Monitoring of gas diffusion in air using the TWI technique: Thermal diffusivity measurements made easy

J. A. P. Lima, M. G. da Silva, M. S. O. Masssunaga, S. L. Cardoso, H. Vargas, E. Marn, and L. C. M. Miranda

Articles you may be interested in
Measurement of Thermal Diffusion in Coatings and Films by Traveling Thermal Wave Technique
AIP Conf. Proc. **1349**, 469 (2011); 10.1063/1.3605937

Self-consistent photothermal techniques: Application for measuring thermal diffusivity in vegetable oils
Rev. Sci. Instrum. **74**, 700 (2003); 10.1063/1.1517727

Monitoring of hydrocarbon vapor diffusion in air using a thermal wave interferometer
J. Appl. Phys. **91**, 5581 (2002); 10.1063/1.1465104

Thermal-wave resonator cavity design and measurements of the thermal diffusivity of liquids
Rev. Sci. Instrum. **71**, 2933 (2000); 10.1063/1.1150713

Measurement of thermal diffusivity of air using photopyroelectric interferometry
Rev. Sci. Instrum. **70**, 2372 (1999); 10.1063/1.1149765

Monitoring of gas diffusion in air using the TWI technique: Thermal diffusivity measurements made easy

J. A. P. Lima[a], M. G. da Silva, M. S. O. Massunaga, S. L. Cardoso, and H. Vargas
Universidade Estadual do Norte Fluminense, Centro de Ciência e Tecnologia, Av. Alberto Lamego 2000, Campos dos Goytacazes, RJ, 28015-620, Brazil

E. Marín
Facultad de Física, Universidad de La Habana, San Lázaro y L, Vedado 10400, Ciudad de La Habana, Cuba

L. C. M. Miranda
Instituto Nacional de Pesquisas Espaciais Av. dos Astronautas, 1758, Cx Postal 515, S.J. Campos, SP, 12201-970, Brazil

(Presented on 27 June 2002)

The thermal wave interference technique (TWI) has been explored in recent years for the investigation of the thermal and transport properties of gases and liquids. In this article we address ourselves to the quantitative understanding of the transient thermal wave interference signal of air:hydrocarbon vapor mixtures. This is the situation one faces when placing a given portion of liquid hydrocarbon inside an initially air-filled thermal wave interference. What is observed in this case is the thermal wave interference signal decay as a function of the time as a result of the change of the gas thermal diffusivity with time due to the increase of the hydrocarbon vapor concentration in air. In this article we show that value of the thermal diffusivity of the saturated mixture is readily obtained from the saturation value of the normalized signal amplitude, without the need of performing the conventional L scan. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1524008]

I. INTRODUCTION

In recent years a growing number of articles have recently applied thermal wave interference (TWI) to the investigation of the thermal properties of gases and liquids.[1-6] The TWI method consists essentially in recording the temperature fluctuation of the pyroelectric sensor as a function of the cavity gap length. This fact renders this technique well suited for gas and liquid samples analysis. One of the immediate applications of the TWI technique is to evaluate the thermal diffusivity of air:hydrocarbon vapor mixtures. In these experiments a liquid portion of the hydrocarbon under investigation is placed inside the cell in which the initially air filled TWI cavity is assembled. The hydrocarbon vapor resulting from the evaporation process diffuses into the air inside the TWI cavity. As a result of this, the thermal properties of the resulting gas mixture changes with time, following the changes of the vapor concentration in the air. This process evolves with time until the hydrocarbon vapor inside the cell reaches saturation. In this article we explore the TWI signal amplitude saturation value to determine the thermal diffusivity of air:hydrocarbon vapor mixtures.

