the two oils. The mixture of pumpkin and sunflower oil shows high absorption at 3006 and 3010  $\text{cm}^{-1}$ , bands assigned to the oleic and linoleic acids, but there is not a linear dependence between the absorbance and the sunflower oil content in the mixture with the pumpkin oil.

**Region C** corresponds to the interval 1800-1600  $\text{cm}^{-1}$  and has two major bands near 1750 and 1660  $\text{cm}^{-1}$ . The absorption at 1753  $\text{cm}^{-1}$ , feature to the oils with a high content in saturated fatty acids and short carbohydrate chain, does not show significant variations by modifying the content of sunflower oil in olive oil, because of the low content of saturated acids in both olive and sunflower oil.

The second part of the region presents important information on the oils. At 1665  $\text{cm}^{-1}$  the signal intensity increases along with increasing the content of sunflower oil in olive oil. This spectral band near to 1665  $\text{cm}^{-1}$  corresponds to the double  $\text{C}=\text{C}$  link and may be correlated with the content of polyunsaturated fatty acids in the molecule, which were determined by HPLC (Table 6). Along with the increased content of sunflower oil in olive oil the sample's

absorbance increases too, so that the signal received at this frequency may constitute a criterion for identifying the addition of sunflower oil in olive oil.

The mixture of corn germ and sunflower oil can be measured quantitatively by determining the absorbance at 1752  $\text{cm}^{-1}$ . Increasing the content of sunflower oil in the mixture increased the intensity of absorption at this frequency (Table 3, Fig. 3). The correlation coefficient was  $R = 0.98892$  and  $SD = 0.02755$ .

For the peanut + sunflower oil mixture, spectral differences were observed at 1735  $\text{cm}^{-1}$ , where peanut oil presented high absorbance, due to higher content of saturated fatty acids compared with sunflower oil and because of fatty acids with less carbon atoms in the triglycerides composition. The intensity of the absorption at this frequency may be a criterion for the identification of peanut oil forgery with sunflower oil (Table 4, Fig. 4). The data obtained by plotting the concentrations of the adulterant oil against the absorbance intensity showed linear relationships with very good mathematical proprieties ( $R = 0.98919$ ,  $SD = 0.05455$ ).

Also, at 1654  $\text{cm}^{-1}$  the absorbance increased with the content of sunflower oil in the mixture. This frequency is assigned to the *cis* isomers of the molecule, and because the intensity of the absorption at this frequency is higher, the content of *cis* isomers is greater. Because the relation of dependence between the absorption intensity and the content of sunflower oil in the sample is linear, one can make a calibration scale at this frequency in order to identify the addition of peanut oil in the sunflower oil.

For the mixture of pumpkin and sunflower oil the highest absorption was observed at 1734  $\text{cm}^{-1}$ , band characteristic to the saturated fatty acids; the explanation is that palmitic acid has a high concentration in the pure pumpkin oil.

**Region D** (1600-1390  $\text{cm}^{-1}$ ) comprises a single spectral band near 1440-1445  $\text{cm}^{-1}$  proper to the vibrations of deformation  $\delta(\text{CH})$ . This band can be used to determine the total unsaturation. In the 1600-1390  $\text{cm}^{-1}$  region, the IR spectrum of olive and sunflower oils has a maximum at 1463  $\text{cm}^{-1}$ , but its intensity doesn't have a linear variation with the modification of the sunflower oil content in olive oil and therefore cannot be used for identifying forgery.

**Region E** (1390-1200  $\text{cm}^{-1}$ ) includes two bands near 1303  $\text{cm}^{-1}$  and 1270  $\text{cm}^{-1}$ . The first band corresponds to the deformation vibration in the phase of methylene group, while the second band corresponds to the deformation vibration in the plan of the group  $=\text{CH}$ , from the double links *cis* unconjugated. The region E has two maximums at 1377  $\text{cm}^{-1}$  and 1234  $\text{cm}^{-1}$ . The intensity of the absorption at these frequencies is similar for both oils and is not useful in forgery identification.

