Simultaneous determination of the thermal properties for liquid and pasty materials from photopyroelectric measurements


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In this work we are proposing a new experimental configuration based in the use of two sensors to allow the simultaneous measurement of both thermal diffusivity and effusivity of the sample. This Dual Sensor Photopyroelectric – DSPPE configuration implies in a single experiment and any calibration is required. Temperature dependent experiments are allowed from a cell equipped with Peltier elements. Substituting the upper sensor for a quartz window spectroscopic experiments are permitted. Water and margarine with different fat content were used as testing samples.

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Photopyroelectric – PPE schemes have been used in the determination of the dynamic (diffusivity \( \alpha \), effusivity \( e \) and conductivity \( k \)) and static (specific heat \( c \)) thermal properties of liquid and pasty materials [01-06]. Two main configurations have been usually employed, namely the SPPE (Standard or Back) and the IPPE (Inverse or Front), depending upon which surface the modulated incident light reaches first, of the sample or of the pyroelectric sensor, respectively. For some specific thermal and optical features of sample and sensor, usually one obtains the thermal diffusivity \( \alpha \) from an experiment using the SPPE configuration (which serves also for spectroscopic purposes) and the thermal effusivity \( e \) from an experiment using the IPPE configuration. In the last case it is still necessary to calibrate the experiment using a standard, usually water. Being in possession of \( \alpha \) and \( e \) data one can obtain the value for the thermal conductivity \( k \) from \( k = e / \sqrt{\alpha} \). Provided we know about the specific mass \( \rho \) of the sample.

In this paper we are proposing a new configuration based in the use of two sensors to allow the simultaneous measurement of both \( \alpha \) and \( e \) of the sample. This Dual Sensor Photopyroelectric – DSPPE configuration implies in a single experiment for the determination of both thermal parameters and any calibration is required. Our setup permits temperature dependent experiments as free conditions are necessary in other situations [07]. To assure the optical and thermal thick conditions we have to consider the radiation reflection at the interfaces and the sample and sensors as optically opaque or transparent materials and for thermally thick or thin materials, but most of them have not experimental interest. We have considered the sample and sensors as optically opaque and the upper sensor as thermally thin and the sample as thermally thick. Also we fixed sensors 1 and 3 as done of the same pyroelectric material (geometrical conditions are free). They are experimentally easy conditions to reproduce and feasible for most of purposes. Choosing these conditions we have not to consider the radiation reflection at the interfaces as is necessary in other situations [07]. To assure the optically opaque or transparent materials and for thermally thick or thin materials, but most of them have not experimental interest. We have considered the sample and sensors as optically opaque and the upper sensor as thermally thin and the sample as thermally thick. Also we fixed sensors 1 and 3 as done of the same pyroelectric material (geometrical conditions are free). They are experimentally easy conditions to reproduce and feasible for most of purposes. Choosing these conditions we have not to consider the radiation reflection at the interfaces as is necessary in other situations [07].

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Figure 1 shows the one-dimensional geometry of a DSPPE cell. To find the photopyroelectric signal equations for each sensor we have to determine the average temperature in each sensor solving the coupled heat diffusion equations for the five layers of the system in the Fig. 1. Their solutions supplies the temperature stationary field for each layer under the boundary conditions for this case, that is, temperature and heat flux continuity through the layer interfaces. We supposed the backing layer thickness much greater than that of the sum for sensors and sample. We still considered that in air and in the backing material one has not heat sources and found complete equations of the pyroelectric signals for the upper and the lower sensors. They are very long expressions that were simplified applying specific optical and thermal conditions for sample and sensors. One has in this case 64 different combinations for

\[
\frac{V_p}{V_p f} = \frac{A}{\xi} \frac{\sqrt{2\pi f}}{\sqrt{1+(2\pi f\tau_{el})^2}} \frac{1}{\sqrt{\eta+\sqrt{f}}} \frac{1}{\sqrt{\eta+\sqrt{f}}} + \frac{\pi}{4}
\]

where \( A = I_0 R_{el} A_t P \) and \( \tau_{el} \) is the detection electronics + sensor 1 equivalent RC circuit time constant.

