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On the optimization of experimental parameters in photopyroelectric investigation of thermal diffusivity of solids

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Abstract

In this paper, the possibility of optimizing the experimental conditions for a correct photopyroelectric evaluation of the thermal diffusivity of solid samples is studied. For this purpose, a glassy carbon sample, with known thermal properties, was selected as test material and two types of techniques were applied in order to get the value of its thermal diffusivity: (i) the photopyroelectric calorimetry in back detection configuration and (ii) the infrared thermography. Assuming that the values of thermal diffusivity obtained by thermography are correct (a non-contact technique), we studied how to eliminate the underestimation (due to the presence of the coupling fluid) of the results in the back photopyroelectric calorimetry investigations. Experiments with different types of coupling fluids and numerical simulations were performed in order to evaluate the influence of the coupling fluid on the value of the thermal diffusivity. The conclusion is that a proper choice of the type of coupling fluid and some improvements performed in the experimental design of the photopyroelectric calorimetry detection cell (with the purpose of reducing the coupling fluid's thickness), can eliminate the difference between the results obtained with the two photothermal (contact and non-contact) techniques.

Keywords: Coupling fluid; Lock-in thermography; Photopyroelectric calorimetry; Thermal diffusivity.

1. Introduction

The photopyroelectric method (PPE), in various detection configurations, has been extensively applied to study the thermal properties of condensed matter samples; see for example [1-4] among others. The major advantages of this technique are its simplicity, high sensitivity, non-destructive character and its easy adaptation to the experimental restrictions imposed by the theoretical requirements. It is now well-known that using the two detection configurations, “back” (BPPE) and “front” (FPPE), and the information contained in the amplitude and/or phase of the PPE signal, one can directly measure two dynamic sample’s related thermal parameters, thermal diffusivity and effusivity. The remaining thermal parameters can be then calculated and so, PPE is able to offer a complete thermal description of the investigated material. Concerning the investigated materials, the liquids are the most suitable samples due to the perfect sample-sensor thermal contact. For solid samples, a coupling fluid is always necessary between the sensor and the sample and, unfortunately, this coupling fluid influences the quantitative results. When accurate results are required, people try to eliminate or, at least, to reduce the influence of coupling fluid on the measurement’s accuracy [5-8].

During the last decades, the thermal-wave resonator cavity (TWRC) method [9] was probably the most successful in controlling the influence of coupling fluid on the values of the investigated thermal parameters. However, sometimes this method cannot be used and, in such cases, one has to act on other experimental parameters as type of coupling fluid, chopping frequency, etc. The TWRC method was used mainly to characterize liquid samples. It was used to increase the accuracy for both thermal diffusivity (back PPE configuration) and effusivity (front PPE configuration) investigations. The main reason was that in the frequency scanning procedures the exact thickness of the liquid under investigation was not known [10].

In the case of solid samples the TWRC method can be applied only in the front configuration and it is only the thermal effusivity coming out from the measurement (the solid under investigation is in a back position). In the same time, even in this configuration, TWRC cannot be applied if the solid sample is porous, pressed powder or very thin [11]. Consequently the TWRC method cannot be applied for thermal diffusivity investigations of solids and this is the reason for which we propose in the paper to optimize the frequency scanning procedure.

In this paper we will focus only on solid samples, on one thermal parameter, thermal diffusivity [12-16] and on one detection configuration BPPE (associated with the chopping frequency as scanning procedure) [11]. This is a simplified classical and largely used configuration, composed by 4 layers (air/sample/sensor/air) in which, if we assume optical opacity for the sample and thermally thick regime for the sample and sensor, we can obtain the value of the sample’s thermal diffusivity from the slope of the amplitude and/or phase of the signal as a function of square root of the chopping frequency (see Eq. (1)-(2)) [11]:

$$\ln|V_n| = \ln \frac{2}{b_{sp} + 1} - L_s \left(\frac{\omega}{2\alpha_s} \right)^{1/2} \quad (1)$$

$$\Theta = \Theta_0 - L_s \left(\frac{\omega}{2\alpha_s} \right)^{1/2} \quad (2)$$

In Eq. (1)-(2) the standard notations have been used: s and p represent the sample and pyroelectric sensor, respectively, $b_{sp} = e_s/e_p$ where e is the thermal effusivity, a is the reciprocal of the thermal

diffusion length μ , $a = 1/\mu$, $\mu = (2\alpha/\omega)^{1/2}$, α is the thermal diffusivity, ω is the angular modulation frequency and L_s is the thickness of the sample (the sensor is considered semi-infinite). Θ is the phase of the signal (Θ_0 is a frequency independent offset) and V_n is the normalized amplitude of the BPPE signal (the normalization was performed with the signal obtained with empty sensor).

