International Journal of Thermophysics, Vol. 27, No. 3, May 2006 (© 2006)
DOI: 10.1007/s10765-006-0070-1

Measurement of the Thermal Conductivity and Thermal Diffusivity of Liquids. Part I: "Pure Conduction and an Example of a Solution"[1]

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The measurement of the thermal conductivity of liquids is rather complicated due to the nature of the fluid. To the conduction, which has to be characterized, are added the natural convection, the radiative transfer, and the perturbations caused by the presence of enclosure walls. The goal of this work, composed of two parts, is to implement an experimental bench allowing the measurement of the thermal diffusivity and thermal conductivity of liquids. The first part (Part I) presented here, is about pure conduction and focuses on several aspects involved in this measurement, which will lead one, based on theoretical and practical considerations, to choose a pulse method in a one-dimensional (1D) and cylindrical geometry to solve the problem. In the second section of this part, the problem of the parameters estimation is investigated with the presence of the walls of the measuring cell and this will allow us to define the characteristics of the walls (thickness and thermophysical properties). The entire problem is treated through the thermal quadrupoles method. Finally, in a last section, a setup at room temperature is described. The second part (Part II) of this work that is presented in another paper will show how it is possible to get rid of the convection by a judicious choice of the extension of the measuring cell and how the radiation effects can be taken into account to perform measurements at high temperatures (up to 500°C).

KEY WORDS: fluids; parameter estimation; thermal conductivity; thermal diffusivity; transient technique.

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[1] Paper presented at the Seventh Asian Thermophysical Properties Conference, August 23–28, 2004, Hefei and Huangshan, Anhui, P. R. China.

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1. INTRODUCTION

The determination of the thermal conductivity of a liquid is particularly difficult since one is in the presence of several modes of heat transfer: conduction, convection, and radiation disturbed by the presence of solid boundaries, which also play a key role in the heat transfer. The goal in this study is to show, from an example, the different steps to follow for setting-up a device allowing the measurement of thermal properties of fluids.

2. PROBLEM

As one thinks about thermal conductivity measurement, one considers the steady-state hot-wire method; and as one thinks about thermal diffusivity, one considers the flash method. The main drawbacks of the steady-state hot-wire method are:

- Only the thermal conductivity can be determined (assuming that no convection and no radiation are present in the measuring cell).
- In most cases, natural convection that appears as a power-dependent apparent thermal conductivity cannot be neglected and must be modeled in cylindrical geometry, which makes the problem difficult to solve.
- Radiation is difficult to take into account in this geometry and is bi-dimensional.

Conversely, the flash method presents some advantages:

- The ability to work in Cartesian coordinates with the assumption of one-dimensional (1D) heat transfer.
- The possibility to obtain the thermal conductivity and thermal diffusivity of the fluid at the same time choosing an appropriate geometry and materials for the measuring cell.
- Taking into account the radiation in a 1D geometry and in Cartesian coordinates is analytically possible.
- In this geometry, conductive and convective heat transfers can be uncoupled.

These are the reason why we have chosen (contrary to what is usually done for fluids [1–16]) the "*flash*" method. Two configurations can be considered: the classical plane geometry (Fig. 1), or cylindrical geometry (Fig. 2). Each of them has its own advantages.

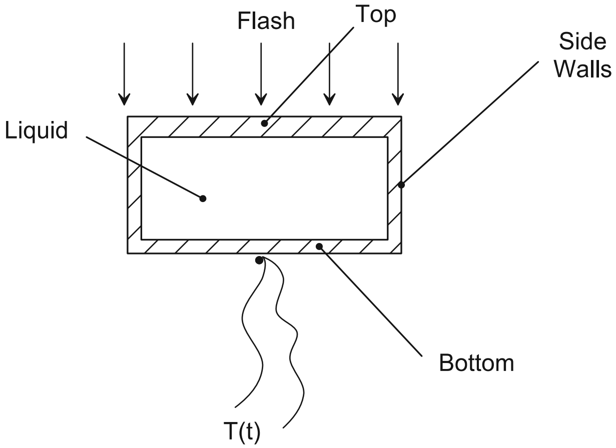


Fig. 1. Principle of the measurement (plane geometry).

