Measurements of the thermal effusivity of transparent liquids by means of a photopyroelectric technique

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A new photopyroelectric methodology for thermal effusivity measurements in transparent liquids is presented. This methodology involves the photopyroelectric technique in the standard front-surface configuration. A signal normalization procedure, which avoids the conventional requirement for transfer function determination is implemented. The thermal effusivity of three liquids was measured by means of this device and very good agreement was found with the corresponding values reported in the literature.

Keywords: Photopyroelectric techniques; thermal effusivity; transparent liquids.

Se presenta una nueva metodología fotopiroeléctrica para la medición de la efusividad térmica de líquidos transparentes. Esta metodología involucra la técnica fotopiroeléctrica en la configuración estándar. Se implementa un procedimiento de normalización con el que se evita el requerimento de conocer la función de transferencia. Dicho procedimiento se utilizó para medir la efusividad térmica de tres líquidos transparentes encontrándose excelente acuerdo con los valores reportados en la literatura.

Descriptores: Técnicas fotopiroeléctricas; efusividad térmica; líquidos transparentes.

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1. Introduction

The thermal effusivity, defined as $e = (k\rho c)^{1/2}$ in units of $\mathrm{Ws}^{1/2}\mathrm{K}^{-1}\mathrm{m}^{-2}$, is an important thermophysical property, which characterizes the thermal impedance of matter, *i.e.*, its ability to exchange thermal energy with the surroundings [1]. Its importance lies not only on the aforementioned thermal exchange characteristics, but also on its utility in making complete thermal characterization of materials through combinations with other thermophysical properties.

Photothermal techniques have proved to be useful experimental methodologies for carrying out thermal characterizations in the liquid and the solid state [2–10]. Several photothermal methodologies, involving photoacoustic [6, 7] and photopyroelectric [8, 10] detection, have been reported for measuring thermal effusivity for liquids. The photoacoustic methodologies reported for the direct measurement of this thermal property [6,7], one of these [6] suitable only for thermal effusivity measurements in transparent liquids, involves the ligth absorber in the thermally thin regime. The reported photopyroelectric technique for the direct measurement of the thermal effusivity for liquids [10], on the other hand, involves the inverse configuration assuming the thermally thin behavior of the pyroelectric sensor and, even more, requires the use of a reference sample for the matter of calibration of the sensor. In this paper the utility of the standard photopyroelectric configuration [10] (front photopyroelectric configuration) for performing high precision measurements of thermal effusivity in transparent liquids, is shown. As opposite to the fore described reported photothermal techniques the one reported in this paper makes use of the ligth absorber (py-

roelectric sensor) in the thermally thick regime. The overall methodology is based on the asymptotic behavior of the normalized pyroelectric signal, as a function of the modulation frequency, when the modulated beam impinges on the pyroelectric surface by crossing the liquid sample. A constant value for this normalized signal, which depends on the thermal effusivity of the liquid in question, is obtained for each case. This constant is measured from signals at high modulation frequencies and its average value is used for evaluating the sample thermal effusivity. The procedure is illustrated through measurements of the thermal effusivities for three liquid samples: distilled water, ethylene glycol, and olive oil. Excellent agreement was obtained with the values reported in the literature.

2. Theory

By considering the one dimensional heat diffusion problem of Fig. 1, where light, with intensity I_0 and angular modulation frequency $\omega = 2\pi f$, is impinging on the upper surface of medium 2, which absorbs light on its surface with optical absorption coefficient β, the corresponding coupled differential equations for the one-dimensional heat diffusion are

$$\frac{\partial^2 T_1}{\partial x^2} - \frac{1}{\alpha_1}\frac{\partial T_1}{\partial t} = 0, \quad 0 \leq x,$$

$$\frac{\partial^2 T_2}{\partial x^2} - \frac{1}{\alpha_2}\frac{\partial T_2}{\partial t} = -\frac{\beta I_0 \delta(x)}{2k_2}\left[1 + e^{i\omega t}\right], \quad -L \leq x \leq 0,$$

