Recent measurements of thermal diffusivity for mexican edible oils in food industry

Rigoberto Carbajal-Valdez[1], Alfredo Cruz Orea[1], J.L. Jiménez-Pérez[2]

[1]CINVESTAV-IPN, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Delegación Gustavo A. Madero, Código Postal 07360, Ciudad de México, México.

e-mail: rcarbajal68@gmail.com
URL ORCID: https://orcid.org/0000-0002-0755-3842
e-mail: alfredo.cruzorea@cinvestav.mx
URL ORCID: https://orcid.org/0000-0002-4329-5449

[2]Unidad Profesional Interdisciplinaria en Ingeniería y Tecnologías Avanzadas, Av. Instituto Politécnico Nacional No. 2580, Col. Barrio la Laguna Ticomán, Del. Gustavo A. Madero, C.P. 07340, Ciudad de México, México.

e-mail: jimenezp1957@gmail.com
URL ORCID: https://orcid.org/0000-0001-8324-7428

Resumen

La difusividad térmica (D) de aceites comestibles mexicanos (nuez, semilla de uva y ajonjolí) se estudió mediante espectroscopia de lente térmica (TLS). En la técnica TLS se utilizó la configuración de alineación de lente térmica de doble haz en modo desacoplado, con un láser He-Ne como haz de prueba y un láser de iones Ar+ como haz de excitación. La determinación experimental del tiempo característico de la señal transitoria de la lente térmica se obtuvo ajustando la ecuación teórica de la TLS a los datos experimentales. A partir del tiempo característico obtenido de la muestra, fue posible calcular la difusividad térmica de la muestra mediante la TLS, la cual que se calibró con agua. Los valores fueron: ($D = 8.47 \times 10^{-4}$ $cm^2 \cdot s^{-1}$, $\theta = 32.72 \times 10^{-2}$, $t_c = 4.73 \times 10^{-3} \cdot$ s), ($D = 8.13 \times 10^{-4}$ $cm^2 \cdot s^{-1}$, $\theta = 58.14 \times 10^{-2}$, $t_c = 4.92 \times 10^{-3} \cdot$ s) y ($D = 8.57 \times 10^{-4}$ $cm^2 \cdot s^{-1}$, $\theta = 51.96 \times 10^{-2}$, $t_c = 51.96 \times 10^{-3} \cdot$ s) para los aceites de nuez, semillas de uva y ajonjolí, respectivamente. La técnica TLS demostró ser no destructiva, con alta sensibilidad y versátil para el estudio de las propiedades térmicas de los aceites comestibles utilizados en la industria alimentaria.

***Palabras Clave*, Lente térmica, Técnica fototérmica, Difusividad térmica, aceites comestibles**

Abstact

Thermal-diffusivity (D) of Mexican edible oils (nut, grape seed and sesame) were studied by thermal lens spectroscopy (TLS). In the TLS technique the mode-mismatched dual-beam thermal lens alignment configuration was used, with a He-Ne laser as a probe beam and an Ar+ ion laser as excitation one. Experimental determination of the characteristic time constant of the transient thermal lens signal was obtained by fitting the theoretical equation of TLS to the experimental data. From the obtained characteristic time constant of the sample it was possible to calculate the sample thermal diffusivity by TLS, which were calibrated with water. Values were: ($D = 8.47 \times 10^{-4}$ $cm^2 \cdot s^{-1}$, $\theta = 32.72 \times 10^{-2}$, $t_c = 4.73 \times 10^{-3} \cdot$ s), ($D = 8.13 \times 10^{-4}$ $cm^2 \cdot s^{-1}$, $\theta = 58.14 \times 10^{-2}$, $t_c = 4.92 \times 10^{-3} \cdot$ s) and ($D = 8.57 \times 10^{-4}$ $cm^2 \cdot s^{-1}$, $\theta = 51.96 \times 10^{-2}$, $t_c = 51.96 \times 10^{-3} \cdot$ s) for nut, grape seed and sesame oils, respectively. The TLS technique was shown to be non-destructive, with high sensitivity and versatile for the study of thermal properties of edible oils used in food industry.

Keywords, Thermal lens, Photothermal technique, Thermal diffusivity, edible oils

I. INTRODUCTION

Edible oils extracted from plant and animal sources are important in foods and other industries, such as cosmetics, pharmaceuticals, and lubricants. During extraction, purification and usage, oils undergo a variety of processing operations, including frying, distillation and chemical modification which may alter their physical properties of edible oils. These oils depend primarily on composition and temperature [1, 2]. There is a great interest to determine in edible oils their relative concentration of different carboxylic acids and fatty acids. The main variations in composition are the chain length and the degree of instauration of these fatty acids. Different analytical techniques used for these purposes, are based on infrared spectroscopy in the middle region (IR) and near-infrared (NIR) or liquid chromatography (HPLC) [3]. However, these systems are liquid and semi-transparent in the visible region, then they are very appropriate to be studied through thermal lens spectroscopy (TLS).