- For plane geometry:
  The upper face being heated, natural convection can always be neglected. Nevertheless, it is very difficult in practice to have perfect contact between the liquid and the top of the measuring cell, which introduces an unknown additional parameter, a contact resistance. It is also necessary to take into account conduction through the lateral walls of the cell, and this makes the implementation of estimation models difficult.
- For cylindrical geometry:
  - The contact between the liquid and walls is good.
  - The heat transfer is 1D.
  - Free convection is always present, which requires work in a "pseudo-conduction" regime and a proper choice of the aspect ratio of the measuring cell (its extension e/h). We will see more precisely in Part II how it is possible to overcome this difficulty.

These physical considerations and other more practical reasons (filling and cleaning of the cell) led us to consider a cylindrical geometry as given in Fig. 2. The liquid is located between two metallic, coaxial cylinders. The cell is subjected to a heat impulse stimulation on the inner face of the internal cylinder and the temperature is measured on the back face of the external cylinder (technique known as "back-face" measurement).

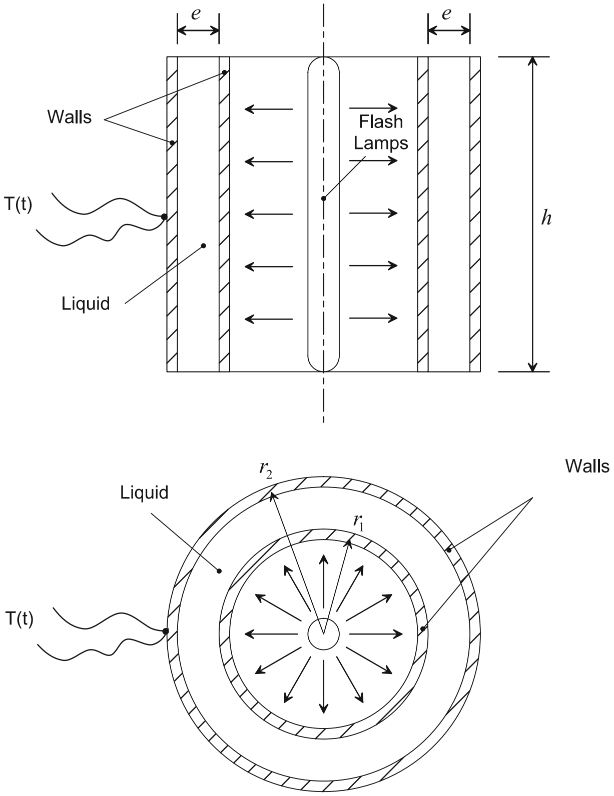


Fig. 2. Principle of the measurement (cylindrical geometry).

A study has been carried out here in an effort to minimize the disturbing effects introduced by the measuring cell.

3. PROBLEM IN PURE CONDUCTION AND ESTIMATION METHOD

In this part, we make the assumption of purely conductive heat transfer. The effects of metallic walls are investigated, and a model allowing the measurement of both the thermal diffusivity and thermal conductivity of fluids by an inverse technique will be presented.

The thicknesses of the three layers are small compared to their radii (aspect ratio less than 0.1), and the differences between the temperatures calculated in Cartesian and cylindrical coordinates are less than 0.01%. Thus, we will consider a Cartesian coordinate system in the next section.

3.1. Direct Model

From the preceding remarks, we will consider a Cartesian coordinate system and we will use the thermal quadrupole method to solve the problem.

3.1.1. Model

The problem is described in Fig. 3. The implementation of the analytical model is simplified by using thermal quadrupoles [17]. After a Laplace transform, the solution is obtained from a chain of quadrupoles. A diagram of the system is given in Fig. 4 with