**Region F** (1200-700  $\text{cm}^{-1}$ ) contains bands characteristic to the C-C links and to the vibration links  $\text{C}=\text{O}$ . Carbohydrate chain is characterized by a series of bands of vibration due to the C-C links at 1100-1000  $\text{cm}^{-1}$  and 900-800  $\text{cm}^{-1}$  domains, while  $\text{C}=\text{O}$  link has two characteristic bands at 1150-1060 and 970-800  $\text{cm}^{-1}$ . Carbohydrate chain vibrations of deformation were detected in the region 450-150  $\text{cm}^{-1}$  too. Absorption in the domain 700-1200  $\text{cm}^{-1}$  is similar as intensity for the samples of sunflower oil and corn germ oil, and this is due to the carbohydrate radical from the triglyceride structure of oils.

**Table 1.** Maximum absorption frequency of the major molecules of vegetable oils.

| Region | Frequency (cm <sup>-1</sup> ) | Molecule          | Group | Vibration      |
|--------|-------------------------------|-------------------|-------|----------------|
| B      | 3015                          | RCH=CHR           | =CH   | v asymmetrical |
|        | 2970                          | -CH3              | C-H   | v asymmetrical |
|        | 2940                          | -CH2              | C-H   | v asymmetrical |
|        | 2900                          | -CH3              | C-H   | v symmetrical  |
|        | 2860                          | -CH2              | C-H   | v symmetrical  |
| C      | 1750                          | RC=OOR            | C=O   | v              |
|        | 1670                          | Trans RCH=CHR     | C=C   | v              |
|        | 1660                          | cis RCH=CHR       | C=C   | v              |
| D      | 1445                          | -CH2              | C-H   | δ              |
| E      | 1310                          | -CH2              | C-H   | δ              |
|        | 1275                          | cis RCH=CHR       | =C-H  | δ              |
| F      | 1100-1000                     | -(CH2) <i>n</i> - | C-C   | v              |
|        | 900-800                       | -(CH2) <i>n</i> - | C-C   | v              |

**Table 2.** IR absorbtion for olive and sunflower oils and for their mixture.

| Sample                  | Frequency (cm <sup>-1</sup> ) |      |      |      |      |      |      |      |      |      |
|-------------------------|-------------------------------|------|------|------|------|------|------|------|------|------|
|                         | 3011                          | 3008 | 3006 | 1753 | 1663 | 1445 | 1377 | 1234 | 914  | 720  |
| Olive oil               | 1.64                          | 2.38 | 2.71 | 3.83 | 0.41 | 2.68 | 2.04 | 2.95 | -    | 1.80 |
| Olive+5% sunflower oil  | 1.67                          | 2.44 | 2.29 | 3.16 | 0.41 | 2.68 | 2.12 | 2.59 | 0.52 | 1.10 |
| Olive+10% sunflower oil | 1.71                          | 2.56 | 2.45 | 3.56 | 0.47 | 2.65 | 2.11 | 2.87 | 0.59 | 1.77 |
| Olive+25% sunflower oil | 2.21                          | 2.74 | 3.13 | 3.58 | 0.48 | 2.45 | 2.05 | 2.99 | 0.65 | 1.96 |
| Olive+50% sunflower oil | 2.61                          | 2.96 | 3.33 | 3.54 | 0.76 | 2.43 | 2.21 | 3.19 | 0.92 | 2.19 |
| Angelli oil             | 2.65                          | 3.02 | 2.80 | 3.54 | 0.81 | 2.32 | 2.05 | 3.01 | 0.82 | 2.10 |
| Sunflower oil           | 2.75                          | 3.25 | 2.20 | 3.47 | 0.86 | 2.20 | 1.90 | 2.73 | 0.67 | 1.86 |

**Table 3.** IR absorbtion for corn germ and sunflower oils and for their mixture.

| Sample                       | Frequency (cm <sup>-1</sup> ) |      |      |      |      |      |      |      |      |  |
|------------------------------|-------------------------------|------|------|------|------|------|------|------|------|--|
|                              | 3011                          | 3006 | 1752 | 1654 | 1463 | 1377 | 1234 | 914  | 720  |  |
| Corn germ oil                | 2.76                          | 2.65 | 3.09 | 0.47 | 3.34 | 2.06 | 2.96 | 0.72 | 2.03 |  |
| Corn germ +10% sunflower oil | 3.00                          | 3.11 | 3.10 | 0.45 | 3.40 | 2.04 | 2.76 | 0.69 | 1.91 |  |
| Corn germ +25% sunflower oil | 3.07                          | 2.87 | 3.15 | 0.44 | 3.42 | 1.90 | 2.30 | 0.62 | 1.67 |  |
| Corn germ +50% sunflower oil | 3.22                          | 2.99 | 3.23 | 0.48 | 3.48 | 2.11 | 2.96 | 0.73 | 1.97 |  |
| Sunflower oil                | 2.75                          | 2.20 | 3.47 | 0.86 | 2.20 | 1.90 | 2.73 | 0.67 | 1.86 |  |

