

Specific Heat Measurements by a Thermal Relaxation Method: Influence of Convection and Conduction¹

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This paper involves the well-known thermal relaxation method for measurement of the specific heat (c) of thin solid samples. Although this method was applied successfully in recent years for the characterization of different materials, in this work some aspects that must be taken into account in order to avoid problems based on satisfying the required experimental conditions of heat flux imposed by the physical model used for data analysis and processing will be discussed. For this purpose, for a given experimental geometry, the heat diffusion equation will be solved in order to obtain the sample's requirements for reliable measurements of c , regarding its thickness and thermal conductivity. An experimental device is described that can be used for the study of the influence of heat dissipation by convection on the method. A computer simulation was performed for comparing the simple model with one that takes to in account the gradient of temperature inside the sample. The results of measurements are presented.

KEY WORDS: heat conduction; heat convection; specific heat capacity.

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1. INTRODUCTION

This work deals with an experimental approach currently used for the measurement of the specific heat capacity, C , of small solid samples at room temperature. This property is defined as a product of the specific heat, c , and the density, ρ , and expresses the amount of heat developed per mass unit in a sample of unit volume when its temperature is varied by 1 K. Its knowledge is of great importance in solid-state physics because it provides us with a direct means to test theoretical models of a given physical system and because of its sensitivity to phase transitions, etc.

There are several methods for the experimental determination of this parameter in solids. Some of them are discussed in detail by Touloukian [1], while in the work of Kraftmakher [2] an overview of the most useful calorimetric methods is given. Recently, photo acoustic methods have also been reported for the same purpose [3,4].

The temperature relaxation method offers the advantages of an inexpensive and relatively simple experimental setup. It is based on first disturbing an adiabatically isolated sample from its state of equilibrium by light irradiation, and then measuring the time changes in its absolute temperature, T . If the deviation of the system from the state of equilibrium is small, the relaxation is described by the equation $T(t) = T_0 \exp(-t/\tau)$, where T_0 is the initial value of the temperature and τ is the relaxation time of the system. This relaxation time, for the case of thin samples with high thermal conductivity—as we will see later—is related to the sample's specific heat. This method was first proposed by Bachmann et al. [5] for low-temperature (1–35 K) measurements; it was later extended to measurements below 1 K by Schutz [6] and successfully used, with appropriate modifications, by several authors in a higher temperature range. Djurek and Baturic-Rubidic [7] have modified the Bachmann method for measurements above 35 K. Experiments on tungsten in the range 2400–3600 K were performed by Zinov'ev and Lebedev [8]. Hatta [9] has designed a relaxation calorimeter, employing for the first time light heating for measurements on small samples in the temperature range around room temperature. Mansanares et al. [10] have later developed Hatta's approach for simple measurements of C at room temperature. This variant of the temperature relaxation method, designed by the last mentioned authors as the temperature rise method under continuous illumination, has been used in recent years for a characterization of different materials such as semiconductors [11], foods [12], wood [13], zeolites [14], clays [15], and ferroelectric ceramics [16,17], among others.

In this work we will discuss some aspects related to the relaxation method that must be taken into account in order to avoid problems based

on satisfying the required experimental conditions of heat flux imposed by the physical model used for data analysis and processing. For this purpose, for a given experimental geometry, we will solve the heat diffusion equation in order to obtain the sample's requirements for reliable measurements of C , regarding its thickness and thermal conductivity. The influence of heat dissipation by convection on the method will also be analyzed. For this purpose calculations taking into account convection heat losses were performed, and a measurement cell was designed and constructed allowing measurements to verify the reliability of the theoretical model. The results of these measurements confirm our theoretical predictions.

2. EXPERIMENTAL DETAILS AND THEORY

2.1. Experimental Setup

Our typical experimental setup (Fig. 1) is a straightforward modification of the widely used arrangement described elsewhere [10–17]. The samples of thickness L were horizontally (minimizing, in this way, convection effects due to buoyancy forces) and adiabatically supported in a constant temperature reservoir (with the help of thin, low thermal-conductivity isolating wires, because it is important that there is minimal energy exchange between the sample and everything else other than the reservoir), which has an optical glass window through which a white light beam is uniformly focused onto the upper surface of the sample. On the opposite side, a chromel–alumel thermocouple is attached mechanically to the sample. A good contact is achieved by the vertical movement of the sample using screws on which their supporting wires are firmly attached, as shown in the Figure. The temperature evolution of the back surface could be monitored as a function of time. A vacuum system consisting of a mechanical oil pump and a Pirani vacuum meter is connected to the reservoir. Before the samples are mounted on the support, they are cut to the desired dimensions (they are typically shaped as 1 cm diameter discs or 1 cm side squares, each about 0.1 cm thick) and their surfaces are sprayed with a thin black paint layer to assure good light absorption.

