

Thermal Diffusivity Measurements in Edible Oils using Transient Thermal Lens¹

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Time resolved thermal lens (TL) spectrometry is applied to the study of the thermal diffusivity of edible oils such as olive, and refined and thermally treated avocado oils. A two laser mismatched-mode experimental configuration was used, with a He-Ne laser as a probe beam and an Ar⁺ laser as the excitation one. The characteristic time constant of the transient thermal lens was obtained by fitting the experimental data to the theoretical expression for a transient thermal lens. The results showed that virgin olive oil has a higher thermal diffusivity than for refined and thermally treated avocado oils. This measured thermal property may contribute to a better understanding of the quality of edible oils, which is very important in the food industry. The thermal diffusivity results for virgin olive oil, obtained from this technique, agree with those reported in the literature.

KEY WORDS: degradation; oils; photothermal phenomena; thermal diffusivity; thermal lens.

1. INTRODUCTION

Thermal lens (TL) spectroscopy is a high-sensitivity optical technique that has been applied to study samples with small optical absorption, by measuring the thermal properties of solids and liquids, as well as other complex systems. This technique is attractive because it is nondestructive, noninvasive, and, in many cases, can be very sensitive [1]. The thermal

¹ Paper presented at the Seventeenth European Conference on Thermophysical Properties, September 5-8, 2005, Bratislava, Slovak Republic.

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lens effect is observed when an excitation light beam passes through the sample; the light is tuned to a sample absorption line, and the energy is absorbed by the sample. The molecules are excited into vibrational, rotational, or electronic states; the excited molecules lose energy in the form of heat through nonradiative relaxation processes. The heating of the sample causes a change of the refractive index, as determined by convergence or divergence of a probe laser beam when it passes through the sample. Under equilibrium conditions, the temperature change is related to the refractive index. Measurements of the change in convergence or divergence of a laser beam after the formation of the thermal lens, which results in the so-called thermal lens signal (TLS), and its time evolution is analyzed to obtain the physical parameters of the sample [2].

Monitoring of the functional properties and quality of edible oils is an area of research involving not only the quantification of the chemical and physical properties of oils, and their changes during industrial processing, but also diverse other subjects such as the deterioration of these products induced by their exposure to temperatures and changes during shelf life. Up to now, the sensitivity of edible oils to temperature changes has not been a subject of much research, and the lack of experimental data in this area has motivated the efforts of the current work.

In this article, an experimental setup of this technique is used to investigate the thermal diffusivity of three samples of vegetable oils, which are refined and thermal treated avocado oils and virgin olive oil. This measured thermal property may contribute to a better understanding of the quality of edible oils, which is very important in the medical, cosmetic, and food industries [3].

2. EXPERIMENTAL SETUP

A schematic diagram of the experimental setup is shown in Fig. 1. An Ar^+ laser, 40 mW of power and 514.5 nm wavelength, was used as the excitation beam, focused onto the sample with 40 μm of a waist radius. The probe beam was a He-Ne laser, 632.8 nm wavelength and 4 mW power, with a waist radius on the sample of 190 μm . An electronic circuit controls a shutter, which consists of a mechanical diaphragm that was used for limiting the exposure of the sample to the light; when it was opened, the sample was illuminated, and the shutter driver sent a signal to initialize the data acquisition [4]. The maximum intensity of the probe beam was centered on the photodiode detector, and its time variation, in the form of a voltage, was registered by a digital oscilloscope (Hewlett-Packard 54502A), recorded and sent to the pc, as a function of time, through a GPIB interface bus.

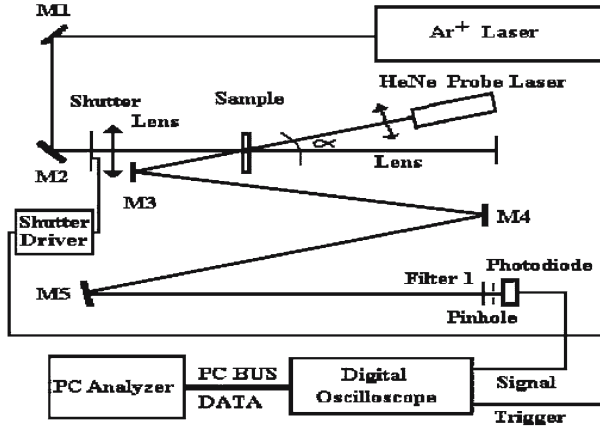


Fig. 1. Thermal lens experimental setup.