**Table 4.** IR absorbtion for peanut and sunflower oils and for their mixture.

| Sample                    | Frequency (cm <sup>-1</sup> ) |      |      |      |      |      |      |      |      |  |
|---------------------------|-------------------------------|------|------|------|------|------|------|------|------|--|
|                           | 3011                          | 3006 | 1737 | 1654 | 1452 | 1377 | 1234 | 914  | 720  |  |
| Peanut oil                | 2.63                          | 2.60 | 3.58 | 0.40 | 3.02 | 2.03 | 2.70 | 0.58 | 1.78 |  |
| Peanut +10% sunflower oil | 2.34                          | 3.02 | 3.55 | 0.60 | 3.00 | 2.10 | 2.90 | 0.65 | 1.97 |  |
| Peanut +25% sunflower oil | 3.11                          | 3.06 | 3.53 | 0.62 | 2.84 | 2.10 | 3.04 | 0.83 | 2.10 |  |
| Peanut +50% sunflower oil | 3.89                          | 3.51 | 3.32 | 0.70 | 2.68 | 2.18 | 3.18 | 0.84 | 2.07 |  |
| Sunflower oil             | 2.75                          | 2.20 | 3.25 | 0.86 | 2.47 | 1.87 | 2.73 | 0.67 | 1.86 |  |

**Table 5.** IR absorbtion for pumkin and sunflower oils and for their mixture.

| Sample                     | Frequency (cm <sup>-1</sup> ) |      |      |      |      |      |      |      |      |  |
|----------------------------|-------------------------------|------|------|------|------|------|------|------|------|--|
|                            | 3011                          | 3006 | 1753 | 1654 | 1463 | 1377 | 1234 | 914  | 720  |  |
| Pumkin oil                 | 2.80                          | 2.59 | 3.40 | 0.45 | 3.44 | 2.15 | 2.23 | 0.66 | 1.63 |  |
| Pumkin + 5% sunflower oil  | 2.73                          | 3.09 | 3.49 | 0.65 | 3.36 | 2.13 | 2.2  | 0.85 | 2.02 |  |
| Pumkin + 10% sunflower oil | 2.98                          | 2.98 | 2.87 | 3.40 | 0.61 | 3.27 | 2.85 | 0.79 | 1.96 |  |
| Pumkin + 25% sunflower oil | 3.00                          | 2.85 | 3.63 | 0.68 | 3.36 | 2.19 | 3.13 | 0.89 | 0.75 |  |
| Pumkin + 50% sunflower oil | 1.97                          | 1.95 | 2.81 | 0.49 | 4.69 | 2.32 | 1.39 | 0.68 | 1.28 |  |
| Sunflower oil              | 2.75                          | 2.20 | 3.47 | 0.86 | 2.20 | 1.90 | 2.73 | 0.67 | 1.86 |  |

**Table 6.** Correlation between IR absorbtion at 1660 cm<sup>-1</sup> and unsaturation degree of sample determined by HPLC.

| Sample                    | Absorption at 1660 cm <sup>-1</sup> | Total unsaturation (%) |
|---------------------------|-------------------------------------|------------------------|
| Olive oil                 | 0.41                                | 79.42                  |
| Olive + 5% sunflower oil  | 0.41                                | 79.78                  |
| Olive + 10% sunflower oil | 0.47                                | 80.17                  |
| Olive + 25% sunflower oil | 0.48                                | 81.29                  |
| Olive + 50% sunflower oil | 0.76                                | 83.18                  |
| Sunflower oil             | 0.81                                | 87.73                  |