\[
\phi_{pl} = -\tan^{-1}\left(\sqrt{\frac{f}{\eta+\sqrt{f}}}\right) - \tan^{-1}\left(2\pi f \tau_{el}\right) + \frac{\pi}{4}
\]
\( V_{p3} = \frac{B}{\xi} \left[ 1 + \frac{1}{(2\pi \eta \xi e_3)^2} \left[ \frac{\eta}{\eta + \sqrt{f^2 + (\sqrt{f})^2}} \right] \right] - L_2 \frac{\eta}{\eta^2} \phi \) (3)

where \( B = \frac{2}{I_3} I_0 R_{e3} A_3 P \left( \frac{e_2}{e_1 + e_2} \right) \sqrt{\alpha_1} \) and \( \tau_{e3} \) is the detection electronics + sensor 3 equivalent RC circuit time constant.

\( \phi_{p3} = -\tan^{-1} \left( \frac{\sqrt{f}}{\eta + \sqrt{f}} \right) - \tan^{-1} \left( 2\pi R e_3 \right) - L_2 \frac{\eta}{\alpha_2} \) (4)

where, for all equations,

- \( \xi = e_1 L_1 \sqrt{\frac{\pi}{\alpha_1}} \)
- \( \eta = \frac{e_g + e_2}{\xi} \)
- \( f \) = radiation modulation frequency
- \( I_0 \) = is the light intensity incident on sensor 1
- \( R \) = equivalent resistance of the electronics detection + sensor
- \( A, P \) = sensor area and pyroelectric coefficient
- \( e_g \) = thermal effusivity of the gas in front of sensor 1 (air)
- (1) – upper sensor, (3) – lower sensor, (2) – sample.

One can see from equations (1) and (2), for sensor 1, that carrying out experiments as a function of the modulation frequency and adjusting data to the equations one obtains three parameters, namely \( A, \tau_1, \eta \). From the \( \eta \) parameter one obtains the sample thermal effusivity \( e \). Similarly, and provided we already know \( e \), one can obtain the thermal diffusivity \( \alpha \) of the sample from equations (3) or (4), for the sensor 3. In the case of the effusivity determination one should care about the value of \( \eta \) compared with \( \sqrt{f} \). For higher values of \( e \), as is the case of water (\( e = 1600 \text{ Ws}^{1/2}/\text{m}^2/\text{K} \)), we have to choose a suit sensor material and thickness to do the \( \xi \) parameter (which depends only on thermal and geometrical conditions of the sensor) high enough to preserve \( \eta \) comparable with \( \sqrt{f} \). On the other hand, if the sample \( e \) value to be determined is too small (one extreme case is air with \( e = 5.5 \text{ Ws}^{1/2}/\text{m}^2/\text{K} \)), one should choose an upper sensor that produces a \( \xi \) value small enough to preserve \( \eta \) comparable with \( \sqrt{f} \). We have commercially many choices for pyroelectric sensors, then, with our methodology it is possible to measure effusivity values within the whole range they exist. One can observe that for extreme high or low \( \eta \) values the sensitivity is not good; one have to choose a sensor 1 that produces intermediate \( \eta \) values for high sensitivity.

### Experimental

Figure 2 presents details of the DSPE cell used in our experiments. The sample is placed between the two pyroelectric sensors and its thickness is precisely defined by the mask 2 thickness. In order to preserve the sample thickness during temperature dependent experiments the cell is designed with small escape tracks. The signals from both sensors are detected in amplitude and phase by two lock-in amplifiers at the chosen modulation frequencies. The Peltier elements permit the control of the experiment temperature. Replacing the upper pyroelectric for a quartz window the apparatus is allowed to proceed spectroscopic measurements. The system is fully computer controlled.

In order to characterize the built apparatus we have carried out experiments with water as sample, finding results in good agreement with literature data. The sensors are chosen of PVDF (polyvinylidene fluoride), the upper 28 \( \mu \text{m} \) and the lower 100 \( \mu \text{m} \) thickness. Hence, to fulfill the methodology conditions we operate within the 1.7 Hz – 21.9 Hz modulation frequency region. The sample thickness was fixed in 450 \( \mu \text{m} \) and the temperature in 24°C. During data acquisition the control software waited for stabilization at each modulation frequency and then took the average of 10 measurements.