3. THEORY

The theoretical treatment of the thermal lens effect takes into account the spherical aberration of the thermal lens and also considers the whole optical path length change with temperature. Shen's model [5] considers that a heat source is induced by the laser beam, which is proportional to the Gaussian intensity profile, and can be expressed as: $I_e(r) = (2P_e/\pi\omega_e^2) \exp(-2r^2/\omega_e^2)$, where P_e is the excitation beam power and ω_e is the excitation beam waist at the sample position. The solution of the heat conduction equation depends on the employed boundary conditions. This theory was used to develop the infinitive aberrant model for the mode-mismatched configuration. The temporal evolution of the temperature profile $T(r, t)$ induced by the TL, in the sample is given by [5]

$$\Delta T(r, t) = \frac{2P_e A_e}{\pi c \rho \omega_e^2} \int_0^t I_0 \left(\frac{1}{1 + (2t'/t_c)} \right) \exp \left(\frac{2r^2/\omega_e^2}{1 + (2t'/t_c)} \right) dt', \quad (1)$$

where ρ is the density, c is the specific heat, A_e is the optical absorption coefficient at the excitation beam wavelength, and t_c is the characteristic TL time constant, defined as

$$t_c = \frac{\omega_e^2}{4D}, \quad (2)$$

where D is the thermal diffusivity. As was mentioned previously, this temperature rise, which carries a Gaussian profile, induces a slight distortion in the probe beam wave front that can be associated with the change in

the sample refractive index with respect to the beam axis, and can be expressed as follows:

$$\phi = \frac{2\pi}{\lambda_p} \ell_0 \left(\frac{dn}{dT} \right)_p [\Delta T(r, t) - \Delta T(0, t)], \quad (3)$$

where ϕ is the phase shift induced when the probe beam passes through the TL, λ_p is the probe beam wavelength, ℓ_0 is the sample thickness, and $(dn/dT)_p$ is the temperature dependence of the sample refractive index. Finally, using the Fresnell diffraction theory, the probe beam intensity at the detector plane can be written as an analytical expression for the absolute determination of the thermo-optical properties of the sample, as

$$I(t) = I(0) \left[1 - \frac{\theta}{2} \tan^{-1} \left(\frac{2mV}{[(1+2m)^2 + V^2] \frac{t_c}{2t} + 1 + 2m + V^2} \right) \right]^2, \quad (4)$$

where

$$m = \left(\frac{\omega_{1p}}{\omega_c} \right)^2; \quad V = \frac{Z_1}{Z_c}; \quad \theta = -\frac{P_e A_e \ell_0}{k \lambda_p} \left(\frac{dn}{dT} \right)_p.$$

In Eq. (4), $I(t)$ is the temporal dependence of the probe laser beam intensity at the detector, $I(0)$ is the initial value of $I(t)$, θ is the thermally induced phase shift of the beam after it passes through the sample, Z_c is the confocal distance of the probe beam, and Z_1 is the distance of the probe beam waist from the sample.

The avocado oil samples were thermally treated, and placed in pyrex tubes of 1.5 cm diameter and 5 cm height. These tubes were heated in a bath of thermal oil (IKA-Hiezbad HB-250, Germany), with the temperature controlled using thermocouples (digitally monitored by using an Ogden monitor, ETR-9090, U.S.A.) in contact with the oil samples, at 160 and 180°C for 30 minutes. After this, the samples were naturally cooled until room temperature was reached. The oil samples, used in the TL experiments, were placed in a quartz cuvette of 1 cm thickness.

4. RESULTS AND DISCUSSION

The time evolution of the TL signal from olive, and refined and thermally treated avocado oils are shown in Figs. 2–5 (the symbols are the experimental points and the solid lines represent the best fit of Eq. (4) to the experimental data). Figure 2 shows a typical transient TLS for olive oil at room temperature. The solid line corresponds to the best fit of Eq. (4) to the TL experimental data with θ and t_c as adjustable parameters.