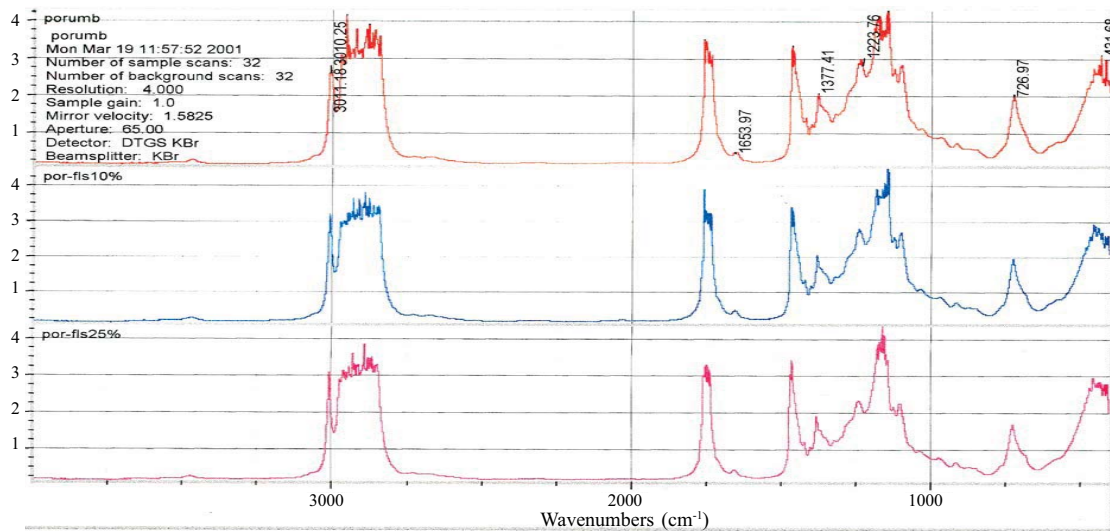


Figure 1. IR spectra for pure peanut and sunflower oil and for their mixture.

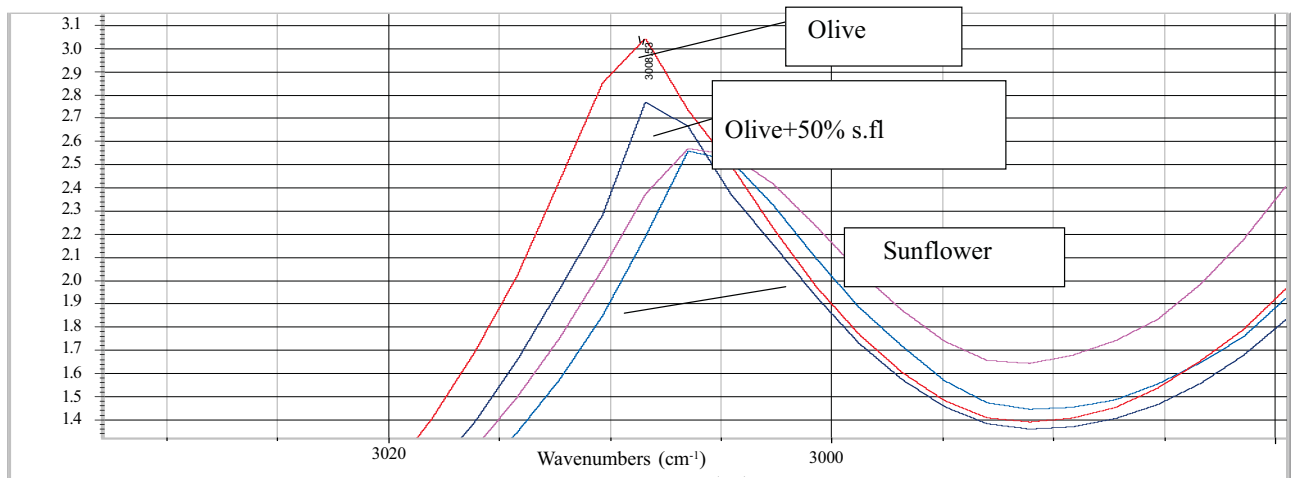


Figure 2. IR spectra for pure olive and sunflower oil and for their mixture at 3011  $\text{cm}^{-1}$ .

