Application of the thermal wave resonator cavity sensor to the measurement of the thermal diffusivity in air contaminated with vapours of different liquid hydrocarbons

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A measuring device based in thermal wave interference in a cavity is described. It was tested measuring the air thermal diffusivity with good accuracy. The device is further applied to the measurement of the thermal diffusivity of air mixed with the vapors of liquid hydrocarbons of the paraffin family (n-pentane, n-hexane and n-heptane). Our results illustrate how the diffusion of their vapors in air can be monitored by a simple method and how the thermal properties (i.e. the thermal diffusivity) of the gas mixture change as a result of this mechanism. Based in the former results a device suitable for in field measurements is predicted.

Introduction

Despite the increasing number of techniques and methods suitable for materials characterization, their applications to gases have been limited to a few examples, mainly spectroscopic in nature. These traditional techniques are based on the absorption of certain characteristic laser lines by gas atoms or molecules, typically in the infrared range of the electromagnetic spectrum, thus leading to the use of expensive signal generation and detection schemes used mainly for low concentration measurements [1]. As there is a well known expanding demand for reliable and precise measurement of basic properties of gases and as there exist some lack of information related to their thermal properties, such as thermal diffusivity [2], we discuss an alternative method for measurement of this parameter in gas mixtures. It is based on the phenomena of thermal wave interference. The method is another application of photothermal (PT) techniques [3], a field that has experienced enormous expansion in many directions as a result of its general applicability and adaptability to several areas of research. It was proposed recently by Shen and Mandelis [4], who's succeeded to measuring the air thermal diffusivity with high accuracy by detecting the temperature resulting from the propagation of a thermal wave through the air filling a cavity formed between a PVDF pyroelectric sensor and an Al foil, namely a Thermal Wave Resonator Cavity (TWRC). In the present paper, the method is applied to measure the thermal diffusivity of air saturated with different concentrations of vapors of different liquid hydrocarbons of the paraffin family.

Experimental

The instrument designed in our laboratories consists of a chamber of total volume 210 cm^3, containing the gas under investigation, in which a TWRC [3] is enclosed. This is shown in Fig. 1. The cavity, of variable length L, is formed between a 15 μm thick Al foil and a pyroelectric temperature sensor (a 25 μm thick Polyvinyledene Fluoride (PVDF) film with Al-coated surfaces). Light chopped at a frequency f illuminates the external surface of the Al foil, which is painted black and acts as a light absorber. The
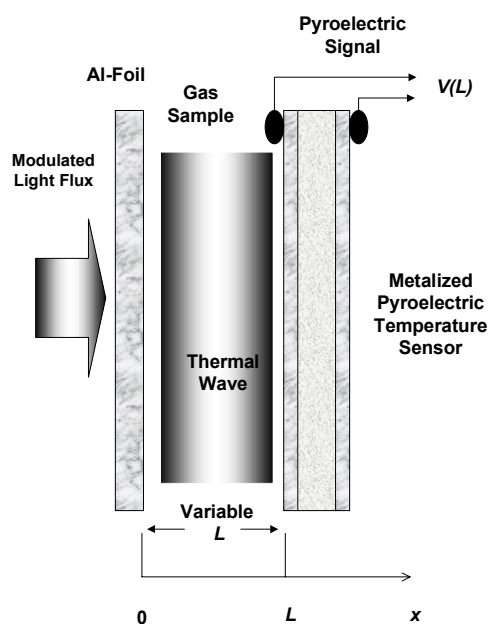

Fig. 1. Schematic view of the TWRC sensor.

foil temperature therefore oscillates periodically and generates a thermal wave that diffuses through the gas filling the cavity and causes a temperature fluctuation at the surface of the pyroelectric detector.

The temperature distribution $T(x,t)$ within the gas region along the longitudinal x coordinate follows the periodic heating of the Al foil and can be obtained by solving the heat diffusion equation with the boundary condition that light energy is totally absorbed at the foil surface. The solution of physical interest for applications in PT techniques is related to the time-dependent

component of the light flux. If we take this component, the general solution of the problem is referred to as a thermal wave [3], $\mu_g=(2\alpha_g/w)^{-1/2}$ is the thermal diffusion length, $i=(-1)^{1/2}$ and $w=2\pi f$ is the angular frequency.