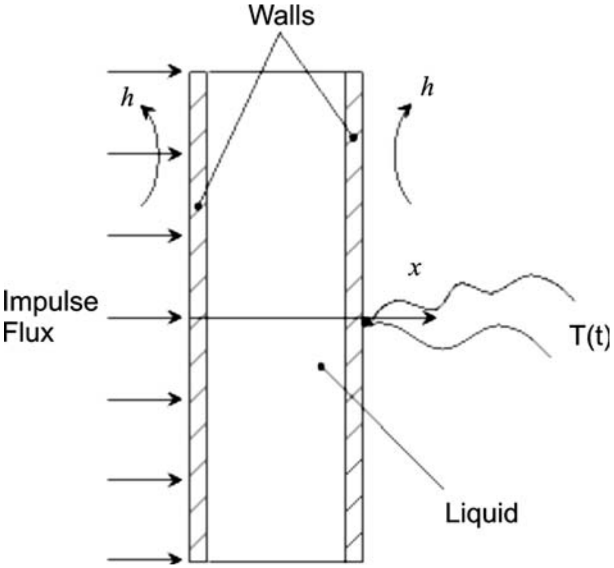


Fig. 3. Model.

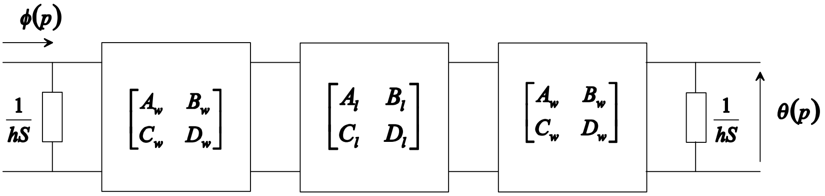


Fig. 4. Quadrupole representation.

- $1/(hS)$ being the convective heat losses with the surroundings,
- A, B, C, and D are coefficients of the inverse transfer matrices to account for the effects of the walls and liquid. Their expressions are given by

$$A_i = D_i = \cosh\left(\sqrt{\frac{pe_i^2}{a_i}}\right), \quad B_i = \frac{1}{\lambda_i S\sqrt{\frac{p}{a_i}}}\sinh\left(\sqrt{\frac{pe_i^2}{a_i}}\right), \text{ and}$$

$$C_i = \lambda_i S\sqrt{\frac{p}{a_i}}\sinh\left(\sqrt{\frac{pe_i^2}{a_i}}\right), \tag{1}$$

(subscript i refers to the fluid or to the walls)
and e_i is the thickness of the material, a_i is the thermal diffusivity, and λ_i is the thermal conductivity

3.1.2. Solution

The rear-face temperature $\theta(p)$ in a Laplace domain is given by

$$\theta(p) = \frac{\phi(p)}{C + 2\mathrm{A}hS + \mathrm{B}(hs)^2}. \tag{2}$$

A, B, and C represent the coefficients of the equivalent transfer matrix obtained by taking the product of the transfer matrix of each layer:

$$\begin{bmatrix} \mathrm{A} & \mathrm{B} \\ \mathrm{C} & \mathrm{D} \end{bmatrix} = \begin{bmatrix} A_\mathrm{w} & B_\mathrm{w} \\ C_\mathrm{w} & A_\mathrm{w} \end{bmatrix}\begin{bmatrix} A_l & B_l \\ C_l & A_l \end{bmatrix}\begin{bmatrix} A_\mathrm{w} & B_\mathrm{w} \\ C_\mathrm{w} & A_\mathrm{w} \end{bmatrix}, \tag{3}$$

with:

$$\begin{aligned} \mathrm{A} &= (A_\mathrm{w}A_l + B_\mathrm{w}C_l)\,A_\mathrm{w} + (A_\mathrm{w}B_l + B_\mathrm{w}A_l)\,C_\mathrm{w} \\ \mathrm{B} &= (A_\mathrm{w}A_l + B_\mathrm{w}C_l)\,B_\mathrm{w} + (A_\mathrm{w}B_l + B_\mathrm{w}A_l)\,A_\mathrm{w} \\ \mathrm{C} &= (C_\mathrm{w}A_l + A_\mathrm{w}C_l)\,A_\mathrm{w} + (C_\mathrm{w}B_l + A_\mathrm{w}A_l)\,C_\mathrm{w}. \end{aligned}$$

By assuming that the heat pulse $\varphi(t)$ received by the system is infinitely short (Dirac of flux), then $\phi(p)$ is a constant equal to the pulse energy.

