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Detection of Olive Oil Adulteration by Visible Spectroscopy Technique

In this study, simple, fast and cost-effective analytical technique based on visible fluorescence spectroscopy was employed for adulteration detection in the olive oil. Olive oil was mixed with three low quality edible oils in Iraq; sunflower, vegetable and corn, in volume concentrations of 25, 50, 75, and 100%. The excitation-fluorescence map shows that the luminescence of the olive oil occurred at around 675 nm when it excited in UV-NIR region. Therefore, a 532 nm green laser was used as an excitation source for olive oil adulteration. In pure olive oil, a clear orange color was shown and it became faint color gradually by only adding a small concentration of the mixed oils and disappeared with a high concentration. Moreover, the emitted intensity peaks at 675 nm showed a linear decay with increasing the concentration of adulterant oils; this is true for sunflower and vegetable oils. However, impurity with corn oil showed nonlinear trend with the concentration. The technique used in this study can pave the way for fast and real time detection for olive oil quality.

Keywords: Virgin olive oil; Adulteration; Fluorescence spectroscopy; Health effects
Received: 28 August 2023; **Revised:** 02 October 2023; **Accepted:** 09 October 2023

1. Introduction

Olive oil is one of the most popular oils in Iraqi meals because of its healthy contents, particularly for patients with high cholesterol who can consume it in healthy habits. However, the adulteration olive oil with less expensive edible oil is currently a concern in the market, as it has serious problems about the health of consumers. Therefore, determining the authenticity of olive oil is the primary challenge, and consequently, many techniques have been growing to detect frauds of the pure olive oil [1]. So, the adulteration has become an important issue in the industry as well as due to the legal requirements and public concern, the demand on the need of inexpensive, direct and real-time monitoring of olive oil adulteration is increased continuously. Sunflower, corn, hazelnut and soybean oils (due to their low cost and chemical similarity with pure olive oil) [2-3] or even low-grade olive oils (refined or pomace olive oil) [4], are the most popular oil adulterants.

Olive oil contains many remarkable components such as monounsaturated fatty acids [5,6] and minor components such as carotenoids, phenolics and sterols [7-9]. On the other hand, recently, high demand on using olive oil in main foods based on some research that olive oil can help to prevent cancers and reduce potential risk of coronary heart diseases [10,11], diabetes and obesity [12-14]. Consuming virgin olive oil (25–50 ml/day) has been linked to increase lifespan, maintain good health and reduces possibility of Alzheimer's [15]. Generally, three types of olive oils are categorized by Food and Agriculture Organization (FAO): virgin olive, refined olive, and refined olive-pomace oils. They are then categorized into several grades based on, among other things, their organoleptic characteristics, median flaws, and color [16]. Many analytical methods have been reported for olive oil adulteration and among them are spectroscopic techniques [17-19] which include Raman spectroscopy, nuclear magnetic resonance spectroscopy (FTNMR), infrared spectroscopy (NIR), ultraviolet-visible spectroscopy (UV-visible) and fluorescence spectroscopy (FS) [20, 21]. In comparison to other techniques, fluorescence spectroscopy has a growing interest in detection of olive oil impurity with other adulterants [22] such as sunflower oil [23], corn oil [1], soybean oil [24] and lower quality olive oil in extra virgin olive oil [4,25]. In recent years, laser-induced fluorescence (LIF) spectroscopy is well established technique to be used in this field as it has the possibility of choosing the laser excitation wavelength based on the peak absorption of the oil [26]. In contrast to many detection techniques, LIF is a direct detection technique that offers very attractive inexpensive, simple and direct detection solutions; it is a small size and fast response and direct detection that can be even seeing by eyes in a very short measurement time.

In this study, LIF spectroscopy with compact and inexpensive green diode laser was employed to quantify olive oil adulteration with most common edible oils in Iraq, sunflower, vegetable and corn oils. This technique provides important advantages in practical applications of fast testing, small size, and simplicity of use by characterization of oils via the orange peak spectra emission.

2. Materials and Methods

Extra virgin olive oil with a volume of 6 ml was divided into three samples (2 ml each); each sample was adulterated with one of three different types of most common cooking oils in Iraqi: sunflower (sample 1), vegetable (sample 2) and corn (sample 3), in volume concentration ratios of 25, 50, 75, and 100%. Each olive oil sample (0% adulteration) was mixed thoroughly with 0.5 ml (25%) of one of the adulterant oils and placed in a silica cuvette for analyses. The concentration ratio of the mixture then increased sequentially by 0.5 ml of the adulterant oil to reach 50% (1 ml), 75% (1.5 ml) and 100% (2 ml) as a maximum.

UV-visible spectrophotometer (K-MAC Spectra Academy SV-2100) was used as fluorescence spectroscopy. In this study, a green laser pointer (JD-303, China) with output power of less than 1000 mW and a wavelength of 532 nm was used as an excitation source in the setup (Fig. 1). The measurements were performed at a wavelength from 400 to 800 nm and a spectral resolution of 0.5 nm.

