Thermal-wave resonator cavity design and measurements of the thermal diffusivity of liquids

J. A. Balderas-López,[a] A. Mandelis,[b] and J. A. Garcia
Photothermal and Optoelectronic Diagnostics Laboratories (PODL), Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8, Canada

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A liquid-ambient-compatible thermal wave resonant cavity (TWRC) has been constructed for the measurement of the thermal diffusivity of liquids. The thermal diffusivities of distilled water, glycerol, ethylene glycol, and olive oil were determined at room temperature (25 °C), with four-significant-figure precision as follows: $(0.1445\pm0.0002)\times10^{-2}\ \mathrm{cm^2/s}$ (distilled water); $(0.0922\pm0.0002)\times10^{-2}\ \mathrm{cm^2/s}$ (glycerol); $(0.0918\pm0.0002)\times10^{-2}\ \mathrm{cm^2/s}$ (ethylene glycol); and $(0.0881\pm0.0004)\times10^{-2}\ \mathrm{cm^2/s}$ (olive oil). The liquid-state TWRC sensor was found to be highly sensitive to various mixtures of methanol and salt in distilled water with sensitivity limits 0.5% (v/v) and 0.03% (w/v), respectively. The use of the TWRC to measure gas evolution from liquids and its potential for environmental applications has also been demonstrated. © *2000 American Institute of Physics.* [S0034-6748(00)01407-6]

I. INTRODUCTION

Matter in the liquid state plays a fundamental role in science and technology. Its importance is demonstrated by the variety of scientific disciplines that deal with it (i.e., the biomedical, food, and agricultural sciences). Thus, the design of experimental techniques to carry out measurements of the properties of a substance in the liquid state becomes very relevant. Especially important is the measurement of the thermophysical properties of liquids because of their widespread use as refrigerants, lubricants, and heat exchangers. The utility of the photothermal techniques for measuring thermal properties of materials has been well documented in the literature.[1–7] The basic principle of these techniques consists of measuring the temperature fluctuations in a sample as a result of the nonradiative deexitation process that takes place following the absorption of intensity-modulated radiation. The thermal-wave propagation in a material depends on its thermal diffusivity. Traditionally this thermal property has been determined from the frequency- and time-domain behavior of the thermal wave in a fixed volume of the material. The development of the thermal wave resonant cavity (TWRC)[8–10] has introduced the possibility of measuring thermal properties by monitoring the spatial behavior of the thermal wave through cavity-length scans, instead of scanning the modulation frequency. The major advantages of cavity-length scans are the fixed noise bandwidth of the system, which improves the signal-to-noise ratio (SNR), as well as disposing with the requirement for instrumental transfer-function normalization. This kind of device has been successfully utilized to measure the thermal diffusivity of gases, particularly air,[8,9] and vapors[10] to a high degree of precision. Although it is possible to carry out thermal diffusivity measurements in the frequency domain with the TWRC, cavity scans on this device have shown further advantages in terms of precision and stability.[11] This article reports a new liquid-state compatible design of the TWRC, and its application to the measurement of the thermal diffusivity of liquids. The sensitivity of this technique is also evaluated by examining various liquid mixtures. Finally, the potential of the TWRC as an environmental sensor is demonstrated in detecting dissolved gases in liquids.

II. THEORY

According with the mathematical theory of the TWRC,[8] it has been shown that the pyroelectric signal from this device, Fig. 1, at a fixed thermal-wave oscillation frequency $f=\omega/2\pi$ is given by

$$V(L,\alpha_l,\omega)=\mathrm{Const}(\omega)\,\frac{e^{-\sigma_l L}}{1-\gamma_{ls}\gamma_{lp}e^{-2\sigma_l L}},\tag{1}$$

where V is the voltage signal across the pyroelectric detector in the open-circuit configuration, L is the cavity length, and σ_l is the complex thermal diffusion coefficient, defined by

$$\sigma_l=(1+i)\sqrt{\omega/2\alpha_l}.\tag{2}$$

Here α_l is the thermal diffusivity of the liquid sample. The interfacial thermal coefficients γ_{jk} are defined as

$$\gamma_{jk}=\frac{(1-b_{jk})}{(1+b_{jk})},\tag{3}$$

where $b_{jk}=e_j/e_k$ is a thermal coupling coefficient, the ratio of thermal effusivities of media j and k; the subscripts s, p, and l refer to the thermal-wave source (a plane metallic light absorber, such as a copper or aluminum strip; see Fig. 1), the

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[a] On leave from Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN, Av. Legaria 694, Col. Irrigación, C.P. 11500, México, D. F., México.