For $h = 0$, the temperature at long times is given by

$$T_\infty = \lim_{t\to\infty} T(t) = \lim_{p\to 0} p\theta(p). \tag{4}$$

Thus,

$$T_\infty = \lim_{p\to 0} \frac{p\phi(p)}{\mathrm{C}(p)}, \tag{5}$$

and:

$$T_\infty = \frac{Q}{S\,(2\rho c_{\mathrm{w}} e_{\mathrm{w}} + \rho c_l e_l)} \quad (T_\infty \text{ is called the adiabatic temperature}). \quad (6)$$

Then, the inverse Laplace transform of Eq. (2) is implemented numerically. Several algorithms, either the Stehfest algorithm [18], the De Hoog algorithm [19], or a numerical inverse fast Fourier transform (IFFT) [20], which lead in our case to the same results, can be used.

Figure 5 gives an example of results obtained for two liquids (water and oil) and two different fluid thicknesses (0.5 and 2 mm). The thermophysical properties used are:

- $e_{\mathrm{l}} = 4.5\,\mathrm{mm}$, $h = 5\mathrm{W}\cdot\mathrm{m}^{-2}\cdot\mathrm{K}^{-1}$
- Water: $\lambda_{\mathrm{l}} = 0.597\ \mathrm{W}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}, a_{\mathrm{l}} = 1.43\times10^{-7}\ \mathrm{m}^2\cdot\mathrm{s}^{-1}$
- Oil: $\lambda_{\mathrm{l}} = 0.132\,\mathrm{W}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}, a_{\mathrm{l}} = 7.33\times10^{-8}\,\mathrm{m}^2\cdot\mathrm{s}^{-1}$
- Walls (copper): $\lambda_{\mathrm{w}} = 395\,\mathrm{W}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}, a_{\mathrm{w}} = 1.15\times10^{-4}\,\mathrm{m}^2\cdot\mathrm{s}^{-1}$
- $e_{\mathrm{w}} = 0.5$ or $2\,\mathrm{mm}$
- $Q/S = 4\times10^4\ \mathrm{J}\cdot\mathrm{m}^{-2}$

3.1.3. Sensitivity Study

The model depends on several parameters. Some of them are assumed known, and others will be estimated. The initial goal in this study is to

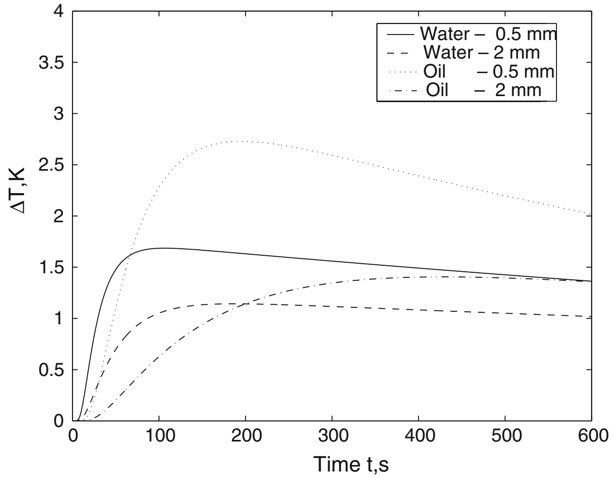


Fig. 5. Simulation examples (impulse responses).

thermally characterize the fluid, i.e., to estimate two quantities, the thermal diffusivity and conductivity (or any other set of parameters as, for instance, the effusivity or the specific heat). Assuming that the thermal properties of the walls and the geometry of the system are known, the model is a function of four unknown parameters:

$$\begin{array}{ll} e_1/\sqrt{a_1} & e_1/\lambda_1 \\ Q/S & h. \end{array}$$

The question is to know if it is possible to determine these four parameters from only one experimental thermogram. Generally, it is a difficult problem because of the measurement noise, which involves an error in the estimated values of parameters that is necessary to quantify. Beck and Arnold [21] showed that one of the most powerful tools for that is a sensitivity study, associated with a stochastical approach.

Letting β_i represent the unknown parameters; the temperature evolution can be written as

$$T = f\,(t, \beta_1, \beta_2, \beta_3, \beta_4) = f\,(t, \beta)\,. \tag{7}$$

The measured temperature being disturbed, one can write by assuming an additive noise:

$$Y_i = T\,(t_i, \beta) + \varepsilon_i, \tag{8}$$

where ε_i is the random noise, associated with measurement Y_i at time t_i.