2.2. Basic Theory

The variation with time of the generated heat in the sample, due to the absorption of light of incident power P_0 , is given by

$$\frac{\partial Q}{\partial t} = P_0 - R \quad (1)$$

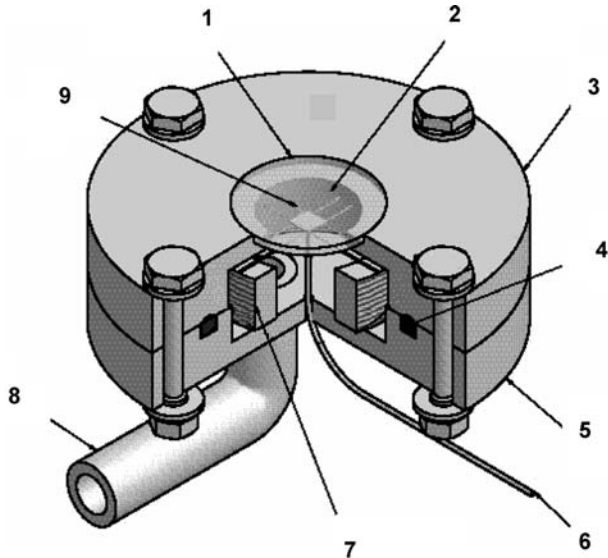


Fig. 1. Schematic view of the measurement cell. 1-optical glass window; 2-sample; 3-upper part of the (Stainless Steel) measurement reservoir (consisting on two dismountable parts); 4-vacuum o-ring; 5-lower part of the reservoir; 6-thermocouple; 7-screw allowing the up (down) vertical movement of the sample and its good mechanical thermal contact with the thermocouple; 8-valve to vacuum system; 9-nylon wires forming the sample's support.

where R represents the power lost by radiation, given by the Stefan–Boltzmann law of radiation, which for temperature variations in the sample ΔT much lower than the ambient temperature T_0 is reduced to

$$R \approx 4A\varepsilon\sigma T_0^3 \Delta T \quad (2)$$

where A is the sample's surface area, ε is the emissivity ($\varepsilon \approx 1$ if the sample's surfaces are black painted, as in our case), T is the sample temperature, and σ is the Stefan–Boltzmann constant. In Eq. (1) we have considered only heat losses by radiation.

Neglecting the temperature gradient present in the sample, it has been obtained [10] that the rise in temperature of the back surface is given by [10]

$$\Delta T_{\uparrow}(t) = \frac{P_0}{AH} \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (3)$$

When the illumination is interrupted, the sample's temperature decreases as follows:

$$\Delta T_{\downarrow}(t) = \frac{P_0}{AH} \exp\left(-\frac{t}{\tau}\right), \quad (4)$$

In the above equations

$$\tau = \frac{LC}{2H} \quad (5)$$

Here, L is the sample thickness and $H = 4\sigma T_0^3$. We can determine τ by fitting the experimental results with Eq. (3) or (4). Then, the specific heat capacity C can be obtained from Eq. (5).

2.3. Influence of Convection

Assuming convection losses, one should introduce in the energy balance equation, Eq. (1), a term given by Newton's cooling law:

$$K = hA\Delta T \quad (6)$$

where h is a characteristic parameter that encompasses the effects of the fluid (air in our case) that flows near the sample surface, the fluid properties, and the surface geometry. The H term in Eqs. (3) and (4) must be replaced now by [18],[19]

$$H = H_K = 4\sigma T_0^3 + h \quad (7)$$

If we denote τ_k as the relaxation time measured under atmospheric pressure, one can easily demonstrate from the above equations that

$$h = 4\varepsilon T_{\text{amb}}^3 \left(\frac{\tau}{\tau_K} - 1 \right) \quad (8)$$

2.4. Consideration of Heat Conduction

In the above-described model an important approximation was made that allows simplification of the mathematical treatment of the problem. This approximation consisted of neglecting the temperature gradient present in the sample due to heat conduction. If we consider it, we can obtain the temperature field $T(x,t)$ solving the one-dimensional heat diffusion problem with surface energy losses, i.e., the third kind boundary condition.