$$\frac{\partial^2 T_3}{\partial x^2} - \frac{1}{\alpha_3}\frac{\partial T_3}{\partial t} = 0, \quad -\infty < x \leq -L, \tag{1}$$
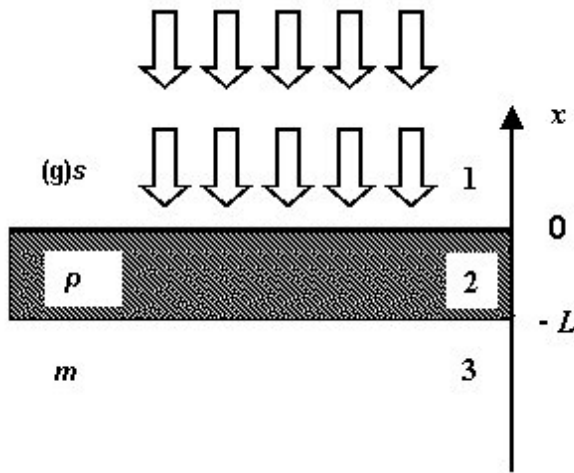
FIGURE 1. Schematic representation of the one-dimensional heat diffusion model with surface absorption on the pyroelectric element.

with boundary conditions

$$T_1(0) = T_2(0),$$

$$T_2(-L) = T_3(-L),$$

$$-k_1 \frac{dT_1}{dx}\Big|_{x=0} = -k_2 \frac{dT_2}{dx}\Big|_{x=0},$$

$$-k_2 \frac{dT_2}{dx}\Big|_{x=-L} = -k_3 \frac{dT_3}{dx}\Big|_{x=-L},$$

and the physical requirement of finite solutions as $x \to \pm\infty$

$$\lim_{x \to +\infty} T_1(x) = 0,$$

$$\lim_{x \to -\infty} T_3(x) = 0,$$

where T_i $i=1,2,3$ is the temperature distribution inside medium i; σ_2 is the complex thermal diffusion coefficient for medium 2, which is defined as $\sigma_2 = (1+i)(\pi f/\alpha_2)^{\frac{1}{2}}$, and α_2, k_2 and L are the corresponding thermal diffusivity, thermal conductivity and thickness, respectively. Solving this system of equations it is easy to show that the temperature distribution inside medium 2 is given by

$$T_2(x,t) = \frac{I_0 \beta d(1 + \gamma_{12})}{4k_2\sigma_2}$$

$$\times \frac{\left[e^{\sigma_2 x} - \gamma_{23}e^{-2\sigma_2 L}e^{-\sigma_2 x}\right]}{\left[1 + \gamma_{12}\gamma_{23}e^{-2\sigma_2 L}\right]}e^{i\omega t}. \quad (2)$$

In this equation βd is the absorbance of the infinitesimal surface layer of material 2, where the total absorption of light takes place; γ_{12} and γ_{23} are thermal coupling coefficients [5, 11, 12], defined by $\gamma_{ij} = (1 - e_i/e_j)/(1 + e_i/e_j)$, with e_i been the thermal effusivity of medium i. From Eq. (2) the spatially averaged temperature, $T_2^{AV}(f)$, inside

medium 2 is

$$T_2^{AV}(f) = \frac{I_0 \beta d(1 + \gamma_{12})(1 - e^{-\sigma_2 L})}{4Lk_2\sigma_2^2}$$

$$\times \frac{\left[1 - \gamma_{23}e^{-\sigma_2 L}\right]}{\left[1 + \gamma_{12}\gamma_{23}e^{-2\sigma_2 L}\right]}e^{i\omega t}. \quad (3)$$

Considering that medium 2 is a pyroelectric transducer, with induced voltage proportional to its thickness-averaged temperature rise, [13] it is evident that the voltage signal can be written as

$$V_2(f) = \frac{G(f)\beta I_0 d}{4Lk_2\sigma_2^2}(1 + \gamma_{12})(1 - e^{-\sigma_2 L})$$

$$\times \frac{\left[1 - \gamma_{23}e^{-\sigma_2 L}\right]}{\left[1 + \gamma_{12}\gamma_{23}e^{-2\sigma_2 L}\right]}e^{i\omega t} \quad (4)$$

