Non-linear optical response of edible oils by means of the Z-scan technique

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Abstract. Oils of vegetable origin are classified as organic compounds, which have become the object of study in the field of photonics and non-linear optics, because they have a characteristic chemical bond with the presence of delocalized electrons, which gives them a high non-linear response. In the food industry, non-destructive or invasive studies are required to establish the quality and conservation indices of the chemical, physical and nutritional properties of edible products. The non-linear optic response of different oils of vegetable origin was evaluated: extra virgin olive oil, extra virgin sesame oil, extra refined linseed oil and virgin avocado oil using the Z-scan technique. The absorption and transmission spectra were taken to establish the coefficient of linear absorption of the sample as a function of the wavelength. For each compound, the variations of the nonlinear optical properties were analyzed as a function of the excitation power, using the closed cell and open cell configurations; where the third-order electrical susceptibility ($\chi^{(3)}$), the non-linear refraction index ($\eta_2$) and the non-linear absorption coefficient ($\beta$) were determined. Subsequently, a comparison of the non-linear response was made according to the type of oil and the degree of refinement. It was found that extra virgin olive oil and virgin avocado oil presented a better non-linear response at low laser power as a consequence of the low thermal influence, which makes them possible candidates in the development of photonic devices.

1. Introduction
Vegetable oils are mainly composed of triglycerides and fats, both belonging to the lipids group. Many of the organic components present in these oils have large dielectric properties due to their distinctive chemical bonds with delocalized electrons, a conjugated double bond and also a huge dipole moment; properties that provide a high response to non-linear phenomena such as non-linear absorption and the nonlinear refraction [1,2].

The great advances in optics and photonics have caused a big demand in the study of non-linear optical materials and their application in optical limitation and optical switches; Many of the investigations are focused on organic materials [3–5]. In the present investigation was performed the study using the closed cell configurations, for the measurement of the non-linear refraction index $\eta_2$ and the real part of the third order electric susceptibility using an aperture of 0.32 mm radius, and the configuration in open cell for the non-linear absorption coefficient $\beta$ and the imaginary part of the third order electric susceptibility, of the four study oils (extra
virgin olive oil (EVOO), extra virgin sesame oil (EVSO), extra refined linseed oil (ERLO) and virgin avocado oil (VAVO)). The study was performed for evaluating the depending with the power of the laser using the z-scan technique, that is based on the distortion that experiences a laser beam of Gaussian profile when going through a non-linear sample [6, 7]. This technique is one of the most used due to its relative simplicity and sensitivity in comparison with other techniques, which have rigorous assemblies and low precision [8].

2. Theory

2.1. Chemical structure of a vegetable oil

Fats and oils are divided in two fractions, a lipid or saponificable fraction and an unsaponificable fraction, each consisting of several compounds. In general they are composed of triglycerides, which in turn have waxes and fatty acids. The oils correspond to triglycerides of vegetable origin, which contain saturated fatty acids, omegas fats and mostly unsaturated fatty acids [9].

2.2. Z-scan technique

To develop the Z-scan theory, we follow the theoretical model proposed by Sheik Bahae et.al [6].

We performed the theoretical model with the following equations:

\[ \Delta T_{PV} = 0.406(1 - S)^{0.25} |\Delta \Phi_0| \]  

(1)

with \( \Delta \Phi_0 \):

\[ \Delta \Phi_0 = (2\pi/\lambda) \eta_2 I_0 L_{eff} \]  

(2)

where the Equation (1) shown the \( \Delta T_{PV} \), that represents the difference in the normalized transmittance curve between the maximum and minimum value \( [T_P - T_V] \), \( I_0 \) y \( \lambda \) represent the irradiancy and wavelength parameters of the laser. The term \( \Delta \Phi_0 \) shown in Equation (2) represents the change in the phase produced in the sample. The terms of transmittance at the opening \( (S) \) and effective length \( (L_{eff}) \) are defined by the Equation (3) and Equation (4):

\[ S = 1 - \exp \left[ -2r_s^2/w_0^2 \right] \]  

(3)

\[ L_{eff} = [1 - \exp (-\alpha L)] \alpha^{-1} \]  

(4)

where \( L \) is the total length of the sample and \( \alpha \) is the linear absorption coefficient. The phenomena of non-linear refraction and non-linear absorption are related to the existence of a complex factor called third-order electrical susceptibility, denoted as \( \chi^3 = \chi^3_R + i\chi^3_I \), this factor has a fourth order tensor representation [10].

