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Thermal diffusivity studies in edible commercial oils using thermal lens spectroscopy

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The thermal diffusivity of edible commercial oils (canola, peanut, olive, sunflower, maize and soy bean) was determined using thermal lens spectroscopy in the unmatched mode. The measurements were made using the 632.8 nm He-Ne and 488 nm Ar laser beams as the probe and excitation beams, respectively. The thermal lens effect (ΔI) showed a strong dependence on the thermo-optical properties of these oils. This fact was used to construct a curve in which each oil is distinguished by its thermal lens signal for a given constant excitation beam power.

Thermal diffusivity as a function of temperature increased significantly for the samples with lower thermal diffusivity (soy bean and canola) at around T=32ºC. This parameter was constant from 32ºC until 58ºC and increased at about 72ºC for the soy bean case.These results were compared using principal component analysis (PCA) of near infrared spectra. The spectra information was analyzed using PCA to classify oils under heat treatment and to relate the different groups in terms of thermal diffusivity.

Keywords: Optical properties; Thermal diffusivity; Thermal lens; Edible oils

Se determino la difusividad térmica de aceites comestibles de origen comercial (canola, cacahuate, olivo, girasol, maíz y soya), mediante espectroscopia de lente térmico en el modo desempalmado. Las mediciones se realizaron utilizando las líneas de haz laser 632.8nm de He-Ne y 488 nm de Ar, operando como el haz de prueba y de excitación respectivamente. El efecto de lente térmico (ΔI) mostró una fuerte dependencia sobre las propiedades termo-ópticas de estos aceites. Este hecho fue utilizado para construir una curva en la cual cada aceite se distingue por su señal de lente térmico para una potencia constante del haz de excitación. La difusividad térmica en función de la temperatura mostró un incremento significativo alrededor de 32°C para las muestras con menores valores de difusividad térmica (soya y canola). Este parámetro fue constante desde 32°C hasta 58°C y nuevamente se incrementó en torno a 72°C para el caso de la soya. Estos resultados fueron comparados utilizando el análisis de componentes principales (PCA) de los espectros en el cercano infrarrojo. La información espectral fue analizada utilizando PCA para clasificar aceites bajo el tratamiento térmico y relacionar los diferentes grupos en términos de la difusividad térmica.

Palabras clave: Propiedades ópticas; Difusividad térmica; Lente térmico; Aceites comestibles

1. Introduction

In edible commercial oils, determining the relative concentrations of the different carboxylic acids, saturated and unsaturated fatty acids is of great importance. Among the analytic techniques available for this purpose are those based on IR or NIR analysis spectra or high performance liquid chromatography (hplc)[1-4]. Edible commercial oils differ in terms of their composition and the relative concentration of fatty acids. The main variations in composition are the chain length and the degree of unsaturation of these fatty acids. Recently, some photothermal techniques have been used to study fatty acids, determining phase transitions and some thermal transport parameters [5-10]. Thermal lens effect (TL) is a powerful tool for determining thermal diffusivity and the optical parameters of semitransparent materials, solids and liquids [11-17]. In this study, the thermal lens technique is used to determine the thermal diffusivity in several edible commercial oils. Additionally, the thermal lens signal is used to study the thermo-optical behavior of these oils. The principal aim is to determine the range values of thermal diffusivity (α) for the more common edible commercial oils and the enhancement factor of the absorption coefficient (θ). Another goal is to unequivocally identify these oils by means of thermal diffusivity measurements and variations in the thermal lens effect. The measurements were made using pure oils, and the thermal parameters were determined as a function of temperature for soy bean and canola oils.

In order to evaluate the thermal diffusivity results and the thermo-optical behavior of this set of oils, we used chemometric treatment, such as principal component analysis (PCA), in association with vibrational spectroscopy, which makes classification of this set of oils possible without any chemical analysis. This classification is correlated with the thermal diffusivity results. In this study, the NIR spectra for the oils were recorded using optical fiber analysis. The spectra information constitutes the experimental data which are analyzed by PCA to classify oils under heat treatment and to relate the different groups in terms of thermal diffusivity.

