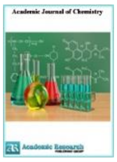

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The Use of Fourier-Transform Infrared Spectroscopy to Assess Libyan Virgin Olive Oil Adulteration with Corn and Sun Flower Oils

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Abstract

Modern improvements in Fourier transform infrared spectroscopy instrumentation spread out the application of this technique to the field of food research. This study is focused to evaluate the efficiency of FT-IR spectroscopy in order to assess the Libyan virgin olive oil adulteration with cheaper vegetable oils: sunflower oil and corn oil. Taking a closer inspection to different regions of recorded IR spectra of both pure oil sample (virgin olive oil, sun flower oil, corn oil) and their mixture: It is noticed that an absorbance shift was identified at about 3000 cm-1 due to the C-H stretching vibration of the cis-double bond proved to be reliable index for assessing of virgin olive oil adulteration by vegetable oil addition. Also, the absorbance at about 3008 cm-1, characteristic to the oils with a high saturated fatty acids content and short carbohydrate chain, recorded appreciable changes by increasing of vegetable oil percent added in virgin olive oil. Based on the calibration curve (absorbance versus percent of vegetable oil added in virgin olive oil), it is possible to determine the degree of virgin olive oil adulteration. A significant positive correlation for both adulterant oils (R2 > 0.97) at wavenumber 3008.3 cm-1 was observed in our study. Our data demonstrated that FT-IR spectroscopy proved to be a valuable tool to identify the differences recorded in oil samples spectra and finally, to appreciate the degree of virgin olive oil adulteration.

Keywords: Adulteration; Corn oil; FT-IR spectroscopy; Olive oil; Sun Flower oil.

1. Introduction

Although many methodologies have been applied in the detection of olive oil adulterants, these methods are time consuming and involved complicated chemical treatments using sophisticated instruments. Until, FTIR applications were strongly used more than 10 years ago due to its simplicity, sensitivity and rapidness. [1, 2] Olive oil (OO) is an important production in Mediterranean countries and can be used directly without any treatment for several purposes. Consumption of olive oil in Libya is a daily habit in cooking and used as a public remedy due to its pleasant taste and high nutritional and health value. Olive oil is very expensive in comparison with other vegetable oils. Nowadays virgin olive oil (VOO) is about four times more expensive than sunflower oil (SFO) in Libyan market. Because of its expense and its unique properties such as stability, fine aroma and reported health benefits, olive oil has been subjected to adulteration, fraud mixing with less expensive edible oils. Adulteration is usually done either by dilution or substituting with other lower cost oils containing additional chemicals resulting in oils with higher quality appearance. [3] Two types of adulterations may be applied to olive oil, first is dealt with the blending of virgin olive oil with refined olive oils whilst the second is based on the addition of lower price edible vegetable oils**.**

Adulterants may be corn oil, soyabean oil, sunflower oil and olive pumice oil. As a result, adulteration represents a big danger for economic and health issues for virgin olive oil consumers [1]. Therefore, the validity of OO has become an important issue for producers, consumers and quality control authorities [1, 4].

Previous applied analytical techniques in the detection of authenticity of olive oil are as follows: chromatographic techniques GC [5-7], GC-MS [8], UV-VIS-NIR [9], headspace-mass spectrometry [10, 11], nuclear magnetic resonance (NMR) spectroscopy [12-14]. However, in this study Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) technique is used to investigate the authenticity of Libyan olive oil.

