



Use of Raman Spectroscopy for Analysis and Detection of Some Sudanese Edible Oils

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Abstract: Vegetable edible oils provide high nutritional and health value in the Sudanese diet. It is also used in the pharmaceutical industry and an essential ingredient in cosmetics. This paper reviews the use of Raman spectroscopy for the analysis, quality and characterization of edible oils, including six types of oils (corn, extra virgin olive, sunflower, factory sesame, presses sesame, and peanut) purchased from local Sudanese stores. The results showed that the spectra of edible oils are similar, but they show some differences that, despite their smallness, allow them to be distinguished from each other. Divide the spectrum into the fingerprint region. The range ranges between (600 and 1800) cm^{-1} the silent region", this spectral region is (1800 to 2500) cm^{-1} , and range is from (2500 to 3400) cm^{-1} , known as the "high wave number region". Raman spectra also pliable the determination of the degree of saturation and unsaturation of oils. This characteristic is related to the value of iodine, and the degree of unsaturation can be used to classify and approve oils, which is especially useful with high-quality oils in the appearance of the vibration modes at 1155 cm^{-1} and 1525 cm^{-1} . Adulteration of edible oils with cheaper oils is a major concern in the oil industry. The capabilities of a Raman spectrometer were checked to assess the purity of the samples (peanut spectrum and presses sesame spectrum). Raman spectroscopy allowed the examination of secondary components such as sterols, hydrocarbons, terpene alcohols and polyphenols. Raman spectroscopy is used because this innovative method provides fast, non-destructive and reagent-free measurements, samples do not need to be processed and do not require large volumes.

Keywords: Edible Oils, Raman Spectroscopy, Unsaturation, Adulteration

1. Introduction

Vegetable edible oils are substances extracted from plants that are composed of triglycerides and represent a major component [1]. The minor components of edible oils are formed of, free fatty acids, phosphatide, pigments, fat-soluble vitamins, tocopherol, sterols, fatty alcohol and waxes [2, 3]. Normally, oils are liquid at room temperature [4]. The connexion between health and food has been proven for the maintenance of life, but the notion has now been changed from conservation to better health quality. Among all the diet ingredients, fats become more important for both health specialists and the public. Fatty acids play an important role

in the cardiac cells because they are essential fuels for the electrical and mechanical activities of the heart [5]. The modern way of processing vegetable oils is through chemical extraction and the use of solvent extracts, Physical extraction, a method that does not use a solvent, is another way of processing vegetable oils through traditional mechanical extraction [6]. Oilseed presses are commonly used in developing countries, amid people for whom other extraction procedures would be prohibitively costly [7]. The refinement of edible oils means the elimination of smell, natural color, free fatty acids and odour. The final product of refinement is transparent edible oil. It involves chilling plant, neutralization (to remove soap); Bleaching (to remove color), Filtration (use the wax filter and use pressure leaf filter), and

cooling. The stability or shelf-life of the edible oil is important globally, especially in developing countries where the storage condition for the edible oils is not ideal. A major influence on the stability of storage edible oils is the type of fatty acid practically the unsaturated. However, cultivars types, maturity and environmental condition are known to influence the composition of fatty acids e.g. groundnut oil is more stable than safflower and sunflower, because both oils contain high amounts of polyunsaturated fatty acids [8, 9]. The objectives of the present study are to use Raman spectroscopy for analyzing and to characterize edible oils of the six edible oil of sesame, groundnut, sunflower, corn, olive. Raman spectroscopy analyses is a spectroscopic procedure based on Raman scattering effects of molecular vibrations, elastic individual molecular spectra, that can serve as fingerprints for compounds and mixtures [10]. Its advantages encompass non-destructive influences on samples, low costs, high efficiency, absence of specimen preparation, and small specimen sizes [11, 12]. Raman spectroscopy has been extensively utilized in various domain, including physics, environmental science, biology, medicine, and chemistry [13, 14]. Of the identifier that the shape of a Raman spectrum is related to the molecular structure of the sample. Therefore, even if samples, such as oils, have the same functional groups, Raman spectra will present various shapes, despite having Raman peaks at or around the same wavenumber [15]. This happens because of the various molecular structures.