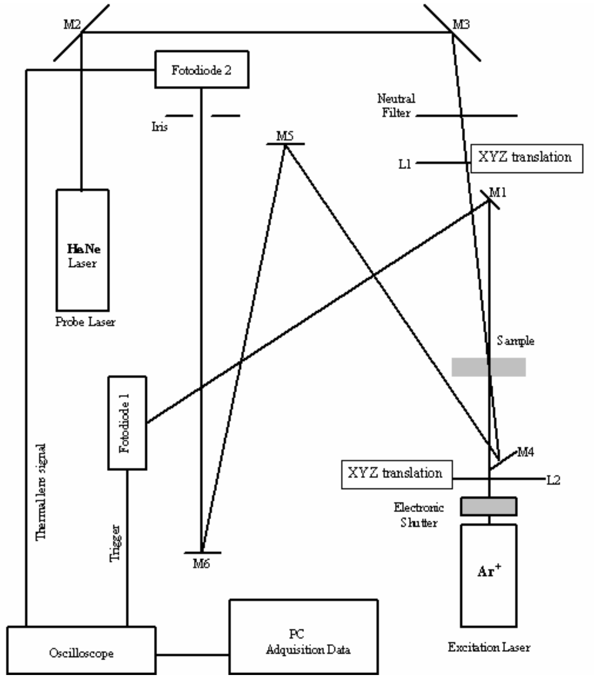


Figure 1. Experimental Set-Up for the thermal lens system in the unmatched mode. For the chopped thermal lens signal, the electronic shutter is changed by a mechanical chopper.

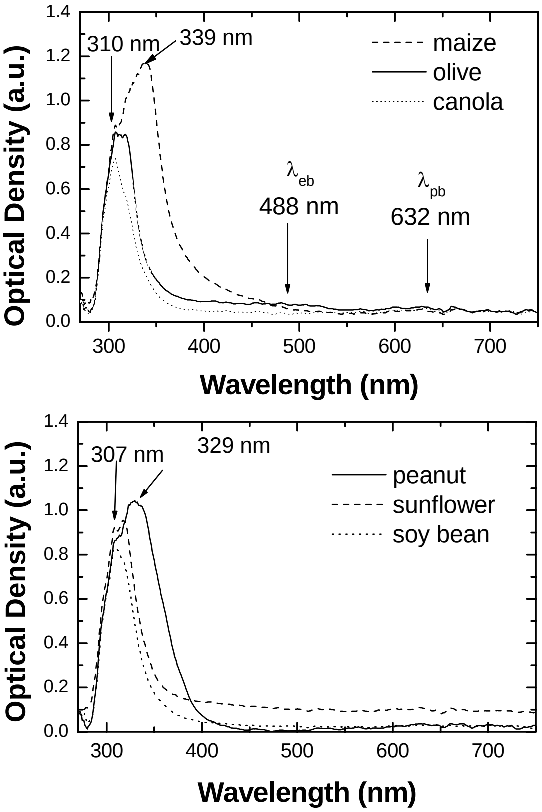


Figure 2. Optical absorption spectra for the set of edible oils studied.

2. Materials and methods

Six edible commercial oils were analyzed. Their purity, according to the specifications of the different suppliers, is as follows: canola (generic, 100% pure), peanut (generic, 100% pure), olive (Ibarra, 100% pure), sunflower (generic, 100%), maize (Mazola, 99.99 % pure), soy bean (Hogar, 100% pure).

The optical absorption spectra were obtained using a Perkin-Elmer lambda2 spectrometer with a quartz cuvette with a 1 cm path length and a 250 to 750nm wavelength range. For the thermo-optical measurements, oil samples in a quartz cuvette were located in the thermal lens set-up. Fig. 1 shows the experimental set-up for the thermal lens system with two beams in the unmatched mode (there is a difference of one in the ratio of the radius of the probe beam to that of the excitation beam).

The sample is centered in the waist of the excitation laser beam (Ar laser, Lexel 95), at 23 cm from the L2 lens. After passing through the sample, mirror 1 deflects the excitation beam to photodetector 1, whose signal is directed to a oscilloscope trigger (Tektronics TDS340). When the electronic shutter (Newport 845 Hp) is opened, the trigger is activated and the measurement process begins.

The probe beam (He-Ne laser, Melles Griot) is directed to the same point in the sample where the excitation beam hits. Then, by a set of M4-M6 mirrors, the probe beam is directed to photodetector 2, whose signal is analyzed in the far field (about 2 m from the sample). This signal is directed to the oscilloscope. The experimental data are averaged in the oscilloscope and the final curve is acquired with a PC using a RS232 communication port. The experimental data are fitted to a theoretical model [12,13].

