Application of ultrasound for green extraction of proteins from spirulina. Mechanism, optimization, modeling, and industrial prospects

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An improved model for the parallel hot wire: application to thermal conductivity measurement of low density insulating materials at high temperature

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Abstract

This paper presents a new model of the the transient temperature at a point situated at a distance d of the heating wire, in a parallel hot wire measurement device. A preliminary theoretical study shows the limits of the estimation method proposed by the standard ISO8894-2. First, we proposed an optimal processing method, based on the model used in the standard, to improve the estimation of the thermal conductivity. Then, a new model based on the quadrupolar formalism is developed, it takes into account: the mass and the radius of the heating wire, the thermal contact resistance between the heating wire and the sample and the mass of the thermocouple. A theoretical study shows that this model enables a precise estimation of the thermal conductivity of a large range of materials and that it makes also possible to obtain an estimation of the volume heat capacity. An experimental study has been realized using a very low density material (polystyrene with $\rho = 15\ \mathrm{kg\,m^{-3}}$) at ambient temperature and a reference material (Silcal 1100) at temperatures varying from 200°C to

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1000°C to validate the results of the theoretical study. Compared to known thermal properties of these two materials, the thermal conductivity was estimated with a deviation lower than 3.4 % and the volume heat capacity was estimated with a deviation lower than 10%.

1. Introduction

A variant of the hot wire method consists in placing in the medium to characterize a thermocouple parallel to the heating wire and to record its temperature. The measurement of this temperature makes it possible to estimate the thermal conductivity and the thermal diffusivity of the medium. This transient method called the parallel hot wire method was the object of the standard ISO 8894-2 [1] concerning the determination of the thermal conductivity of refractory materials.

The device of the parallel hot wire associated with the estimation method defined by the standard was used to characterize various types of materials among them: refractories [2-3], polymers [4], soils [5] and insulating materials [6].

The model used by the standard is based on the simplifying hypothesis that the radius of the heating wire is null. Hakansson et al [7] took into account the variation of the supply power that may be negligible if the temperature coefficient of the electrical resistance is low. Pettersson [8] studied the influence of the thermal conductivity of the wire and concluded that it has no influence on the estimation of the thermal conductivity. Grazzini et al [9] proposed a model taking into account the heating wire radius and the thermal contact resistance, leading to an analytical expression of Laplace transform $\theta_t(p)$ of the temperature rise $T_t(t)$ of the thermocouple. Nevertheless, some approximations are necessary to obtain an analytical expression of $T_t(t)$ and these authors conclude that their model does not provide better estimation of the thermal conductivity than the simplified model (heating wire with a null radius).

Furthermore, one can notice that the thermal capacity of the thermocouple was never taken into account in all the previously cited models.

Some studies based on numerical simulations have also been realized to estimate the time limit for the validity of the semi-infinite medium hypothesis (always considered in the hot wire methods) [10], [11], [12].

The aim of this paper is to propose a more complete quadrupolar analytical model and to estimate the error caused by the simplified model used in the standard, for various types of materials. The presented model takes into account the radius and the thermal capacity of the heating wire, the thermal contact resistances between the heating wire and the sample on one hand and between the thermocouple and the sample on the other hand, as well as the thermal capacity of the thermocouple. It will be shown that the analysis of the residues of estimation makes it possible to determine easily the time limit of validity of the hypothesis of the semi-infinite medium. An experimental study realized on two reference materials will validate the results of the theoretical study

2. Models

The schematic diagram of the method is presented in figure 1.