2. Materials and Methods

2.1. Raman Spectroscopy

Raman spectra were measured for edible oil samples using

a Raman microscope (Thermo Scientific DXR), from Thermo Fisher, the USA equipped with a confocal microscope, with a depolarization laser at an excitation wavelength at 532 nm green lasers and voltage (2.33 volts). All samples were measured directly without any physical or chemical treatment. Six accumulations with an exposition time (5-10 s). For the peak fitting procedure, all basic spectra were corrected using the Origin Pro 2017 software, (Origin Lab, Northampton, USA), presenting the information about: peak position, peak height, and peak intensity.

2.2. Materials

Six types of Sudanese edible oils (corn oil, extra virgin olive oil, presses sesame oil, factory sesame oil, peanut, and sunflower oils) were selected as the experimental samples. Four types of edible oils were produced producer in Sudan, and corn oil and extra virgin olive oil was an import commodity. The oil samples used in this work were purchased as commercial products from as commercial products from a local supermarket in Khartoum, Sudan.

3. Results

Raman spectra of six different edible oils (Corn, Olive, Sunflower, Presses Sesame, Factory Sesame and Peanut) oils were measured under green laser excitation at 532 nm. The Raman spectra were recorded in the spectral region (50–3100) cm^{-1} , as shown in Figures 1 to 6. While the various oil spectra presentation changes in the Raman intensities of many lines, there are remarkable changes in the position (Raman shift) of these bands. The band assignments, Molecule/group, vibrational mode, and peak intensity of the Raman spectra of edible oil. Reported in Tables 1 to 6.

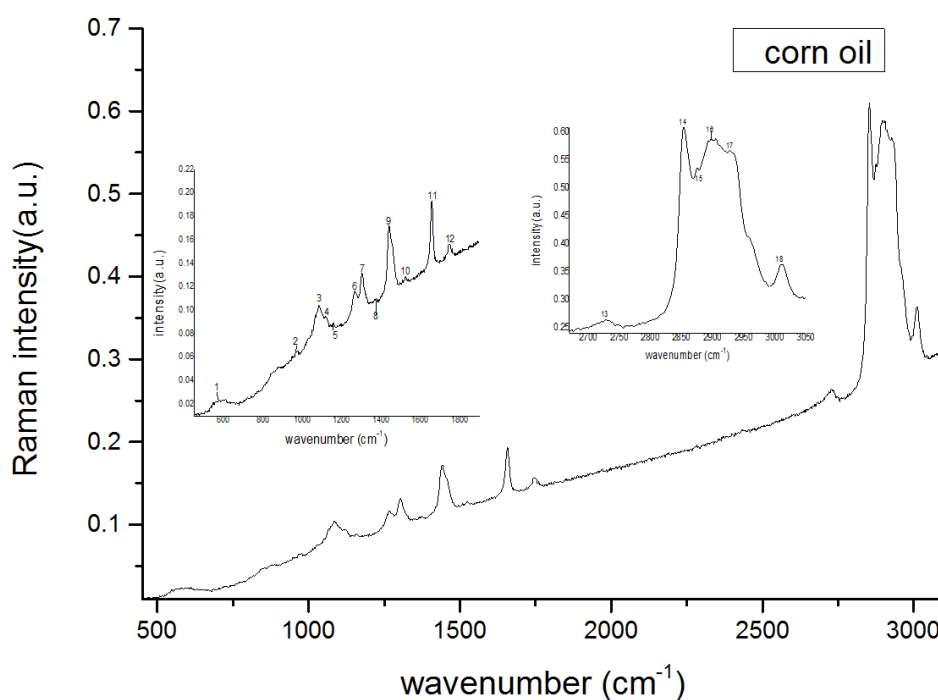
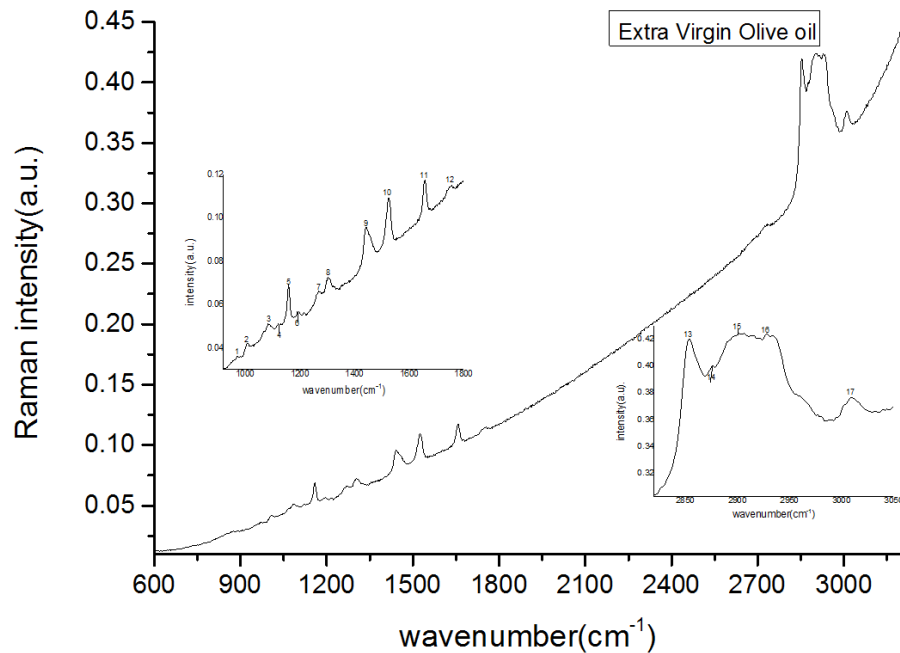


