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Photothermal techniques applied to thermophysical properties measurements (plenary)

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In this article, we present a bird’s eye view of applications of photothermal techniques for evaluation of the thermal properties of different materials. This is followed by the presentation of specific techniques for direct measurements of thermal diffusivity and thermal effusivity and indirect measurements of heat capacity. The presentation finishes by discussing the use of alternative photothermal techniques for the investigation of thermal and transport properties of gases and liquids. © 2003 American Institute of Physics. [DOI: 10.1063/1.1519682]

I. INTRODUCTION

In the last 25 years we have witnessed great expansion and development of photothermal techniques for the nondestructive characterization of thermal, optical and structural properties of different materials. In this article we will be focusing on the application of photothermal methods for the thermal characterization of liquids, solids, and gases. Information on the thermophysical properties of solids, liquids, and gases is of great importance for engineering design and science as well as for environmental monitoring.

In spite of the large demand for thermophysical characterization of solids, liquids, and gases, widely used conventional techniques are, in some cases, unsuitable for many materials and conditions. The present review article intends to discuss several aspects regarding photothermal techniques for thermophysical characterization of solids, liquids, and gases. We will focus our attention principally on recent photothermal techniques and their applications. For a more detailed discussion we refer the reader to the existing review articles published in the literature and the books by Rosencwaig, Almond, and Patel.

The quantity that measures the rate of heat diffusion in a sample is the thermal diffusivity, \( \alpha \), whereas measurement of the heat exchange rate or the thermal impedance for heat exchange of a given material is essentially determined by its thermal effusivity, \( e \). Thermal diffusivity and thermal effusivity are defined by

\[
\alpha = k / \rho c, \quad e = (k \rho c)^{1/2},
\]

where \( k \) is the thermal conductivity, \( c \) is the heat capacity, and \( \rho \) is the mass density. Knowing \( e \) and \( \alpha \), sample thermal conductivity \( k \) and heat capacity per unit volume \( \rho c \) can be obtained from the relations

\[
k = e (\alpha)^{1/2} \quad \text{and} \quad \rho c = e (\alpha)^{1/2}.
\]

II. THERMAL PROPERTIES MEASUREMENTS

There are several photoacoustic and photothermal methods devoted to determination of the thermal properties of solids, liquids, and gases. These techniques can be classified into two main categories, one in which the sample is in contact with the detection system, and another one involving a remote detection system. Remote, noncontact, techniques are especially adequate in situations where the sample is exposed to severe environmental conditions. In what follows we present a brief summary of the most widely used techniques.

A. Photoacoustic (PA) technique

Photoacoustic (PA) detection is probably the best example of a contact technique. The general idea in measuring the thermal diffusivity is based upon the evaluation of the phase change or the signal attenuation as a heat pulse travels through a sample. Usually, this is carried out by depositing modulated heat at a given sample surface and probing the sample temperature at the opposite surface. In conventional photoacoustic detection this is done by shining a modulated light beam in a previously blackened surface, and measuring the amplitude and phase of the resulting temperature fluctuation on the opposite surface, as a function of the modulation frequency. In contrast to this signal attenuation type, a “time-of-flight” type of experiment may be also envisaged. In this type of experiment, carried out at a single modulation frequency, one tries to directly access the sample heat diffusion time. This is done by carrying out a simultaneous illumination of the sample surfaces and measuring the phase difference between the front and rear illumination signals.

Thermal diffusivity and thermal effusivity are key parameters affecting heat transport and exchange capabilities in a wide range of applications involving materials performance.
This is essentially what Pessoa et al. have proposed and demonstrated in their phase-lag method. The usefulness of this single modulation frequency PA method for measuring the thermal diffusivity of solid samples is described in detail in Ref. 6. It consists of measuring the relative phase lag $\Delta \phi = \phi_F - \phi_R$ at a single modulation frequency between rear-surface illumination ($R$) and surface illumination ($F$). This method, called the two-beam phase lag method, is an alternative to the one proposed by Yaza and Amer. Figure 1 shows the typical schematic arrangement for two-beam photoacoustic measurement of the thermal diffusivity. This method has an additional advantage that is valid regardless of whether the sample is thermally thick ($l_a > 1$) or thermally thin ($l_a < 1$). Several authors have directly compared the rear and front surface signals with simultaneous excitation, the main interesting feature of the latter arrangement is that it avoids the buckling of the samples and the spurious signals associated with it.