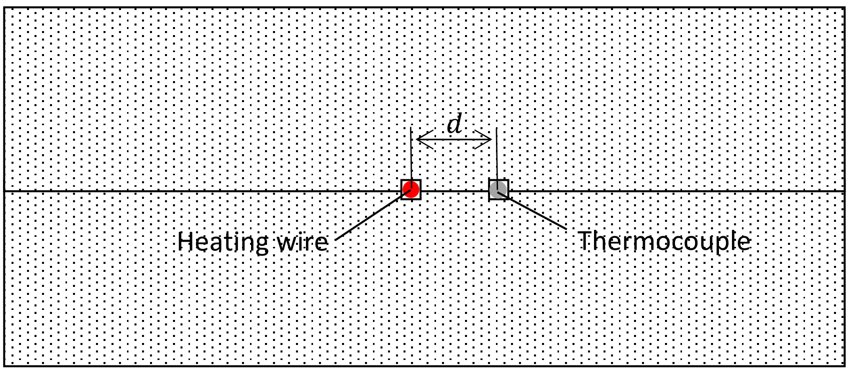

Figure 1: Schematic diagram of the parallel hot wire method

A resistive wire with a radius r_w is inserted in a groove realized on the surface of the bottom sample. A thermocouple is inserted in another groove realized at the surface of the same sample at distance d of the heating wire. A second sample with the same dimensions as the bottom sample is then placed on it.

Quadrupolar model

A quadrupolar model M1 will now be developed considering the following hypotheses:

- The samples are semi-infinite
- The heating wire and the thermal contact resistance between the wire and the samples are taken into account
- The thermocouple is not taken into account: the thermal properties of the sample and of the thermocouple are the same and the thermal contact resistances between the thermocouple and the samples are negligible.
- The sample is optically thick

One can write the following quadrupolar relation [13] between the heating wire and a point in the solid at a distance d from the wire:

$$\begin{bmatrix} \theta_w \\ \frac{\varphi_w}{p} \end{bmatrix} = \begin{bmatrix} A_w & B_w \\ C_w & D_w \end{bmatrix} \begin{bmatrix} 1 & R_c \\ 0 & 1 \end{bmatrix} \begin{bmatrix} A_s & B_s \\ C_s & D_s \end{bmatrix} \begin{bmatrix} \theta_d \\ \frac{\theta_d}{Z} \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \theta_d \\ \frac{\theta_d}{Z} \end{bmatrix} \qquad (1)$$

With:

$A_w = 1$

$B_w = \frac{1}{2\pi\lambda_w L q_w r_w} \frac{I_0(q_w r_w)}{I_1(q_w r_w)} - \frac{1}{\rho_w c_w \pi {r_w}^2 L p}$

$C_w = \rho_w c_w \pi {r_w}^2 L p$

$D_w = \frac{q_w r_w}{2} \frac{I_0(q_w r_w)}{I_1(q_w r_w)}$

$A_s = q_s d[K_1(q_s d) I_0(q_s r_w) + K_0(q_s r_w) I_1(q_s d)]$

$$B_s = \frac{1}{2\pi\lambda_s L}[K_0(q_s r_w)I_0(q_s d) - K_0(q_s d)I_0(q_s r_w)]$$

$$C_s = 2\pi L\rho_s c_s r_w dp[K_1(q_s r_w)I_1(q_s d) - K_1(q_s d)I_1(q_s r_w)]$$

$$D_s = q_s r_w[K_1(q_s r_w)I_0(q_s d) + K_0(q_s d)I_1(q_s r_w)]$$

$$\frac{1}{Z} = 2\pi\lambda_s L q_s d\,\frac{K_1(q_s d)}{K_0(q_s d)};\ q_w = \sqrt{\frac{p}{a_w}}\quad;\ q_s = \sqrt{\frac{p}{a_s}}$$

Where:

θ_w Laplace transform of the temperature rise of the wire

θ_d Laplace transform of the temperature rise at a distance d in the solid

I_0, I_1, K_0, K_1 modified Bessel function of the first and second kind

λ_w thermal conductivity of the heating wire

$\rho_w c_w$ volume heat capacity of the heating wire

a_w thermal diffusivity of the heating wire

L length of the heating wire

r_w radius of the heating wire

d distance between the heating wire and the thermocouple

λ_s thermal conductivity of the sample

$\rho_s c_s$ volume heat capacity of the sample

a_s thermal diffusivity of the sample

R_c thermal contact resistance between the heating wire and the sample

p Laplace parameter

φ_w Heat flow rate in the heating wire

Then:

