Calorimetric investigations of solids by combined FPPE – TWRC method

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Abstract. An alternative photopyroelectric (PPE) technique that combines the front detection configuration (FPPE) with the thermal-wave-resonator-cavity (TWRC) method is proposed for direct measurement of thermal effusivity of solid materials inserted as backings in the FPPE detection cell. The method uses the scan of the normalized PPE phase as a function of sample’s thickness, in the thermally thin regime for the sensor and liquid layer, and thermally thick regime for the backing material. The value of backing’s thermal effusivity results from the optimization of the fit of the phase of the signal, performed with sample’s thickness and backing’s thermal effusivity as fitting parameters. The paper presents experimental results on several solid materials (inserted as backing in the cell), with different values of thermal effusivity (brass, steel, wood) and two liquids (ethylene glycol, water) largely used in the FPPE-TWRC cells. The paper stresses mainly on the sensitivity of the technique to different liquid/backing effusivity ratios. It seems that the method is suitable especially when investigating solids with values of thermal effusivity close to the effusivity of the liquid layer.

1. Introduction

In a photopyroelectric (PPE) experiment, one may combine detection configurations (back or front), sources of information (PPE amplitude or phase) and scanning parameters (chopping frequency or sample’s thickness), in order to obtain one dynamic thermal parameter (usually, thermal diffusivity or effusivity) of one of the specific layers (sample, backing or pyroelectric sensor) of the detection cell [1-3].

Recently, we proposed an alternative technique that combines the front detection (FPPE) configuration [4] with the thermal-wave resonator cavity (TWRC) method [5-7]; in this configuration, by monitoring the thickness of a fluid sample, the thermal effusivity of a solid material, used as backing in the detection cell, can be measured. In such a way the coupling fluid (i.e. liquid sample) is not anymore a disturbing factor, but its properties can be used in order to obtain the value of the thermal effusivity of a solid [8].

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The value of the thermal effusivity of the backing material is obtained by performing a sample’s thickness scan of the phase of the normalized PPE signal, given by the equation [8]:

\[ V_n = \frac{\sigma_p L_p + b_w}{(\sigma_p L_p) + b_w} \left( \frac{1 + R_{bs} \exp(-2\sigma_s L_s)}{1 - R_{bs} \exp(-2\sigma_s L_s)} \right) \]  

Equation (1) is valid in the optically opaque and thermally thin regime for the pyroelectric sensor and thermally thick regime for the backing [8]. The PPE signal depends on liquid’s thermal effusivity, \( e_s \), \( (b_{sp} = e_s / e_p) \) and diffusivity \( \alpha_s \), \( (\alpha_s = (2\alpha p / \mu_p)^{1/2}) \), and on backing’s thermal effusivity, through the reflection coefficient of the thermal wave at the “bs” interface, \( R_{bs} = (b_{bs} - 1) / (b_{bs} + 1) \). Symbols “p”, “s” and “b” denote the pyroelectric sensor, liquid layer (sample) and (investigated) backing material.

Even if the theory of the configuration was presented before [8, 9], we want to perform in this paper an investigation on the sensitivity of the technique in investigation of thermal effusivity of different type of solids. In a FPPE-TWRC cell, one uses as a liquid layer stable liquids as ethylene glycol, silicon oil or water, with thermal effusivities ranging from about 800 W s^{1/2} m^{-2} K^{-1} to 1600 W s^{1/2} m^{-2} K^{-1}. Concerning solid materials, the value of the thermal effusivity has a very large variation range, from about 35000 W s^{1/2} m^{-2} K^{-1} for copper, down to 100-200 W s^{1/2} m^{-2} K^{-1} for wood or porous materials [10, 11]. Equation (1) depends on the backing/liquid effusivity ratio \( (b_{bs}) \) and consequently, a study of the sensitivity of this parameter as a function of this parameter is requested. This is in fact the purpose of this paper.