Figure 1. Typical Raman spectrum of Corn oil.

Table 1. Raman data of Corn oil and their peaks assignments.

| Peak number | Wavenumber (cm ⁻¹) | Molecule/group | Vibrational mode | Intensity (a.u.) | Reference |
|-------------|--------------------------------|-------------------|---|------------------|------------------|
| 1 | 580.6 | - | - | 0.023 | - |
| 2 | 969.1 | RHC=CHR | C=C bending form trans | 0.065 | [16, 18] |
| 3 | 1084.9 | C-C | Aliphatic stretch | 0.104 | [17, 18] |
| 4 | 1122.5 | C-C | Aliphatic in phase stretch | 0.093 | [18] |
| 5 | 1158.1 | CH ₂ | Bending | 0.089 | [23] |
| 6 | 1266.1 | Cis RHC=CHR | =CH symmetric rock Cis isomer | 0.116 | [16, 18] |
| 7 | 1303.7 | CH ₂ | Bending (twisting) from methylene | 0.131 | [15, 17, 18, 21] |
| 8 | 1374.1 | CH ₃ | Symmetric bending | 0.110 | [22, 23] |
| 9 | 1441.6 | -CH ₂ | C-H bending (scissoring) from methylene | 0.171 | [15-17, 19-21] |
| 10 | 1524.5 | RHC=CHR | C=C stretching | 0.128 | [16, 17] |
| 11 | 1657.6 | RHC=CHR | C=C stretching from Cis | 0.193 | [17, 18, 20] |
| 12 | 1749.2 | RC=OOR | C=O stretching from ester | 0.156 | [15-19] |
| 13 | 2727.9 | C=O | Fermi resonance | 0.263 | [23] |
| 14 | 2853.3 | -CH ₂ | Symmetric aliphatic C-H stretch | 0.610 | [16, 15, 22, 23] |
| 15 | 2875.4 | CH ₂ | Symmetric stretching | 0.535 | [15, 16 22, 23] |
| 16 | 2898.6 | CH ₂ | Asymmetric stretching | 0.588 | [16, 23] |
| 17 | 2927.5 | -C-H ₂ | C-H asymmetric stretching | 0.568 | [16, 15] |
| 18 | 3010.4 | Cis RHC=CHR | =C-H symmetric stretching | 0.362 | [16, 15, 19, 20] |

