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New Photopyroelectric Technique for Precise Measurements of the Thermal Effusivity of Transparent Liquids

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A new photopyroelectric methodology for thermal effusivity measurements in transparent liquids is presented. The new methodology involves the thermally thick limit of the pyroelectric signal 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 five liquids was measured by means of this technique, and very good agreement was found with corresponding values reported in the literature.

KEY WORDS: photopyroelectric; thermal effusivity; transparent liquids.

1. INTRODUCTION

The thermal effusivity, defined as $e = (k\rho c)^{1/2}$ ($k =$ thermal conductivity, $\rho =$ density and $c =$ specific heat), in units of $\mathrm{W \cdot s^{1/2} \cdot K^{-1} \cdot m^{-2}}$, 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 characteristic, but also on its utility in making complete thermal characterization of materials through combinations with other thermophysical properties.

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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. In this paper the utility of the standard photopyroelectric technique [10] for performing high precision measurements of the thermal effusivity in transparent liquids is shown. 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. This normalization involves the ratio of pyroelectric signals with and without the liquid sample. A (theoretically constant) value for this normalized signal, which depends on the thermal effusivity of the liquid in question, is obtained for each case, and it is shown to be directly related to the thermal effusivity of the liquid, thus avoiding the requirement for instrumental calibration, unlike other photopyroelectric techniques reported in the literature [10]. This constant is measured from signals at high modulation frequencies and its value, averaged over an experimental data set, is used for evaluating the sample thermal effusivity through a simple equation. The precision of the thermal effusivity measurement is thus directly related to the data-set standard deviation, making the analytical procedure simpler and more reliable than those reported in the literature [6, 7, 10]. The procedure is illustrated through measurements of the thermal effusivities for five liquid samples: distilled water, glycerol, ethylene glycol, olive oil, and castor oil. Excellent agreement is 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

$$\begin{aligned}
&\frac{\partial^2 T_1}{\partial x^2} - \frac{1}{\alpha_1}\frac{\partial T_1}{\partial t} = 0 && 0 \leqslant x \\
&\frac{\partial^2 T_2}{\partial x^2} - \frac{1}{\alpha_2}\frac{\partial T_2}{\partial t} = -\frac{\beta I_0\, \delta(x)}{2k_2}[1+e^{i\omega t}] && -L \leqslant x \leqslant 0 \qquad (1)\\
&\frac{\partial^2 T_3}{\partial x^2} - \frac{1}{\alpha_3}\frac{\partial T_3}{\partial t} = 0 && \infty < x \leqslant -L
\end{aligned}$$

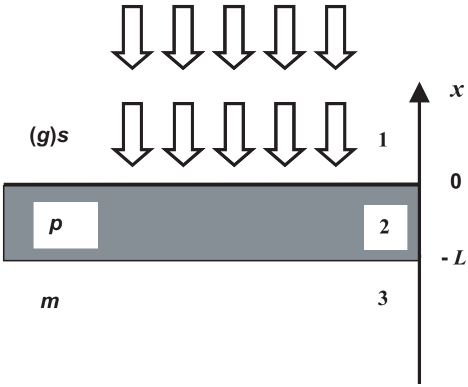

Fig. 1. Schematic representation of the one-dimensional heat diffusion model with surface absorption on the pyroelectric element.

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 $\sigma_2 = (1+i)(\pi f/\alpha_2)^{1/2}$, and α_2, k_2, and L are the corresponding thermal diffusivity, thermal conductivity and thickness, respectively. Solving this system of equations with the proper boundary conditions of heat flux and temperature continuity at all interfaces, it is easy to show that the temperature distribution inside medium 2 is given by

$$T_2(x, t) = \frac{I_0 \beta d (1+\gamma_{12})}{4k_2\sigma_2} \frac{[e^{\sigma_2 x} - \gamma_{23} e^{-2\sigma_2 L} e^{-\sigma_2 x}]}{[1+\gamma_{12}\gamma_{23} e^{-2\sigma_2 L}]} e^{i\omega t} \tag{2}$$

In this equation βd is the absorbance of the infinitesimal surface layer of material 2, where total light absorption 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 being the thermal effusivity of medium i. From Eq. (2) the spatially averaged temperature inside medium 2 is

$$T_2(f) = \frac{\beta I_0 d (1+\gamma_{12})(1-e^{-\sigma_2 L})}{4Lk_2\sigma_2^2} \frac{[1-\gamma_{23} e^{-\sigma_2 L}]}{[1+\gamma_{12}\gamma_{23} e^{-2\sigma_2 L}]} e^{i\omega t} \tag{3}$$