[b] Electronic mail: mandelis@mie.utoronto.ca

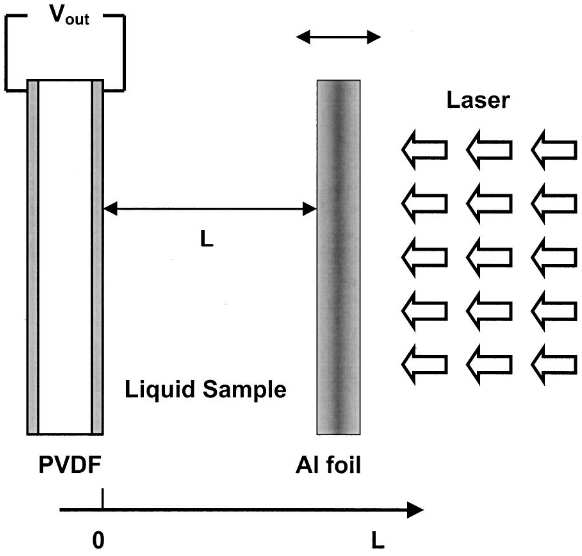

FIG. 1. Side view of a schematic of the TWRC configuration.

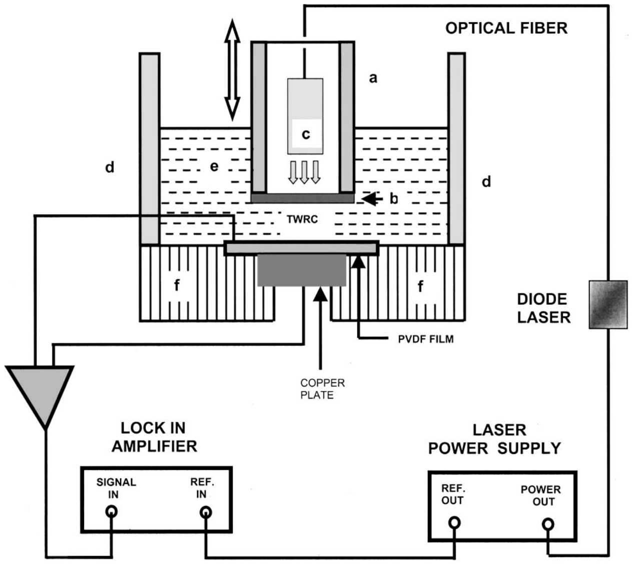

FIG. 2. Schematic representation of the experimental setup. (a) Cylindrical thermal-wave emitter head containing the aluminum foil absorber, (b), and the photothermal chamber with the optical fiber, (c); (d) container walls, (e) liquid sample filling the TWRC and (f) dielectric substrate. The bottom surface of the PVDF was attached to a copper plate. This plate worked as electric contact and support. A current-modulated laser diode was used.

pyroelectric material and the liquid sample, respectively.

The magnitude of the complex expression given in Eq. (1) can be written as

$$|V(L,\alpha_l,\omega)| \approx \mathrm{Const}(\omega)e^{-A_l L}, \tag{4}$$

where $A_l=(\pi f/\alpha_l)^{1/2}$. To obtain this expression, only the forward thermal wave has been considered. The remaining terms form an infinite series of exponential factors, exp $(-nA_lL)$, $n=2,3,\ldots$, constituting coherent thermal-wave power accumulation in the intracavity region of length L. They have been neglected compared to $n=1$. This approximation is valid, since the product of the interfacial thermal coefficients γ_{jk} and the exponential term in the denominator of Eq. (1) is $\ll 1$ (by taking water for reference, with thermal diffusivity 0.001 45 cm^2/s, this term decreases to 0.001 for a 0.03 cm cavity length). Equation (4) shows that it is possible to carry out *simple* TWRC measurements of the thermal diffusivity of liquids by monitoring the polyvinylidene fluoride (PVDF) signal as a function of the cavity length, and fitting the data to a linear equation in a semilog scale. The thermal diffusivity can be obtained from the slope fitting parameter A_l.