### Results and Discussion

Figure 3 represents the fitting of experimental data to the equations (1) and (3) in the case of water. We have adopted the same procedure for the phase data and equations (2) and (4).

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**Figure 2 – Details of the DSPE cell. Sample is placed between the two sensors.**

**Figure 3 – Fitting of the signal amplitude data for the sensor 1 (upper curve) and sensor 3 (lower curve) to the equations (1) and (3) for the determination of thermal effusivity and thermal diffusivity of water. The air effusivity \( e_a \) was assumed as 5.5 \( \text{ Ws}^{1/2}/\text{m}^2/\text{K} \). Triangles represents experimental data and solid curve the best fitting.**
In the Table are summarized the results found for the thermal effusivity and thermal diffusivity of water at room temperature using the DSPPE configuration. One can see that the precision obtained for the parameters (showed between parenthesis in the Table), and taken from the root-mean-square deviation, are better than the usual expected for PPE experiments [03, 05, 06]. Comparison with the literature available experimental data shows an accuracy less than 0.7% for the diffusivity and 2.5% for effusivity values, a quite expressive result considering the many different compositions one can find water.

Table – DSPPE thermal diffusivity and thermal effusivity obtained results at room temperature for distilled water. The values indicated between parenthesis are the precision of each measurement, that is, $\Delta\alpha/\alpha$ or $\Delta\varepsilon/\varepsilon \times 100\%$.

<table>
<thead>
<tr>
<th>parameter</th>
<th>equation (1)</th>
<th>equation (2)</th>
<th>literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal diffusivity $10^{-3}$ cm$^2$/s</td>
<td>1.47 $\pm$ 0.08 (5%)</td>
<td>1.5 $\pm$ 0.1 (7%)</td>
<td>1.40 – 1.50</td>
</tr>
<tr>
<td>thermal effusivity $10^3$ Ws$^{1/2}$/m$^2$K</td>
<td>1.62 $\pm$ 0.02 (1%)</td>
<td>1.64 $\pm$ 0.09 (5%)</td>
<td>1.58 – 1.60</td>
</tr>
</tbody>
</table>

In order to proceed the characterization of our apparatus for spectroscopic purposes we carried out experiments with a 1000 W Xenon-arc lamp for both a photoacoustic cell (carbon black as sample) and the photopyroelectric one (sensor surface metallic deposit as sample). We have obtained spectra with both cells for the visible and the near infra-red spectral region. The PPE spectra reproduces reliably the Xenon lamp spectra with a better signal to noise ratio compared with the Photoacoustic ones, a very well recognized technique for optical spectroscopy. We have applied the DSPPE methodology to a set of five commercial Brazilian margarine in order to exemplify its potential to the study of pasty materials as some foodstuffs. Figure 4 presents results for the thermal diffusivity and thermal effusivity as a function of the fat (or water) content in the five different margarine. As expected the values of both thermal parameters increase with the decrease of fat content (water content increase). One should remind the values for water: $\alpha = 1.47 \times 10^{-3}$ cm$^2$/s and $\varepsilon = 1.62 \times 10^{3}$ Ws$^{1/2}$/m$^2$K (Table). The large value for the effusivity of 72% fat content margarine can be due to variations in the production process of the producer (we have used commercially available margarine samples), given that two different operators carried out our experiments finding very close values. The methodology behaved very sensitive to the fat/water content of the samples. In the fat content range of our experiment the thermal diffusivity values changed 35% and those of thermal effusivity changed 24%.

In the Table are summarized the results found for the thermal effusivity and thermal diffusivity of water at room temperature using the DSPPE configuration. One can see that the precision obtained for the parameters (showed between parenthesis in the Table), and taken from the root-mean-square deviation, are better than the usual expected for PPE experiments [03, 05, 06]. Comparison with the literature available experimental data shows an accuracy less than 0.7% for the diffusivity and 2.5% for effusivity values, a quite expressive result considering the many different compositions one can find water.

Figure 4 – DSPPE results for the thermal diffusivity and thermal effusivity at room temperature of 05 different fat content margarine available in the Brazilian market. Data represents an average over 03 measurements.

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References