Apart from the measurement of the thermal diffusivity, a great flexibility of the photoacoustic detection system is that it also allows us to carry on both thermal effusivity measurements and dynamical studies. This is usually done in a front (inner) illumination configuration in which an aluminum foil closes the PA cell and acts as the light absorber. The sample under investigation is then placed in close contact with this aluminum foil. We refer the reader to Refs. 10 and 11 in which the use of PA detection for thermal effusivity evaluation is discussed in detail: Finally, we should mention that apart from being extensively used for evaluation of thermal diffusivity and effusivity, the PA technique has also been applied to the investigation of several transport phenomena and phase transition studies in solid samples.

**B. Open-photoacoustic-cell (OPC) technique**

An improved gas-microphone detection technique especially suitable for measuring thermal diffusivity in attenuation-type measurement is that of the so-called open-photoacoustic-cell (OPC) technique. The schematic cross section of the OPC configuration is shown in Fig. 2. This open-cell configuration is an attractive and simple technique presenting some advantages over conventional closed-cell detection. The use of a minimal gas chamber ensures an enhanced signal-to-noise ratio, and, consequently, higher accuracy in the value of $\alpha$, and offers greater adaptability to practical restrictions imposed by experimental system requirements, especially when minimal preparation is required. The OPC technique is widely used for several applications aiming at the thermal characterization of a great variety of samples such as instant corn dry masa flour, wood, two-layer systems, semiconductors, food products, polymers, clays, and so on. In Fig. 3 we show a typical application of the OPC method for the characterization of kaolinite clays. The overall behavior of the thermal diffusivity of the heat-treated clay samples was explained by these authors with the help of both crystallinity and porosity measurements. The sharp increase in the thermal diffusivity between 800 and 950°C was attributed to the observed sharp increase in the sample crystallinity in this temperature range. On further increasing the heat treatment temperature the sample porosity decreases considerably at the same time that the sample density increases. As a result, the thermal diffusivity decreases.

**C. Optical beam deflection technique**

The optical beam deflection, or “mirage” effect technique was first introduced in the early 1980s by Boccara, Fournier, and Baldoz and subsequently developed by Aamodt and Murphy and by Jackson et al. This remote technique is well suited for investigation of the thermo-optical properties and nondestructive evaluation of solid samples, especially in severe environmental conditions. In a

![FIG. 1. Schematic arrangement for two-beam photoacoustic measurement of thermal diffusivity.](image1)

![FIG. 2. Cross section of the open-photoacoustic cell using the front air chamber of a common electret microphone as the transducer medium.](image2)

![FIG. 3. Thermal diffusivity of heat-treated kaolinite clay as determined by the open-photoacoustic cell.](image3)
D. Photopyroelectric (PPE) technique

The photopyroelectric method (PPE) is another example of a contact photothermal technique that has been widely used for the optical and thermal characterization of different materials. This technique consists essentially of using a pyroelectric sensor in close contact with the sample under investigation. A modulated light beam is shown on the sample, causing its temperature to fluctuate as a result of the light into heat conversion following the absorption of light. As the temperature fluctuation reaches the pyroelectric sensor–sample interface the pyroelectric sensor senses an electric current carrying information on the structure as well as the thermal and optical properties of the sample. A variant configuration of the standard photopyroelectric method, well suited for thermal effusivity measurements, is the so-called inverse photopyroelectric technique (IPPE). The inverse configuration was introduced by Chirtoc and co-workers. Figure 5 shows a typical inverse photopyroelectric experimental setup. In this configuration the light impinges directly on the surface of the pyroelectric transducer and the substrate is substituted by the sample. The measurement of the thermal effusivity by the IPPE technique has been applied to binary liquid systems as a way to determine the relative concentrations of the components as in the case of the ethanol–water mixtures presented by Chirtoc and co-workers. Application of the IPPE technique for measurement of thermal effusivity of margarines, cultured milk, and pastry materials in general is a typical example of the potential of this technique for foodstuff quality control. Direct determination of the thermal conductivity of solids and liquids at very low frequencies using the IPPE technique was recently discussed by Thoen and co-workers.