The near infrared spectra were obtained using an Oceanoptics NIR512 spectrometer with an InGaAs detector and a halogen tungsten lamp in a wavelength range from 850 to 1700 nm.

Principal Component Analysis (PCA) of the NIR spectral data was performed using functions we implemented in MatLab. PCA is a method for extracting systematic variations in non-deterministic data sets. This method can be used for classification as well as for description and interpretation. We used PCA for edible oil classification by temperature. Our results were compared with the thermal diffusivity measurements.

3. Thermal diffusivity measurements using the thermal lens effect

The TL effect is produced when an excitation laser beam passes through the sample and the absorbed energy is converted into heat, producing a temperature gradient in the sample. At the same time, a refractive index gradient is established, producing a lens-like optical element in the sample. Projecting the probe laser beam through the same region of the sample results in defocusing (dn/dT<0) or focusing (dn/dT>0) of the probe beam. The theoretical

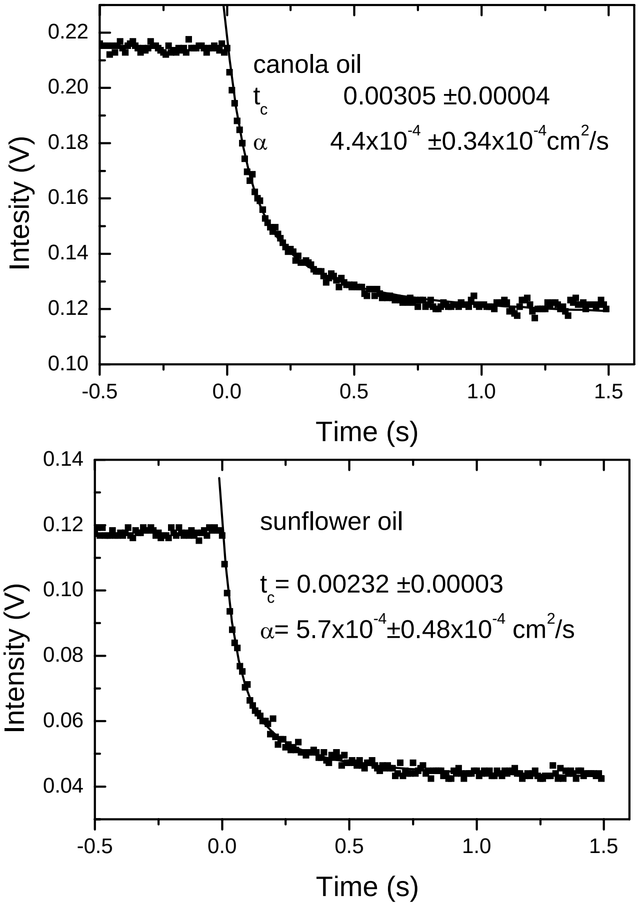


Figure 3. Typical curve for the transient thermal lens effect in two representative edible oils. The thermal diffusivity (α) and the absorption coefficient enhancement factor are determined (θ) from this curve.

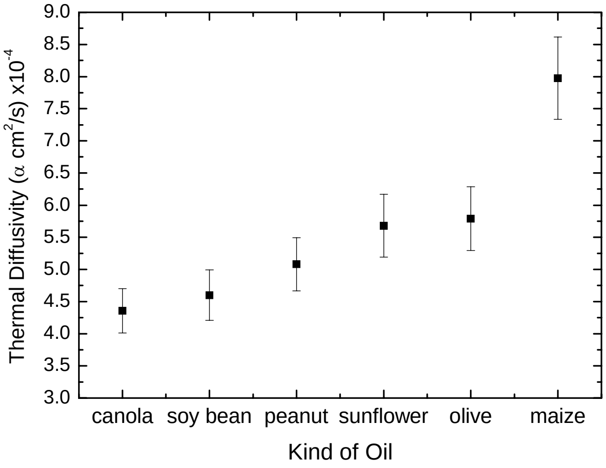


Figure 4. Thermal diffusivity for several edible commercial oils.