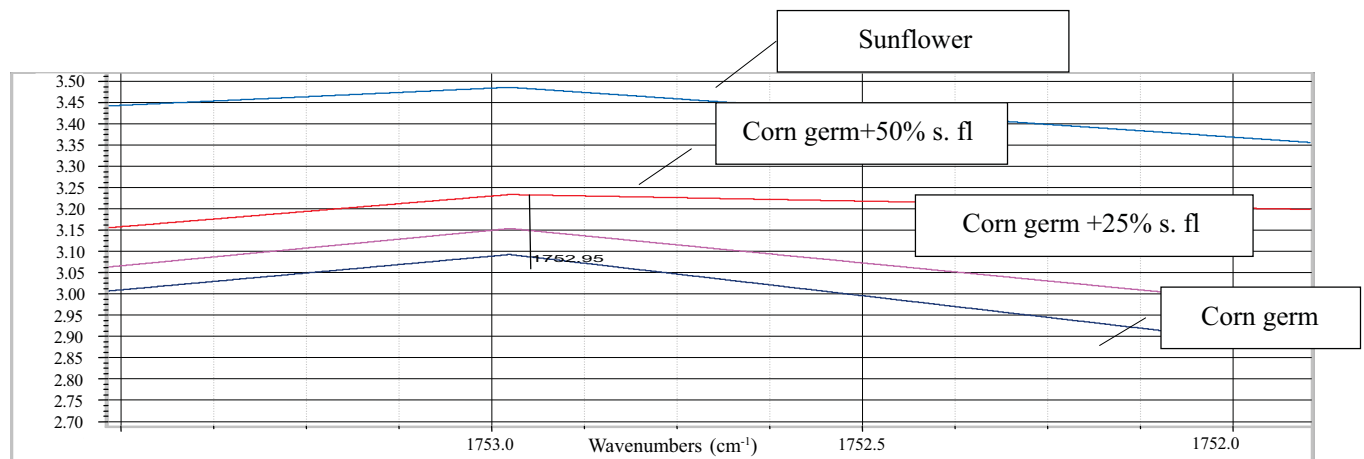


Figure 3. IR spectra for pure corn germ and sunflower oil and for their mixture at 1752  $\text{cm}^{-1}$ .

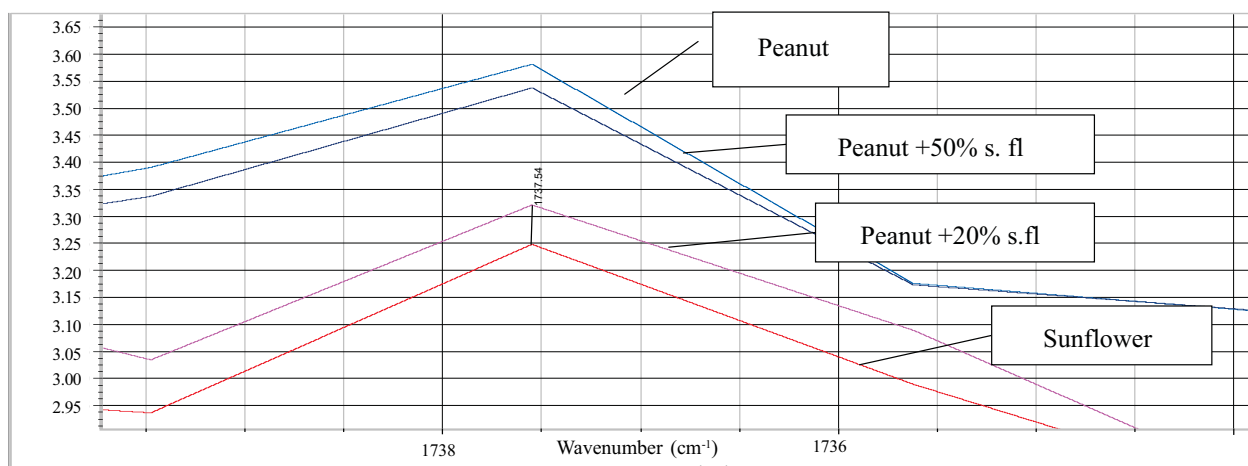


Figure 4. IR spectrum for pure peanut and sunflower oil and for their mixture 1735  $\text{cm}^{-1}$ .

### Conclusions

Even if differences in the infrared middle spectra are very low, because most of vegetable oils contain the same type of fatty acids (especially those with C16 and C18) and triglyceride content is similar (C50, C52, C54), however, subtle spectral differences exist in various types of vegetable oils, so it is possible to identify the addition of foreign oil in an oil sample, using calibration curves established for certain characteristic frequencies in the known mixed oils.