2. Experimental results and discussions

The experimental set-up and detection cell were largely described elsewhere [9, 12]. We will give here only the values of the thermal parameters of interest for the first two layers of the detection cell: 100 \( \mu \)m thick LiTaO\(_3\) pyroelectric sensor \( (e_p = 3.66 \times 10^8 W s^{1/2} m^{-2} K^{-1}; \alpha_p = 1.36 \times 10^{-6} m^2 s^{-1}) \), water \( (e_s = 16.0 \times 10^8 W s^{1/2} m^{-2} K^{-1}; \alpha_s = 14.6 \times 10^{-8} m^2 s^{-1}) \) and ethylene glycol \( (e_s = 8.14 \times 10^8 W s^{1/2} m^{-2} K^{-1}; \alpha_s = 9.36 \times 10^{-8} m^2 s^{-1}) \). In all experiments the chopping frequency was 1 Hz.

![Figure 1](image)

*Figure 1.* Normalized phase of the FPPE signal as a function of sample’s absolute thickness, for a detection cell with ethylene glycol as liquid layer and two different solids as backing materials (brass and wood).

2.1. Good and bad thermal conductors

The results obtained on a good (brass) and a bad (wood) thermal conductor, together with the contour maps of the precision of the fit performed with equation (1) on the experimental data, are displayed in figures 1-3. The conclusions coming out from the shape of the contour maps are: (i) the localization of
The position of the backing is better in the case of good thermal conductors; (ii) the value of the thermal effusivity is more precise in the case of bad thermal conductors.

**Figure 2.** Contour map of the precision of the fit performed with equation (1) on the experimental data obtained with brass as backing. X-axis represents the correction term in the measurement of the absolute liquid’s thickness. The shape of the contour curves indicates a good localization of the position of the backing, but rather low precision in the value of thermal effusivity.

**Figure 3.** Contour map of the precision of the fit performed with equation (1) on the experimental data obtained with wood as backing. X-axis represents the correction term in the measurement of the absolute liquid’s thickness. The shape of the contour curves indicates a bad localization of the position of the backing, but good precision in the value of thermal effusivity.

**Figure 4.** Normalized phase of the FPPE signal as a function of sample’s absolute thickness, for a detection cell with steel as backing materials and two different coupling fluids (ethylene glycol and water).

**Figure 5.** Normalized phase of the FPPE signal as a function of sample’s absolute thickness, for a detection cell with ethylene glycol as coupling fluid and glass as backing material. In one investigation 100 µm Al foil was glued on the glass backing.
2.2. Influence of coupling fluid (liquid layer)
The results of the investigations performed on the same backing material (steel), but with two different coupling fluids (water and ethylene glycol) are presented in figure (4). The same value for the thermal effusivity was obtained in both cases for the investigated material.

2.3. Influence of a metallic foil deposited on the backing
Concerning the suitability of this method, a possible challenge can be the investigation of porous solid materials. In such a case the coupling fluid can penetrate the backing, changing its thermal properties. In order to prevent this, a thin metallic layer is interposed (glued or deposited) between the coupling fluid and the backing; the influence of such a layer on the results is the target of this section.

The results obtained with a cell based on ethylene glycol as fluid and glass as backing are displayed in figure 5. In one of the measurements a 100 µm Al foil was glued with silicon grease to the glass backing. The results show that the influence of the metallic layer on the thermal effusivity of glass is of about 7%.

3. Conclusions
The FPPE-TWRC method was used to measure the room temperature value of the thermal effusivity of several solid materials. The results are in good agreement with literature data [10, 11]. The paper was focused mainly on the investigation of the suitability of the FPPE-TWRC technique in measuring the thermal effusivity of various solid materials. The accuracy of the measurement depends on the effusivity ratio of the backing/fluid materials; the method seems to be suitable mainly for solids with values of thermal effusivity close to that of the coupling fluid. Porous materials can be investigated by this technique if they are isolated from the coupling fluid with a thin metallic layer.

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