Let us denote

$$u = u(x, t) = \Delta T = T(x, t) - T_0 \quad (9)$$

Taking into account the existence of a temperature gradient across the sample, the temperature rise during illumination, u_{\uparrow} , is described by the following set of equations:

$$\frac{\partial u_{\uparrow}(x, t)}{\partial t} = \alpha \frac{\partial^2 u_{\uparrow}(x, t)}{\partial x^2} \quad 0 < x < L \quad t > 0 \quad (10)$$

$$u_{\uparrow}(x, t=0) = 0 \quad (11)$$

$$\gamma_1 u_{\uparrow}(0, t) - k \left. \frac{\partial u_{\uparrow}(x, t)}{\partial x} \right|_{x=0} = P_0 \quad (12)$$

$$\gamma_2 u_{\uparrow}(0, t) - k \left. \frac{\partial u_{\uparrow}(x, t)}{\partial x} \right|_{x=0} = 0 \quad (13)$$

When the illumination is interrupted, the system of equations becomes

$$\frac{\partial u_{\downarrow}(x, t)}{\partial t} = \alpha \frac{\partial^2 u_{\downarrow}(x, t)}{\partial x^2} \quad 0 < x < L \quad t > 0 \quad (14)$$

$$u_{\downarrow}(x, t=0) = w(x) \quad (15)$$

$$\gamma_1 u_{\downarrow}(0, t) - k \left. \frac{\partial u_{\downarrow}(x, t)}{\partial x} \right|_{x=0} = P_0 \quad (16)$$

$$\gamma_2 u_{\downarrow}(0, t) - k \left. \frac{\partial u_{\downarrow}(x, t)}{\partial x} \right|_{x=0} = 0 \quad (17)$$

where $w(x)$ is the saturation temperature, α is the thermal diffusivity, and k is the thermal conductivity. The later parameters are related by $\alpha = k/C$. In the above equations γ_1 and γ_2 are the heat exchange parameters at the front and rear surfaces of the sample, respectively. In general, we can write

$$\gamma = \gamma_1 = \gamma_2 = H \quad (18)$$

where H is given by Eq. (7).

Using the well known method of separation of variables, we can propose

$$u_{\uparrow}(x, t) = w(x) + v(x, t) \tag{19}$$

and

$$u_{\downarrow}(x, t) = -v(x, t) \tag{20}$$

Substituting in Eqs. (10)–(19), one obtains

$$w(x) = \frac{-\gamma_2 P_0 x + (\gamma_2 L + k) P_0}{(\gamma_2 + \gamma_1) k + \gamma_2 \gamma_1 L} \tag{21}$$

$$v(x, t) = \sum_{n=1}^{\infty} A_n e^{-\lambda_n a^2 t} \left[\frac{k\sqrt{\lambda_n}}{\gamma_1} \cos(\sqrt{\lambda_n} x) + \sin(\sqrt{\lambda_n} x) \right] \tag{22}$$

where we have set $\alpha = a^2$. For the eigenvalues we have

$$\lambda_n = \left(\frac{\mu_n}{L} \right)^2 \tag{23}$$

$$tg(\mu) = \frac{\frac{L}{k} (\gamma_1 + \gamma_2) \mu}{\left(\frac{\gamma_1 \gamma_2 L^2}{k^2} - \mu^2 \right)} \tag{24}$$

and

$$A_n = \frac{1}{\|X_n\|} \int_0^L -w(\xi) X_n(\xi) d\xi \tag{25}$$

with

$$\|X_n\|^2 = \int_0^L \left[\frac{k\sqrt{\lambda_n}}{\gamma_1} \cos(\sqrt{\lambda_n} x) + \sin(\sqrt{\lambda_n} x) \right]^2 dx \tag{26}$$

Similar results can be found in many problems related to heat propagation in materials following the absorption of laser pulses [18–20], such as the transient heat transport by electrical carriers and phonons in semiconductors [21, 22], among others.