It is to mention that, in the theoretical development of this particular detection case, the layer of coupling fluid was neglected. Experimentally, the presence of a thin (but uncontrolled in thickness) layer of coupling fluid cannot be avoided; this additional layer changes the slope of the phase (amplitude) curve and, consequently, the obtained value of thermal diffusivity is always underestimated [5-8]. The influence of the coupling medium in pyroelectric measurements of solids becomes significant especially for high conductive samples and at high modulation frequency of the incident radiation. Different solutions have been proposed in order to obtain correct values of thermal diffusivity. Some are based on non-contact techniques as photothermal radiometry (PTR) [17-19], others try to modify the experimental set-up of the PPE technique itself. Salazar *et al* [5-7], for instance, used transparent electrodes (ITO) deposited on the sensor (LiTaO_3) surface, and introduced a self-normalization procedure [6,7]. In doing so, the thermal diffusivity of opaque solid samples could be measured with high accuracy. However, by using the proposed technique, each sample has to be measured in both, back and front configurations.

The research performed in this work is focused on finding a different solution in order to minimize the undesired effect of the coupling fluid by a proper selection of the coupling fluid and by performing a simple experimental modification of the detection cell (reduction of the coupling fluid thickness). The final goal is to obtain similar results with both photopyroelectric calorimetry and infrared lock-in thermography (IRT) techniques.

2. Material preparation and experimental methods

A glassy-like square shape carbon sample (GC) with known thermal properties [20] was used as test solid sample. The thickness of the GC sample (1 mm) and the other geometrical parameters were measured with a micrometer with an accuracy of 10 μm . The sample was weighted with a Discovery OHAUS laboratory analytical balance (DV215CDM model) of sensitivity of 0.1 mg. The experimental setup for the BPPE measurement [11] consisted of a green, current-modulated DPSS (Diode Pumped Solid State) laser (532 nm) with the output power of about 50 mW, a LiTaO_3 detector (0.54 mm thick) provided with Cr+Au electrodes and a SR830 lock-in nanovoltmeter for signal processing. In this configuration the sample is placed onto the sensor and is directly excited by the incident radiation. A thin layer of different fluids served as a coupling medium between the sample and the sensor. The following coupling fluids were tested: standard silicon grease, commercial ceramic thermal paste used in computers, silicon oil, glycol, ethylene glycol and distilled water. Some typical values of the dynamic thermal parameters of these coupling fluids found in literature [21,22] are presented in Table 1.

Table 1. Values of the dynamic thermal parameters of tested coupling fluids [21,22].

The thermal parameter	Silicon grease	Thermal paste	Silicon oil	Glycol	Ethylene glycol	Distilled water
Th. Diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$) $\times 10^{-6}$	0.01	-	0.097	0.09	0.0936	0.143
Th. Effusivity ($\text{W} \cdot \text{s}^{1/2} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$)	720	-	-	-	890	1586
Th. Conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	0.23	0.5-5	0.1	0.16	0.27	0.6

The sample under investigation was stuck to the sensor with a small amount of coupling fluid. Once the sample was placed onto the detector, some pushing force together with some gentle movements was applied. A black diaphragm was used in order to protect the detector from the scattered light. Frequency scans were performed in the range 0.3 Hz - 15 Hz with 0.3 Hz or 0.5 Hz single step. Standard normalization procedure with empty sensor was applied.

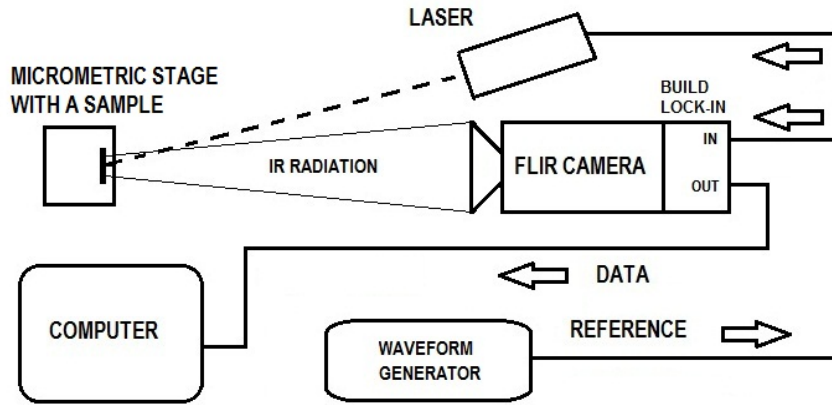


Fig. 1. Experimental setup for the lock-in thermography technique.