**Figure 2.** Typical Raman spectrum for Olive oil.**Table 2.** Raman data of Olive oil and their peaks assignments.

| Peak number | Wavenumber (cm ⁻¹) | Molecule/group | Vibration mode | Intensity (a.u.) | Reference |
|-------------|--------------------------------|--------------------|---|------------------|------------------|
| 1 | 970.1 | RHC=CHR | C=C bending from Trans | 0.036 | [16-18] |
| 2 | 1007.7 | HC-CH ₃ | CH ₃ bending | 0.042 | [16, 25] |
| 3 | 1088.7 | C-C | Stretching | 0.050 | [20] |
| 4 | 1125.3 | C-C | Aliphatic in phase stretch | 0.051 | [18, 24, 25] |
| 5 | 1158.1 | CH ₂ | Bending | 0.086 | [23] |
| 6 | 1195.7 | CH ₂ | Bending | 0.056 | [23] |
| 7 | 1268.1 | Cis RHC=CHR | =CH symmetric rock cis isomer | 0.066 | [16, 18] |
| 8 | 1303.7 | CH ₂ | Bending (twisting) from methylene | 0.072 | [15-18, 21] |
| 9 | 1441.6 | -CH ₂ | C-H bending (scissoring) from methylene | 0.095 | [15-17, 19] |
| 10 | 1525.5 | RHC=CHR | C=C stretching | 0.109 | [16, 17] |
| 11 | 1657.6 | RHC=CHR | C=C stretching from Cis | 0.117 | [15-17, 20, 21] |
| 12 | 1756.0 | RC=OOR | C=O stretching | 0.115 | [15, 16, 19, 25] |
| 13 | 2854.2 | -CH ₂ | C-H symmetric stretching | 0.419 | [23, 25] |
| 14 | 2876.4 | C-H ₂ | Symmetric stretching | 0.400 | [15, 16] |
| 15 | 2901.5 | CH ₂ | Asymmetric stretching | 0.424 | [15, 16, 22, 23] |
| 16 | 2928.5 | -CH ₂ | C-H asymmetric stretching | 0.423 | [16, 23] |
| 17 | 3009.5 | Cis RHC=CHR | =C-H symmetric stretching | 0.376 | [15, 16, 20, 25] |

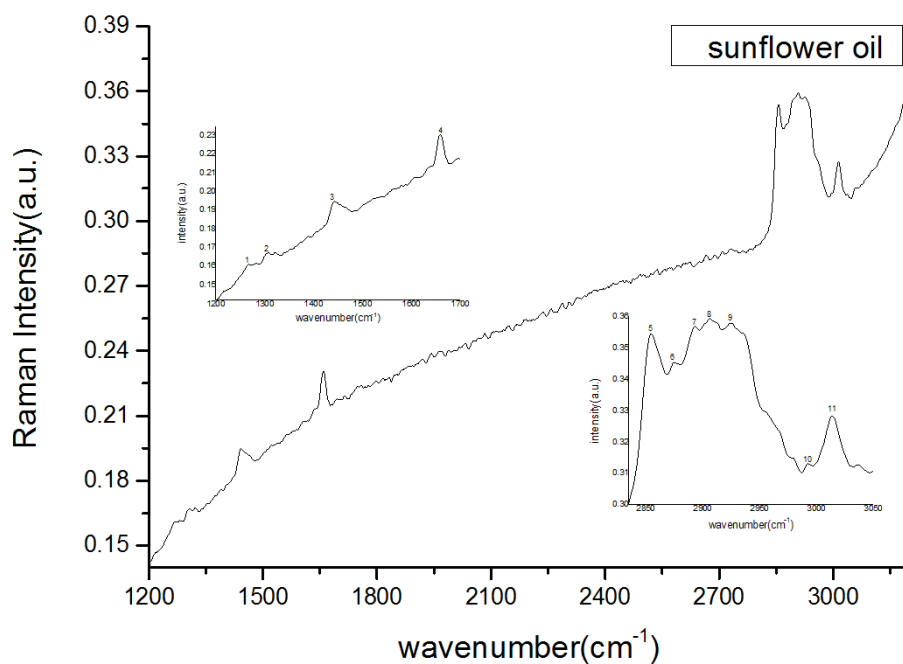


Figure 3. Typical Raman spectrum of Sunflower oil.