2. Practical

A virgin olive oil (VOO), sunflower oil (SFO) and corn oil (CO) samples were provided from Libyan market. Sunflower oil and corn oil samples were each mixed directly with the virgin olive oil sample in a series of 0-90% at 10% increments using accurate burettes. The mixtures were vigorously shaken at room temperature to obtain

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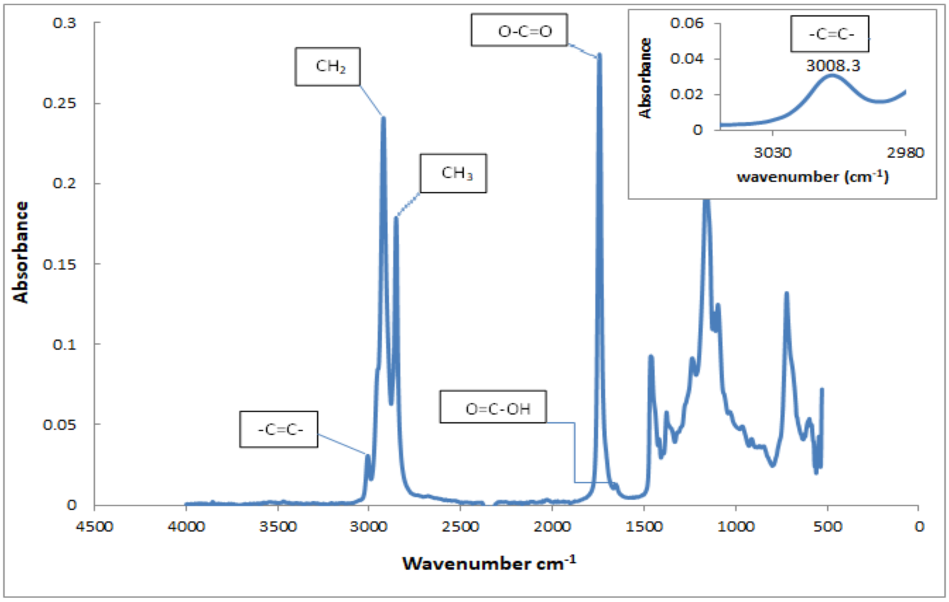
homogeneous solutions and scanned using FT-IR (Bruker TENSOR II) in the range (4000 to 400 cm^{-1}) equipped with MIRacle ATR device and processed with the computer software program OPUS7. The system was designed to carry out sixteen replicates for each scan. After every scan Hexane was used for cleaning the crystal surface and a sample background was obtained.

3. Results and Discussion

Edible oils show similar Infrared spectrum since they constitute the same chemical groups. This is clear from figures 1, 2 and 3 that represent the spectra of the pure vegetable oils used in this study, olive oil, corn oil and sun flour oil respectively. These figures represent the recorded FTIR spectra of the pure oils under investigation illustrated with the specific stretching and vibration bands signifying different groups. The various bands shown in these figures are assigned and are consisted with that reported in literature [15-17].

Fig-1. ATR-FTIR Spectrum of pure olive oil sample



All recorded spectra showed similar absorption bands at different wavelengths with no spectral differences apart from slight changes in absorbance and shifts of some bands. Some of which are 3009 cm^{-1} (C-H stretching of cis =CH), shoulder 2922 cm^{-1} (asymmetric stretching vibration of C-H of CH_2 group), shoulder at 2852 cm^{-1} (asymmetric stretching vibration of C-H of CH_3 group), 1743 cm^{-1} (stretching vibration of C=O of ester group).