III. INSTRUMENTATION AND EXPERIMENT

The experimental setup used for the thermal diffusivity measurements of liquids, shown in Fig. 2, consisted of an infrared (806 μm) semiconductor laser (Opto Power Corporation), operating at powers up to 200 mW. The intensity-modulated laser light was incident on an aluminum foil (80 μm thick and 1 cm in diameter). Thermal waves were generated in this foil which was mounted on a micrometer stage. This stage allowed the cavity length, L, to vary with 10 μm step resolution. The cross-sectional design of the signal generation head (a cylinder) is also shown in Fig. 2. The bottom was sealed hermetically with a highly conducting thin metal (aluminum) foil acting as an optical-to-thermal power converter, as thermal-wave generator, and as a sealant to prevent liquids from seeping into the photothermal signal-generation chamber. The cylindrical module was dipped in various liquids as shown in Fig. 2. Thermal waves conducted across the liquid interface (‘‘intracavity region’’), reached the pyroelectric sensor, which consisted of a PVDF pyroelectric film (25 μm thickness and 1.5 cm diameter) with metal electrodes (Ni–Al) on both sides. To avoid vibrations and possible contributions of the piezoelectric response of the PVDF sensor, its bottom face was attached to a metal (copper) electrode with conductive epoxy. The pyroelectric voltage signal generated in the sensor was preamplified (ITHACO model 1201) and then sent to a lock-in amplifier (EG&G model 5210) for further amplification and demodulation.

For sensitivity analysis of the liquid-state TWRC sensor, time scans were used to observe the changes in the pyroelectric signal when small amounts of various substances were added to distilled water. The signal output with the sensor immersed in distilled water was used as the base line. The sensitivity analysis procedure was as follows: The container with the TWRC was filled with 10–13 ml of distilled water. By maintaining the cavity length constant (about 200 μm), the PVDF signal was recorded as a function of time. As soon as a steady-state signal was obtained (about 600 s), the solute substance (methanol or a saturated solution of sodium chloride in distilled water) was added. The experiments were performed at a modulation frequency of 4.35 Hz. This frequency was chosen because it combined a good SNR and a satisfactory signal amplitude in our system. The test consisted of establishing the minimum volume necessary to obtain a change in the signal base line. This procedure helped determine the sensitivity limit of the TWRC device.

The next step was to measure the thermal diffusivity of various liquid mixtures obtained by cavity length scanning on the TWRC. For comparison purposes, the thermal diffusivity of some pure substances (glycerol and ethylene glycol)

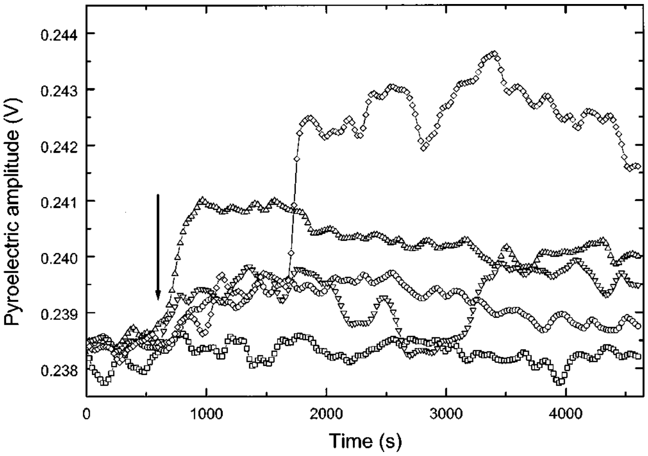

FIG. 3. PVDF signals recorded vs time for the mixtures of methanol and salt dissolved in distilled water used in this work. The correspondences between different lines and substances is as follows: (–□–) Distilled water in distilled water, (–▽–) five drops of methanol in 10 ml of distilled water, (–◇–) ten drops of methanol in 10 ml of distilled water, (–○–) one drop of saturated solution of salt in 13 ml of distilled water, and (–△–) three drops of saturated solution of salt in 10 ml of distilled water. The arrow indicates, approximately, the time at which the various substances were added to the water.

whose thermal diffusivity values have been reported in the literature were also measured. The thermal diffusivity values were obtained by fitting the experimental data to the model described in the theory. Fitting was done by the least-squares minimization method.

IV. RESULTS AND DISCUSSION

In order to ensure that base line changes were only due to the addition of a different substance in distilled water, the following experiment was conducted. Once a base line time scan for the given volume of distilled water was obtained, ten drops of the same distilled water were added. Following this experiment the container was emptied and filled again with the 10 ml of reference sample for the next time scan. This time five drops of methanol were added to the distilled water. The procedure was repeated with ten drops of methanol and three drops of a saturated solution of sodium chloride in distilled water. In order to determine the sensitivity of the sensor to smaller concentrations of salt solutions, the experiment was carried out with only one drop of saturated solution of salt in 13 ml of distilled water. All solutes were added, drop by drop, by means of a high precision syringe. The variation on the base line signal due to various concentrations of methanol and salt in distilled water is shown in Fig. 3. In this figure the line-symbol trace –□– corresponds to the base line for distilled water and the line-symbol trace –○– to the mixture obtained by the dilution of one drop of salt solution in 13 ml of distilled water (0.03% w/v). It is clear that this concentration is close to the sensitivity limit of the sensor. It was verified that there was no significant variation on the pyroelectric signal following the addition of distilled water in distilled water.