The experimental IRT setup included a heat source, a waveform generator, an infrared camera and a computer for data acquisition (see Fig. 1). The intensity-modulated optical stimulation ($f_0=2$ Hz) was delivered by a Nd:YAG laser (Laser Quantum OPUS, with $\lambda=532$ nm and $P=0.5$ W). The IR camera (FLIR 7200 series, with a 256x320 pixel array of InSb detectors sensitive in the 1.5 μm -5.1 μm wavelength range, working at a sampling frequency of 100 Hz) recorded the changes of the surface temperature of the specimen. The noise equivalent temperature difference (NETD) of this camera is lower than 20 mK. The signals delivered by the infrared camera and the reference frequency f_0 were sent to the lock-in detection module incorporated into the camera, which outputs the continuous component image ($f=0$) as well as the amplitude and phase images of the f -component to a PC. The optical axis of the camera was set perpendicular to the investigated surface, at a distance of 300 mm. The value of a pixel in the obtained images is 30 μm . All the measurements presented in this paper were computer-controlled and performed at room temperature.

3. Theoretical aspects

The equations describing the amplitude and phase of the BPPE four-layer system (without taking into account the coupling fluid) were listed in the Introduction.

In this theoretical section, in order to evaluate the influence of the coupling fluid on the thermal diffusivity, a 5-layer system air/sample/coupling fluid/pyro/air model (see Fig. 2) is considered.

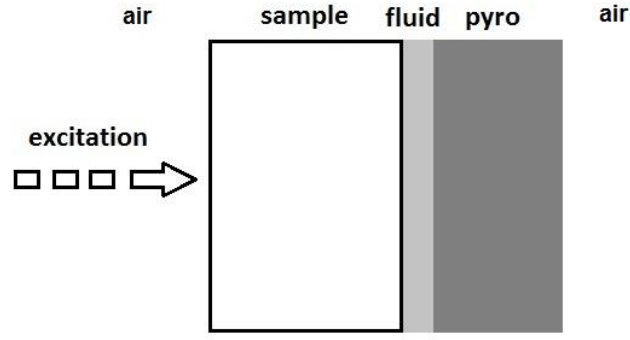


Fig. 2. The model of the three layer system.

The theoretical equation describing such a system proposed by Salazar [5] has the following form:

$$V_n = 4 \frac{1 - R_s}{1 - R_p} \frac{e^{-\sigma_s L_s}}{(1 + b_{sf})(1 + b_{fp})e^{\sigma_f L_f} + (1 - b_{sf})(1 - b_{fp})e^{-\sigma_f L_f}} \quad (3)$$

where V_n is the normalized complex signal, R_i is the optical reflection coefficient, $\sigma_i = (1+i)a_i$ is the complex diffusion coefficient and indexes s , f and p refer to the opaque sample, fluid and pyroelectric sensor, respectively.

It has been shown that the lock-in thermography allows the determination of thermal diffusivity and thermal conductivity of solid samples [23]. The heat wave equation generated by a time-periodic spot heating in an isotropic and homogeneous medium with thermal diffusivity α , can be written as [24]:

$$T(x,t) = T_0 e^{j(2\pi ft - \vec{k}\vec{x})} \quad (4)$$

where x is the thermal wave propagation direction, T_0 is the surface temperature, f is the excitation frequency, t is the time and \vec{k} is the wave vector. In one direction, the thermal diffusion equation can be expressed by:

$$\alpha \frac{\partial^2 T(x,t)}{\partial x^2} = \frac{\partial T(x,t)}{\partial t} \quad (5)$$

where:

$$k = \pm(1-j) \sqrt{\frac{\pi f}{\alpha}} \quad (6)$$

is the wave vector. For physical reasons, the thermal wave must converge at infinity, which requires:

$$k = (1-j) \sqrt{\frac{\pi f}{\alpha}} \quad (7)$$

The thermal wave can thus be written as follows:

$$T(x,t) = T_0 e^{-\sqrt{\frac{\pi f}{\alpha}} x} e^{j\left(2\pi f t - \sqrt{\frac{\pi f}{\alpha}} x\right)} \quad (8)$$

At a large distance from the point heat source, the thermal wave can be approximated by a plane wave. The propagation of a plane thermal wave through a homogeneous medium causes a phase shift $\Delta\phi$ (a delay in the propagation of thermal wave as compared to a reference signal) having the following expression:

$$\Delta\phi = -\sqrt{\frac{\pi f}{\alpha}} x = px \quad (9)$$

where p is the slope of the phase-distance graph and x is the distance from the point heat source. The thermal diffusivity can thus be calculated according to Eq. (9).

4. Results and discussion

The behavior of the BPPE phase for the GC sample, for different coupling fluids, as a function of the square root of the modulation frequency is presented in Fig. 3. For low chopping frequencies, the nonlinear behavior of the phase of the signal as a function of square root of the modulation frequency is attributed to the thermally thin regime for ($\mu > L$) sample and/or the sensor. Starting from $f=2$ Hz, the sensor and the sample are thermally thick. Consequently, linear fits have been performed in the frequency range from 4 Hz up to 15 Hz, using the least square method. The value of the thermal diffusivity of the specimen was calculated according to Eq. (2).