Fig-2. ATR-FTIR Spectrum of pure Corn oil sample

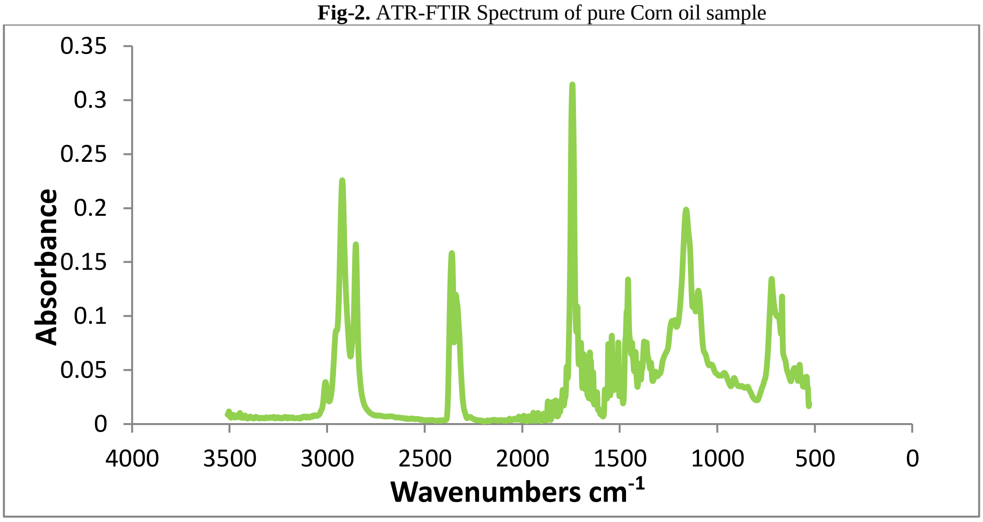
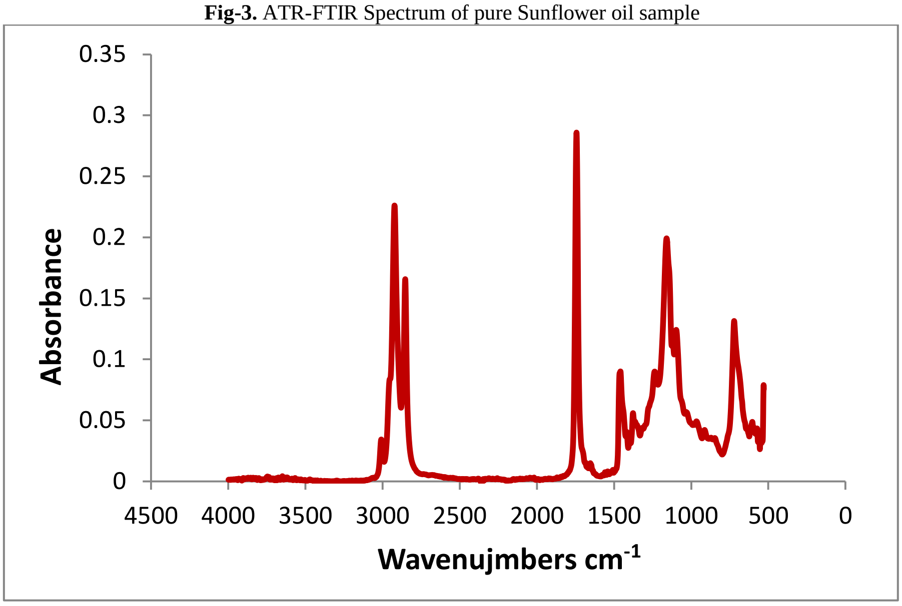


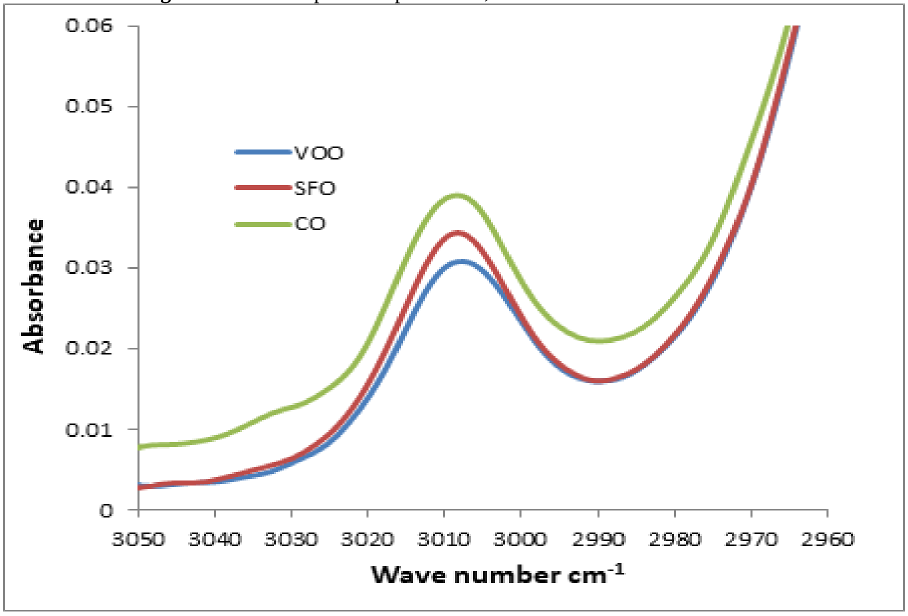
Fig-3. ATR-FTIR Spectrum of pure Sunflower oil sample