The TLS is a powerful tool to obtain the thermal diffusivity and optical parameters of semitransparent materials, solids and liquids [4-6]. 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.

In this paper, the TLS was used to determine the thermal diffusivity of three edible oils: nut, grape seed and sesame, used in typical Mexican dishes.

II. Methodology

TLS technique is well known for its sensitivity to measure very small refractive index (as small as 10^{-8}), across the beam width resulting from a temperature variation of ~ 10^{-5} °C in liquids. A laser beam can thermally induce such refractive index changes, which is the fundamental principle behind TLS. The TLS effect is caused by the deposition of heat via non-radiative decay processes, after the laser beam with Gaussian profile has been absorbed by the sample. In this situation, a transverse temperature profile, $\Delta T(r,t)$, is established. The temporal evolution of $\Delta T(r,t)$, is scaled according to characteristic time constant $t_c = \omega_e^2 /4 D$, where ω_e is the excitation laser beam radius at the sample and D is the thermal diffusivity. The heating of the sample causes a change of the refractive index (dn/dT), as determined by convergence or divergence of a probe laser beam when it passes through the sample: the so-called Thermal Lens (TL) effect. The propagation of a probe laser beam through this TL results in a variation of its on-axis intensity, $I(t)$, which can be calculated using aberrant model theory, the time evolution of the probe beam intensity $I(t)$ at the detector is [4]:

$$\mathrm{I(t)} = \mathrm{I_0}\left(1-\frac{\theta}{2}\tan^{-1}\left(\frac{2mV}{[(1+2m)^2+V^2]\frac{t_c}{2t}+1+2m+V^2}\right)\right)^2 \quad (1)$$

The parameters m, V, t_c and θ are defined as:

$$m = \left(\frac{\omega_{1p}}{\omega_e}\right)^2; \qquad V = \frac{Z_1}{Z_c};$$

$$t_c = \frac{\omega_e^2}{4D}\left(\frac{dn}{dT}\right)_p;$$

$$\theta = -\frac{P_e A_e l_0}{k\lambda_p}\left(\frac{dn}{dT}\right)_p$$

In Eq. 1, I (0) is the initial value of $I(t)$; θ is the thermally induced phase shift of the probe beam after passing through the sample; Z_c (12.89 cm) is the confocal distance of the probe beam and Z_1 (8.0 cm) is the distance from the probe beam waist to the sample. ω_e (ω_p) is the spot size of the excitation (probe) laser beam at the sample, ω_{1p} the radius of beam at distance Z relative to the beam waist; $k(D)$ is the thermal conductivity (diffusivity) of the sample; P_e is the incident power; A_e is the optical absorption coefficient at the excitation beam wavelength λ_e and probe beam wavelength λ_p; l_0 is the length of the sample cell and dn/dT is the temperature dependence of the sample refractive index. The so-called characteristic time of TL t_c, is defined as $D = \omega_e^2/ 4\, t_c$ with $D = k/\rho c$ where ρ is the density and c is the heat capacity of the sample. The experimental value of the beam waist of the excitation laser beam is $\omega_e = 40$ µm. Equation 1 describes the probe beam intensity at the center of the detector.
Then by fitting the equation $I(t)$ (Eq. 1) to the experimental data, as a function of time (t), it is possible to obtain the sample thermal diffusivity D from t_c as adjustable parameter.

The TL experiments were performed using the time resolved mode-mismatched, the schematic experimental setup which is given in references [5, 6]. The excitation laser source is provided by an Ar^+ laser, 40 mW at 514 nm wavelength. The excitation laser was focused by a converging lens f_1, and the sample cell, 10.0 mm quartz, was placed at the focal plane. Exposure of the cell to the excitation beam was controlled by means of a shutter. The probe beam was supplied from a He-Ne laser, 1 mW at 632 nm wavelength. The probe beam was focused by lens f_2 at small angle with respect to excitation beam and carefully centered to pass through the thermal lens to maximize the TL signal. The intensity probe beam was detected by a photodiode (P), located in the far field, by placing a pinhole in front of it. The small angle was used to deviates the probe beam to the TL detection plane (photodiode P).

The experimental setup was calibrated by measuring the thermal diffusivity of de-ionized water (1.43×10^{-3} cm$^2 \cdot$s^{-1}).

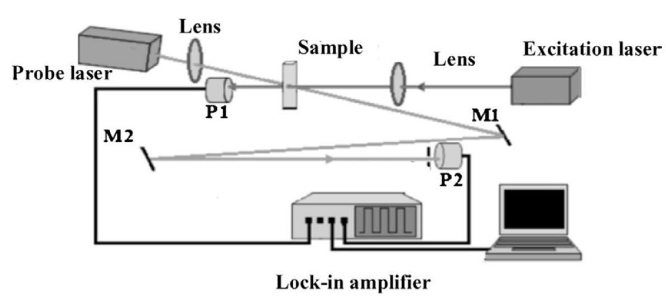

Fig. 1 Experimental setup.