Table 3. Raman data of Sunflower oil and their peaks assignments.

| Peak number | Wavenumber (cm ⁻¹) | Molecule/group | Vibration mode | Intensity (a.u.) | Reference |
|-------------|--------------------------------|------------------|---|------------------|------------------|
| 1 | 1268.1 | =C-H | Symmetric rock Cis isomer | 0.161 | [16-18] |
| 2 | 1303.7 | -CH ₂ | C-H bending (twisting) from methylene | 0.166 | [15-18, 21] |
| 3 | 1442.6 | -CH ₂ | C-H bending (scissoring) from methylene | 0.194 | [15, 16, 20] |
| 4 | 2854.2 | -CH ₂ | C-H symmetric stretching | 0.354 | [15, 16] |
| 5 | 2874.5 | C-H | Symmetric stretching | 0.345 | [15, 16, 22, 23] |
| 6 | 2892.8 | CH ₃ | symmetric stretching | 0.356 | [16, 22] |
| 7 | 2906.3 | CH ₂ | Asymmetric stretching | 0.359 | [22] |
| 8 | 2923.6 | CH ₂ | Asymmetric aliphatic C-H stretching | 0.357 | [15] |
| 9 | 2992.1 | CH ₂ | symmetric stretching | 0.313 | [23] |
| 10 | 3013.3 | =CH | Asymmetric olefinic C-H stretch | 0.328 | [15, 16, 19] |

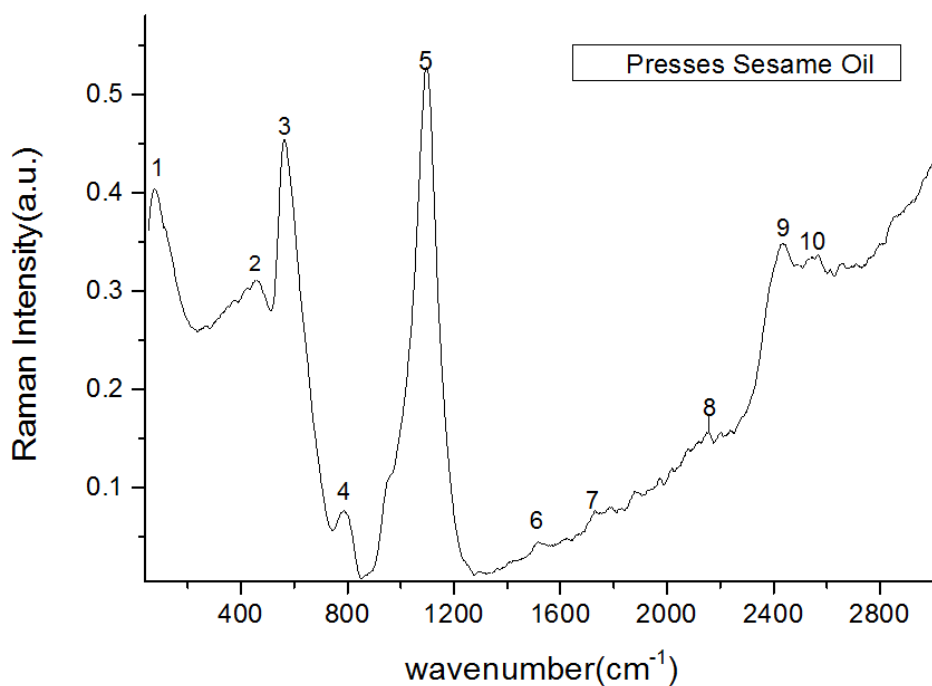


Figure 4. Typical Raman spectrum of Presses Sesame oil.