The sensitivity coefficient of temperature T to parameters β_j at time t is defined by

$$X_j\,(t, \beta) = \frac{\partial T}{\partial \beta_j}\,(t, \beta)\,. \tag{9}$$

Later on, we will use the reduced sensitivity coefficients, which are easier to use for comparisons:

$$X_j{}^*\,(t, \beta) = \beta_j \frac{\partial T}{\partial \beta_j}\,(t, \beta)\,. \tag{10}$$

We can also define a sensitivity matrix ($m \times n$ dimensions), where each column corresponds to a sensitivity coefficient X_j and each line to one measurement at time t_i. The sensitivity curves give us information on the estimation error in parameters (the error is small when the sensitivity coefficient is maximum) and in their possible correlations. The parameters are correlated if the sensitivity coefficients are proportional and it is then that the simultaneous estimation of these parameters is difficult.

In our case, the problem is also nonlinear. Thus, the sensitivity curves and consequently the estimation will depend not only on the nominal values of the unknown parameters but also on the known parameters and on the geometry of the system. This is the reason why, for instance, we can show that there exists an optimum thickness for the walls.

As an example, Fig. 6 gives the sensitivity curves for water and oil with 0.5 and 2-mm wall thicknesses, respectively.

The curves seem to show that some parameters are more or less correlated, particularly $\beta_1\left(e_1/\sqrt{a_1}\right)$ and $\beta_3\left(Q/S\right)$ or β_1 and $\beta_2\left(e_1/\lambda_1\right)$, which would not allow simultaneous estimation of these parameters and consequently the thermal diffusivity. In addition, one can note that for a time larger than twice the maximum, the parameters are strongly correlated. Indeed, one is for the case of the cooling of a system with a quasi-uniform temperature (lumped body). The thermogram is a pure decaying exponential, which depends on only one parameter, the time-constant of the system $h/(2\rho c_w e_w + \rho c_1 e_1)$. This remark leads us to limit the estimation interval to short times. We have chosen to work between $t=0$ and $t=1.5\,t_{\max}$.

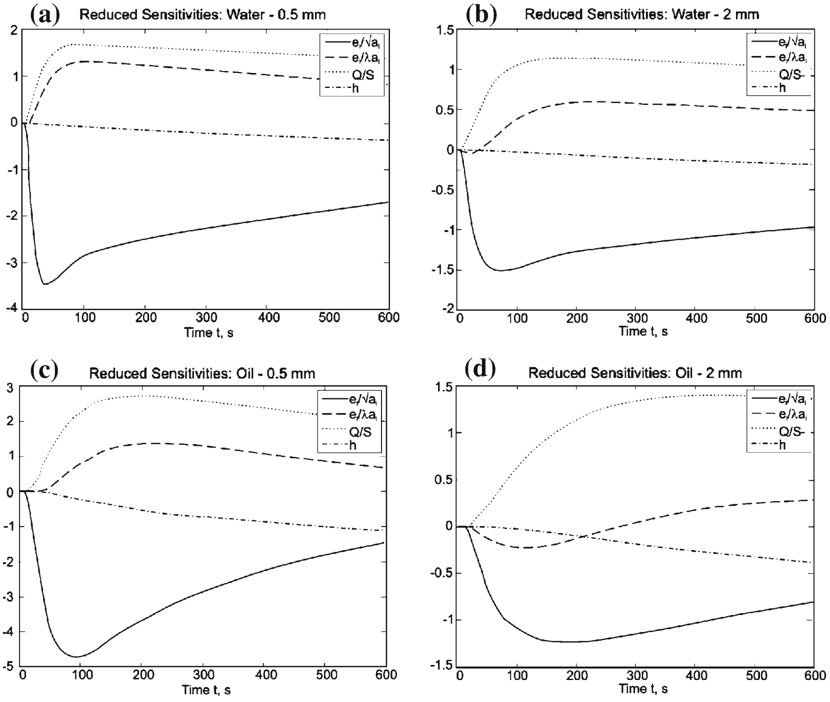


Fig. 6. Sensitivity curves for water and oil (0.5 and 2 mm).