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

$$V_2(f) = \frac{G(f)\, \beta I_0 d}{4Lk_2\sigma_2^2} (1+\gamma_{12})(1-e^{-\sigma_2 L}) \frac{[1-\gamma_{23} e^{-\sigma_2 L}]}{[1+\gamma_{12}\gamma_{23} e^{-2\sigma_2 L}]} e^{i\omega t} \tag{4}$$

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:

$$V_p^g(f)=\frac{G(f)\,\beta I_0 d}{4Lk_p\sigma_p^2}(1+\gamma_{gp})(1-e^{-\sigma_p L})\frac{[1-\gamma_{pm}e^{-\sigma_p L}]}{[1+\gamma_{gp}\gamma_{pm}e^{-2\sigma_p L}]}e^{i\omega t} \tag{5a}$$

$$V_p^s(f)=\frac{G(f)\,\beta I_0 d}{4Lk_p\sigma_p^2}(1+\gamma_{sp})(1-e^{-\sigma_p L})\frac{[1-\gamma_{pm}e^{-\sigma_p L}]}{[1+\gamma_{sp}\gamma_{pm}e^{-2\sigma_p L}]}e^{i\omega t} \tag{5b}$$

Taking the ratio of these two equations we obtain

$$R(f)=\frac{V_p^g}{V_p^s}=\frac{(1+\gamma_{gp})}{(1+\gamma_{sp})}\frac{[1+\gamma_{sp}\gamma_{pm}e^{-2\sigma_p L}]}{[1+\gamma_{gp}\gamma_{pm}e^{-2\sigma_p L}]} \tag{6}$$

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,

$$R_{TG}=\frac{(1+\gamma_{gp})}{(1+\gamma_{sp})}=\frac{1+e_s/e_p}{1+e_g/e_p} \tag{7}$$

Taking into account that gas thermal effusivity, e_g, and the effusivity of the pyroelectric sensor, e_p, usually satisfy the relation $e_g \ll e_p$, it follows from Eq. (7) that

$$R_{TG}=1+\frac{e_s}{e_p} \tag{8}$$

where e_s is the thermal effusivity of the liquid under study. From Eq. (8) the thermal effusivity for a liquid can be found, once the asymptotic value R_{TG} is known, from the relation,

$$e_s=e_p(R_{TG}-1) \tag{9}$$

The constant R_{TG} can be obtained for a given transparent liquid, by taking the signal ratio $\mathrm{R_{TG}}$ 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 setup is shown in Fig. 2. The intensity-modulated laser light crossing the liquid sample (with $\lambda = 660$ nm, power of 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

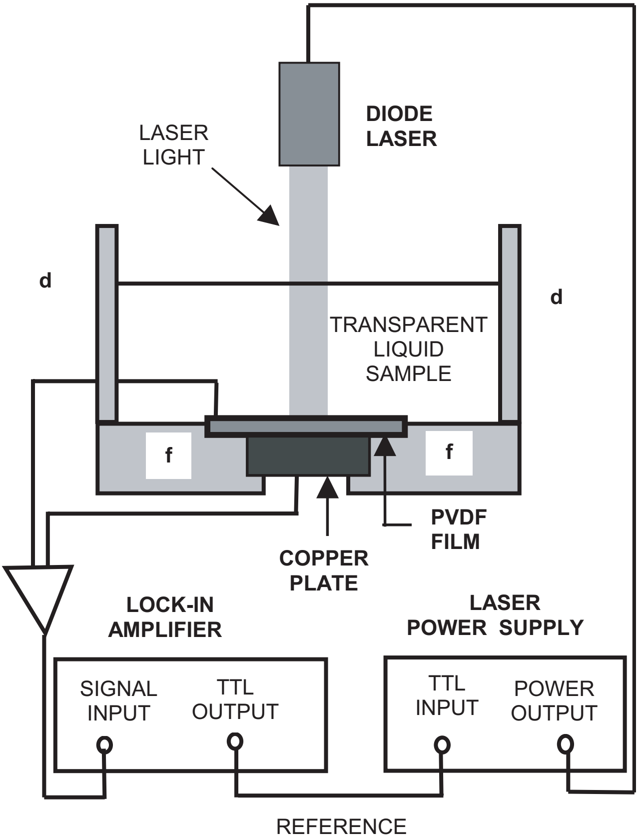

Fig. 2. Schematic cross section of the standard photopyroelectric configuration for liquids; d, container walls, f, dielectric substrate.