Fig. (1) UV-visible spectrophotometer used in the study

3. Results and Discussion

Firstly, the absorption-emission map of the pure olive oil was examined in the UV, visible and NIR regions as shown in Fig. (2). As can see from this figure, the olive oil has three absorption peaks; the first one is between 350-400 nm which is the tail of UV and near to the blue wavelength. The second absorption peak is in the visible region between 500-550 nm, and the third one is between 650-700 nm. In meanwhile, through all three absorption peaks, pure olive oil has only one emission peak wavelength which is around 675 nm. Based on this map, a green laser was used as a source for excitation and the luminescence (emission) of 675 nm which is an orange color was investigated that is easily seen by the eye as shown in Figure 3. The emission of the orange color is mainly associated to chlorophylls and pheophytins and considered as an indication of virginity of the olive oil [27-29]. However, this color was changed to light orange by slightly adding a small quantity of one of the proposed edible oils in this study, while the color was disappeared by adding a high quantity.

In this study, UV absorption peak at 350-400 nm was avoided because this region of the wavelength is unsafe and 675 nm absorption peak was also avoided because it overlaps with the emission wavelength from the sample. Therefore, green laser as 532 nm is the best source cost-effective and safe to be used for this study.

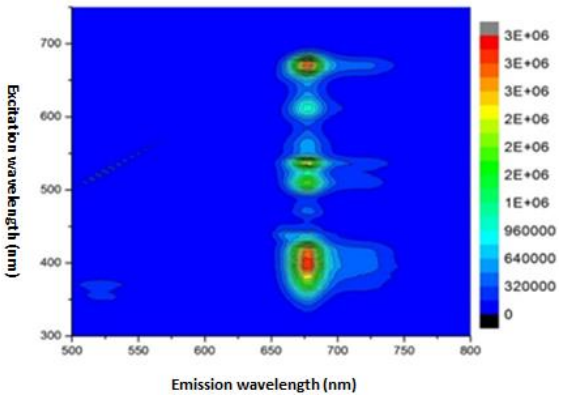

Fig. (2) Excitation-emission map of the pure olive oil

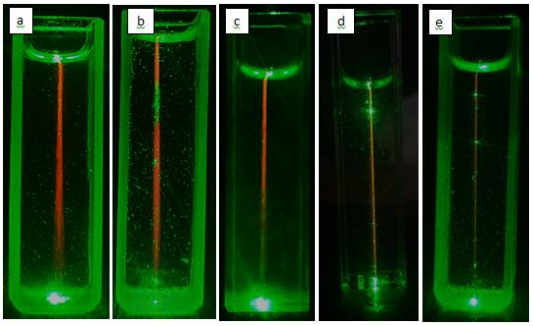

Fig. (3) Orange color emission from the pure olive oil and adulterated with different concentrations of vegetable oil excited using green laser (a) pure olive oil, (b) 0.5 ml, (c) 1.0 ml, (d) 1.5 ml and (e) 2.0 ml

Therefore, the olive oil purity was investigated with the mixed three different traditional edible oils: sunflower, vegetable and corn in different volume of concentrations using a 532 nm laser diode and K-MAC Spectra Academy SV-2100 UV-visible spectrophotometer.

The results of the olive oil mixed with sunflower, vegetable and corn oil with different mixture ratio are illustrated in figures (4), (5) and (6), respectively. It is clearly that the pure olive oil has a high absorption and emission peaks compared to other adulterant oils. The variation in the excitation intensity was due to the difference in the concentration of olive oil with the adulterant oils.

As can be seen from the figures, sunflower, vegetable and corn oils all have very close synchronous fluorescence emission with a maximum intensity around the same position of the olive oil emission. The highest intensity is associated to pure olive oil and then the peaks for the three mixtures were decreased with increasing of the concentration of the adulterant oil. This decrease could be attributed to the change in the luminescent concentration in

some components such as pigments (chlorophyll and carotenes), phenols and tocopherols in the adulterant oils which have negative linear relationship with the formation of oxidation products of fatty acids such as hydroperoxides [30].