treatment of the TL effect considers the temperature distribution in the sample produced by the excitation laser beam. The effect of this temperature distribution on the probe laser beam is an optical path length change, which can be expressed as an additional phase shift on the probe beam wave front after passing it through the sample. The central intensity of the probe beam in the far field as a function of time is given by [12, 13, 15-17].

$$I(t) = I(0)\left\{1 - \frac{\theta}{2}\operatorname{atan}\left[\frac{2mV}{\left[(1+2m)^2+V^2\right]\frac{t_c}{2t}+1+2m+V^2}\right]\right\}^2 \qquad (1)$$

where $\theta = -\frac{P_e A_e l_0}{K\lambda_p}\left(\frac{ds}{dT}\right)$, $V = \frac{Z_1}{Z_c}$, $m = \left(\frac{\omega_p}{\omega_e}\right)^2$, $t_c = \frac{\omega_e^2}{4\alpha}$ (2)

It is the temporal dependence of the probe laser beam at the detector. I(0) is the initial value of I(t). θ is the approximate phase difference of the probe beam at r=0 and $r = \sqrt{2}w_e$ induced by the thermal lens and can be determined by a curve fit to Eq. (1). The θ parameter is also known as the enhancement factor of the absorption coefficient, and ω_p and ω_e are the probe and excitation beam radius at the sample, respectively. P_e is the excitation beam power (mW). A_e is the optical absorption coefficient at the excitation beam wavelength (cm^{-1}). Z_c is the confocal distance of the probe beam. Z_1 is the distance from the probe beam waist to the sample; l_0 is the sample thickness; K is the thermal conductivity; λ_p is the probe beam wavelength; t_c is the characteristic thermal lens time constant; α is the thermal diffusivity of the sample, and (ds/dT=dn/dT in the liquid case) is the temperature coefficient of the sample refractive index at the probe beam wavelength.

In the transient thermal lens measurements, the parameters θ and t_c are determined directly by fitting the experimentally observed time profile of the developing thermal lens effect to Eq. (1). Table 1 summarizes the experimental parameters used in the experimental set-up. The excitation power beam at the sample was in the range from 1 to 6 mW, and the probe beam power was around 0.5 mW. The lower power and the higher radius of the probe beam compared to the respective excitation beam parameters, at the sample are other conditions for the respective excitation beam parameters, at the sample, are other conditions for the thermal lens measurements, ensuring that the thermal lens effect is only due to the excitation laser beam.

4. Results and discussion

Fig. 2 shows the optical absorption spectra of the different edible commercial oils from 250 to 750 nm. Sunflower, canola, soy bean and olive oils have a maximum absorption peak around 310 nm. Peanut and maize oils show a maximum absorption peak at 329 and

Table 1. Experimental parameters for thermal diffusivity measurements.

Probe beam wavelength	λ_{pb}=632.8 nm
Excitation laser spot size at sample (λ_e=488 nm)	ω_{pb}= 23x10^{-4} cm
Probe laser spot size at sample (λ=632.8 nm)	ω_{eb} =693.2x10^{-4} cm
M	297.35
Z_c	1.0404
V	15.203

339 nm, respectively. The absorption bands are broader for the last two oils.

In these samples the optical absorption is due to absorption groups of type -(C=C)- [18] in the chain of unsaturated carboxylic acids. From these spectra it can be observed that oils with higher unsaturated acid concentrations have an absorption band shifted to higher energies (canola, olive and soy bean), and oils with higher saturated acid concentrations have absorption bands at lower energies (maize, peanut and sunflower) [8,9,18,19].

From the UV/VIS spectra it was possible to identify the influence of the concentration of saturated and unsaturated carboxylic acids, due to the shift in the absorption band maximum (shifted to higher energies for oils with higher unsaturated carboxylic acid concentrations).

From Fig. 2 it can be observed that the wavelength of the excitation (488 nm) and probe (632.8 nm) beams are far from the principal absorption band. This fact is one of the experimental conditions for studying semitransparent materials.