$$\frac{\varphi_w}{p} = \left(C + \frac{D}{Z}\right)\theta_d \qquad (2)$$

And finally: $\theta_d(p) = \dfrac{\frac{\varphi_w}{p}}{C+\frac{D}{Z}}$ (3)

with:

$$C = A_s C_w + C_s(C_w R_c + D_w) \quad (4)$$

$$D = B_s C_w + D_s(C_w R_c + D_w) \quad (5)$$

If the thermal resistance of the heating wire can be neglected, relation (3) becomes:

$$\theta_d(p) = \frac{\frac{\varphi_w}{p\,L} K_0(q_s d)}{\rho_w c_w \pi r_w{}^2 p\, K_0(q_s r_w) + 2\pi\lambda q_s r_w [1 + \rho_w c_w \pi r_w{}^2 p R_c L] K_1(q_s r_w)} \quad (6)$$

Relation (6) is identical to the one given by Grazzini et al [9].

<u>Case where the thermocouple properties are very different from those of the samples</u>

In this case, one can no longer consider that the thermocouple's properties are identical to those of the material to characterize. If we also consider the simplifying hypothesis that the temperature field in the sample close to the thermocouple is not modified by the thermocouple, the Laplace transform $\theta_t(p)$ of the temperature rise $T_t(t)$ at a distance d from the heating wire can always be calculated using relation (3).

Since the thermocouple does not produce any heat, if $\theta_t(p)$ is the Laplace transform of the mean temperature of the thermocouple, one can write [12]:

$$\begin{bmatrix} \theta_t \\ 0 \end{bmatrix} = \begin{bmatrix} A_t & B_t \\ C_t & D_t \end{bmatrix} \begin{bmatrix} 1 & R_t \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \theta_d \\ \Phi_\mathrm{d} \end{bmatrix} \quad (7)$$

Where:

$\begin{bmatrix} A_t & B_t \\ C_t & D_t \end{bmatrix}$ is the quadrupolar matrix of the thermocouple

Φ_d is the Laplace transform of the heat flow rate at a distance d from the heating wire.

R_t is the thermal contact resistance between the thermocouple and the sample.

Neglecting the thermal resistance of the thermocouple material compared to the thermal contact resistance between the thermocouple and the sample (hypothesis of uniform temperature), one can write:

$$A_t = 1\ ;\ B_t = 0\ ;\ C_t = \rho_t c_t \pi {r_t}^2 L\, p\ ; D_t = 1 \quad (8)$$

Where r_t is the radius of the thermocouple, L is its length, ρ_t is its density and c_t its specific heat.

Then, the relation (7) leads to the model that we will call M2:

$$\theta_t(p) = \frac{\theta_d(p)}{1+C_t p} \quad (9)$$

Where $C_t = \rho_t c_t \pi {r_t}^2 L\, R_t$ can be considered as a time constant (s).

Model used in the standard ISO 8894-2

The model used in the standard ISO 8894-2 (that we will call M0) is an approximation calculated for a heating wire having a null radius ($r_w = 0$). One can use the limited developments of the Bessel functions in the vicinity of zero:

$$K_0(x) \approx -ln(x)\ ; K_1(x) \approx \frac{1}{x}\ ; I_0(x) \approx 1\ ; I_1(x) \approx \frac{x}{2} \quad (10)$$

Hence:

$$A_w \approx 1$$

$$B_w \approx 0$$

$$C_w \approx 0$$

$$D_w \approx 1$$

Considering these approximations:

$$C = A_s C_w + C_s(C_w R_c + D_w) = C_s \quad (11)$$

and:

$$D = B_s C_w + D_s(C_w R_c + D_w) = D_s \quad (12)$$

Thus:

$$C_s = 2\pi L \rho_s c_s r_w d p [K_1(q_s r_w) I_1(q_s d) - K_1(q_s d) I_1(q_s r_w)] \approx 2\pi L \sqrt{\lambda_s \rho_s c_s} d \sqrt{p} I_1(q_s d) \quad (13)$$

$$D_s = q_s r_w [K_1(q_s r_w) I_0(q_s d) + K_0(q_s d) I_1(q_s r_w)] = I_0(q_s d) \quad (14)$$