Table I. Thermal Effusivities of Some Liquids Measured at 22°C by the Photopyroelectric Technique (e_s), and Some Literature Values (e_R)

Liquid sample	R_{TG}	e_s ($\mathrm{W \cdot s^{1/2} \cdot cm^{-2} \cdot K^{-1}}$)	e_R ($\mathrm{W \cdot s^{1/2} \cdot cm^{-2} \cdot K^{-1}}$)
Distilled Water (Commercial)	3.8476 ± 0.0289	0.1593 ± 0.0016	0.1579 (22°C) Refs. 15 and 16
Ethylene Glycol (Analytical Reagent)	2.4610 ± 0.0113	0.0817 ± 0.0006	0.0813 (20°C) Ref. 17
Glycerol (U. S. P.)	2.2713 ± 0.0092	0.0711 ± 0.0005	0.0929 (20°C) Ref. 17
Olive Oil (Commercial)	2.0867 ± 0.0072	0.0608 ± 0.0004	0.0621 Ref. 10
Castor Oil (U. S. P.)	1.7609 ± 0.0093	0.0419 ± 0.0005	–

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. Five 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 so that the liquid thickness was approximately three mm 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 of the non-soluble water liquids, like olive and castor oils, 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°C).

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. (6). The results are shown in Fig. 3. It is clear from this figure that the asymptotic behavior, predicted by the theory, Eq. (7), 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. (8), 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], $e_p = 0.05594\ \mathrm{W \cdot s^{1/2} \cdot cm^{-2} \cdot K^{-1}}$, the thermal effusivity of the liquid sample can be easily evaluated from Eq. (9). The experimental error of the thermal effusivity measurements was estimated by using the usual formula for error propagation [14] in the form $\Delta e_s = e_p\ \Delta R_{TG}$, 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 been evaluated up to four significant figures, and the 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

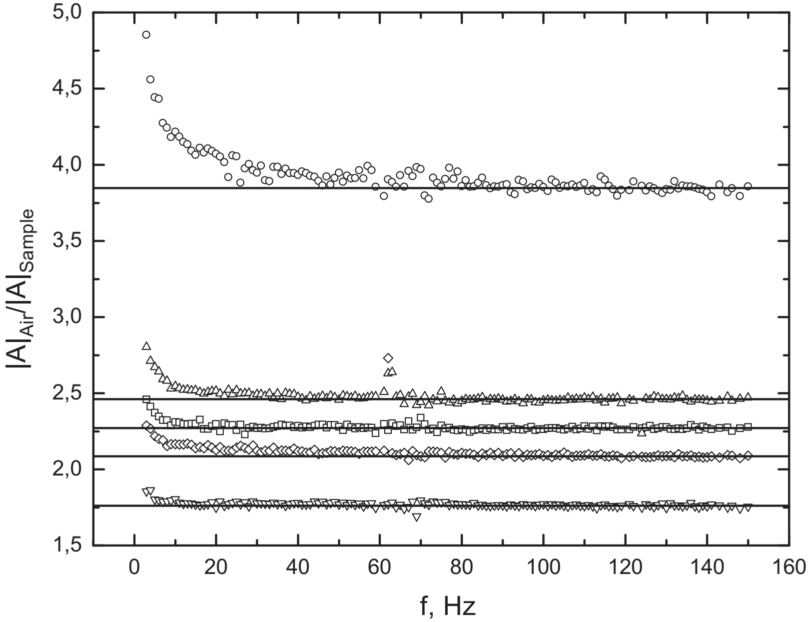

Fig. 3. Results of the normalized photopyroelectric amplitudes for the liquid samples used for this work vs. modulation frequency. (○) distilled water, (△) ethylene glycol, (□) glycerol, (◇) olive oil, (▽) castor oil. The horizontal lines represent the corresponding asymptotic values, R_{TG}, for the normalized pyroelectric signal for each liquid substance.

work is remarkable, especially for distilled water and ethylene glycol. The large disagreement in the case of glycerol is most likely due to the fact that the glycerol sample used for this work was not of high purity.

5. CONCLUSIONS

A new photopyroelectric technique for absolute thermal effusivity measurements in transparent liquid samples has been presented. The high measurement precision of thermal effusivity by means of the present frequency-scanned photopyroelectric technique suggests the future exploration of the related higher signal-to-noise ratio photopyroelectric thermal-wave methodologies, such as the thermal-wave resonant cavity [4, 5, 11], as a means of 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 lies in 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. (9), and calculating the R_{TG} value.

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