Fig. 3 shows the typical curve of the thermal lens effect in these oils; signal intensity against time for: a) canola and b) sunflower oils. (Until time t=0, the signal of the photo-detector is due to the intensity of the probe beam; at t=0 the shutter is open and the excitation beam, after passing through the sample, is directed to photo-detector 1, which activates the oscilloscope trigger and thermal lens effect data acquisition begins). The solid line is the best fit for the experimental data to Eq. 1. By this fitting procedure, parameters θ and t_c are obtained. Using the expression for t_c, the thermal diffusivity values obtained were (4.4x10^{-4} $\pm 0.34x10^{-4}$) and 5.7x10^{-4} $\pm 0.48x10^{-4}$ cm^2/s for canola and sunflower oils, respectively. Similar measurements were made for the rest of the oils. The results are presented in Fig. 4. As a reference, we measured the thermal diffusivity of glycerol and obtained the value of 9.94x10^{-4} cm^2/s, which is very close to the reported value in the literature, 9.22x10^{-4} cm^2/s [5] and 9.45x10^{-4} cm^2/s [20]. Canola oil shows the lowest thermal diffusivity value, sunflower oil shows an intermediate value, and maize oil shows the highest thermal diffusivity value, approximately two times that of canola oil. The increasing thermal diffusivity values for canola, soy bean and peanut oils run in the same direction as the saturated carboxylic acid concentrations, around 8.3, 15.4 and 19.4 % respectively. For sunflower, olive and maize oils the trends are not clear. Nevertheless, the complete set of analyzed oils can be divided into two groups: the first group consists of canola, soy bean and peanut oils, and the second includes sunflower, olive and maize oils. Both groups show increasing thermal diffusivity values with palmitic acid concentrations of 0.3, 10.6 and 11 % in the first group and 7, 9 and 10.9 % in the second group. Fig. 5 shows the signal of the thermal lens effect for the set of oils in the modulated mode as a function of excitation laser beam power. For this measurement, the same experimental set-up is used, but the excitation laser beam is chopped with a mechanical chopper at 12 hz and the photodiode-2 signal of the thermal lens effect in the probe beam is measured with a lock-in amplifier. In Fig. 5, two important aspects of the thermal lens effect in these oils as a function of laser beam power can be observed. The first one is the strong dependence of signal intensity on excitation power, and the second is the different curve slope for each sample.

The peanut, maize, olive and sunflower oils show a higher effect than do the canola and soy bean oils. This fact permits an identification of the kind of oil in accordance with its thermal lens signal at a fixed excitation laser beam power. For example, for an excitation power of P_e= 1 mW, the thermal lens signals are 7.9, 11.3, 17.6 and 28.2 mV for sunflower, peanut , maize and olive oils, respectively. For P_e=5 mW, the thermal lens signals are 13.8, 19.6 and 30.1 mV for glycerol, soy bean and canola, respectively.

Fig. 6 shows the quotient of the enhancement factor of the absorption coefficient for the excitation beam power. In accordance with expression 3, this quotient involves the ratio of the optical absorption coefficient to the thermal conductivity, multiplied by the temperature coefficient of the optical path length change (ds/dT=dn/dT) [16].

$$\frac{\theta}{P_e} = -\frac{A_e l_0}{K\lambda_p}\left(\frac{dn}{dT}\right) \qquad (3)$$

In accordance with the optical density data from Fig. 2, the optical density values for olive, maize and peanut oils at the excitation beam wavelength (488 nm) show the same decreasing behavior (0.077, 0.056 and 0.0068 respectively) as does the (θ/P_e) parameter. For the rest of the curve, there is similar behavior for sunflower, canola and soy bean oils. (The optical density decreases by 0.103, 0.036 and 0.027 respectively.) The fact that the global behavior of (θ/P_e) parameter is not the same as the optical density behavior is due to the contribution of the (dn/dT) parameter which is dependent on the refractive index, the polarizability and the volume expansion coefficient [12,16,17]. For liquids in general, the principal contribution comes from the volume expansion coefficient. The decrease in the (θ/P_e) parameter for olive, maize and peanut oils coincides with a decreasing percent composition of unsaturated carboxylic acids: 97.9, 86.4 and 80.6 respectively [19,21].