The real component of \( \chi^3 \) is related to the kerr effect, an effect that associates the variation of the refractive index as a function of intensity. The real third-order susceptibility component also has a direct proportion with the non-linear refraction index \( \eta_2 \) as shown the Equation (5) [6,11].

\[ \chi^3_R = \frac{4}{3} \eta_0^2 \varepsilon_0 c \eta_2 \]  

(5)

In Equation (5), for measurement \( \eta_2 \) the configuration called closed cell was used, where the parameter \( S \) defined in the Equation (3) is generally small, experimentally this geometry is achieved by placing a collimator or iris; but, physically, the transmittance for this configuration
is proportional to the phase change $\Delta \Phi_0$ produced when the sample is transferred through the focal plane as shown in the Equation (6):

$$T(z, \Delta \Phi_0) = 1 + \frac{4(Z/Z_R)\Delta \Phi_0}{((Z/Z_R)^2 + 1)((Z/Z_R)^2 + 9)}$$  

(6)

In Equation (6), the term $Z_R$ represents the Rayleigh dispersion defined as $Z_R = \pi \omega_0^2/\lambda$. Furthermore to the transmittance, $\eta_2$ is also proportional to the parameter $S$, therefore it is important to estimate it for know the value of $\eta_2$ of the Equation (7).

$$\eta_2 = \frac{\Delta T_{PV} \omega_0^2/\lambda}{1.624(1-S)^{0.25}P L_{eff}}$$  

(7)

On the other hand, the non-linear absorption coefficient $\beta$ is proportional to the imaginary component of the third-order susceptibility $\chi_3$. To measure the coefficient $\beta$ defined in Equation (8); the Z-scan must be applied under the open cell geometry, which implies a value of $S = 1$, in other words the equation that describes the transmittance when absorption effects change, because other effects such as absorption are considered saturable absorption and absorption of multiple photons [12].

$$\beta = \frac{2\sqrt{2}\Delta T}{T_0 L_{eff}}$$  

(8)

The transmittance form for this configuration, is shown in the Equation (9):

$$T(z) = q_0(z)^{-1} \ln(1 + q_0(z))$$  

(9)

In the isolated study of the non-linear absorption (configuration in open cell) are considered small losses with a response much smaller than the width of the pulse $q(z) = \beta IL_{eff} \ll 1$, therefore the transmittance is expressed in terms of a summation, which involves the term $q_0$ as the Equation (10) shows [6–8].

$$T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[q_0(z, 0)]^m}{(m + 1)^{3/2}}$$  

(10)

3. Experimental setup

Figure 1 represents a diagram of the Z-scan assembly in closed cell configuration; for our study an ND-YAG laser of 532 nm wavelength was used, emitting in CW mode, this laser is focused through a lens of 100 mm of focus, towards a glass cell where the study sample is deposited; the sample was moved a distance of 60 mm (taked of $-30 \text{ mm} a + 30 \text{ mm}$) measured symmetrically from the focus of the lens used.

![Figure 1. General scheme of the Z-scan assembly by closed cell.](image)
The transmittance of the samples was monitored from a computer and collected through an LBP-1-USB CCD, camera; the system was controlled through an interface created in LabVIEW; the value of the non-linear refractive index was calculated using the closed cell configuration using an aperture of 0.64 mm in diameter, on the other hand, the non linear absorption coefficient was calculated using the open cell configuration, which involves removing the iris in front of the photodetector. For the calculation of \( \chi^3 \); the values of the refractive index and the linear absorption coefficient are required, these were found using an ABBE Refractometer and taking the absorption spectrum of the oils in study through of a Spectrophotometer UV-Vis EVOLUTION 60S. Figure 2 and Table 1 show the absorption spectrum obtained for each oil and the values of \( \eta_0 \) and \( \alpha \).