According to the previous results we recommend the application of the spectral characteristics in assessment of the authenticity of edible oils. For each analyzed mixture of vegetable oils a calibration curve was made in a characteristic frequency with which the addition of foreign oil may be determined. Determining in advance of the fatty acid composition of pure samples and of counterfeit sample facilitates the interpretation of IR spectra, and thus leads to additional data related to the adulterant agent nature and to the quantity of added oil.

### References

- <sup>1</sup>Alexa, E., Nistor, M. and Jianu, I. 2003. The UV-VIS spectroscopy, a mean to detect vegetable oils adulteration. Proceedings of the Fourth International Symposium Young People and the Multidisciplinary Research, România-Iugoslavia-Ungaria, Timisoara, Sudura Edition, pp. 409-416.
- <sup>2</sup>Amr, A.S. and Abu-Al-Rub, A. I. 2006. Evaluation of the Bellier test in the detection of olive oil adulteration with vegetable oils. *J. Sci. Food and Agriculture* **61**(4):435-437.
- <sup>3</sup>Alexa, E., Poiana, M., Peev, C. and Dehelean, C. 2006. Detection of vegetable oils adulteration using RP-HPLC of fatty acids. *Revue of Chemistry* **57**(3):283-287.
- <sup>4</sup>Gurdeniz, G., Ozen, B. and Tokatli, F. 2008. Classification of Turkish olive oils with respect to cultivar, geographic origin and harvest year using fatty acid profile and mid-IR spectroscopy. *European Food Research and Technology* **227**:1275-1281.
- <sup>5</sup>Hilali, M., Charrouf, Z., Soulhi, A., Hachimi, L. and Guillaume, D. 2007. Detection of argan oil adulteration using quantitative campesterol GC-analysis. *Journal of the American Oil Chemists' Society* **84**(8):761-764.
- <sup>6</sup>Guimet, F. and Boque, J.F. 2005. Rapid detection of olive-pomace oil adulteration in extra virgin olive oils from the protected denomination of origin Siurana using excitation-emission fluorescence spectroscopy and three way methods of analysis. *Analytica Chimica Acta* **544**:143-152.
- <sup>7</sup>Lorenzo, I., Pavón, J. L. P., Laespada, E.F., Pinto, C.G. and Cordero, B.M. 2002. Detection of adulterants in olive oil by headspace-mass spectrometry. *J. Chromatography A* **945**(1-2):221-230.
- <sup>8</sup>Pasca, A. and Dadarlat, D. 2007. Study of edible oils adulteration by ultrasonic attenuation. *Romanian J. Physics* **52**(5-7):641-644.
- <sup>9</sup>Prado, B.M., Kim, S., Ozen, B.F. and Mauer, L.J. 2005. Differentiation of carbohydrate gums and mixtures using Fourier-transform infrared spectroscopy and chemometrics. *Journal of Agricultural and Food Chemistry* **53**:2823-2829.
- <sup>10</sup>Downey, G. and McIntre, P. 2002. Detecting and quantifying sunflower oil adulteration in extra virgin oil from the Eastern Mediterranean by visible and near-infrared spectroscopy. *J. Agric. Food Chem.* **50**(20):5520-5525.
- <sup>11</sup>Gurdeniz, G., Tokatli, F. and Ozen, B. 2007. Differentiation of mixtures of monovarietal olive oils with mid-infrared spectroscopy and chemometrics. *European Journal of Lipid Science and Technology* **109**:1194-1202.
- <sup>12</sup>Baeten, V., Hourrant, P., Morales, M. and Aparicio, R. 1998. Oil and fat classification by FT-Raman Spectroscopy. *J. Agric. Food Chem.* **46**:2638-2646.
- <sup>13</sup>Ozen, B. and Mauer, L. 2002. Detection of hazelnut oil adulteration using FT-IR spectroscopy. *J. Agric. Food Chem.* **50**(14):3898-3901.
- <sup>14</sup>Allam, M. and Hamed, S. F. 2007. Application of FT-IR spectroscopy in the assessment of olive oil adulteration. *Journal of Applied Sciences Research* **3**(2):102-108.