So that:

$$C + \frac{D}{Z} = 2\pi L \sqrt{\lambda_s \rho_s c_s} d \sqrt{p} I_1(q_s d) + 2\pi \lambda L q d \frac{K_1(q_s d)}{K_0(q_s d)} I_0(q_s d) \quad (15)$$

$$C + \frac{D}{Z} = 2\pi L \sqrt{\lambda_s \rho_s c_s} d \sqrt{p} \left[\frac{I_1(q_s d) K_0(q_s d) + K_1(q_s d)\, I_0(q_s d)}{K_0(q_s d)}\right] = \frac{2\pi \lambda L}{K_0(q_s d)} \quad (16)$$

We have: $\theta_t(p) = \frac{\varphi_w}{p} \frac{K_0(q_s d)}{2\pi \lambda_s L}$ (17)

According to Carslaw and Jaeger [14]:

$$L^{-1}\left[\frac{1}{p}\, K_0\left(x\sqrt{p}\right)\right] = \frac{1}{2} \int_{\frac{x^2}{4t}}^{\infty} \frac{e^{-u}}{u}\, du \quad (18)$$

with: $-E_i(y) = \int_y^{\infty} \frac{e^{-u}}{u}\, du$ (19

Thus: $T_t(t) = -\frac{\varphi_w}{4\pi \lambda_s L}\, E_i\left(\frac{d^2}{4 a_s t}\right)$ (20)

Where E_i is the exponential integral

This solution was given by Carslaw and Jaeger [14], it was deducted from the temperature field in a semi-infinite medium in which a heat flow rate step is applied on a line.

Figure 2 shows the temperature simulated using the relations (3) and (20). The value of the temperature calculated by the relation (20) (standard) is always lower than the value calculated by the quadrupolar model. The two models converge for long times. Table 1 gives the parameters values used for the simulation

Table 1: Values of the parameters used for the simulations in figure 2

	r_w	λ_w	$\rho_w c_w$	d	λ_s	$\rho_s c_s$	R_c
	mm	W m^{-1} K^{-1}	J m^{-3} K^{-1}	mm	W m^{-1} K^{-1}	J m^{-3} K^{-1}	K W^{-1}
Figure 2a)	0.25	11.3	3.78×10^6	5	0.1	5×10^5	3.5
Figure 2b)	0.25	11.3	3.78×10^6	5	0.2	5×10^5	3.5

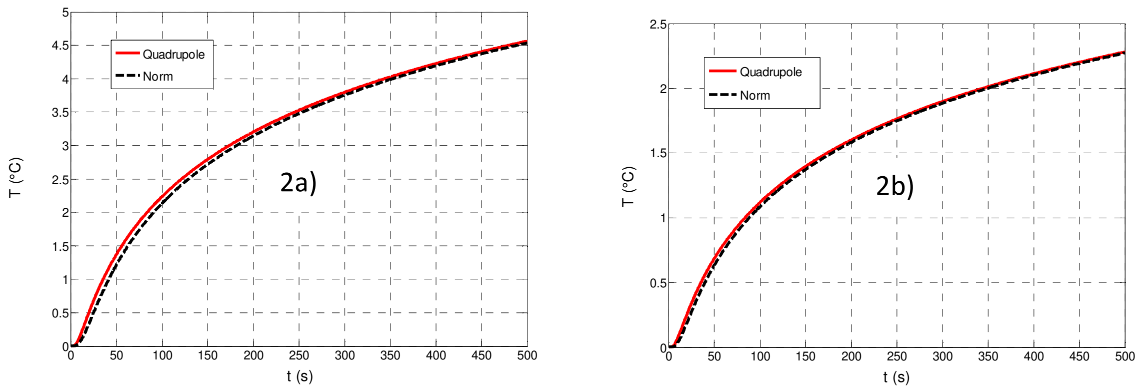

Figure 2: Temperature of the thermocouple simulated with the model of the standard and with the quadrupolar model: 2a) $\lambda_s = 0.1\ \mathrm{W\ m^{-1}\ K^{-1}}$ *; 2b)* $\lambda_s = 0.2\ \mathrm{W\ m^{-1}\ K^{-1}}$