Trace amount (approximately, 10^{-5} M) of rhodamine 6G dye was added to de-ionized water for the thermal diffusivity measurements. Since water has thermal diffusivity compared to common organic solvents, it shows poor thermal blooming effects. Small amount of dye helps in improving the light absorption, also it is reported that, very little amount of dye will not affect the thermal diffusivity of the medium [7, 8].

III. Results and Discussion

Thermal diffusivity results were obtained for three edible oils: nut, grape seed and sesame; typical spectra obtained by thermal lens are shown in Fig. 2 a), b), and c), respectively.

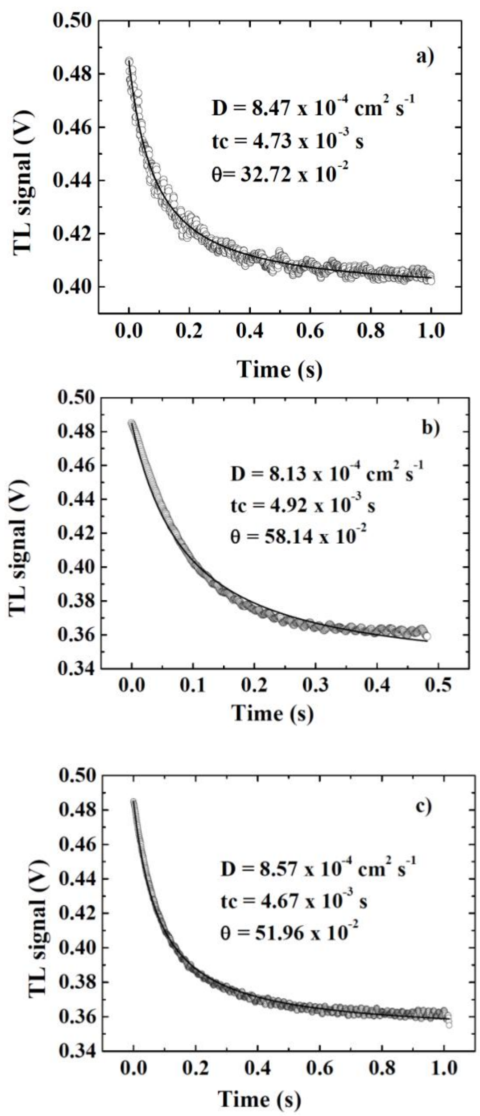

Fig. 2 Typical curve for the transient thermal lens effect for: a) nut, b) grape seed and c) sesame oil. The thermal diffusivity (D) and tc were determined from this curve.

The experimental TL signal evolution has a behavior as described by the theoretical expression for TL (Eq. 1). Figure 2 shows the typical evolution of the TL signal intensity: the symbols (o) represent the experimental points, and the solid line corresponds to the best fit of the theoretical TLS signal amplitude to the experimental data. By this fitting procedure, parameters θ and tc are obtained, where (D= 8.47 × 10-4 cm2•s−1, θ = 32.72 × 10-2, tc = 4.73 × 10-3• s), (D= 8.13 × 10-4 cm2•s−1, θ = 58.14 × 10-2, tc = 4.92 × 10-3• s) and (D= 8.57 × 10-4 cm2•s−1, θ = 51.96 × 10-2, tc = 51.96 × 10-3• s) for nut, grape seed and sesame oils, respectively. The standard deviations of the obtained thermal diffusivities for these edible oils were around of ± 1.5 %. Sesame oil shows the highest thermal diffusivity value, nut oil shows an intermediate value, and grape seed oil shows the lowest thermal diffusivity value. The thermal diffusivity of nut oil is reported for the first time, to our knowledge, and therefore could not be compared with any reported value however the thermal diffusivity values obtained for this oil is in the range of the thermal diffusivity values for some other oil samples reported in the literature as olive, corn and sunflower oils [5, 6].

IV. Conclusions

As shown in this paper, thermal lens spectroscopy is a technique that has applications in different areas as well as in the food technology area. With this technique it is possible to determine the thermal diffusivity of edible oils used every day in the typical Mexican cuisine. The Thermal lens spectrometry is an analytical tool with high sensibility for chemical analysis of solutions that can be complementary with other techniques such as UV-vis and standard methods of analysis. The thermal characterization of these oils, at room temperature, was obtained from the definition of the thermal diffusivity (D).

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Declarations

Conflict of interest. The authors declare that they have no known competing financial interests to influence the work reported in this paper.

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