Visual examination of the whole spectra of these oils makes it challenging to spot the differences between them. All spectra showed two significant bands in the region of 3000 cm^{-1} and 1740 cm^{-1} due to –CH stretching and carbonyl groups of the triglyceride. On closer examination of the recorded spectra, the prominent feature of the spectrum is the band around 3000 cm^{-1} that showed significant changes from one type of oil to another as observed in figure 4.

As a comparison Figure 4 shows the region 3050-2960 cm^{-1} of ATR-FTIR spectra recorded for the pure oils used in this study (VOO, SFO and CO). After close examination clearly, from these spectra we can declare that the absorbance value at the band 3008 cm^{-1} varied from one type of oil to another. The absorbance values at the maximum 3008 cm^{-1} were 0.03077, 0.03435, 0.03900 for VOO, SFO and CO respectively.

Fig-4. ATR- FTIR spectra of pure VOO, SFO & CO at around 3008 cm^{-1}



This may be explained due to the difference in the fatty acid composition of the different types of oils. VOO contains higher proportion of oleic acid (monounsaturated fatty acid) whereas SFO and CO contain higher proportions of linolenic or linoleic acyl groups (polyunsaturated fatty acids). Therefore VOO has the lowest degree of unsaturation among the SFO and CO under investigation, this may be revealed by figures 5 and 7.

On careful examination of the insets in figures 5 and 7 one can accomplish that the absorbance value increased according to the extent of adulteration of VOO with both the SFO and CO. This may be explained due to the increase in the unsaturation degree in SFO and CO compared to that of VOO. These findings are consistent with those reported by Poiana, *et al.* [18], and others where they reported both shifts in the position and changes in the absorbance value of some bands from 3005-3009 cm^{-1}.

As shown in Figure 5 (VOO & CO) and Figure 7 (VOO & SFO) the ATR-FTIR spectra represent that the band absorbance around 3008 cm^{-1} increased with the increase in the percent of adulterants.