### Table 1. Values of \( \alpha_0 \) and \( n_0 \) obtained.

| type of oil | \( \alpha_0 \) (mm\(^{-1}\)) | \( n_0 \) |
|------------|-----------------|-----|
| EVOO       | 0.229           | 1.4678 |
| EVSO       | 0.157           | 1.474 |
| ERLO       | 0.066           | 1.481 |
| VAVO       | 0.361           | 1.4685 |

4. Analysis and results

4.1. Study in function of the power

For each one of the oils, a wide range of powers between 10 and 120 mW was worked, with some exceptions due to the low response of some oils. Figure 3 shows the data obtained for each oil in the corresponding powers, the graphs were treated using Origin, where a Savitsky Golay smoothing of 85 points was applied in order to appreciate better the behavior of the graphs.
The sign of $\eta_2$ is determined by the relative position of the peak and the transmittance valley, if the sample has a $\eta_2 > 0$ the graph of $T(Z)$ has first the valley and then the peak while for a $\eta_2 < 0$ it is presented first the peak and then the value of the valley; for each of the oils under study, evidently, the value of the non-linear refraction index is negative; for powers greater than 60 mW the symmetry of the curve is lost and at the same time the curve is distorted further, all this due to the contribution or thermal influence [4,13,14].

In the same way, the transmittance analysis was carried out using the configuration, as shown in the Figure 4, where again it can be seen that for low power the thermal influence is low and there is a great symmetry in the curve as is characteristic of this configuration [6].

To compare behavior of the oils, we choose the two potencies where the oils showed the best non-linear response, this comparison is shown the Figure 5. Olive oil showed the best performance, the transmittance curves show high symmetry and the thermal contribution at low power is negligible; followed by the EVOO is the VAVO which has nonlinear optical properties from powers even lower than the EVOO with the exception that the VAVO is more susceptible to thermal influence. the other two oils (ERLO y EVSO) have a very low effect compared to the other two (EVOO and VAVO).

Figure 4. Measurement of transmittance using the open cell configuration of the Z-scan.

Figure 5. Comparison at 15 mW (a), and 25 mW (b) of the four oils under study.
The calculations of $\eta_2$, $\beta$ and the two components of the susceptibility shown in Table 2 and Table 3 shows that the order of magnitude of the parameters found for the sample of AOEV and AAGV are much bigger than the other two oils, therefore it is correct to conclude that they have the highest non-linear response.

Table 2. Comparison of nonlinear parameters for each oil at a power of 15 mW.

| Type of Oil | $\eta_2 \times 10^{-6}$ | $\beta \times 10^{-3}$ | $\chi_R^3 (\times 10^{-6})$ | $\chi_i^3 (\times 10^{-5})$ |
|-------------|--------------------------|------------------------|---------------------------|---------------------------|
| EVOO        | -0.819556                | 0.7899                 | -4.4726                   | 1.7777                    |
| EVSO        | -0.111307                | 0.1769                 | -0.6126                   | 0.4015                    |
| ERLO        | -0.026685                | 0.3388                 | -0.1482                   | 0.7762                    |
| VAVO        | -1.58469                 | 0.4254                 | -8.6565                   | 0.9583                    |

Table 3. Comparison of nonlinear parameters for each oil at a power of 25 mW.

| Type of Oil | $\eta_2 \times 10^{-6}$ | $\beta \times 10^{-3}$ | $\chi_R^3 (\times 10^{-6})$ | $\chi_i^3 (\times 10^{-5})$ |
|-------------|--------------------------|------------------------|---------------------------|---------------------------|
| EVOO        | -0.75358                 | 0.9107                 | -4.1126                   | 2.0475                    |
| EVSO        | -0.11219                 | 0.4484                 | -0.6174                   | 1.0166                    |
| ERLO        | -0.02513                 | 0.4288                 | -0.1396                   | 0.9815                    |
| VAVO        | -0.95071                 | 0.8884                 | -5.1933                   | 1.9992                    |

5. Conclusions
The variation of the nonlinear optical parameters of 4 oils of vegetable origin using the Z-scan technique was studied, observing the behavior of the transmittance curve as a function of the incident power of a Nd: YAG laser of 532 nm emission wavelength. From the results obtained, it can be emphasized that each of the oils presents a non-linearity of self-defocusing which means a negative non-linear refraction index; the effects of saturation and deviation are present in the transmittance curves due to the temperature gradient caused by the continuous and focused incidence of the laser beam on the study sample. When carrying out the separate study of each oil, a common potency was determined in which the response of each oil was well behaved, to make a detailed comparison of its behavior. In the comparative study it was graphically and quantitatively evidenced that extra virgin olive oil is the one that presents a better non-linear response, at low and medium potencies, followed by virgin avocado oil, therefore these two oils are presented as the best candidates for application in photonics and electro-optical devices.

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