The thermal wave model assumes reflection at interfaces [6,8]. If we consider that a plane wave propagates from a medium 1 to a medium 2, then for normal incidence the reflection coefficient at a boundary between the two media is given by $R_{12}=(1-b)/(1+b)$, where $b=\varepsilon_2/\varepsilon_1$ and ε represents the thermal effusivity. This parameter may be regarded as a measure of the thermal mismatch between the two media.

Consider now the propagation of a thermal wave through a gas (denoted by g) contained between the Al foil and the PVDF sensor. Once striking the gas-Al and gas-sensor boundaries, the wave will be partially reflected and interference between the reflected and incident wave trains takes place. The temperature $T(L)$ at the surface $x=L$ is obtained by summing the intensities of all the waves arriving at this point. Defining a parameter $\gamma=R_{gA}R_{gP}$, after some mathematical manipulation we obtain:

$$T(L) = \frac{T_0\,exp(-qL)}{1-\gamma\,exp(-2qL)} \quad , \tag{1}$$

where the indices A and P stand for the Al foil and the PDVF sensor respectively; T_o is the temperature at the surface of the Al foil. The temperature oscillation at the PVDF sensor induces an electric field between its opposite surfaces. The resulting voltage V can be written as

$$V=V_oT(L) \quad , \tag{2}$$

where V_0 is a complex function related to the frequency response of the sensor and geometrical parameters characterizing the whole measurement system. The real (in-Phase) and imaginary (Quadrature) parts of V are measured as function of cavity length by phase sensitive detection using a model 5210 EG&G lock-in amplifier interfaced with a personal computer. The sensor side of the cavity was assembled on a micrometer stage which allows a 4 mm variation in cavity length with a step resolution of 10 μm. The light source employed was a 20 mW Meredith Instruments He-Ne laser, modulated at 10 Hz with a model 650 EG&G chopper. A least-squares fit of Eq. (2) to the experimental data was performed, taking T_0, γ and μ_g as adjustable parameters. This allows the measurement of α with remarkable reliability for different gases or gas mixtures. It is worth noticing that although at a first glance the effusivity could be extracted from the parameter γ, the adjusted value of this factor can differ from the theoretically one due to eventual differences in the geometry of cavity [5,6]. The

characterized by a complex wave number $q=(iw/\alpha_g)^{1/2}=(1+i)/\mu_g$, where α_g is the gas thermal diffusivity, uncertainty in the zero thickness of the cavity [6] was also taking into account by us in the fitting procedure considering the existence of a systematic error in the L value.

The device was first tested performing measurements in air at a temperature of 20°C and atmospheric pressure. Fig. 2a shows the In-Phase (In-P) signal as a function of cavity length (L), whereas fig 2b presents the measured Quadrature (Q) signal vs. L. The solid and dashed lines correspond respectively to the best fit of the experimental data to the real and imaginary parts of eq. (2). The value obtained, of $\alpha = (0.244 \pm 0.002)\,cm^2/s$ was in very good agreement with values reported in the literature [2].

Results and discussion

To further demonstrate the analytical potential of the method we have performed experiments with gas mixtures of hydrocarbon vapors in air. We used spectroscopic grade (99% purity) n-pentane, n-hexane and n-heptane. The possibility to identify hydrocarbons from such a measurement was pointed out for a first time by Mandelis and Shen [7]. In our present work the experimental procedure was the following. At the bottom of the cell, a recipient containing approximately 20 cm^3 of a liquid sample was screwed. The magnitude of the TWRC signal was then recorded as a function of time while the vapor resulting from evaporation of the hydrocarbon sample diffused through the air filling the cell. The thermal diffusivity of the gas mixture changes continuously as a consequence of the increase in concentration caused by diffusion of vapor molecules in the air. When saturation is reached, i.e. the vapor pressure of both components (air and hydrocarbons vapors) equals, the thermal diffusivity of the mixture takes a constant equilibrium value.

We have measured the time evolution of the signal amplitude for several concentrations of hydrocarbon vapor in air using a fixed cavity length of $L=2mm$. Different concentrations of each hydrocarbon vapor were obtained varying the temperature of the system using a Neslab RTE-111 constant temperature bath.