Table 4. Raman data of Presses Sesame oil and their peaks assignments.

| Peak number | Wavenumber (cm ⁻¹) | Molecule/group | Vibration mode | Intensity (a.u.) | Reference |
|-------------|--------------------------------|--------------------|--------------------------|------------------|------------------|
| 1 | 80 | Lattice vibrations | | 0.404 | (m r) |
| 2 | 460.0 | - | - | 0.311 | - |
| 3 | 567.1 | - | - | 0.454 | - |
| 4 | 785.9 | CH ₂ | Rocking | 0.076 | [23] |
| 5 | 1098.4 | C=O | Stretching for ester | 0.528 | [23, 24] |
| 6 | 1523.6 | RHC=CHR | C=C stretching | 0.044 | [16] |
| 7 | 1730.6 | RC=OOR | C=O stretching for ester | 0.075 | [15, 16, 21, 24] |
| 8 | 1888. | - | - | 0.096 | - |
| 9 | 2433.8 | - | - | 0.348 | - |
| 10 | 2561.1 | - | - | 0.337 | - |

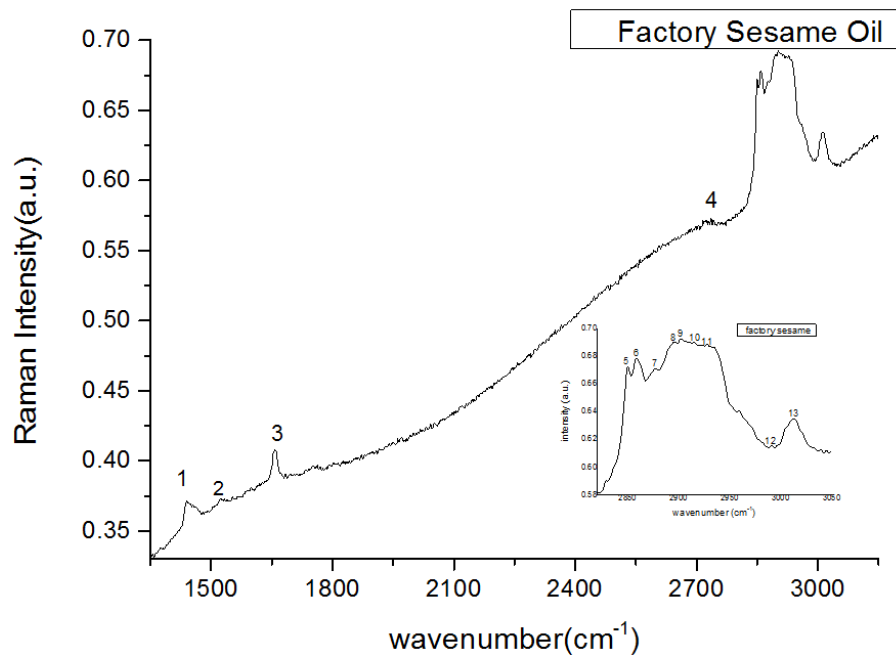
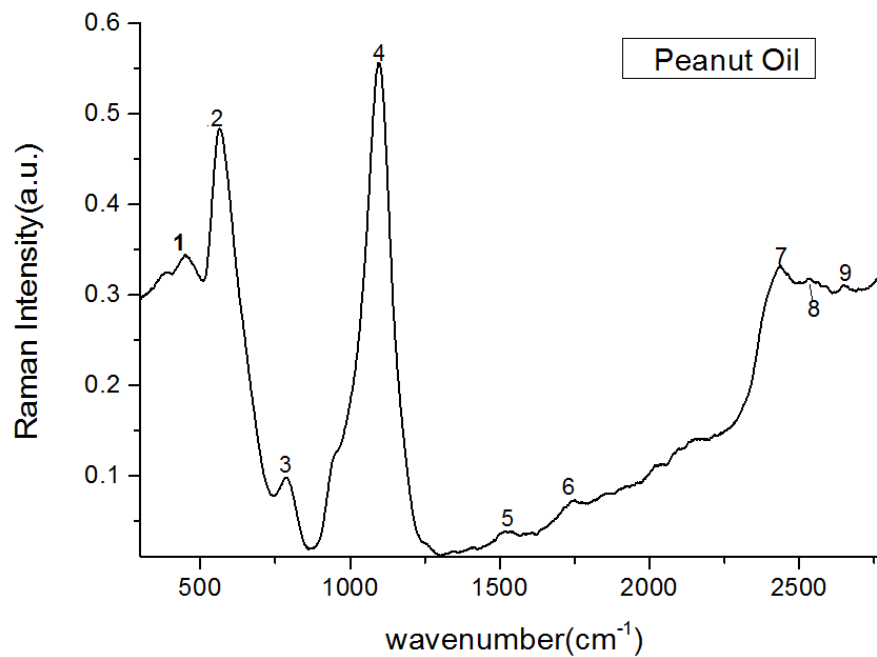
**Figure 5.** Typical Raman spectrum of Factory Sesame oil.**Figure 6.** Typical Raman spectrum of Peanut oil.