Considering that the volume of ten drops of methanol (and the same number of drops of the saturated solution of salt) were approximately 0.1 ml, it was concluded that the sensor has enough sensitivity to detect at least 0.5% (v/v) of methanol, or as low as 0.03% (m/v) of salt in distilled water. To obtain a saturated solution of salt in distilled water about 35 g of salt in 100 ml of distilled water are required.[12]

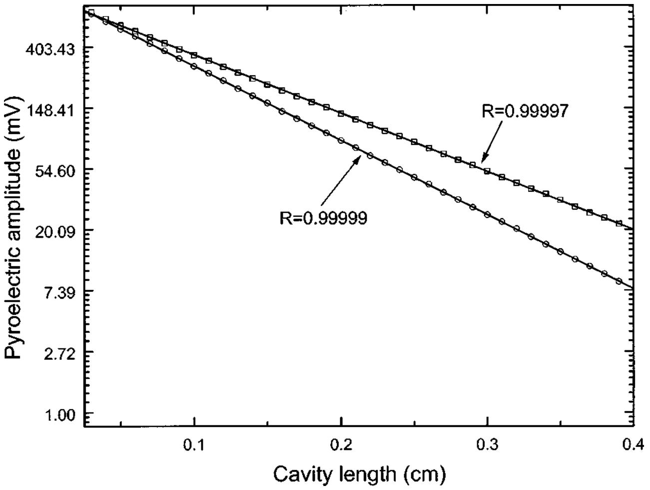

FIG. 4. Typical results of the pyroelectric signal amplitude vs relative cavity length for two liquid substances: glycerol (○) and distilled water (□). The continuous lines correspond to best fits to Eq. (4).

To complete the analysis, the thermal diffusivities of the mixtures described previously and of some other homogeneous liquid substances (distilled water, glycerol, ethylene glycol, and olive oil) were measured by performing a cavity-length scan of the TWRC device. This cavity-length scan was carried out in 10 μm steps and at a modulation frequency of 4.35 Hz. All the measurements were made at room temperature (25 °C). In Fig. 4 a typical behavior of the amplitude of the pyroelectric signal is shown versus the cavity length for two substances. The continuous lines are the best fits to Eq. (4). The resulting thermal diffusivity values measured with this technique are summarized in Table I. The thermal diffusivities reported in this table are averages over, at least, five measurements. The reported uncertainties therefore constitute the standard deviation. Despite the fact that

TABLE I. Thermal diffusivities obtained using the TWRC technique and comparison with (some) known literature values.

Liquid sample	TWRC technique $\alpha_s(\times 10^{-2}\ \mathrm{cm}^2/\mathrm{s})$	Literature $\alpha_s(\times 10^{-2}\ \mathrm{cm}^2/\mathrm{s})$	Reference
Distilled water	0.1445 ± 0.0002	0.1456 (24 °C)	16
Lake water	0.1446 ± 0.0004	⋯	⋯
Tap water	0.1448 ± 0.0003	⋯	⋯
Salt in dist. water (0.03%)	0.1442 ± 0.0003	⋯	⋯
Salt in dist. water (0.1%)	0.1439 ± 0.0004	⋯	⋯
Methanol in dist. water (0.5%)	0.1438 ± 0.0002	⋯	⋯
Methanol in dist. water (1%)	0.1425 ± 0.0004	⋯	⋯
Glycerol	0.0922 ± 0.0002	0.0929 (30 °C)	16
Ethylene glycol	0.0918 ± 0.0002	0.0939 (20 °C)	17
Olive oil	0.0881 ± 0.0004	0.145	5
		0.0799 [a]	3, 14

[a] Calculated from the specific heat and the thermal conductivity for olive oil given in Ref. 3, and the density for olive oil reported in Ref. 14.

there are other experimental channels of information (in-phase, quadrature and phase channels) from the lock-in, the amplitude channel gave a more steady signal, with a better signal to noise ratio. Moreover, the analytical expression for measuring the thermal diffusivity from the amplitude is simpler, having only one parameter (A_i), to be determined from the best fit of Eq. (4). The expressions of the other channels of information (in-phase, quadrature, and phase) are more complex and have more parameters to be fitted.