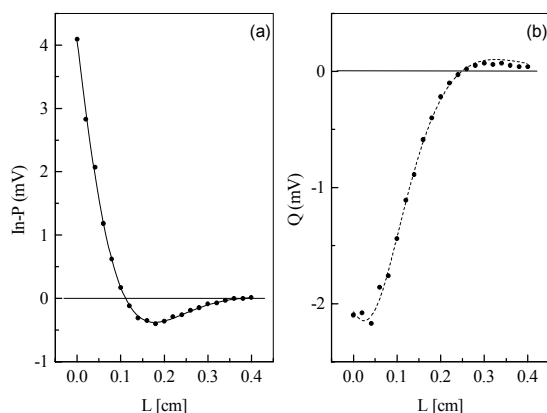This temperature dependence of the vapor concentration

Fig. 2. In-Phase and Quadrature Signals for air. The solid and dashed lines are the best fit of the data to the real and imaginary parts of Eq. (2) respectively.
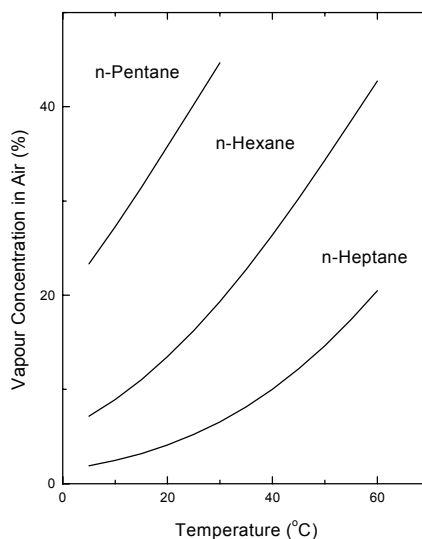
Fig. 3. Calculated hydrocarbon vapors concentration at equilibrium in air as a function of temperature.

in air is shown in Fig 3 and was calculated using literature values [8] of boiling temperature and vaporization enthalpy and well-established formulae.

Typical signal curves as the function of time are represented in Fig. 4. The solid lines represent the best fit to an exponential decay law. We will come to this point later. In each case, as soon as the signal stopped its time evolution (i.e. when saturation is reached), we performed measurements of the signal as a function of the cavity length. The values of thermal diffusivity of the gas mixtures were obtained using the fitting procedure described for air in the preceding section. We plot these values in Fig. 5 as a function of temperature, where the solid lines represent the result of a linear curve fit. The corresponding experimental errors were estimated in about 1%. Our results illustrate how the diffusion of their vapors in air can be monitored by a simple method and how the thermal properties (i.e. the thermal diffusivity) of the gas mixture change as a result of this mechanism. The results indicate that, at a given temperature α is unique for each mixture. For each temperature value we observe that the thermal diffusivity of the mixture corresponding to the n-heptane hydrocarbon vapor has a higher value than those corresponding to the other vapors. This behavior could be explained considering that the measured thermal diffusivity is in fact an effective value for the gas mixture. The concentration of n-heptane vapor in the cell is lower than those of the other ones, as shown in Fig. 3.

the present case of binary mixtures, these parameters are not only strongly correlated, but also that by measuring, say, τ in an unknown binary mixture we can determine the corresponding value of α, and vice-versa.

In conclusion, we have proposed a device suitable to the development of gas analyzers, based on a Thermal Wave Resonator Cavity and on a phenomenological model of thermal wave interference. The main advantage of the technique is that it can be applied to the characterization of both light absorbing gases and optically transparent gases. This can be accomplished employing a very simple apparatus of reduced cost, particularly when compared to spectroscopic techniques. For example, the heat source does not need to be a laser, but can be replace by a radiator driven by an oscillating voltage, so that a compact equipment suitable for field measurements can be devised.