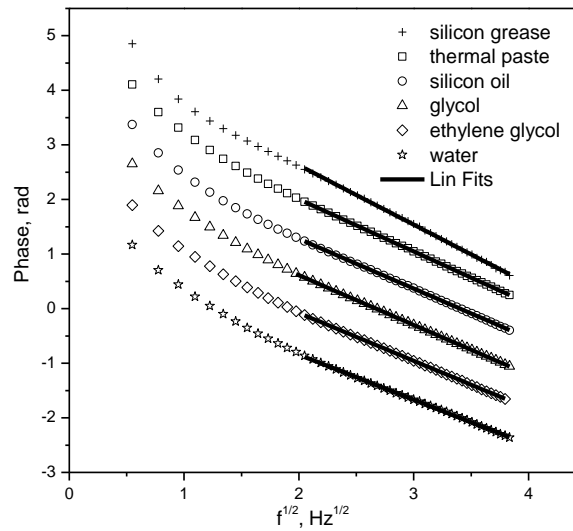


Fig. 3. Phase characteristics of BPPE signal, as a function of the square root of the modulation frequency, for glassy-like carbon and different coupling fluids; the dots are experimental data and lines are linear fits.

Phase images for glassy-like carbon sample, with the corresponding profiles, are shown in Fig. 4 (a) and (b), respectively. The excitation frequency was 2Hz and the corresponding thermal diffusion length is about 800 μm for glassy carbon, which is comparable to the thickness of the investigated sample (around 1mm), so apparently we are not in the thermally thick sample limit case. However,

if a sample is a self-supporting thin film in air, the effective thermal thickness of the sample is always larger than the real thickness of the sample and thus the sample can be considered thermally thick [25]. According to ref. [25] a very thin aluminum foil (10 microns) is thermally thick even at 0.01Hz, despite the fact that the foil should be thermally thick only above 260 kHz. For large thermal effusivity mismatch (in our case the thermal effusivity of glassy carbon is around $3100 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ and respectively $5 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ for air), the corresponding frequency limit is always lower (several orders of magnitude) than the conventional calculated frequency. So, at 2Hz excitation frequency, our sample can be considered as thermally very thick.

The impact area of the laser is represented by the constant phase zone (see Fig. 4b). The thermal wave is propagating continuously, normal to the observed object surface, symmetrically with respect to the excitation source. The diameter of the laser spot is around 5px (150 μm) and the thermal wave is spreading on the surface over a distance of about 3mm around the laser impact zone (see Fig. 5). As the ratio between the two quantities (distance-diameter) is about 20, at this distance from the excitation source the thermal wave can be approximated by a plane wave.

Thus, the theoretical model is fulfilled and equation (9) can be applied in order to determine the thermal diffusivity of the investigated sample.

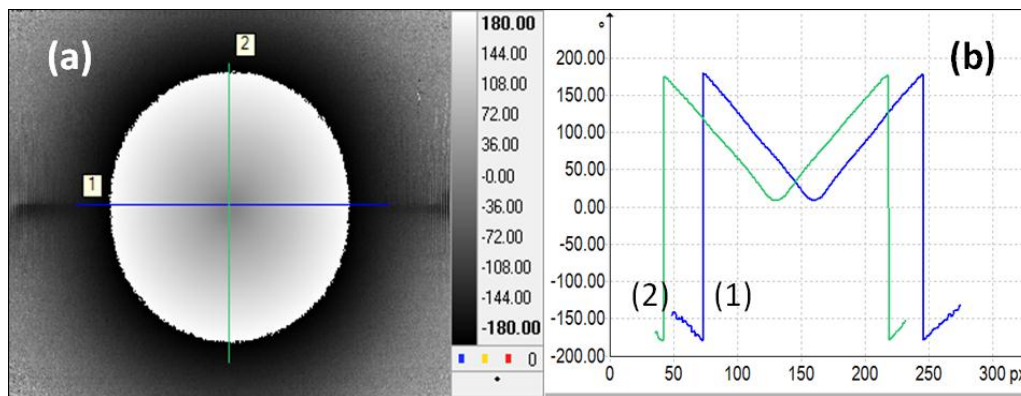


Fig. 4. The phase image of glassy carbon measured at 2 Hz (a) and the corresponding phase profiles (b).