Fig-5. ATR-FTIR spectra of Adulterated VOO samples with CO at 3008 cm^{-1}

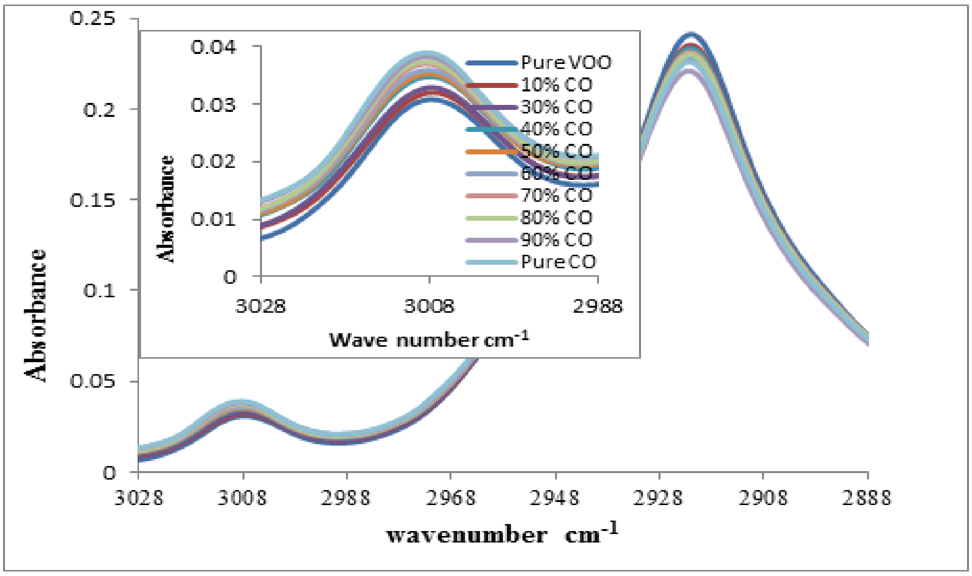
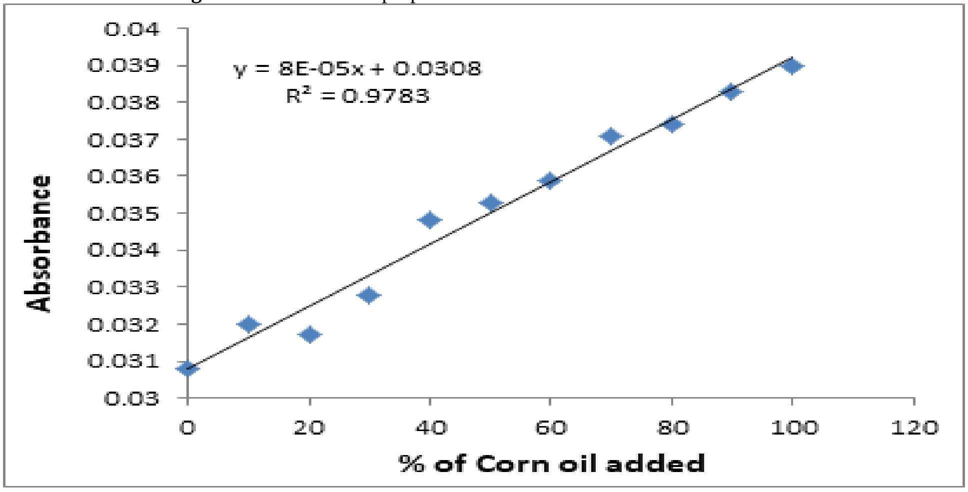
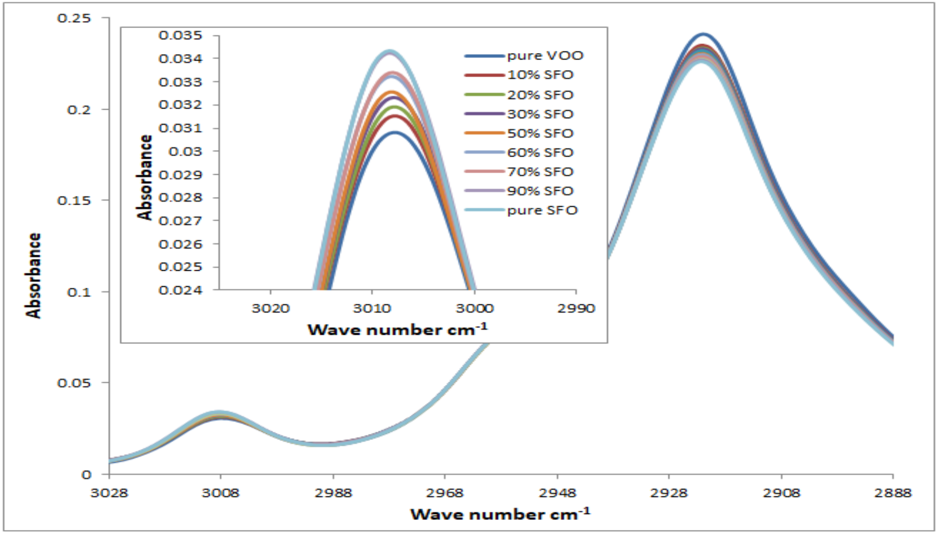


Fig-6. Effect of corn oil proportions on olive oil absorbance at 3008 cm^{-1}



This change in absorbance is due to the C-H stretching vibration of the cis-double bond (=CH). The chemical composition of oil affects the absorbance at a specific band (3008 cm^{-1}) resulting in an increase in absorbance as the adulterant proportion increases. Vlachos and others noted small shift of the band from 3006 cm^{-1} for the pure VOO to 3009 cm^{-1} for sunflower oil, soyabean oil, corn oil and sesame seed oil [15].

