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Thermal properties of centrifuged oils measured by alternative photothermal techniques

R. Carbajal-Valdez[a], J.L. Jiménez-Pérez[b,*], A. Cruz-Orea[a], Z.N. Correa-Pacheco[c], M.L. Alvarado-Noguez[d], I.C. Romero-Ibarra[b], J.G. Mendoza-Alvarez[a]

[a] CINVESTAV-IPN, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Delegación Gustavo A. Madero, Código Postal 07360, Ciudad de México, Mexico
[b] UPIITA, Instituto Politécnico Nacional, Avenida Instituto Politécnico Nacional No. 2580, Col. Barrio la Laguna Ticomán, Gustavo A. Madero, CP 07340, Ciudad de México, Mexico
[c] CONACYT, Centro de Desarrollo de Productos Bióticos-Instituto Politécnico Nacional (CEPROBI-IPN), Carretera Yautepec–Jojutla, km 6. San Isidro, C.P. 62731, Yautepec, Morelos, Mexico
[d] ESIME, Instituto Politécnico Nacional, Av. Instituto Politécnico Nacional Edificio 5, Unidad Profesional Adolfo López Mateos, Zacatenco, Delegación Gustavo A. Madero, C.P. 07738, Ciudad de México, Mexico

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ABSTRACT

In this work, thermal characterization of centrifuged aromatic citrus oils was studied using thermal lens (TL) and open photoacoustic cell (OPC). The thermal diffusivity (D) was obtained by TL, fitting the critical time parameter of the experimental curves to the theoretical values. An experimental arrangement of non-matched mode lasers with a probe and an excitation lasers was used. On the other hand, the thermal effusivity (e) of the samples was obtained by using OPC. The thermal conductivity (k) was calculated from the relationship between D and e. The thermal parameters obtained were compared with theoretical values in the literature. UV–vis spectroscopy, Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR) and ^{1}H Nuclear Magnetic Resonance (NMR) were used to determine the absorption coefficients and chemical structure of the citrus oils. The importance of this research work was the determination of the thermal parameters of essential oils as an alternative technique for quality control application.

1. Introduction

Aromatic essential oils have been used since ancient times in cosmetics, incense or perfumes, as well as for therapeutic, in medicine (microbial and antispasmodic) and culinary applications [1–3]. Citrus essential oils are complex mixtures of chemical compounds that impart characteristic flavor and odor of the fruits. Such chemical compounds can be classified mainly into three groups: terpenes, sesquiterpenes and oxygenates. However, the chemical composition depends on cultivation climate, harvest time, the biotype of plant and finally the process of extracting oils [4–6]. Therefore, it is necessary to determine a profile of the constituents of essential oils, because the variability in chemical composition determines their quality. Citrus essential oils are characterized by a volatile and non-volatile fraction, resulting in a complex product of several hundred compounds. Oils are typically composed of a mixture of a significant volatile fraction (85–99%) that can be further processed by distillation and the remaining 1–15% non-volatile residue. The volatiles are composed of mono- and sesquiterpene hydrocarbons and their oxygenated derivatives, aliphatic aldehydes, alcohols and esters, whereas the non-volatile fraction contains hydrocarbons, sterols, fatty acids, waxes, non-volatile terpenes, carotenoids and flavonoids, as well as coumarins and furocoumarins. The non-volatile residue, which forms from 1% to 15% of the oil, contains hydrocarbons, sterols, fatty acids, waxes, carotenoids, coumarins, psoralens, and flavonoids [7]. Industrially, physical characteristics commonly used as the first parameter for certification are color, taste, odor, density and refractive index. The importance of these substances and the variety of methods of preparation and purification, like the use of analytical techniques make necessary to determine their composition and characterize them for authentication purposes. Among alternative techniques used for these purposes, TL and OPC are important to determine the thermal properties such as diffusivity, effusivity and thermal conductivity. In this work, four centrifuged essential oils were studied: lemon, orange, grapefruit and green mandarin. Our results were compared with the values of the thermal constants of various essential oils from the literature, obtaining optimal values of new compositions of citrus oils using two alternative photothermal techniques.

* Corresponding author.
E-mail address: jimenezp@fis.cinvestav.mx (J.L. Jiménez-Pérez).

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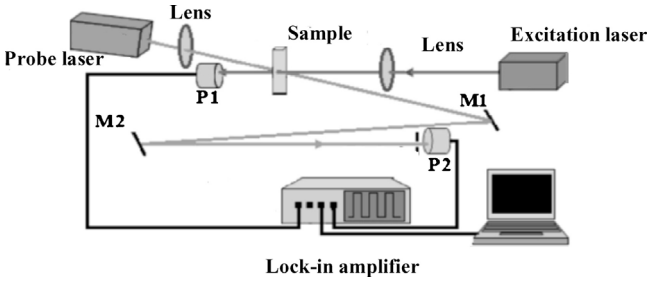

Fig. 1. Themal lens (TL) experimental setup.

2. Experimental

2.1. Thermal lens (TL)

The TL spectrometry experimental setup is observed in Fig. 1. The sample is exposed to an excitation laser beam to generate a local temperature increase and to a probe beam that passes through the sample. There is an increase in temperature because of the heat produced from the absorbed energy in the sample generating a lens-like optical effect detected by the probe. The propagation of the probe beam laser through the TL results in either a defocusing or a focusing of the beam center. Subsequently, the intensity of the probe beam is measured using a detector [8,9].