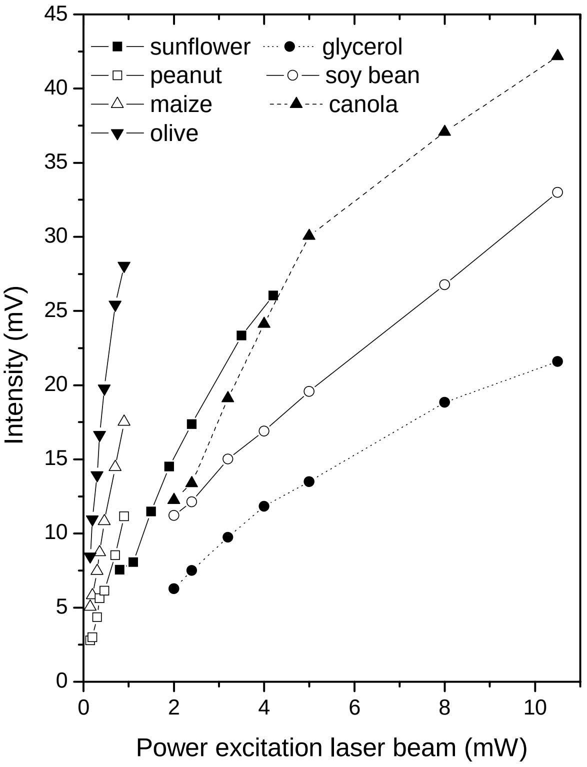


Figure 5. Chopped thermal lens signal as a function of the excitation laser beam power for several edible commercial oils.

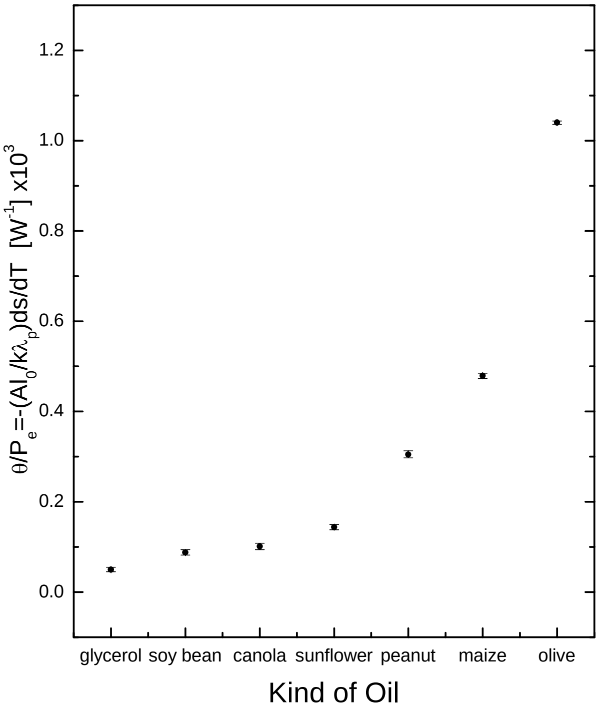


Figure 6. Quotient of the enhancement factor of the absorption coefficient and the excitation laser beam power for the edible commercial oils studied.

Fig. 7 shows the thermal diffusivity behavior as a function of temperature for soy bean and canola oils. Their evolution shows similar trends: around 26 ºC there is a significant increase in the thermal diffusivity value. Canola oil, which has a lower thermal diffusivity value at room temperature, reaches a higher value (the average value is $1.6\text{x}10^3$ cm^2/s) than that of soy bean oil and it does not change even up to 72°C. Around this point, the thermal diffusivity of soy bean oil increases to a value similar to that for canola oil. The temperature range where the thermal diffusivity of soy bean oil increases, is the same temperature at which palmitic and stearic acid fusion takes place: 62.9°C and 69.6°C, respectively. In soy bean oil, these acids are present in proportions of about 10.6 and 4 %, respectively [21].

Fig. 8 shows NIR spectra in the range from 850 to 1700 nm for soy bean and canola oils heated to the indicated temperatures. The heat treatments were performed on a hot plate and measurements were taken in situ using an optical filter. From the figure, we observe that individual spectra look very similar and it is difficult to observe differences. However, bands induced by temperature present slight variations which were analyzed by PCA. The bands obtained are assigned to (carboxylic acids) C-H groups and OH contributions.

The PCA results for canola oil, Figure 9, show two groups: the first for oil at a room temperature of 23ºC, the second for oil heated to temperatures from 26ºC to 65ºC.