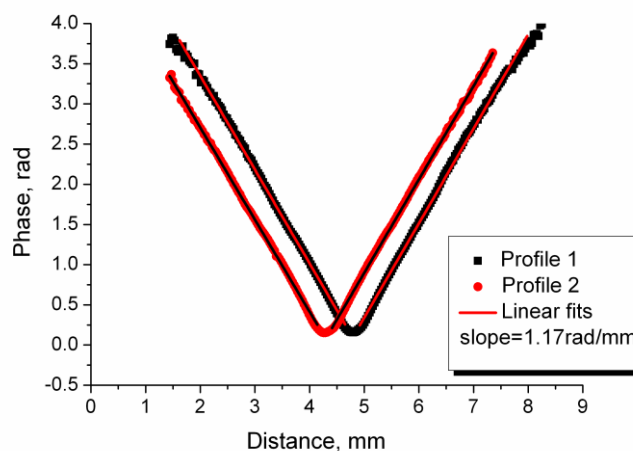


Fig. 5. The phase profiles of the glassy-like carbon at 2 Hz; the experimental data are plotted with dots and the lines are the linear fits.

Under coordinate $x=70\text{px}$ and above coordinate $x=250\text{px}$ (see Fig. 4b, profile 1, for instance), the thermal wave is attenuated and the signal becomes noisy.

Thermal diffusivity was calculated as an average value of the four slopes (taken from two profiles) presented in Fig. 5, according to Eq. (9).

The values of the thermal diffusivity of GC obtained with both BPPE method for different coupling fluids and non-contact lock-in thermography are listed in Table 2. For each technique the measurements were performed three times and the final values from Table 2 represent the average of the results. If we focus on BPPE results, it appears clearly that they are strongly dependent on the type of coupling fluid. For silicon grease and thermal paste the thermal diffusivity of GC sample is underestimated more than 30 % comparing with IRT result. Better coupling fluids seem to be silicon oil and glycol, with an underestimation of about 15 %. The best results were obtained for distilled water. However, in this case, the standard deviation is larger, probably due to some specific water's capillarity properties, evaporation, air bubbles, etc. Considering the investigated coupling fluids, the best solution seems to be ethylene glycol, from both points of view: underestimation value (about 11 %) and standard deviation ($0.022 \times 10^{-6} \text{ m}^2/\text{s}$).

Table 2. Thermal diffusivity of GC obtained with BPPE and different coupling fluids and with IRT.

Coupling fluid	Th. Diffusivity of GC ($\text{m}^2 \cdot \text{s}^{-1}$) $\times 10^{-6}$	Standard dev. ($\text{m}^2 \cdot \text{s}^{-1}$) $\times 10^{-6}$
Silicon grease	2.63	0.034
Thermal paste	3.26	0.025
Silicon oil	3.68	0.028
Glycol	3.65	0.022
Ethylene glycol	3.93	0.022
Distilled water	4.29	0.127
No coupling fluid (IRT)	4.46	0.054

An inspection of Tables 1 and 2 shows that the result obtained for the thermal diffusivity of the investigated sample (GC) is not connected only with the thermal parameters of the coupling fluid. For example ethylene glycol is a rather poor thermal conductor compared with the other coupling fluids (its thermal conductivity is lower than that of thermal paste). The good result obtained with ethylene glycol is probably due to the fact that it creates a thinner layer compared with other liquids. Consequently it seems that an optimization “type of coupling fluid - thickness of layer” is necessary to obtain good results.

Fig. 6 presents theoretical simulations of the phase of the BPPE signal for the 5 layer system (Fig. 2) performed with Eq. (3) for increased thicknesses of the coupling fluid. The sample was a hypothetical solid with thermal diffusivity $2 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$, effusivity $2000 \text{ W} \cdot \text{s}^{1/2} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ and thickness 1 mm.

The thermal parameters of the coupling fluid and the pyroelectric sensor were taken from the literature [21]: for ethylene glycol ($\alpha_f=9.36 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$, $e_f=890 \text{ W} \cdot \text{s}^{1/2} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$) and for LiTaO_3 ($\alpha_p=1.56 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$, $e_p=3600 \text{ W} \cdot \text{s}^{1/2} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$). One can see that the slope a of the curve “phase vs. sqrt. (f)” increases from 1.25 to 1.31 with increasing thickness of the coupling fluid from 0 μm to 10 μm . A similar correspondence “slope of the curve phase vs. sqrt. (f)” vs. “coupling fluid thickness” was obtained in ref. [5].