Fig. 5. Measured Thermal Diffusivity as a function of temperature in the liquid phase for various hydrocarbon vapours-air mixtures
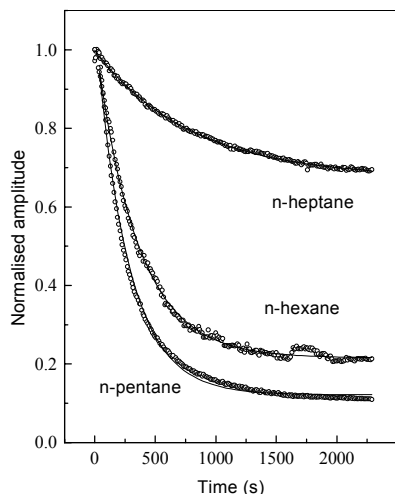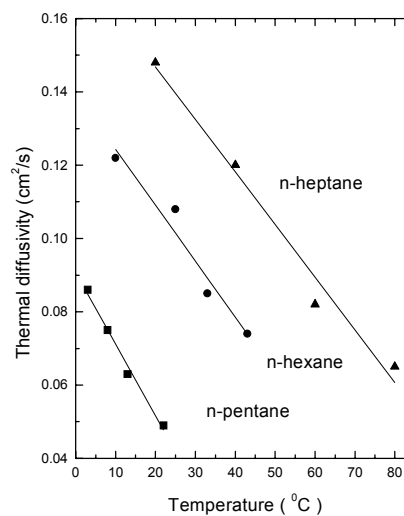

Fig. 4. Normalised amplitude as a function of time for different samples at room temperature

Therefore the measured thermal diffusivity in this case will be closer to that of the air. Conversely, at the same temperature, the vapor concentration in air for the other hydrocarbons is higher, leading to a more pronounced variation in thermal diffusivity as compared to values for the air.

Note that the results presented in Fig. 5 show a behavior analogous to that of the dependence of the vapor pressures from the temperature for the different liquid hydrocarbons. The later dependence is expressed in a well known Reid Diagrams. Therefore, in terms of practical applications, immediate use of our results may be the monitoring of hydrocarbon leakage from storage tanks and the evaluation of the quality of automotive fuels. One should tabulate the characteristic curves of the several air-hydrocarbon mixtures, at different concentrations, and compare the corresponding α value obtained from TWRC signal for the gas sample under test with the corresponding tabulated values.

Finally, in Fig. 6 we plot the correlation between the measured values of α and the decay times (τ) resulting from the fits represented in Fig. 3. The values of τ were estimated within a 10% error. This is an interesting result telling us that, at least for
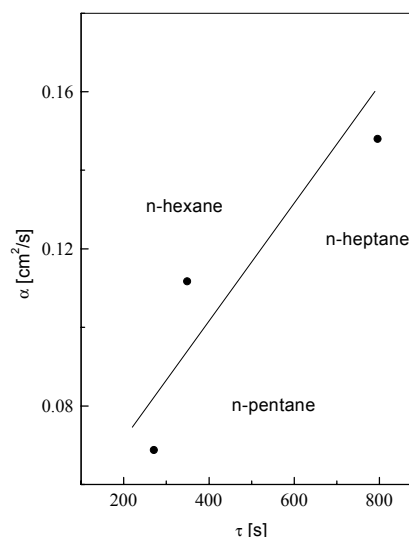

Fig. 6. Thermal diffusivity as a function of the decay times. The solid line has only visualization purposes.

The results presented here open the possibility to perform routine, accurate measurements of thermal diffusivity of gases and, consequently, to monitor environmental air

pollution-related phenomena. Furthermore, a wide range of applications, such as fuel quality control can also be envisaged. The proposed technique may indeed become a quite useful method for the investigation of the thermal properties of binary gas mixtures. We can express the mixture thermal diffusivity dependence on the relative concentration in terms of the thermal properties of the constituent gases combining the appropriate effective thermal conductivity expression with those for the heat capacity per unit volume of the mixture. Due to the complexity of theoretical expressions predicted by the kinetic theory, empirical expressions are often used to analyze the experimental data. Amongst these, the most widely used are the so-called geometric mean model [9] and the logarithm mixing [10] ones. As discussed in [10] the later model is more adequate for random distributions of two-phase systems. Then, from the measured thermal diffusivity value of a mixture as a function of the components relative composition, their thermal properties can be estimated by fitting to the theoretical model. This work is a new step in demonstrating the possibilities of the TWRC technique to perform the characterization and study of gases.

Acknowledgements

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