This classification can be interpreted in terms of changes in thermal diffusivity. The difference between the first and the second group is associated with the drastic change in thermal diffusivity when oil is heated from room temperature to 27ºC. The second group can divided into two subgroups: the first subgroup, labeled 2a, shows a very high correlation, and the second one, labeled 2b, a slight separation between components. In general, the variation between the components (small circles) of group two are low and they have a high correlation, indicating that the variation in thermal diffusivity is very low. In this case, the thermal diffusivity can be considered to be constant. Thus above 30ºC the chemical and physical properties of canola oil remain unaltered.

In the case of soy bean oil, the PCA results (Figure 10) show two isolated points corresponding to oil at room temperature and heated to 80ºC. The isolated character is due to a drastic change in the thermal diffusivity value. The dispersion of components in the intermediate group is associated with slight variations in thermal diffusivity. In particular, the dispersion between the components corresponding to oil heated at 60ºC and the components for the oil heated at 70ºC is higher than the dispersion among the other components of the intermediate group. This dispersion gives us information about an important change in the degradation of the fatty acids and changes in thermal diffusivity.

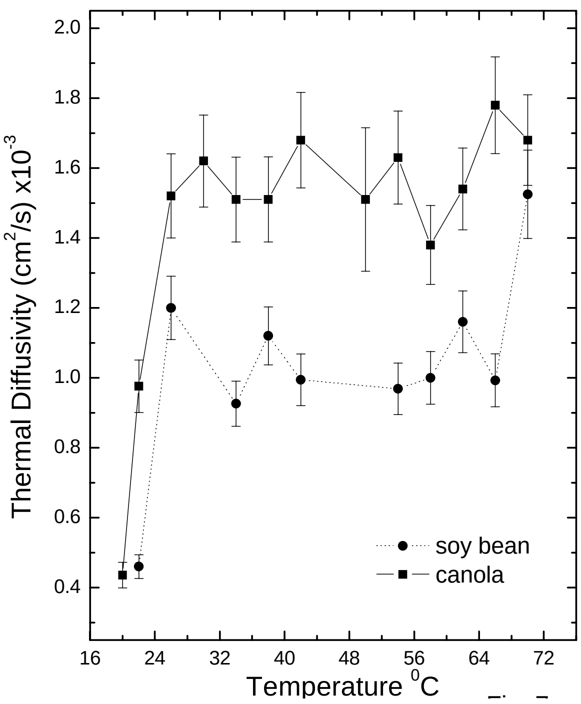
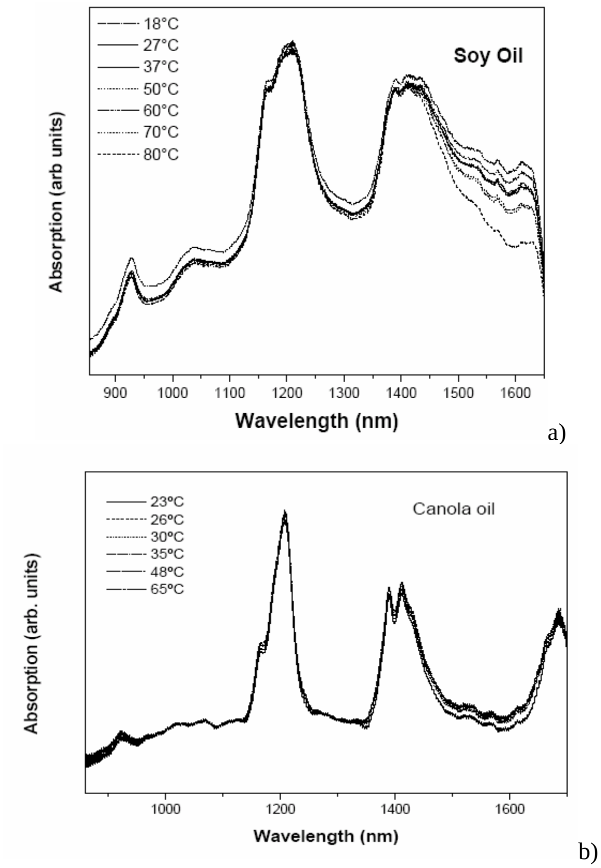


Figure 7. Thermal diffusivity values as a function of temperature for soy bean and canola oils.



a)

b)

Figure 8. Near infrared spectra for a) soy bean oil and b) canola oil in terms of heat treatment at the indicated temperatures.