E. Thermal lens (TL) technique

The thermal lens (TL) technique has proven to be a valuable method to study the thermophysical properties of transparent materials, such as, glasses, liquid crystals, and polymers. It allows determination of the thermal diffusivity and thermal conductivity, the temperature coefficient of the optical path length, optical absorption coefficient, and fluorescence quantum efficiency. Since this is a remote technique, measurements of samples placed inside a harsh environment present no extra difficulties. This is an important aspect if one wants to carry on thermo-optical properties...
measurements at high temperatures where the sample is placed inside a furnace. Extensive use of this technique for investigation of the thermal and optical properties of different materials has been made by Baesso and co-workers. We refer the reader to Refs. 43–46, in which application of the TL technique to glasses, polymers, liquid crystals, as well as foodstuff, is discussed in detail.

F. Thermal wave interferometry (TWI)

The use of different photothermal techniques for gases and liquids, which are of considerable interest in environmental studies and development of new monitoring devices, has been limited to only a few applications.47,48 In the case of gases, most of the investigations have used photoacoustic detection, whereas most of the works with liquids so far have used photoacoustic detection and remote photothermal refractive index modulation techniques, such as the photothermal phase shift technique, thermal lens, and the photothermal optical beam deflection. An alternative photothermal technique for measuring the thermal properties of gases was first discussed by Bennet and Patty49 and later explored by Shen and Mandelis,50–53 who succeeded in demonstrating the feasibility of the pyroelectric detection of thermal wave propagating across an air gap between a pyroelectric sensor and another material acting as the source of thermal waves. These authors showed that the thermal diffusivity of air could be measured with very good accuracy using this configuration for detection of thermal waves. This technique was first named the thermal wave resonant cavity (TWRC) and later denoted thermal wave interferometry (TWI) by other authors.54

More recently, we have designed54 a closed TWI cell suitable for gas exchange and control of ambient parameters. A schematic view of the thermal wave interferometer is shown in Fig. 6. A cavity of variable length is formed between a thin Al foil and a pyroelectric (PVDF) temperature sensor. An intensity modulated light beam impinges on the black-painted external face of the Al foil, which acts as a light absorber. As a result of the absorption of the modulated incident light, the Al foil temperature fluctuates periodically, thereby launching a thermal wave into the gas-filled cavity. On striking the gas–Al and gas–sensor boundaries, the wave will be partially reflected and interference between the reflected and incident wave trains will set in. The temperature distribution \( T(x,t) \) within the gas region along the longitudinal \( x \) coordinate following the periodical heating of the Al foil can be obtained by solving the heat diffusion equation with the boundary condition that the heat generated at the solid surface by light absorption is dissipated in the gas by diffusion. The solution of the physical interest for application in photothermal techniques is the one related to the time-dependent component of the light flux.

As discussed in Refs. 50–54, the pyroelectric signal is proportional to the temperature fluctuation at the sample–PVDF interface at \( x = L \). It can be shown that the temperature fluctuation at \( x = L \) may be written as

\[
T(L) = T_0 e^{-\sigma L} \frac{1 - ye^{-\gamma \sigma x}}{1 - ye^{-2\gamma \sigma x}},
\]

where \( \sigma = (1 + j)/\mu \) is the complex thermal wave number, \( \mu = (\pi f/\alpha)^{1/2} \) is the thermal diffusion length, and \( \gamma \) is a thermal impedance parameter involving the thermal wave reflection coefficients at both \( x = 0 \) and \( x = L \) interfaces. The basic principle for the TWI measurement of the thermal diffusivity is evident from the above expression for the PVDF surface temperature fluctuation; it consists essentially in recording the pyroelectric signal as a function of TWI cell length \( L \).