The function $G(f)$, called the transfer function, represents the frequency response of the sensor and the electronics. By considering two different materials for medium 1 (gas (g) or a transparent liquid (s) in Fig. 1) the following two equations are obtained:

$$V_p^g(f) = \frac{G(f)\beta I_0 d}{4Lk_p\sigma_p^2}(1 + \gamma_{gp})(1 - e^{-\sigma_p L})$$

$$\times \frac{\left[1 - \gamma_{pm}e^{-\sigma_p L}\right]}{\left[1 + \gamma_{gp}\gamma_{pm}e^{-2\sigma_p L}\right]}e^{i\omega t}, \quad (5)$$

$$V_p^s(f) = \frac{G(f)\beta I_0 d}{4Lk_p\sigma_p^2}(1 + \gamma_{sp})(1 - e^{-\sigma_p L})$$

$$\times \frac{\left[1 - \gamma_{pm}e^{-\sigma_p L}\right]}{\left[1 + \gamma_{sp}\gamma_{pm}e^{-2\sigma_p L}\right]}e^{i\omega t}. \quad (6)$$

Taking the ratio of these two equations we obtain

$$R(f) = \frac{V_p^g}{V_p^s} = \frac{(1 + \gamma_{gp})}{(1 + \gamma_{sp})}\frac{\left[1 + \gamma_{sp}\gamma_{pm}e^{-2\sigma_p L}\right]}{\left[1 + \gamma_{gp}\gamma_{pm}e^{-2\sigma_p L}\right]}. \quad (7)$$

It is clear that this normalization procedure eliminates the transfer function and some other parameters, which could complicate the analysis. Equation (6) involves only the thermal response of the materials under examination.

When the pyroelectric element is thermally thick at large enough modulation frequencies, it is clear that R reaches the asymptotic value

$$R_{TG} = \frac{(1 + \gamma_{gp})}{(1 + \gamma_{sp})} = \frac{1 + e_s/e_p}{1 + e_g/e_p} \quad (8)$$

Taking into account that gas thermal effusivities, e_g, and the effusivity of the pyroelectric sensor, e_p, usually satisfy the relation $e_g \ll e_p$, it follows from Eq. (8) that

$$R_{TG} = 1 + \frac{e_s}{e_p} \quad (9)$$

where e_s is the thermal effusivity of the liquid under study. From Eq. (9) the liquid's thermal effusivity can be found, once the asymptotic value R_{TG} is known, from the relation

$$e_s = e_p(R_{TG} - 1). \quad (10)$$

The constant R_{TG} can be obtained for a given transparent liquid, by taking the signal ratio R from the pyroelectric sensor in the thermally thick regime in two different situations: one with the bare sensor, and the other with the liquid sample in place.

3. Experimental

The photopyroelectric experimental set-up is shown in Fig. 2. The intensity-modulated laser light crossing the liquid sample (with λ= 660 nm, power 3.0 mW and electronically chopped by the internal oscillator of the lock-in amplifier), was incident on the metallized surface of a polyvinylidene fluoride (PVDF) pyroelectric sensor (150-μm thick and 1-cm in diameter). The bottom surface of the PVDF film was attached to a metal (copper) electrode with conductive epoxy. The voltage signal generated in the sensor was pre-amplified

(ITHACO model 1201) and then sent to the lock-in amplifier (Stanford Research Systems, model SR830) for further amplification and demodulation. The diode laser (Mitsubishi, model ML1016R), equipped with a collimator lens system, was left unfocussed to illuminate a circular area of the PVDF surface, 5 mm in diameter. Three liquid samples were used for this study (Table I). For a given liquid sample the voltage signal of the bare pyroelectric film was first recorded as a function of the modulation frequency from 2 to 150 Hz, in steps of 1 Hz. Then the liquid was poured in the sample chamber/container in such a way as to approximately be three mm thick above the upper surface of the PVDF sensor. The photopyroelectric signal of the sensor, with the liquid sample in place, was again recorded as a function of the modulation frequency. The complete procedure was repeated for each liquid sample, taking care to completely clean with water and dry the PVDF surface in the interim. For the case

TABLE I. Thermal effusivities of some liquids measured by the photopyroelectric technique (e_s), and some literature values (e_R).