By comparing the thermal diffusivity values measured for one drop of saturated solution of sodium chloride in 13 ml of distilled water (0.03% w/v) with that of pure distilled water (0.001 442 and 0.001 445 cm^2/s, respectively), the high *precision* of the present device is evident. Variations up to the fourth significant figure are meaningful. To further examine the sensitivity of the TWRC, the thermal diffusivity of water samples from various sources was determined. These measurements were made with distilled water, tap water, and a sample of water from Lake Ontario (in Toronto). The measured values of these thermal diffusivities are also reported in Table I. It is seen that the thermal diffusivity values for the various types of water overlap with each other within the reported standard deviations. However, we believe that the small variations observed in the mean values are significant. This issue is currently being investigated more fully, using a novel signal-generation wave form recently introduced in our laboratory, which suppresses the base line of the thermal-wave signal.[13]

The thermal diffusivity value of olive oil determined with the TWRC showed significant differences (~50%) when compared to reported literature values (0.000 881 and 0.001 45 cm^2/s,[5] respectively). By taking the thermal properties reported for olive oil in Ref. 3 and a density of 0.918 g/cm^3 (Ref. 14), a thermal diffusivity value of 0.000 799 cm^2/s is estimated, in close agreement with the one reported by using the TWRC technique. It is worth pointing out that the thermal diffusivity value reported for the olive oil in Ref. 5 was obtained *directly*, by fitting the photothermal phase using the standard photopyroelectric configuration.[15] The thermal properties for the olive oil in Ref. 3 were estimated by using an inverse frequency-domain photopyroelectric configuration and by fitting the data to approximate expressions for the phase and the amplitude.

Finally, in order to evaluate the potential of the liquid TWRC sensor for monitoring gases in liquids and its possible applications in environmental analysis, the time evolution of the pyroelectric signal was monitored as a function of the evolution of CO_2 in carbonated water. To do this a can of commercial carbonated water was opened and some of the liquid was poured in a beaker flask. The liquid was left to rest for 5 min in order to allow for the initial profuse evolution of gas bubbles. After this, the container was filled with this liquid and the PVDF signal was recorded as a function of time. The result is shown in Fig. 5. In this figure the initial flat line corresponds to the distilled water base line (reference). Upon exposure to the carbonated water, a rapid signal decrease followed by an approximately linear increase due to the evolution of the gas was observed. At the end of the gas evolution a flat base line at the distilled-water level was obtained again. The increase of the signal with time for the carbonated water is a measure of the kinetics of gas occlusion from the liquid and the corresponding change on its thermal properties. These results suggest the possibility of using the TWRC in assessing content and evolution of gases (methane, CO_2, O_2, etc.) from water resources, or other biological systems, with important applications to environmental science.

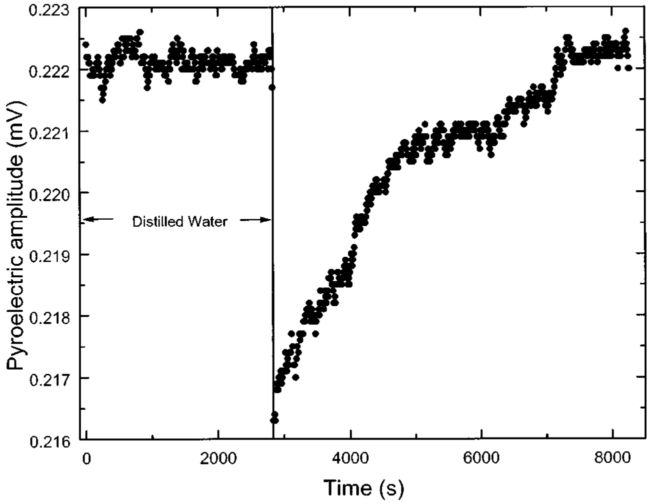

FIG. 5. Evolution of the PVDF signal vs time for carbonated water from a commercial can. The distilled water base line and the transient due to carbon dioxide occlusion are shown.

In conclusion, a novel TWRC design for thermophysical measurements in the liquid state has been demonstrated. The device was shown to be capable of measuring thermal diffusivities of liquids, including mixtures and solutions, with fourth-significant-figure precision. The high sensitivity of the liquid-state TWRC raises the possibility of monitoring the quality of a large range of liquids and liquid compounds, carrying out water pollution assessments based on thermophysical property dependence on gas concentrations (oxygen, methane) or solid-matter content, as well as measuring transient responses due to gaseous occlusions or possibly solid-matter dissolution. The limitations on the current design of this device are associated with the PVDF detector itself, specifically the temperature range of operation[18] (−20 to 80 °C) and the exclusion of aggressive liquids that could be harmful to the sensor material.

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