II. METHODOLOGY

Consider the typical experimental configuration used in the conventional TWI measurements of the thermal diffusivity of, say, air:hydrocarbon mixtures, as shown in Fig. 1. The TWI experimental setup has been discussed in detail elsewhere. It consists of a temperature-controlled closed glass cell, adequately adapted for gas exchange and control of ambient parameters, in which the TWI is enclosed. At the bottom of the glass cell there is a screwed on reservoir of 30 mm diameter on which 18 ml of the liquid hydrocarbon is poured. The vapors resulting from the hydrocarbon evaporation at ambient temperature diffuse into the air cell, filling the TWI cavity with the resulting air:hydrocarbon vapor mixture. The TWI cavity of variable length is formed between a 15-μm thick Al foil and a pyroelectric sensor consisting of a 25-μm-thick polyvinyledene difluoride film with Al metalized surfaces. The surface of this Al foil facing the inner glass tube space is painted with black ink so that it acts as a light absorber. The second glass tube attached to the right glass cell end guides a nylon cylinder on top of which the pyroelectric sensor is assembled. This nylon cylinder is coupled to a translational stage so that the distance L between the Al foil and the pyroelectric sensor can be varied. The light beam from a 20 mW He–Ne laser (Meredith Instruments), modulated at 10 Hz by means of a mechanical chopper (model 650 EG&G), impinges on the black-painted outer surface of the Al foil. The thermal waves thus generated propagate back and forth between the Al foil and the pyroelectric sensor. The temperature rise at the pyroelectric surface is probed using a lock-in amplifier (model 5210 EG&G) interfaced to a personal computer. As discussed in Refs. 1–6, the method consists of measuring the temperature fluctuation at the pyroelectric sensor as a function of the gas layer thickness. To this end the pyroelectric sensor is as-

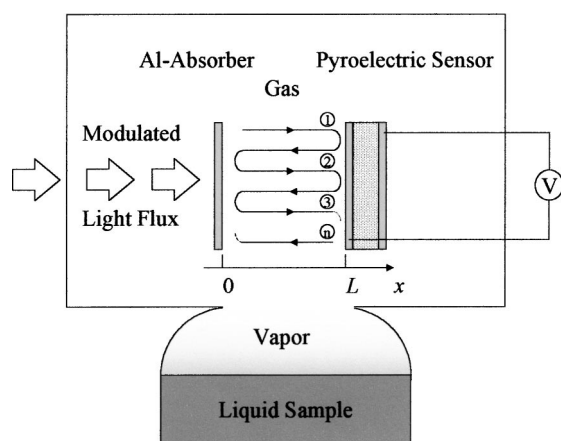[a] Electronic mail: japlima@uenf.br

842

FIG. 1. Schematic view of the TWI.

FIG. 2. Time evolution (normalized signal) of the TWI signal corresponding to different hydrocarbon samples.

sembled on a micrometer stage coupled to a computer controlled stepping motor so that the cavity length can be varied. For a step resolution of 5 μm the time required for the scanning of a 5 mm long cavity is roughly 4 min. The resulting voltage V is proportional to the average temperature rise in the pyroelectric sensor. This, in turn, is proportional to $T(L)$, so that the resulting measurable voltage may be written as

$$V = V_0 \cdot \frac{e^{-L\sigma}}{1 - \gamma e^{-2L\sigma}}, \qquad (1)$$

where V_0 is a complex function containing the frequency response of the pyroelectric sensor signal and geometrical parameters. Here, we note that the pyroelectric sensor output voltage depends explicitly on the modulation frequency and the cavity length L. The basic idea of the steady-state TWI technique consists in using a lock-in detection technique to recording the real (in-phase) and imaginary (quadrature) parts of V, or, equivalently, its amplitude and phase, as a function of the cavity length L. From the resulting dependence of the pyroelectric signal voltage on the cavity length the thermal diffusivity is obtained from two different methods. One of them is based upon the fact that the L dependence of Eq. (1) is such that their in-phase and quadrature signals exhibit maxima and minima Refs. 3–4. The other method,[5–7] consists simply in fitting the recorded signal amplitude as a function of L to Eq. (1), using standard data fitting procedures.

Consider now the typical experimental situation involved in the TWI monitoring of hydrocarbon vapor diffusion in air. In these experiments a liquid portion of the hydrocarbon under investigation is placed inside the cell in which the initially air filled TWI cavity is assembled. The hydrocarbon vapor resulting from its evaporation diffuses into the air inside the TWI cavity. As a result of this, the thermal properties of the resulting gas mixture change with time, following the changes of the vapor concentration in the air. This process evolves with time until the hydrocarbon vapor inside the cell reaches saturation. Once saturation is reached, the standard TWI (L-scan) procedure is then used to measure the thermal diffusivity of the resulting mixture.