3. RESULTS AND DISCUSSION

3.1. Influence of Convection

Figure 2 shows open circles with typical heating and cooling curves measured on a $500\mu\text{m}$ thick copper sample in vacuum of 4×10^{-3} Torr and room temperature of 300 K. The results of measurements at atmospheric pressure on the same sample are plotted as full circles for comparison purposes. As expected, a shift of the curves is obtained as a result of the influence of the convection term. The solid curves, as above, represent the best fit to the theoretical expressions, from which a value of τ was obtained as a mean value from those corresponding to the heating and cooling curves. From the values of τ (at 4×10^{-3} Torr) and τ_k (measured at atmospheric pressure), h was calculated using Eq. (8) as $h = (2.30 \pm 0.50) \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. As discussed in previous studies [23, 24], the value of this parameter can be used for a libration for the given experimental setup (a larger value was obtained for this parameter in our previous studies, where another measurement cell was used) allowing the determination of C by measurements at atmospheric pressure and using Eq. (5), with $H = H_K$ for the calculation of C .

Using this value of h , the results of similar measurements performed in some typical materials are summarized in Table I. The very good agreement between experimental and theoretical values can be observed, as well

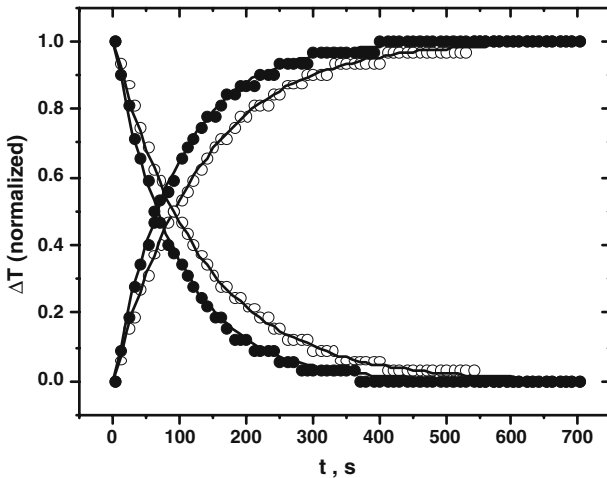


Fig. 2. Typical heating and cooling curves for measurements performed under vacuum conditions (open circles) and without vacuum (solid circles) on copper samples; continuous lines show the best fit of Eqs. (3) and (4) to the experimental data, respectively.

Table I. Experimental Results

Sample	τ_K (s)	τ (s)	L (μm)	h ($\text{W}\cdot\text{cm}^{-2}\cdot\text{K}^{-1}$)	C ($\text{J}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$)	C_{lit} ($\text{J}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$)
Cu	95.2 ± 0.5	130.6 ± 0.5	500 ± 1	$(2.3 \pm 0.2) \times 10^{-5}$	3.20 ± 0.5	3.45
Si		54.9 ± 0.7	400 ± 1	from Eq. (6)	1.68 ± 0.1	1.65
Zn		109.8 ± 0.1	500 ± 1		2.69 ± 0.1	2.77
Al		99.9 ± 0.1	500 ± 1		2.45 ± 0.5	2.43

as the better results compared with previous studies [23,24], presumably due to the improved experimental configuration.

3.2. Consideration of the Gradient of Temperature Inside the Sample: Comparison with the Simple Model

We will begin our analysis looking for a criterion allowing neglecting of losses by heat conduction through the sample and of the temperature gradient. We can define

$$\Delta u_{\text{max}} = u_{\uparrow}(0, \infty) - u_{\uparrow}(L, \infty) = u_{\downarrow}(0, 0) - u_{\downarrow}(L, 0) = w(0) - w(L) \quad (27)$$

as the maximum possible temperature difference between both sides of the sample (Fig. 3).