Table 5. Raman data of Factory Sesame oil and their peaks assignments.

| Peak number | Wavenumber (cm ⁻¹) | Molecule/group | Vibration mode | Intensity (a.u.) | Reference |
|-------------|--------------------------------|-------------------------|---|------------------|------------------|
| 1 | 1302.8 | -CH ₂ | C-H bending (twisting) from methylene | 0.327 | [15-18, 21] |
| 2 | 1439.7 | -CH ₂ | C-H bending (scissoring) from methylene | 0.371 | [15-18, 21] |
| 3 | 1523.6 | RHC=CHR | C=C stretching | 0.373 | [16] |
| 4 | 1657.6 | RHC=CHR | Stretching from Cis | 0.408 | [15-17, 21] |
| 5 | 2728.9 | C=O | Fermi resonance | 0.571 | [16, 23] |
| 6 | 2849.4 | -CH ₂ | C-H symmetric stretching | 0.672 | [15, 16, 20] |
| 7 | 2858.1 | CH ₂ | Symmetric aliphatic CH stretching | 0.678 | [16] |
| 8 | 2877.4 | CH ₂ | Symmetric stretching | 0.670 | [15, 16, 22, 23] |
| 9 | 2895.7 | -CH ₃ | C-H symmetric stretching | 0.690 | [16] |
| 10 | 2901.5 | CH ₂ | Asymmetric stretching | 0.692 | [16, 23] |
| 11 | 2915.9 | -C-H (CH ₂) | Asymmetric stretching | 0.689 | [23] |
| 12 | 2927.5 | CH ₂ | Asymmetric aliphatic CH stretching | 0.688 | [16] |
| 13 | 2991.1 | CH ₂ | symmetric stretching | 0.615 | [23] |
| 14 | 3012.4 | =CH | C-H Asymmetric olefinic stretching | 0.634 | [15] |

Table 6. Raman data of Peanut oil and their peaks assignments.

| Peak number | Wavenumber (cm ⁻¹) | Molecule/group | Vibration mode | Intensity (a.u.) | Reference |
|-------------|--------------------------------|------------------------------------|--------------------------|------------------|-----------|
| 1 | 448.5 | - | - | 0.344 | - |
| 2 | 585.7 | - | - | 0.483 | - |
| 3 | 785.0 | -(CH ₂) _n - | Rocking | 0.097 | [23] |
| 4 | 1097.4 | C=O ester | Stretching | 0.556 | [23, 24] |
| 5 | 1517.8 | RHC=CHR | C=C stretching | 0.038 | [23] |
| 6 | 1748.2 | RC=OOR | C=O stretching for ester | 0.073 | [16-18] |
| 7 | 2435.7 | - | - | 0.332 | - |
| 8 | 2528.3 | - | - | 0.317 | - |
| 9 | 2651.7 | - | - | 0.310 | - |

4. Discussion

In the region from the beginning of the spectrum to 600 cm⁻¹, bands appeared in this region of several oils, corn oil 580 cm⁻¹, pressed sesame oil 80 cm⁻¹ and 567 cm⁻¹, and peanut oil at 448 cm⁻¹ and 585 cm⁻¹.