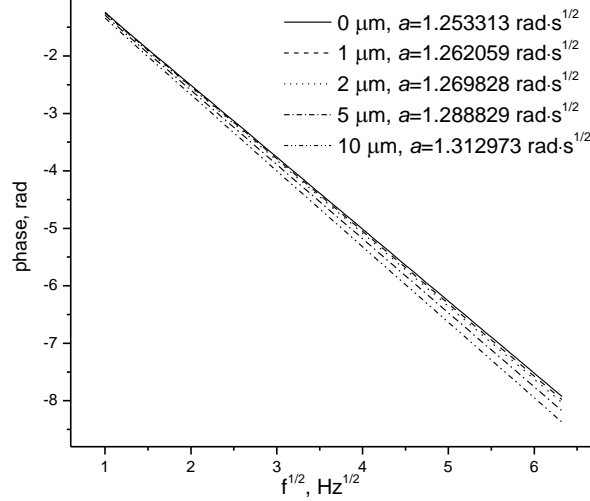


Fig. 6. Theoretical simulations of the phase of the signal for different thicknesses of the coupling fluid. The following set of parameters was used: $\alpha_s=2\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$, $e_s=2000 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $L_s=1 \text{ mm}$, $\alpha_f=9.36\times 10^{-8} \text{ m}^2\cdot\text{s}^{-1}$, $e_f=890 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $\alpha_p=1.56\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$, $e_p=3600 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $L_p=0.5 \text{ mm}$.

The results of the numerical calculation of relative error in thermal diffusivity evaluation, by applying Eq. (3), for different sets of the parameters, are given in Table 3. The error was calculated as relative value taking into account given thermal diffusivity in comparison with value obtained for zero fluid thickness.

The first three rows in Table 3 present the influence of the thickness of the coupling fluid on the value of thermal diffusivity for a solid sample with low (second row) and high (third row) thermal diffusivity. The calculations were performed using the following set of parameters: $e_s=2000 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $L_s=1 \text{ mm}$, $\alpha_f=9.36\times 10^{-8} \text{ m}^2\cdot\text{s}^{-1}$, $e_f=890 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $\alpha_p=1.56\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$, $e_p=3600 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$.

Table 3. Relative error in thermal diffusivity evaluation, for different solid samples.

Fluid thickness (μm)	0	1	2	5	10
Error (%) for $\alpha_s = 2\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$	0	1.38	2.58	5.44	8.90
Error (%) for $\alpha_s = 6\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$	0	2.40	4.45	9.17	14.68
α_L / α_s	1/20	1/10	1/4	1/2	1/1
Error (%) for $\alpha_s = 2\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$ and $L_f=10 \mu\text{m}$	8.68	6.82	4.87	3.70	2.77
e_L / e_s	1/4	1/2	1/1	3/2	5/2
Error (%) for $e_s=2000 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $L_f=5 \mu\text{m}$	6.29	5.25	4.47	4.39	4.75
e_L / e_s	6/1	4/1	2/1	3/2	6/5
Error (%) for $e_L=6000 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $L_f=5 \mu\text{m}$	5.21	5.09	4.81	4.67	4.56

The data presented in Table 3 support our initial statement, that the influence of the coupling medium becomes significant especially for high conductive samples. The dependence of the relative error versus the thermal diffusivity ratio (α_L / α_s) is given in next two rows of Table 3. As expected, when the values of the thermal diffusivity of the coupling fluid and the sample are close, the error decreases. Last four rows in Table 3 evaluate the influence of the difference between the effusivity

of the coupling fluid and that of the solid sample; this difference seems to be not so important like the thickness and the thermal diffusivity of the coupling fluid.

In order to calibrate experimentally the influence of the thickness of the coupling fluid layer on the value of the thermal diffusivity, a double scanning “thickness/chopping frequency” experiment was performed. The carbon sample was placed parallel to the sensor, in a set-up allowing a thickness scanning procedure and ethylene glycol was inserted as coupling fluid between the two solids [11]. The coupling fluid was then compressed with a step of 1 μm , at each step a frequency scan being performed in order to obtain the value of the thermal diffusivity. The starting value of the coupling fluid’s thickness was estimated at about 40 μm , position for which the value of the thermal diffusivity is underestimated (compared with the IRT value) with about 30%. The obtained results are shown in Fig. 7.

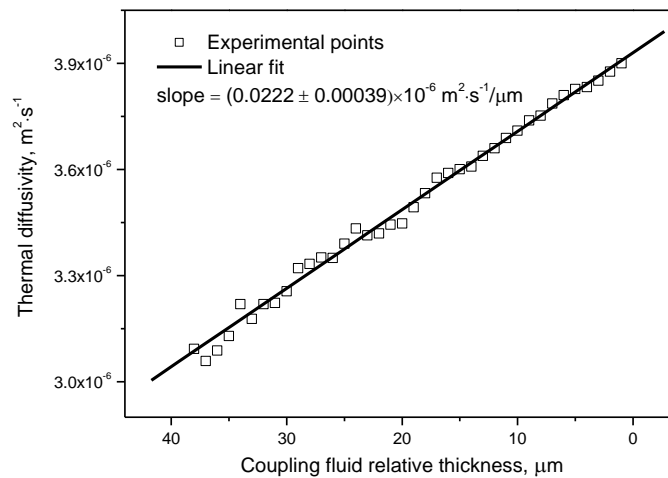


Fig. 7. Thermal diffusivity of the glassy-like carbon as a function of coupling fluid thickness; the squares correspond to measured data and the line represents the linear fit.