3. Parameters estimation

Quadrupolar models (M1 and M2)

The thermal properties of the resistive heating wire are supposed to be known so that the unknowns are the thermal conductivity λ_s and volume capacity $\rho_s c_s$ of the samples and the thermal contact resistance R_c between the heating wire and the samples. The time constant C_t

can be added as an unknown parameter if the sample thermal properties are very different from those of the thermocouple.

The temperature rise $T_t(t)$ can be calculated by an inverse Laplace transform applied to $\theta_t(p)$ realized by using the De Hoog algorithm [15]. The Levenberg-Marquart algorithm [16] is used to find the values of the unknown parameters that minimize the sum of the quadratic errors:

$$S = \sum_{n=1}^{N} \left[T_{t_{exp}}(t) - T_{t_{mod}}(t)\right]^2 \tag{21}$$

The parameters λ_s, $\rho_s c_s$ and R_c must be estimated in the model M1 and the parameters λ_s, $\rho_s c_s$, R_c and C_t must be estimated in the model M2.

Standard ISO 8894-2 (Model M0)

We have: $T_t(2t) = -\frac{\varphi_w}{4\pi\lambda_s L}\, E_i\left(\frac{d^2}{8a_s t}\right)$ (22)

Thus: $U = \frac{T_t(2t)}{T_t(t)} = \frac{E_i\left(\frac{d^2}{8a_s t}\right)}{E_i\left(\frac{d^2}{4a_s t}\right)} = \frac{E_i\left(\frac{u}{2}\right)}{E_i(u)}$ (23)

Where: $u = \frac{d^2}{4a_s t}$

For each value of u one can calculate $E_i(u)$ and $U = \frac{E_i\left(\frac{u}{2}\right)}{E_i(u)}$. Thus the function $E_i(u) = f\left[U = \frac{E_i\left(\frac{u}{2}\right)}{E_i(u)}\right]$ can be plotted and modelled. We have identified the following polynomial function which enables its calculation with a precision better than 1%:

$$E_i(u) = a_0 + a_1 U + a_2 U^2 + a_3 U^3 + a_4 U^4 + a_5 U^5 + a_6 U^6 + a_7 U^7 \tag{24}$$

$a_0 = 474.926168472597$

$a_1 = -1574.223079517534$

$a_2 = 2262.705889755608$

$a_3 = -1816.820318813171$

$a_4 = 877.286213344994$

$a_5 = -254.261946376719$

$a_6 = 40.904415135482$

$a_7 = -2.815400284900$

The principle of the method is the following:

- The temperature rise T_t is recorded during a time $2t_f$
- The ratio $U = \frac{T_t(2t)}{T_t(t)}$ is calculated for each time value comprised in the interval [0 t_f]
- One can deduce $E_i\left(u = \frac{d^2}{4a_s t}\right)$ from relation (24) then λ_s is obtained using the relation:

$$\lambda_s = -\frac{\varphi_w}{4\pi L\, T_t(t)}\, E_i\left(\frac{d^2}{4a_s t}\right) \tag{25}$$

The calculation must be done on a time interval where the hypotheses (negligible mass of the heating wire and semi-infinite medium) are valid, we will see further how this time interval can be determined.

When applying the standard ISO 8894-2, $E_i(u)$ is deduced from $U = \frac{T_t(2t)}{T_t(t)}$ by interpolation in a table of numerical values. The use of relation (24) is more convenient.

Comparison of the models

To evaluate the precision of the estimations based on the two models we have realized 2D numerical simulations of the system represented in figure 1 with COMSOL. The following boundary conditions have been considered:

- The temperature on the unheated face of the samples is uniform and constant
- The heat losses coefficient on the lateral faces of the samples is $h = 20\ \mathrm{W\ m^{-2}K^{-1}}$.