In Fig. 2 we show a typical time evolution of the TWI signal amplitude, normalized to its initial value, for different
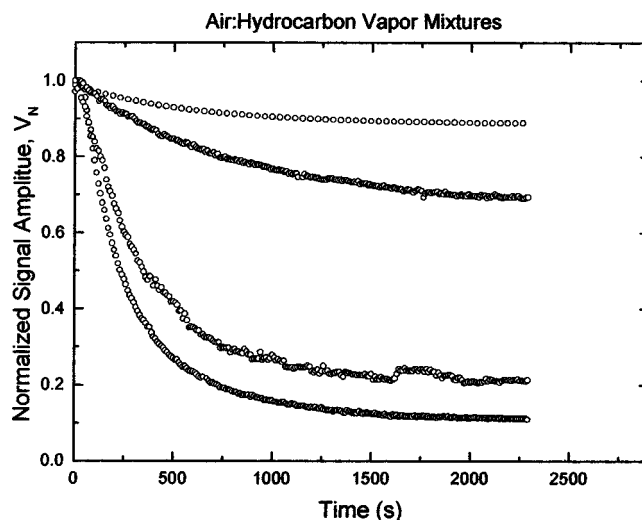
air:hydrocarbon mixtures recorded at 10 Hz modulation frequency for a fixed cavity length of $L = 2$ mm. These measurements were carried out at ambient temperature (23 °C) and pressure (760 mm Hg) with the laboratory relative humidity at 60%. The signal decay as a function of time is reflecting the changes of the gas thermal diffusivity with time as a result of the changes of the hydrocarbon vapor concentration in air until a saturated mixture is formed. For the experimental situation, the gas layer in our TWI cavity may be considered as thermally thick, that is, $L\sigma \gg 1$. Accordingly, the pyroelectric sensor output voltage, as given by Eq. (1), reduces to

$$V = V_0 \cdot e^{-L/\mu} = V_0 \cdot e^{-L(\pi f/\alpha)^{1/2}}. \qquad (2)$$

It follows from Eq. (2) that the decreasing the thermal diffusivity, as a result of the decrease of the gas thermal diffusivity due to the hydrocarbon vapor diffusion into the originally air filled cell, the TWI signal decreases exponentially. Equation (2) is the basic equation we assume to determine the
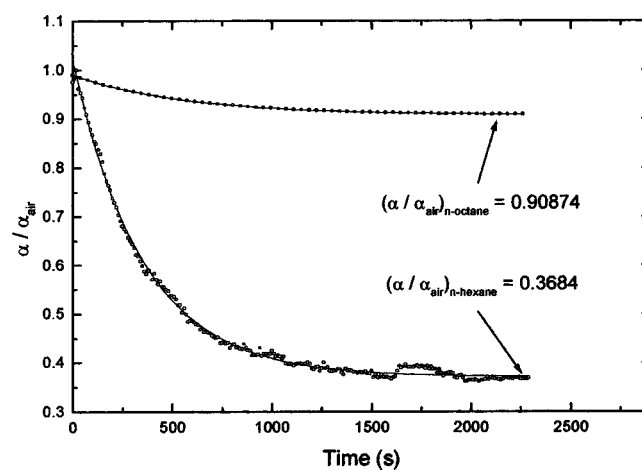

FIG. 3. Time evolution of the thermal diffusivity ratio for two air:hydrocarbon mixtures.

TABLE I. Thermal diffusivity of air:hydrocarbon mixtures at saturation, calculated by three different procedures.

Hydrocarbon	Air:hydrocarbon mixture thermal diffusivity (cm^2/s)		
	Saturation data averaging	Numerical data fitting	Cavity length scanning
n-pentane	$0.0597 \pm 2.0 \times 10^{-4}$	$0.0594 \pm 7.0 \times 10^{-5}$	0.069 ± 0.002
n-hexane	$0.0807 \pm 2.0 \times 10^{-4}$	$0.0816 \pm 2.0 \times 10^{-4}$	0.112 ± 0.002
n-heptane	$0.1652 \pm 3.0 \times 10^{-4}$	$0.1622 \pm 2.0 \times 10^{-4}$	0.148 ± 0.003
n-octane	$0.1999 \pm 4.0 \times 10^{-5}$	$0.1996 \pm 1.0 \times 10^{-6}$	0.201 ± 0.003

thermal diffusivity of our air:hydrocarbon mixtures. At $t = 0$, Eq. (2) is simply that corresponding to the air-filled cell so that the normalized voltage $V_N = V/V_{air}$:

$$V_N = \exp\{L(\pi f/\alpha_{air})^{1/2} \cdot [1 - (\alpha_{air}/\alpha)^{1/2}]\}. \quad (3)$$