The linear fit (least square method) performed on the experimental data from Fig. 7 indicates that, for the specific parameters of our experiment (carbon sample and ethylene glycol as coupling fluid) the reduction of the coupling fluid’s thickness, brings the value of sample’s thermal diffusivity closer to the value obtained with IRT.

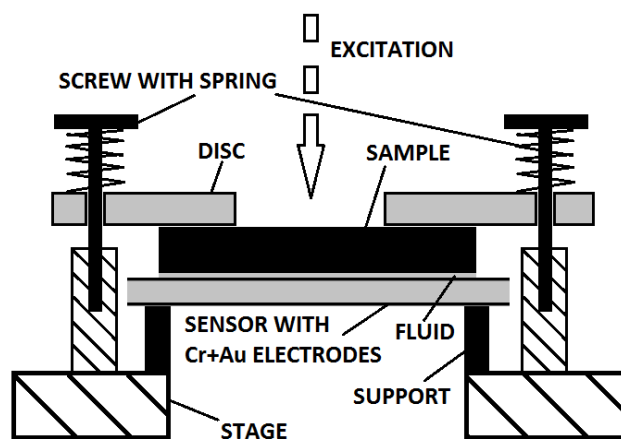


Fig. 8. Improved experimental detection cell.

As a consequence to this important influence of the thickness of the coupling fluid on the value of sample's thermal diffusivity, an experimental improvement of the detection cell is proposed (in order to minimize its thickness) - see Fig. 8. Three screws provided with identical springs and located symmetrically around a textolite ring distribute a uniform pushing force on the surface of the sample, allowing the compression of the coupling fluid. A comparison of experimental results obtained with this modified detection cell, before and after applying the compression force, is shown in Fig. 9.

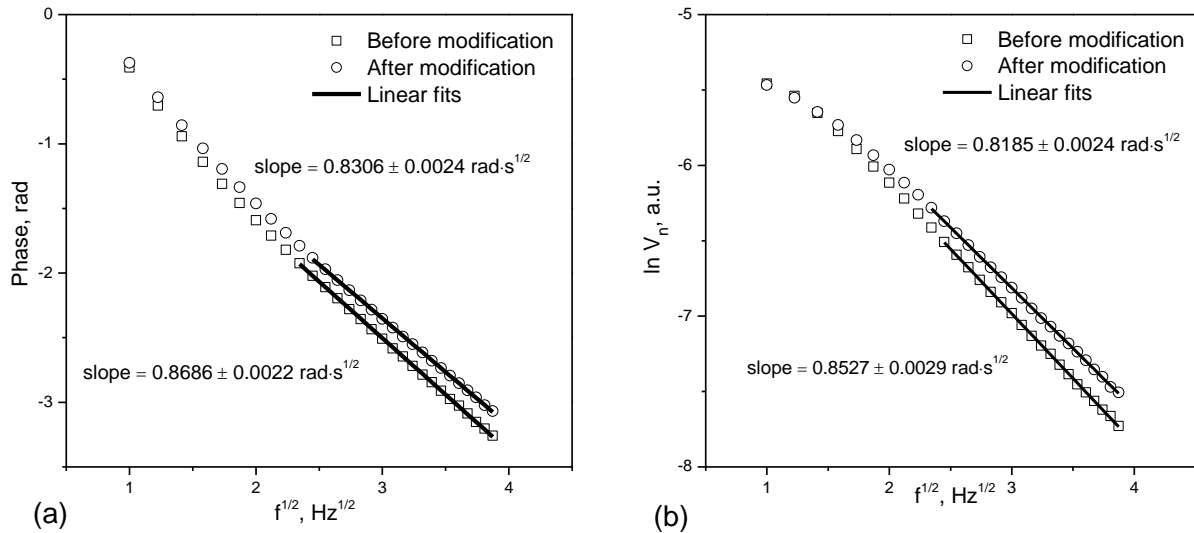


Fig. 9. The behavior of the phase (a) and amplitude (b) of the BPPE signal for GC sample, as a function of the square root of the modulation frequency, measured before (squares) and after (circles) applying the compression force; the points are experimental data and the lines are fits.