The theory of the TL is expressed in terms of the Fresnell diffraction theory based in the phase shift on the probe beam after passing through the sample [9–11]. The analytical expression for the probe beam intensity is as follows:

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

where, $I(t)$ is the time dependence of the probe laser beam at the detector. $I(0)$, is the initial value of $I(t)$ for t zero, θ is the phase shift of the probe beam after passing through the sample due to the increase in temperature.

$V = \frac{Z_1}{Z_c}$; $m = \left(\frac{w_p}{w_e}\right)^2$ (2) where Z_c is the confocal distance of the probe beam, Z_1 is the distance from the probe beam waist to the sample. w_p is the probe beam spot size and w_e is the excitation beam spot sizes at the sample [9].

$$\theta = -\frac{P_e A_e L}{k\lambda}\left(\frac{dS}{dT}\right) \quad (3)$$

where P_e is the excitation beam power, A_e is the optical absorption coefficient of the sample at the excitation beam wavelength, L is the sample thickness, k is the thermal conductivity, λ is the laser wavelength of the probe beam, and (ds/dT) is the temperature coefficient of the optical path length change at the probe beam wavelength.

The characteristic time constant of the thermal lens t_c depends on the excitation beam spot size at the sample w_e, and thermal diffusivity D it can be expressed as:

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

θ and t_c can be determined by fitting Eq. (1) to the experimental data. The TL was calibrated with water to compare with the values reported in the literature. The experimental parameters of TL are summarized in Table 1.

2.2. Open photoacoustic cell technique (OPC)

The Open photoacoustic cell technique (OPC) was used for the thermal effusivity measurements [12]. The thermal effusivity measures essentially the thermal impedance of the sample, or the samplés ability to exchange heat with the environment. The technique consists of a modulated beam, obtained with a mechanical chopper, at an angular frequency of $\omega = 2\pi f$. The OPC experimental setup is observed in Fig. 2. A detail of the cross section of the photoacoustic cell is shown in Fig. 3. In the photoacoustic cell, the liquid sample is placed on the aluminum foil of known thermal effusivity. An electret microphone connected to the cell detects the heat generated due to the temperature rise and then it diffuses into the photoacoustic (PA) gas chamber modulating the pressure (acoustic waves) within the PA cell. A lock-in amplifier interfaced with a data acquisition system measures the microphone-response signal [13].

For the calculation of the thermal effusivity the obtained photoacoustic signal of each sample is normalized, by using the photoacoustic signal when the sample is air, and the following equation is used [14]:

$$e_s = \frac{l_0\rho_0 c_0}{I_R}\sqrt{\omega} \quad (5)$$

where ρ_0 is the density of the used aluminum foil (2.7 g cm^{-3}), c_0 is the specific heat of the aluminum foil (0.9 $Jg^{-1}\,°C^{-1}$), l_0 is the thickness of the aluminum foil (0.0016 cm), $\omega = 2\pi f$ being f the modulation

Table 1
Thermal lens experiment parameters.

P_e - Excitation laser power (at 514.5 nm)	30 mW
P_p - Probe laser power (at 632.8 nm)	1 mW
ω_e - Excitation laser spot size	4.9×10^{-3} cm
ω_{1p} - Probe laser spot size at cell	1.81×10^{-2} cm
m - Constant parameter	13.691
V - Constant parameter	1.22
Z_c - Focal distance	6.56 cm
Z_2 - Distance	~2 m
L - Length of sample cell	1.0 cm
Sample	Essential Oil

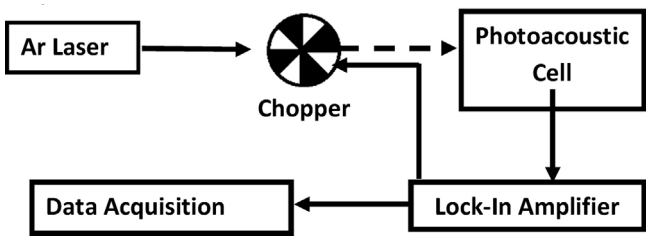

Fig. 2. Open photoacoustic cell (OPC) experimental setup.

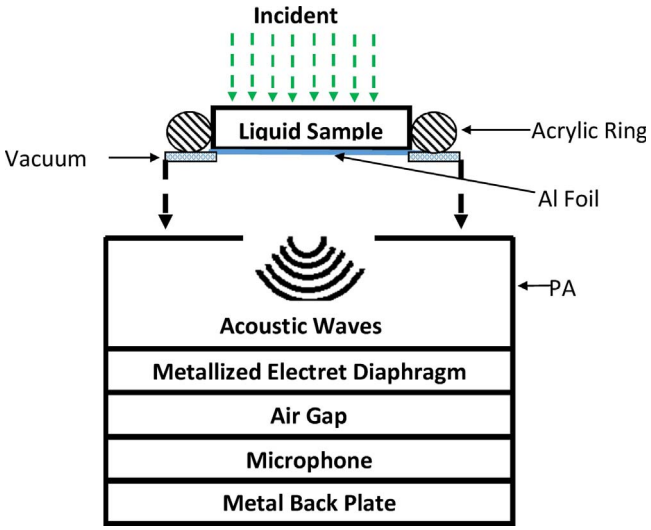

Fig. 3. Cross section of the open photoacoustic cell (OPC).