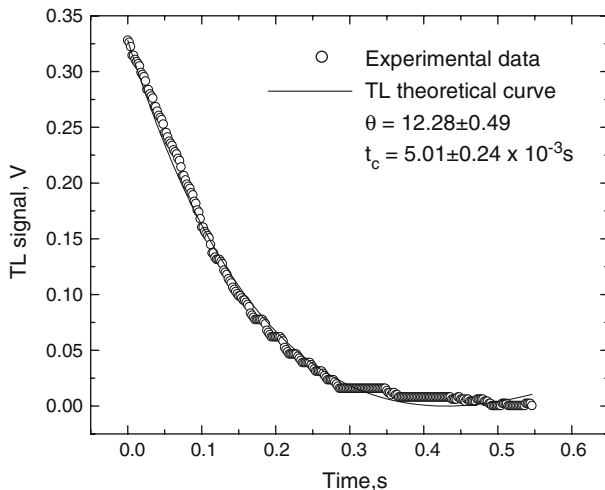


Fig. 2. Time evolution of the thermal lens (TL) signal for virgin olive oil. Solid line corresponds to the best fit of Eq. (4) to the TL experimental data.

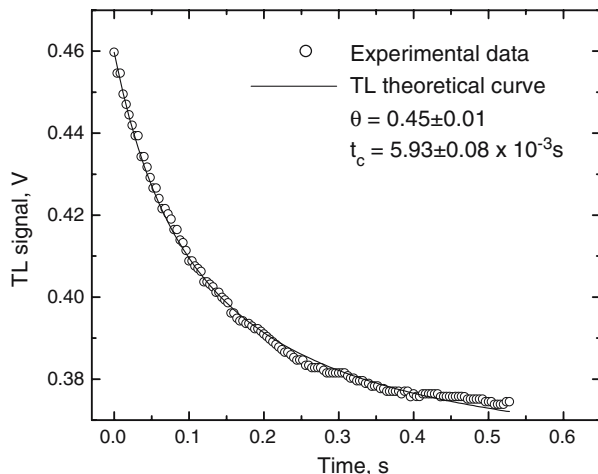


Fig. 3. Time evolution of the thermal lens (TL) signal for refined avocado oil. Solid line represents the best fit with Eq. (4).

The obtained values for these parameters were $\theta = 12.27571 \pm 0.49109$ and $t_c = 5.01 \pm 0.24 \times 10^{-3}$ s. Using Eq. (2) with $\omega_c = 4.0 \times 10^{-3}$ cm, we obtained $D = 7.96 \pm 0.38 \times 10^{-4}$ cm² · s⁻¹, for the thermal diffusivity. This value is in agreement with that reported in the literature, at room temperature

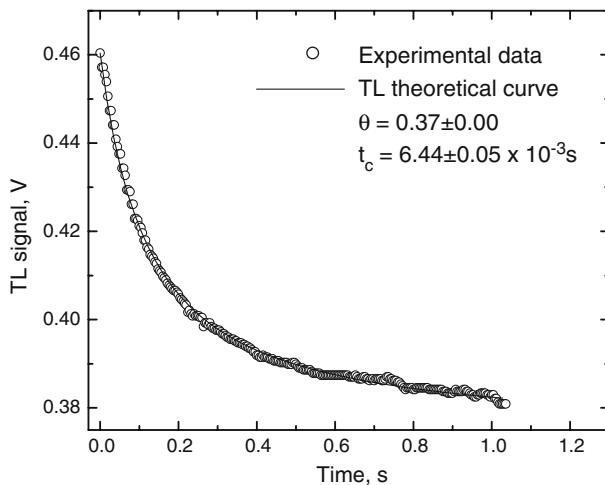


Fig. 4. Time evolution of the thermal lens (TL) signal for thermally treated avocado oil (160°C). Solid line represents the best fit of Eq. (4) to the experimental data