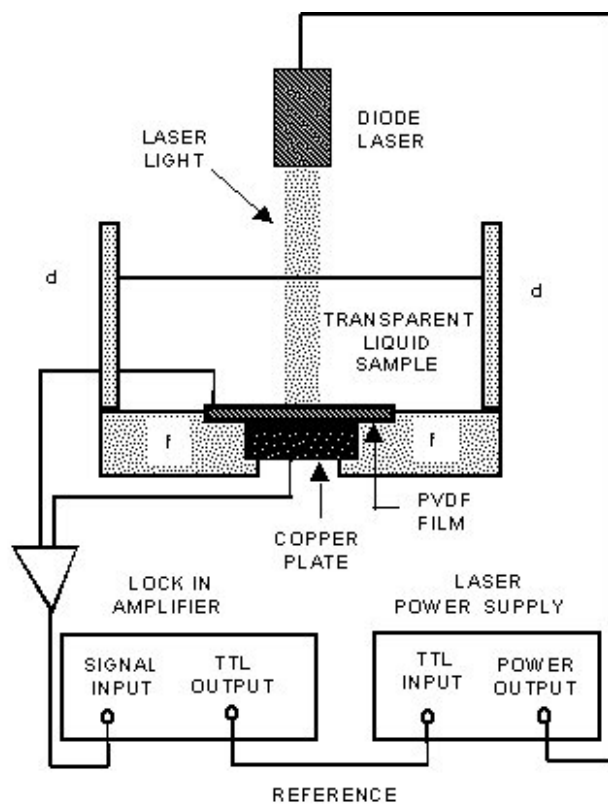| Liquid sample	R_{TG}	e_s(Ws$^{1/2}$/cm^{2}K)	e_R(Ws$^{1/2}$/cm^{2}K)	
Distilled Water (Commercial)	3.8476±0.0289	0.1593±0.0016	0.1579	[Ref. 15 and 16]
Ethylene Glycol (Analytical Reagent)	2.4610±0.0113	0.0817±0.0006	0.0813	[Ref. 17]
Olive Oil (Commercial)	2.0867±0.0072	0.0608±0.0004	0.0621	[Ref. 10]

FIGURE 2. Schematic cross section of the standard photopyroelectric configuration for liquids. d) container walls. f) dielectric substrate.

of the non-soluble water liquid, like olive oil, the sample container and the sensor surface were carefully cleaned with CCl_4 using cotton-wool sticks. All the measurements were made at room temperature (22^0C).