We have obtained after a straightforward calculation the difference between the temperature extreme values:

$$\Delta u_{\text{max}} = \frac{\gamma_2 P_0 L}{k(\gamma_2 + \gamma_1) + \gamma_2 \gamma_1 L} \quad (28)$$

for $\gamma = \gamma_1 = \gamma_2$

$$\Delta u_{\text{max}} = \frac{P_0}{2} \frac{1}{\frac{k}{L} + \frac{\gamma}{2}} \quad (29)$$

and its ratio:

$$\frac{w(0)}{w(L)} = 1 + \gamma_2 \frac{L}{k} = \frac{\frac{k}{L} + \gamma}{\frac{k}{L}} \quad (30)$$

Then, on the basis of Eqs. (29) and (30), the gradient of temperature inside the sample may be neglected when the following criterion is fulfilled:

$$k/L \gg \gamma \quad (31)$$

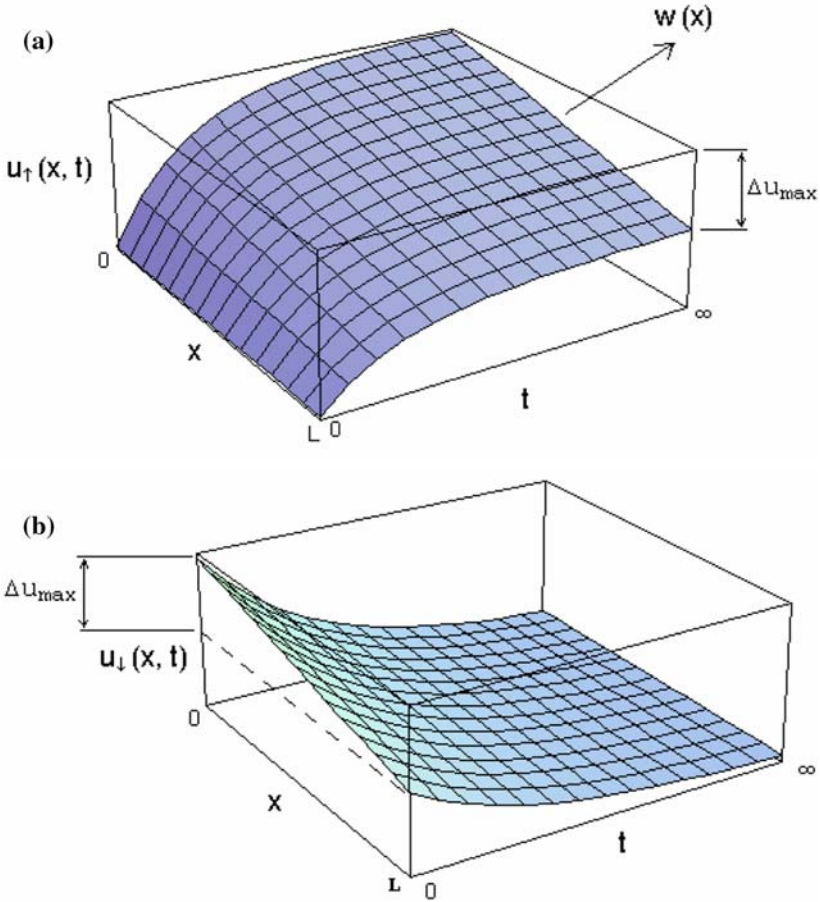


Fig. 3. Graphs of (a) $u_{\uparrow}(x, t)$ and (b) $u_{\downarrow}(x, t)$.

Substituting $\gamma = H$, one obtains

$$k/L \gg H \tag{32}$$

or

$$k/V \gg H/A, \tag{33}$$

where $V = AL$ is the sample volume.

Taking into account the definition of thermal resistance,

$$R_t = L/(Ak) \tag{34}$$

we obtain

$$R_t \ll 1/(HA) \quad (35)$$

The obtained results corroborate that the temperature gradient can be neglected for all materials for which the condition in Eq. (34) is satisfied, i.e., when the thermal resistance of the sample is much less than its resistance to convective and radiation effects, as expressed by the right-hand side of that condition.

A graphic simulation of the temperature behavior in the backside of the sample for the models presented above is shown in Fig. 4. A comparison between the results of a typical simple, phenomenological model of Sections 2.2 and 2.3 and the analytical model considering the temperature gradient described in Section 2.4 is presented. For simplicity we have set $h=0$.

Figure 3a shows the results obtained for a $50\mu\text{m}$ thick typical high conductivity sample such as copper, Cu (thermal conductivity $k=400\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $C=3.45\text{ J}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$). The results for a low conductivity sample (wood, $k=0.04\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $C=1.35\text{ J}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$) are presented in Fig. 4b and c for thicknesses of 500 and $2000\mu\text{m}$, respectively. As one can see, the curves resulting from both models overlap. There is only a small difference for the thicker sample of Fig. 4c.