The following properties have also been considered:

- The heating wire with a 0.5 mm diameter is made of Nickel Chromium 80/20.
- The thermocouple with a 0.5 mm diameter has the same thermal properties as the heating wire
- The heating wire and the thermocouple are placed in grooves with a $0.5 \times 0.5\ \mathrm{mm^2}$ square section filled with still air.

The simulations have been realized with the thermal properties given in the table 2:

Table 2: Thermal properties used for the COMSOL simulations

Material	λ	ρc
	$\mathrm{W\ m^{-1}\ K^{-1}}$	$\mathrm{J\ kg^{-1}\ m^{-3}}$
Air [17]	0.026	1.30×10^{3}
NiCr 80/20 [18]	11.3	3.78×10^{6}
Quartzel felts® [19]	0.035	2.04×10^{4}
Silcal 1100® [20]	0.12	2.50×10^{5}
LUX500® [21]	0.22	7.70×10^{5}
NorFoam® [22]	0.75	7.00×10^{5}

The COMSOL simulations have been realized using the dimensions defined by the standard: the sample dimensions are 200 x 100 x 50 mm and the distance between the heating wire and the thermocouple is $d = 15\ \mathrm{mm}$. The standard recommends considering the values of the thermal conductivity calculated for the values of the ratio $\frac{T_t(2t)}{T_t(t)}$ between 1.5 and 2.4, provided that the maximum deviation from the mean value is lower than 5%.

The simulated curves have been considered as numerical experiments and processed using the three estimation methods to estimate:

- The values of λ_s, $\rho_s c_s$ and R_c with the quadrupolar model M1.
- The values of λ_s, $\rho_s c_s$, R_c and C_t with the quadrupolar model M2.
- A curve $\lambda_s = f(t)$ with the model M0 (standard) enabling the estimation of a mean value.

The estimation time interval for the quadrupolar models M1 and M2 has been adjusted so that the mean value of the estimation residues is null and that the residues are centered on zero. The results are presented in table 3.

The limit of validity of the semi-infinite medium hypothesis appears very clearly on curve of residues even for the lightest material (Quartzel) when the estimation is realized by using the model M2 (cf. figure 3b). This limit cannot be defined with the same accuracy when we use the model M1 for Quartzel since the residues are oscillating around the null value (cf. figure 3a). Compared to reference values, the values of the thermal conductivity estimated with the model M2 present a maximum deviation of 2.3% for Quartzel while it reaches 12.2% with the model M1. This deviation compared with the reference values is lower than 1 % with models M1 and M2 for the 3 other materials, and residues obtained with both models are identical as shown in figure 3c) and 3d).

Table 3: Estimated values of the parameters from COMSOL numerical experiments with samples dimensions $200 \times 100 \times 50$ mm^3 and $d = 15$ mm.

			Quartzel	Silcal 1100	LUX 500	Norfoam

	$t_{estimation}$	s	150	500	400	200
M0 (Standard)	λ_s	W m^{-1} K^{-1}	0.027	0.116	0.219	0.74
	$\left(\lambda_s - \lambda_{s_{ref}}\right)/\lambda$	%	-22.8	-3.3	-0.9	-1.2
M1	λ_s	W m^{-1} K^{-1}	0.0307	0.119	0.22	0.75
	$\rho_s c_s$	kJ m^{-3} K^{-1}	22.2	253	775	704
	$\left(\lambda_s - \lambda_{s_{ref}}\right)/\lambda$	%	-12.2	0.8	0	0
M2	λ_s	W m^{-1} K^{-1}	0.0358	0.119	0.221	0.75
	$\rho_s c_s$	kJ m^{-3} K^{-1}	20.7	253	770	704
	$\left(\lambda_s - \lambda_{s_{ref}}\right)/\lambda$	%	2.3	0.8	0.5	0
Reference values	$\lambda_{s_{ref}}$	W m^{-1} K^{-1}	0.035	0.12	0.22	0.75
	$(\rho_s c_s)_{ref}$	kJ m^{-3} K^{-1}	20.4	250	770	700