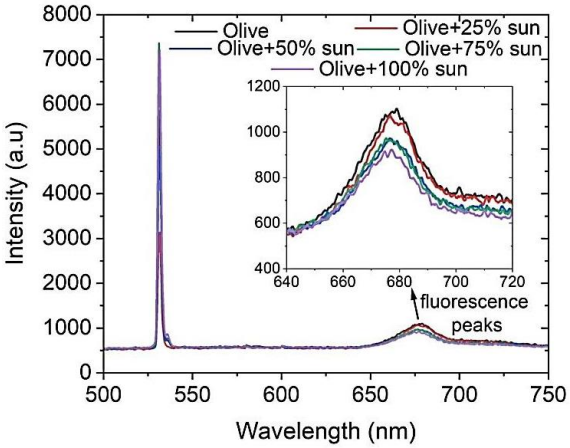

Fig. (4) Photoluminescence spectra of olive oil mixed with different volumes of sunflower oil

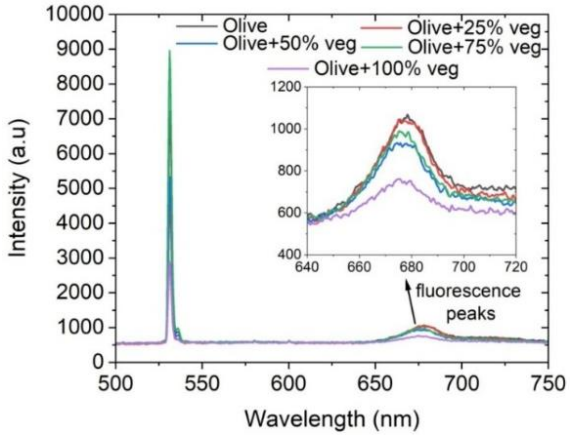

Fig. (5) Photoluminescence spectra of olive oil mixed with different volumes of vegetable oil.

On the other hand, the fluorescence intensity peaks for olive and other adulterants were determined with relative ratio to their concentrations. It was found that the emitted intensity was decreased linearly with increasing the mixture ration for pure olive oil with sunflower and vegetable oils, as shown in (Fig. 7). The reason for the linearity in the relationship is that the two adulterant oils have the same fluorescent components (chlorophylls) to that of pure olive oil but with lower concentrations. However, the mixture of the pure olive oil and corn shows nonlinear drop and this is because corn oil has lesser amounts of chlorophylls [26]. The results indicate that sunflower and corn oils are the most common adulterants used for fraud in Iraqi markets due to their chemical similarity with virgin olive oil and cheap oils. It was tried to find the emitted intensity peak trend at 532 nm with the wavelength, but it was not clear because the emitted peaks are very broad and this due to the presence of tocopherols, a type of vitamin E, and perhaps to some oxidation products [31].

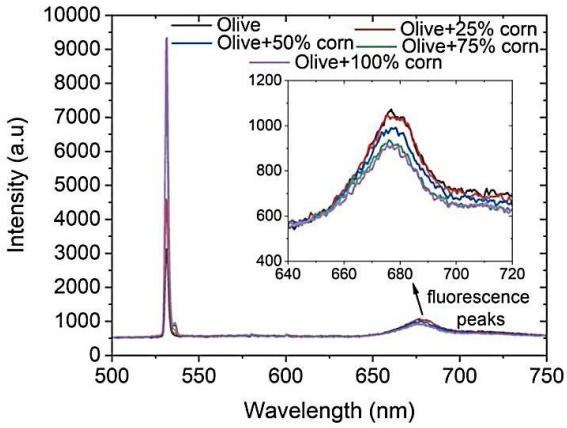

Fig. (6) Photoluminescence spectra of olive oil mixed with different volumes of corn oil

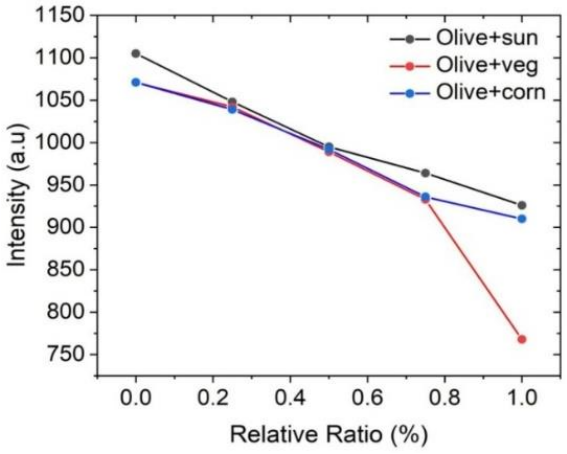

Fig. (7) Emitted peak intensity of the three edible oil concentrations with relative ratio to that of olive oil

4. Conclusions

Virgin olive oil adulteration with sunflower, vegetable and corn oils in Iraqi markets was conducted using visible-fluorescence spectroscopy. The virgin olive oil showed the highest fluorescence emission intensity and this is due to present of pigments and other components. It was shown an emission of clear orange color for pure olive oil and this color became faint and finally disappeared by gradual increase of the concentration of the adulterants. This color is mainly associated to chlorophylls and pheophytins and as a measure of virginity of the oil. However, a linear decay for the emission intensity peaks with relative ratio of concentration was found for olive and two of adulterants: sunflower and vegetable oils, while nonlinear drop was determined for olive and corn oils. This indicated that sunflower and vegetable oils are more probable adulterants in Iraqi markets as they have the same chemical components to that of olive oil.

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