On the basis of the computer simulations, we conclude that although the temperature gradient forming across the sample as a result of heating can play an important role in the model for high values of L/k , the phenomenological model described in Section 2 can be used with confidence for common materials and for thicknesses satisfying the one-dimensional approach.

It should be noted that the results given by Eq. (34) are similar to those obtained by Bachman et al. [5]. In the mentioned work the authors state that the temperature gradient can be neglected when the relaxation time $\tau = LC/2H$ is greater than the internal relaxation time $\tau_i = L^2 C/k$. This is analogous to comparing $1/H$ with L/k , as in Eq. (31), or R_t with $1/HA$, as done above. As the parameter H is not related to the sample dimensions or thermal properties, then the sufficient condition ($\tau \gg \tau_i$), for the same H , will be met for very thin samples with high thermal conductivity.

4. CONCLUSIONS

Convection losses and the temperature gradient inside a sample were taken into account and their influence on the results of the temperature relaxation method has been discussed. An experimental device was

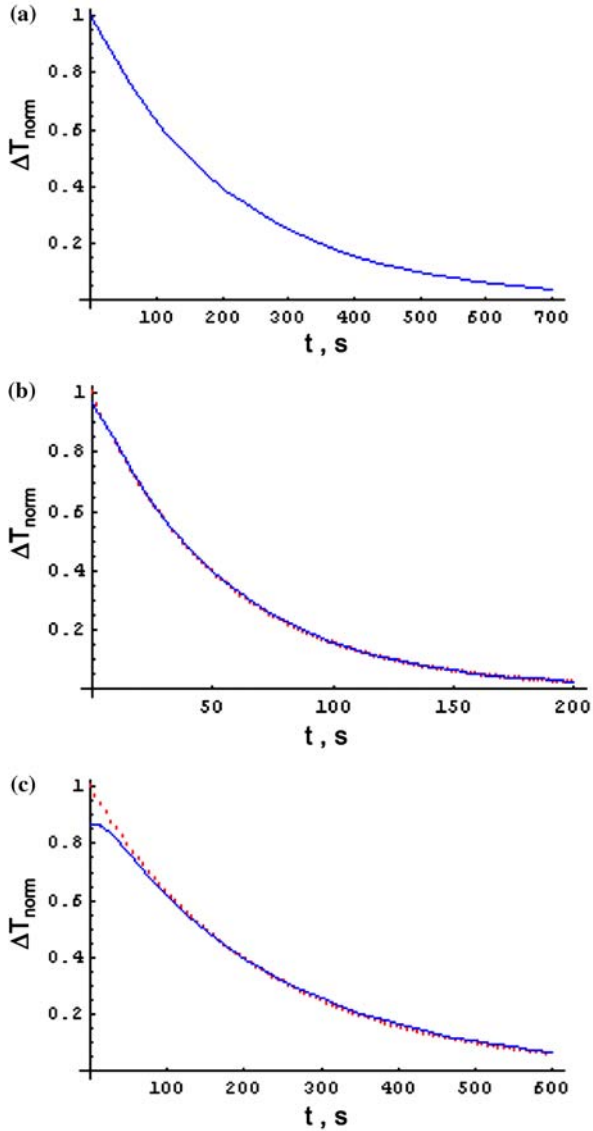


Fig. 4. Normalized temperature relaxation curves predicted by both the simple (dashed curve) and analytical (solid curve) models: (a) 50 μm thick high thermal-conductivity sample, (b) 500 μm thick low thermal-conductivity sample, and (c) 2000 μm thick low thermal-conductivity sample.

designed that can be used for the study of the influence of convection on the experimental results. It is shown that the heat transfer coefficient, characteristic for this phenomenon, can be used to determine the specific heat capacity of solids by measurements performed at atmospheric pressure. Furthermore, a simulation of the temperature evolution was made, comparing the phenomenological model (commonly used in this technique) with a more rigorous one, which takes into account the temperature gradient created in the sample. The obtained results corroborate that the approximation is possible for all materials for which the condition, $R_t \ll 1/HA$, is satisfied, i.e., the phenomenological model described above can be used without problems for common materials and for typical thicknesses for which the one-dimensional approach is valid.

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