In the fingerprint region, the range between (600 and 1800) cm⁻¹. This region gets its name from the variety of localized micro-spectral properties that give particles their unique "fingerprints". Molecular fingerprints can allow classification of samples the s and chemical analysis. Bands appeared in this region in all samples.

The "silent region", this spectral region of (1800 to 2500) cm⁻¹ is mostly devoid of contributions from biological molecules, although there are some exceptions. Bands in this range only appeared in presses sesame oil, peanut oil. It was not possible to interpret the results in this region.

The range from (2500 to 3400) cm⁻¹, which is known as the "high wavenumber region" From the Raman spectrum. changes in Raman ranges in the region of cm⁻¹ are related to modifications of expansion vibrations C-H. Raman indicates the homologous expansion of CH₂, antagonist expansion of CH₂ symmetry, and symmetric stretching movement of CH₃, respectively. This region appears in corn, olives, sunflower, and factory sesame.

Cis-trans appeared in the bands of corn at (969.1, 1266.1, 1657.6) cm⁻¹, olives at (970.1, 1268.1, 1657.6) cm⁻¹ sunflower at (1268.1) cm⁻¹ and factory sesame at (1657.6) cm⁻¹. Cis-trans isomerism is a direct result of the high energy barrier of

rotation at the double bond it is most often encountered in unsaturated compounds. Groups can be arranged around C = C, =CH spatially to give two types of isomers it is called cis (Latin for the same side) and Trans (Latin for the cross). The two shapes it has the same molecular formula but differs in structure. Cis and Tran's isomers have different solubility Points and boiling points [26].

The main difference between low-quality and high-quality edible oils is the appearance of the two vibration modes at 1155 cm⁻¹ and 1525 cm⁻¹. In an oil sample, these two modes can be observed in high quality (corn, olive, sesame) oil, while in a low-quality oil sample, these two modes cannot be detected. Also, the intensity of these two modes varies with the free fatty acids (FFA) content in edible oils samples. The mode at 1155 cm⁻¹ can be assigned to C-C stretching of carotenoids, and the mode at 1525 cm⁻¹ can be assigned to C=C stretching of carotenoids. The carotenoids play an important role as natural antioxidants in edible oils.

The carbonyl group or C = O is the ideal functional group to detect utilizing infrared spectroscopy (IR) because the peak of the expansion vibration is intense and located in a unique wavelength range. It did not appear in the pomegranate studies, but in the research, it was found at the band - at 2728 cm⁻¹ in corn oil and factory Sesame oil.

The spectra for (corn, olive, sunflower, factory sesame) oils were similar and contained the typical strong bands at (267, 1302, 1442, 1655, 1747, 2852 c, and 2970) cm⁻¹.

There is a big difference between the Raman spectrum of factory sesame oil and presses sesame oil, but the Raman spectrum of peanut oil and presses sesame oil are identical.

Detection of adulteration of pressed sesame oil mixed with peanut oil. To confirm this result, more samples must be studied.

5. Conclusions

This article demonstrates that Raman spectroscopy is a valuable, adequate, and useful technique for determining the degree of unsaturation of edible oil. The detection of adulterants and the determination of minor components of vegetable oils can be achieved by Raman spectroscopy. In this work, we have demonstrated that dispersive Raman can be used as a fast and nondestructive method. The results of this study demonstrate that Raman spectroscopy can be useful in detecting adulteration. However repetition is needed.

The domestic edible oils industry must be improved. Raman device must be available in all institutions that control the quality of products.

6. Recommendations

1. Expand the study to include all edible oils used in Sudan.
2. Conducting more experiments by taking samples from different production companies for comparison.
3. Study the effect of low and high temperatures on oils.
4. Investigation of the effect of storage methods.

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