Using the slopes of the phase in Fig. 9(a), the corresponding values of the thermal diffusivity of the GC sample are $(3.95 \pm 0.023) \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ before compression and $(4.29 \pm 0.029) \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ after. The amplitude data shown in Fig. 9(b) lead to similar result. The quantitative data mentioned before for the values of the thermal diffusivity were calculated as average values from three independent measurements. The value of the thermal diffusivity of GC, after compression, indicates an underestimation of only 3.8 %, compared with the value obtained by IRT. On the other hand, if we assume that the value of the thermal diffusivity obtained with IRT technique is correct, we can estimate the coupling fluid thicknesses before (23 μm) and after (7.6 μm) compression, respectively.

The main sources of the systematic error in the investigations performed in this paper were: (i) the experimental reproducibility, (ii) the accuracy of the sample's thickness measurement, and (iii) the theoretical approximations performed in order to derive the detection particular cases. The standard deviation calculated from three independent measurements in the case of ethylene glycol gives an error of about 0.6 %. The thickness of the GC sample (0.98 mm) was measured with a micrometer with an accuracy of 10 μm , which produces additional uncertainty of about 0.2 %. The third contribution connected with the theoretical approximations can be practically neglected if the theoretical conditions, imposed by the particular cases, are largely fulfilled [11,23]. Consequently, we expect a total uncertainty of about 1 % for the measured values of GC thermal diffusivity.

It is well-known that the thermal diffusivity α , effusivity e and conductivity k , are connected with the density ρ and the mass specific heat C by the relationships: $\alpha = k/(\rho C)$, $e = (k\rho C)^{1/2}$ and $k = e\alpha^{1/2}$. Due to the fact that these thermal parameters are not independent, we can use the above mentioned relationships in order to compare our results with previously reported data. The thermal effusivity of the GC sample ($3110 \pm 45 \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$) was previously obtained by using the PPE technique in the front configuration (FPPE), together with the thermal wave resonator cavity (TWRC) method [21]. Using this value of thermal effusivity together with the value of thermal diffusivity measured in this paper, we obtain for the thermal conductivity of the glassy-like carbon $6.34 \pm 0.22 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ value in good agreement with the producer data ($6.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). The specific heat of the glassy-like carbon was found by Pawlak *et al* [26] from differential scanning calorimetry as $1050 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ with the uncertainty of 2-5 %. This value is in very good agreement with the one obtained in this work ($1075.1 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$); the density of the GC sample was estimated from its weight and volume ($1421.8 \text{ kg}\cdot\text{m}^{-3}$).

5. Conclusions

The main purpose of this paper was to optimize the experimental conditions of a BPPE experiment for a correct measurement of the thermal diffusivity of a solid sample. A glassy carbon sample (GC), with known thermal properties, was selected as test material and the BPPE technique was combined with a non-contact photothermal method, the infrared thermography (IRT). Assuming that the values of thermal diffusivity obtained by IRT are correct, we studied how to eliminate the underestimation of the obtained values of the thermal diffusivity in the BPPE experiment, due to the presence of the coupling fluid. The experiments, performed with different types of coupling fluids, and the numerical simulations were focused both on the influence of the coupling fluid's thermal parameters (thermal diffusivity, effusivity and conductivity) and on its thickness.

As a first conclusion, the influence of the coupling fluid is more important for good thermal conducting samples and consequently, a proper choice of the type of coupling fluid with high values of thermal conductivity is necessary. On the other hand, as presented in Table 3, in both cases (good and bad thermal conductors), the accuracy of the measurement increases if one can select a coupling fluid with a thermal diffusivity close to the value of the investigated sample. From the thermal point of view, it seems that water is the best coupling fluid but, due to the above mentioned drawbacks (high capillarity, evaporation, incorporation of air bubbles, etc.), ethylene glycol remains the most suitable one (from the investigated coupling fluids).

The value of the thermal effusivity of the coupling fluid seems to be not an important parameter. However, even if the value of the thermal parameters are important, we are very limited in fact concerning the type and number of coupling fluids : some oils, greases, thermal paste, glycol based liquids and water are the only possibilities.

This is why the study was also focused on another parameter of the coupling fluid, a geometrical one, its thickness. Both experiments and mathematical simulations indicate that a thinner layer of coupling fluid leads to more correct results. This is in fact an expected result (see also ref [5]), at least from a theoretical point of view, because the fittings have been performed with Eq. (2) in which the coupling fluid layer was neglected.

In order to reduce the coupling fluid's thickness, some improvements were performed to the experimental design of the BPPE detection cell. In such a way, the difference between the results

obtained for the thermal diffusivity of GC sample (using ethylene glycol as coupling fluid) with the two photothermal (contact and non-contact) techniques was reduced to 3.8 %.

As a final conclusion, this paper offers a different solution, compared with previously reported methods [1,5,6,11,21] for improving the accuracy of the PPE calorimetric investigations of solids.

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