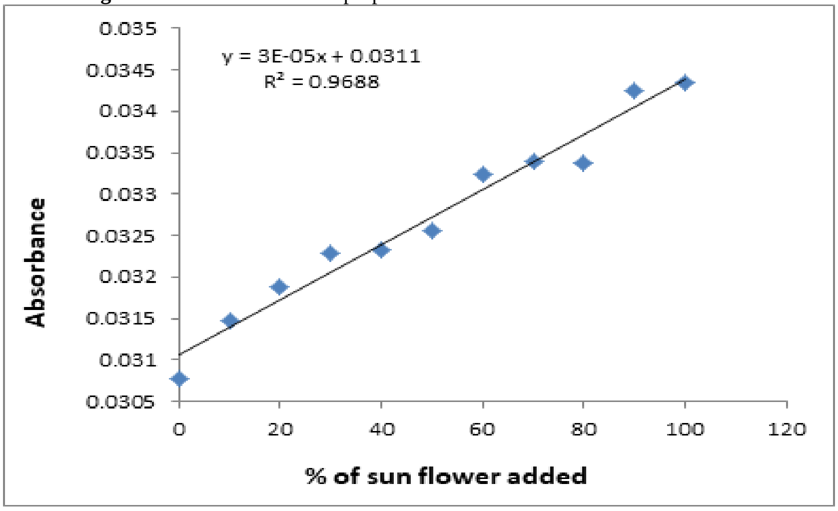
Fig-7. ATR-FTIR spectrum of Adulterated VOO samples with SFO at 3008 cm^{-1}



Based on the curve of Figure 6, absorbance at 3008 cm^{-1} versus the percentage of CO added to VOO have been generated for mixtures of olive oil/CO ranging from 0 to 100% CO, it is possible to determine the degree of VOO adulteration by addition of CO. A significant positive correlation coefficient (R^2 = 0.9783) was obtained. This is compatible with that reported by Poiana and others [1].

The same findings have been obtained for the adulteration of VOO with SFO as shown in Figure 8. Figure 8 shows the curve generated for mixtures of OO/SFO ranging from 0 to 100% SFO giving a good correlation coefficient (R^2 = 0.9688). This result is also in agreement with that found by Poiana and others [1]. This means that the absorbance band at 3008 cm^{-1} can be a reliable index to monitor the extent of adulteration of VOO by SFO and CO. This makes it possible to evaluate the degree of unsaturation and thus the olive oil authenticity.

Fig-8. Effect of sun flower oil proportions on olive oil absorbance at 3008 cm^{-1}



4. Conclusion

This study concern the study on Libyan virgin oil (VOO) by FT-IR spectroscopy in order to assess the adulteration with cheaper vegetable oils: sunflower oil and corn oil..

FTIR spectral regions ascertained to be useful for determination of VOO adulteration by CO and SFO. From this studies we conclude that; the FT-IR technique can be used to assess the adulteration of olive oil with some other cheap vegetable oils in short time with no chemical consumption. The main focus is on the absorbance band at 3008 cm^{-1} identified due to C-H stretching of cis-double bond which showed a significant change with change in the percentage of the cheaper vegetable oils mixed with VOO. On conclusion we can highlight that ATR-FTIR is an effective technique to investigate adulteration of olive oil due to its simplicity, rapidness, minimum sample preparation and low cost compared to other reported techniques.

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