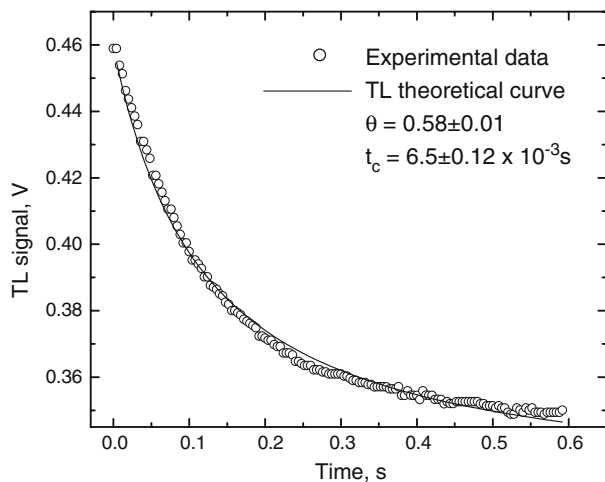


Fig. 5. Time evolution of the thermal lens (TL) signal for thermally treated avocado oil (180°C). Solid line represents the best fit with Eq. (4).

$D = 7.99 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$ [6,7]. Figures 3–5 show the transient signal for refined and thermally treated avocado oils at room temperature. From the best fit of Eq. (4) to the experimental data, t_c was obtained for each sample and then, by using Eq. (2) with $\omega_c = 4.0 \times 10^{-3} \text{ cm}$, we obtained the

Table I. Adjustable Parameters t_c and θ Obtained from the Fits of Eq. (4) to the TL Experimental Data and their Calculated Thermal Diffusivity Values (D)

Oil Sample	Fitting Results $t_c(10^{-3} \text{ s})$	θ	Thermal diffusivity $D(10^{-4} \text{ cm}^2 \cdot \text{s}^{-1})$
Oil olive	5.01 ± 0.24	12.28 ± 0.49	7.96 ± 0.38
Refined avocado	5.93 ± 0.08	0.45 ± 0.01	6.73 ± 0.09
To 160°C	6.44 ± 0.05	0.37 ± 0.00	6.19 ± 0.05
To 180°C	6.5 ± 0.12	0.58 ± 0.01	6.14 ± 0.11

thermal diffusivity for refined and thermally treated (at 160 and 180°C) avocado oils. Table I summarizes the thermal diffusivity values obtained from the analyzed samples.

It is possible to see from Figs. 2–5 that the TL signal decreases with time, indicating that the thermal lens is divergent, thus defocusing the probe beam on the detector. This behavior is due to the fact that the temperature coefficient of the optical path length, ds/dT , is negative for oils and also for transparent liquids [5]. It can be seen that the thermal diffusivity of avocado oil decreases when these oils are thermally treated, which reflects a change in their physicochemical properties. Normally, the thermal treatment promotes transformations in oils, some of the desirables as controlled transformations, and some undesirables due to the rupture of their ester bonds, which generates fat acids and other compounds, which deteriorate the oil [8]. The decrease of thermal diffusivity in the samples under thermal treatment could be due to an acceleration of auto-oxidation processes [9], which promote the formation of unstable compounds (free radicals, hydroperoxide radicals and hydroperoxide) and stable compounds (polymers of higher molecular weight, epoxies, ceto-glycerides and others), which modify the thermal properties. For this reason, it is important to extend the physicochemical studies in the field of food technology to avoid the undesirables involved in the transformation of the oils in the food industry.

5. CONCLUSION

The results showed that the TL technique is a sensitive method to investigate the thermal properties of thermally treated edible oils. Several vegetable oils were studied, and a thermal lens experiment was used to measure their thermal diffusivities. It was found that the thermal diffusivity of avocado oils is smaller when compared with that of olive oil. These studies may contribute to a better understanding of the physical

and chemical properties of edible oils under different storage conditions of these important foodstuffs.

ACKNOWLEDGMENTS

The authors are thankful to the Mexican Agencies, CONACYT, COFAA, CGPI for financial support of this work. One of the authors (A. Cruz Orea) is grateful for partial financial support from CONACYT Project No. 43252-R. Also J.L. Jiménez Pérez wants to thank the support from CGPI-IPN Project No. 20050510. Also the authors are grateful to Ing. Esther Ayala and Ing. Damian Jacinto Méndez for their technical support at Physics Department, CINVESTAV-IPN.

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