Now, the factor $L(\pi f/\alpha_{air})^{1/2}$ in the exponential is a well-known value. For instance, for the current experimental situation in which $L = 2$ mm and $f = 10$ Hz, using the room temperature value of the air thermal diffusivity, namely, $\alpha_{air} = 0.22$ cm^2/s, it is equal to 2.39. Equation (3) can be straightforwardly used to write the thermal diffusivity as

$$\frac{\alpha}{\alpha_{air}} = \frac{1}{\left[1 - \dfrac{\ln(V_N)}{L(\pi f/\alpha_{air})^{1/2}}\right]^2}. \quad (4)$$

Equation (4) provides us with a simple relationship between the thermal diffusivity of the gas mixture and the normalized TWI signal amplitude. In particular, we note that the value of the thermal diffusivity of the saturated mixture is readily obtained from the saturation value of normalized signal amplitude, without the need of performing the conventional L scan, as in the previous articles.[1–6] The use of this new procedure to evaluate the thermal diffusivity of gas mixtures is the point we draw our attention to the remaining.

In Fig. 3, we present the time evolution of the thermal diffusivity ratio data for two of our typical air:hydrocarbon mixtures. To find the saturation value of the thermal diffusivity ratio, α/α_{air}, we have adopted two procedures; a numerical one, and another one based upon the averaging of the last five data points. The numerical evaluation of the saturation value was carried out by fitting the time evolution of the thermal diffusivity ratio to an exponential decay, using the Origin® 5.0 software. The corresponding saturation values we found from this procedure were $0.371\,12 \pm 0.000\,89$ and $0.907\,18 \pm 0.000\,006$, for *n*-hexane and *n*-octane, respectively. Substituting the room temperature air thermal diffu-

sivity by $\alpha_{air} = 0.22$ cm^2/s, we then get the following values for the thermal diffusivity of the air:*n*-hexane and air:*n*-octane mixtures, respectively: $0.0816 \pm 0.000\,02$ cm^2/s and $0.1996 \pm 0.000\,001$ cm^2/s. In contrast, the averaging of the last five data points yielded the following saturation values for the thermal diffusivity ratio: $0.3684 \pm 0.000\,006$ and $0.908\,74 \pm 0.000\,006$, for the case of *n*-hexane and *n*-octane, respectively. The corresponding values of the air mixtures thermal diffusivities were 0.0816 ± 0.0002 cm^2/s and $0.1996 \pm 0.000\,001$ cm^2/s, for the case of air:*n*-hexane and air:*n*-octane mixtures, respectively. In Table I we summarize the results that we got for the thermal diffusivity of our air:hydrocarbon mixtures using both approaches.

III. CONCLUSIONS

The difference in the values of the air:hydrocarbon mixtures thermal diffusivity as obtained by the currently proposed approach and the conventional L-scan method may be summarized as follows. For *n*-octane, there is no difference between the two methods. For *n*-pentane, *n*-hexane, and *n*-heptane the thermal diffusivities differ by 17%, 37%, and 9%, respectively. The main discrepancies appeared in the cases where the experimental data exhibited somewhat larger fluctuations, namely, the cases of *n*-pentane and *n*-hexane.

[1] C. A. Bennett and R. R. Patty, Appl. Opt. **21**, 49 (1982).
[2] J. Shen and A. Mandelis, Rev. Sci. Instrum. **66**, 4999 (1995).
[3] J. Shen, A. Mandelis, and B. D. Aloysius, Int. J. Thermophys. **17**, 1241 (1996).
[4] J. Shen, A. Mandelis, and T. Ashe, Int. J. Thermophys. **19**, 579 (1998).
[5] J. A. P. Lima *et al.*, Rev. Sci. Instrum. **71**, 2928 (2000).
[6] J. A. P. Lima, E. Marin, M. G. Silva, M. S. Sthel, S. L. Cardoso, H. Vargas, and L. C. M. Miranda, Rev. Sci. Instrum. **72**, 1580 (2001).
[7] J. A. P. Lima *et al.*, Meas. Sci. Technol. **11**, 1522 (2000).