5. Conclusions

The UV/Vis spectra show a significant shift in the absorption band maximum, and this shift is highly dependent on the relative concentration of saturated or unsaturated carboxylic acids, (with a shift to higher energies for oils with higher unsaturated carboxylic acid concentrations).

Thermal lens spectroscopy proves to be an appropriate technique for determining thermal diffusivity values of edible commercial oils. The thermal diffusivity values of this set of analyzed oils are perfectly distinguishable with values from 4.35x10^{-4} cm^2/s for canola to 7.97x10^{-4} cm^2/s for maize.

An important result found for these oils is the strong dependence of the chopped thermal lens effect signal on the excitation laser beam power. This signal is dependent on the thermo-optical parameters of the sample; in particular, the samples with the highest thermal diffusivity and (θ/P_e) parameter values (maize, olive, sunflower and peanut) show very different values for the excitation power needed to establish the thermal lens effect than soy bean and canola oils do, whose thermal diffusivity and (θ/P_e) parameter values are lower. For glycerol, soy and canola, a higher excitation power is necessary in order to establish the thermal lens effect, and the signal has an inverse dependence on the thermal diffusivity values.

The (θ/P_e) parameter, which involves thermo-optical parameters, can be used to distinguish two sets of oils (olive, maize and peanut as one set and sunflower, canola and soy bean as the other) with monotonic decreasing behavior and the same tendency as the optical density at the excitation beam wavelength. For olive, maize and peanut oils, this decrease coincides with decreasing concentrations of unsaturated carboxylic acids.

The thermal diffusivity for soy bean and canola oils as a function of temperature shows significant variation around 28°C, and there is an appreciable increase at 72ºC in the case of soy bean oil. The latter is probably related to the fusion of palmitic and stearic acids. This fact will be explored by studies of phase transition in these kinds of oils as a function of temperature. The chopped thermal lens signal will be used to determine the transition temperature and the transient thermal lens effect to obtain the thermal diffusivity values around this transition temperature.

The PCA results obtained via NIR spectroscopy show that thermal lens spectroscopy is an adequate technique for studying oil degradation for the determination of thermal diffusivity and it gives an unequivocal identification of these kinds of oils.

With near infrared absorption, spectroscopy in association with chemometric treatment such as PCA analysis, it was possible to classify the heated oils. These classifications were interpreted in terms of changes in thermal diffusivity.

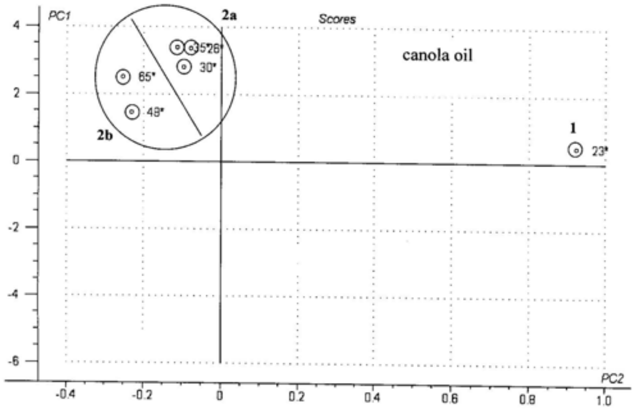


Figure 9. PCA Results from near infrared spectra in terms of heat treatment for canola oil.

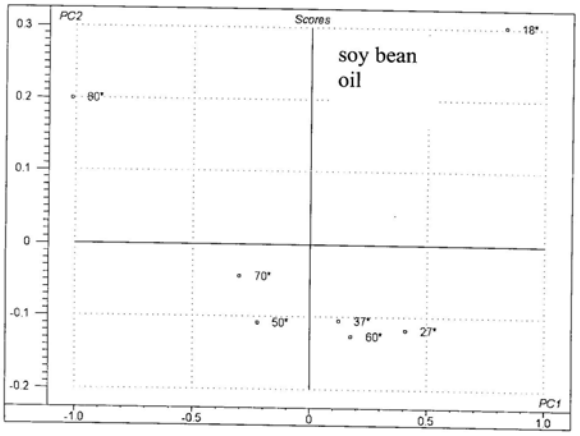


Figure 10. PCA Results from near infrared spectra in terms of heat treatment for soy bean oil.

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