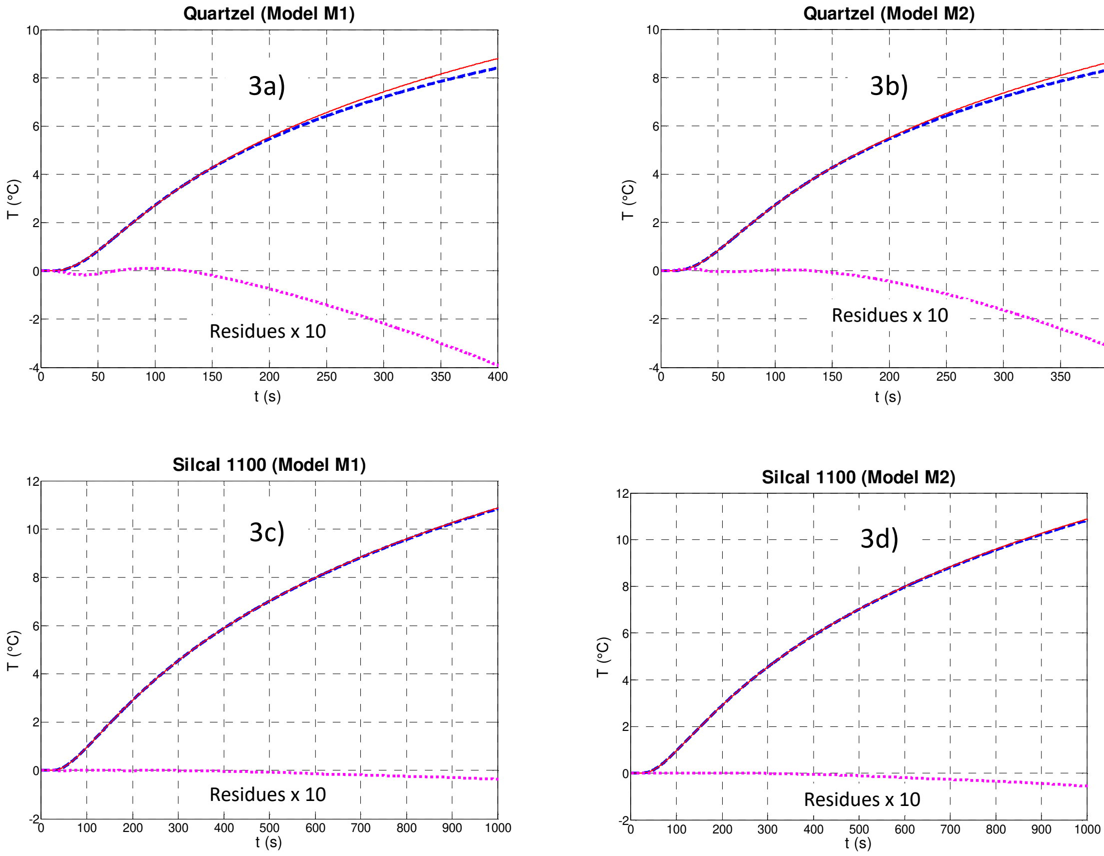

Figure 3: COMSOL simulations (--), quadrupolar model (—) and residues×10 for two materials

The application of the method of the standard leads to less precise results and always to underestimated values. The value obtained before that the hypothesis of the semi-infinite medium is no longer valid (situated in the rectangle in dotted lines on the figure 4) is more precise than the average value calculated between the values 1.5 and 2.4 of the ratio $\frac{T_t(2t)}{T_t(t)}$ (estimation method recommended by the standard). This remark is justified by the fact that the approximation of the standard neglects the heating wire mass and radius, it is thus more precise for long times (cf. figure 2). Furthermore, figure 4 shows that the change of slope of the curve $\lambda = f\left[\frac{T_t(2t)}{T_t(t)}\right]$ occurs in every case for $\frac{T_t(2t)}{T_t(t)} \approx 1.6$.