4. Results and discussion.

Following the collection of the two experimental data sets for the bare PVDF sensor and with the liquid sample in place, the signal amplitude ratios for each modulation frequency were calculated for the analysis, as suggested by Eq. (7). The results are shown in Fig. 3. It is clear from this figure that the asymptotic behavior, predicted by the theory [Eq. (8)] is obtained for all cases for modulation frequencies ranging from 100 to 150 Hz. The corresponding R_{TG} values, needed for the thermal effusivity evaluations of the liquid, through Eq. (10), were obtained as the arithmetic average of the 50 sample set from 100 to 150 Hz. The horizontal lines in the same figure are the corresponding plots of these constant values. Using the known thermal effusivity for PVDF [13], e_p=0.05594 Ws$^{1/2}$/cm^{2}K, the thermal effusivity of the liquid sample can be easily evaluated from Eq. (10). The experimental error of the thermal effusivity measurements was estimated by using the usual formula for error propagation [14] in the form $e_s = e_p \Delta R_{TG}$, where ΔR_{TG} is the standard deviation of the R_{TG} measurements. The results are summarized in columns 2 and 3 of Table I and the corresponding literature values are summarized in column 4 of the same table. From the data in column 3, the high precision of the present methodology becomes evident: the thermal effusivities have
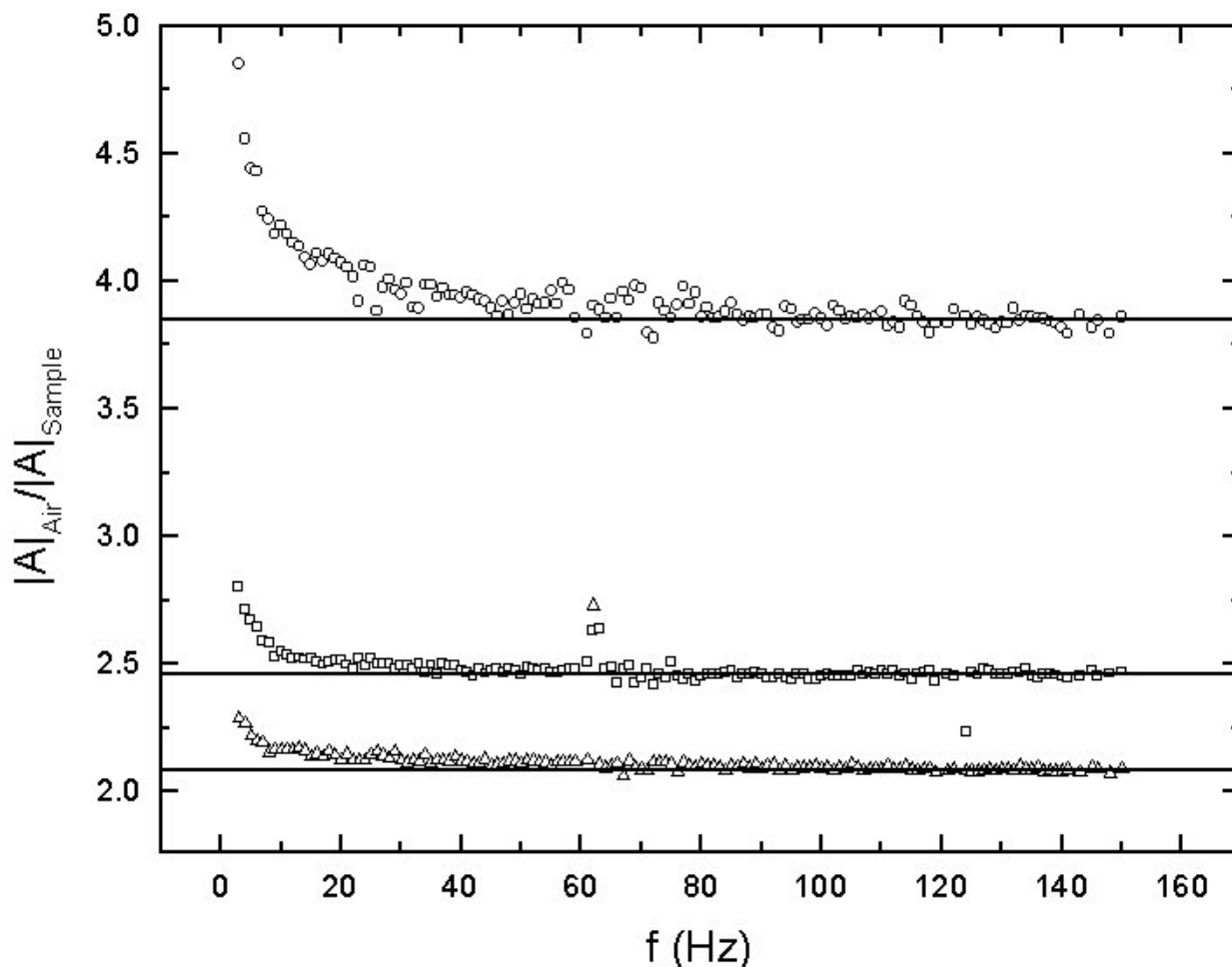
FIGURE 3. Results of the normalized photopyroelectric amplitudes for the liquid samples used for this work vs. modulation frequency. The correspondance between symbols and materials is as follows: (circle) Distilled water, (square) Ethylene Glycol, (triangle) Olive oil. The horizontal lines represents the corresponding asymptotic values, R_{TG}, for the normalized pyroelectric signal for each liquid substance.

been evaluated up to four significant figures and precision improves for the samples of high viscosity, which is reasonable because the magnitude of small convective variations further decreases in these liquids. Moreover, the close agreement between the literature values and the measurements made in this work is remarkable, especially for distilled water and ethylene glycol. The high measurement precision of thermal effusivity by means of the present frequency-scanned photopyroelectric technique suggests the future exploration of the related higher-precision photopyroelectric thermal-

wave methodologies, such as the thermal-wave resonant cavity [4, 5], as a means for complete thermal characterization for liquids of industrial importance, *e.g.* vegetable oils.

Finally, a major advantage of the present methodology over other reported photothermal techniques consists of the possibility to carry out fast estimates of the thermal effusivity of liquids, by measuring the photopyroelectric signals with and without the liquid sample at a conveniently chosen modulation frequency in the asymptotic range of Eq. (7), and calculating the R_{TG} value.

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