The analytical potentialities of the proposed TWI method have been demonstrated in Ref. 54, and later extended in Ref. 55, in which a series of kinetic measurements of gas mixtures consisting of hydrocarbon vapor–air mixtures has been presented. These experiments consisted essen-

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**FIG. 6.** Schematic view of the thermal wave interferometer.

**FIG. 7.** Time evolution of the TWI signal of air–hydrocarbon vapor mixtures.
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tially in pouring some amount of liquid hydrocarbons at the bottom reservoir of the TWI cell depicted in Fig. 6 and recording the pyroelectric signal amplitude, at 10 Hz modulation frequency, as a function of time until the cell was completely saturated with the hydrocarbon mixture. In Fig. 7 we show the typical data of these transient measurements. Once saturation is reached, the TWI signal is then recorded as a function of cell length \( L \), and the resulting data are then fitted to the theoretical expression derived from Eq. (3). In this way, the thermal diffusivity of the saturated air–hydrocarbon vapor mixture is obtained. The results of these transient experiments are shown in Fig. 7. For a more-detailed discussion of the measured thermal diffusivity values, we refer the reader to Ref. 54.

The above TWI technique, with small cell design modifications, has also been explored for measuring the thermal diffusivity of binary gas mixtures and different liquid and liquid mixture samples. We refer the reader to Refs. 56–59, where a detailed discussion of these applications of the TWI technique are described.

Finally, we should mention an interesting and practical application of the TWI technique regarding the monitoring of commercial gasoline fuels on which we have recently reported. The basic idea is that outlined above for air–hydrocarbon vapors. The only difference is that instead of placing pure hydrocarbon samples in the bottom reservoir we have poured it on commercial gasoline collected from different gas stations. These fuels have previously undergone standard octane rating tests yielding the characteristic fuel quality indicators known as the research octane number (RON), motor octane number (MON), and pump octane number (PON). These characteristic fuel quality control numbers, together with the other standard chemical tests, where used to classify the different gasolines as typical, nontypical and nonconforming. Typical and nontypical gasolines are the ones that are acceptable for sale. Gasolines classified as nonconforming are the ones that have been somehow adulterated. From transient data similar to those shown in Fig. 7, we have determined the characteristic decay time, \( \tau \), for each fuel, whereas from the saturated mixture regime we have determined the corresponding thermal diffusivity, as indicated above. In Fig. 8 we show the relationship between decay time and thermal diffusivity for several fuel samples collected at different gas stations. Figure 8 indicates that in the \( \tau, \alpha \) space there seems to exist a square region in which the nonadulterated fuels are supposed to fit in. This promising result is current being extensively explored in order to check whether it may be, in fact, an alternative fuel quality control method or not.

### III. CONCLUSIONS

The field of photothermal science has partially fulfilled some of its promises since its rediscovery almost 30 years ago by Rosencwaig. In the case of solids, its potential as a research and analytical tool seems not to be fully explored and each year new routes for developments are being opened up. Some of these developments are moving closer to industrial applications as testing and quality control techniques. Already, some of these photothermal techniques have been tested in the microelectronics and foodstuff industries. The case of the more recent TWI technique deserves special attention.

In the case of gases and gas mixtures, the TWI technique seems to be an extremely attractive technique for gas characterization. In the case of liquids, the TWI technique has also been demonstrated to be straightforwardly used to perform routine, accurate measurements of the thermal properties of liquids. This is an interesting result especially for the case of liquid mixtures. There is an expanding demand for reliable and precise measurements of the basic properties of a wide range of liquid mixtures in use today or generated by nature and modern industry the knowledge of which can lead scientists to a better understanding of the processes and phenomena governing their production.

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