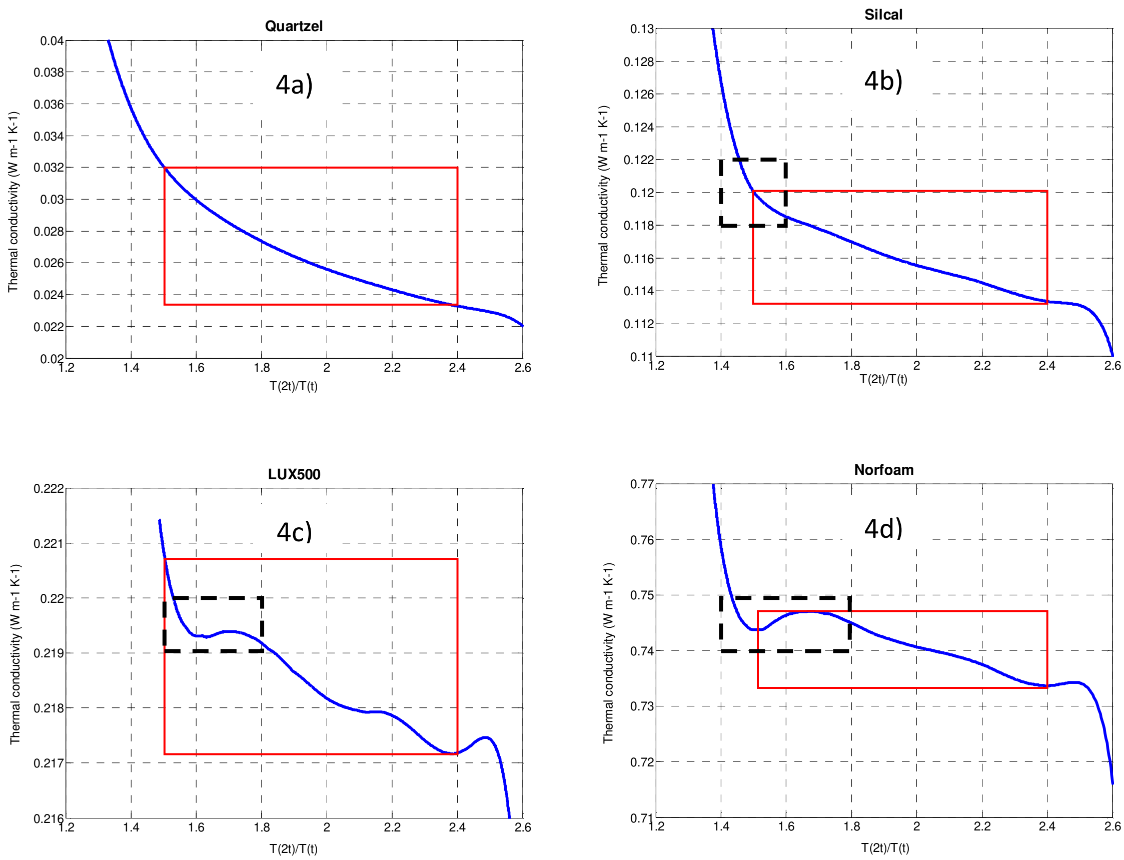

Figure 4: Thermal conductivity of the four materials estimated with the method of the standard ISO 8894-2 with sample dimensions $200 \times 100 \times 50\ mm^3$ *and d = 15 mm.*

The standard method does not enable an accurate estimation of the thermal conductivity of low density materials such as Quartzel. The estimation error can reach 20 % for these materials.

The standard lays down a distance $d = 15\ mm$ between the heating wire and the thermocouple. To test the influence of this distance on the precision of the estimation we have realized the same study but with a distance reduced to $d = 5\ mm$ enabling to use thinner samples; we chose a sample thickness of 30 mm.

Figure 5 presents the values of the thermal conductivity estimated with the standard method and table 4 presents the values obtained with the three methods.