The significant number of parameters (4) and the cross correlations between them make the reading and interpretation of the sensitivity curves difficult. The stochastical and simplified studies in the following sections will allow us to analyze the problem more clearly.

3.1.4. Stochastical Approach

An efficient method to estimate the unknown parameters consists of using an inverse technique. The method we used is based on the nonlinear Gauss–Newton ordinary least-squares method that consists of finding good values for the unknown parameters introduced in the theoretical model to minimize, by an iterative process, the differences between the experimental and theoretical curves. Let S be the sum of the ordinary squared differences:

$$S = \sum_i (Y_i - T(t_i, \beta))^2 \tag{11}$$

Y represents the experimental thermogram, T represents the theoretical thermogram as a function of time t, and β denotes the unknown parameters. The subscript i refers to the time t_i. Minimizing S with respect to β_j is equivalent to make its derivatives equal to zero:

$$\frac{\partial S}{\partial \beta_j} = 0 \Rightarrow \sum_i \frac{\partial T(t, \beta)}{\partial \beta_j} (Y_i - T(t_i, \beta)) = 0 \quad (\forall j). \tag{12}$$

The previously defined sensitivity coefficient $X_j(t, \beta)$ naturally appears in this minimization. Thus, an observation of the sensitivity curves allows us to know if the model we used is adapted or not to measure the parameters we seek. By a linear expansion of the model around the solution, one can obtain an analytical relation between the estimated values $\hat{\beta}$ of the parameters and their real values β that is given by

$$\hat{\beta} = \beta + \left(X^t X\right)^{-1} X^t \varepsilon(t), \tag{13}$$

where $\varepsilon(t)$ is the noise at time t.

From this relation, one shows that

$$E\left(\hat{\beta}\right) = \beta \quad \text{(expected values of parameters (unbiased estimator))} \tag{14}$$

$$V\left(\hat{\beta}\right) = \sigma_n^2 \left(X^t X\right)^{-1} = \sigma_n^2 \begin{bmatrix} \mathrm{Var}(\beta_i) & \mathrm{Cov}(\beta_i, \beta_j) \\ \mathrm{Cov}(\beta_i, \beta_j) & \mathrm{Var}(\beta_j) \end{bmatrix} \tag{15}$$

covariance matrix (σ_n: standard deviation of noise).

The previous relation is very important because it allows us to evaluate the errors in the estimated parameters. It also clearly shows that if the signal is not corrupted by the measurement noise, then one can expect to estimate the unknown parameters with a high accuracy, even if their effects on the signal are strongly coupled. In contrast, in the case of a noisy signal, errors in the values of the estimated parameters directly depend on the noise level, particularly if they are strongly coupled. To know if the parameters that are estimated from the iterative process really correspond to the thermophysical properties of the material, it is also of a great interest to compute the correlation factor between parameters β_i and β_j that is defined by

$$\rho\left(\beta_i, \beta_j\right) = \frac{\mathrm{Cov}\left(\beta_i, \beta_j\right)}{\sqrt{\mathrm{Var}\left(\beta_i\right) \cdot \mathrm{Var}\left(\beta_j\right)}} \tag{16}$$

The measurement will be much better when the variances are small and the correlation coefficients are far from unity in absolute value. The covariance and correlation matrices corresponding to the four preceding parameters are given in Tables I and II. To be compared, these tables are calculated from the reduced sensitivities.

From the covariance matrix, one can notice that the variance in β_1 is the smallest one, which shows that the accuracy for the thermal diffusivity will be better than for the thermal conductivity. In the same way, the estimation will be better for oil than for water. Later on, one will consider water as a test fluid knowing that for less conducting fluids, the results are better. Finally, one can observe that the variances vary strongly with the thickness of the walls, which will thus have to be optimized.

From the correlation matrix, one can note that β_3 is correlated with β_1 and β_2 in most cases, particularly for water. This confirms the preceding results. For case 4, one can note that no parameters are correlated.

Table I. Variance–Covariance Matrices

Water - 0.5 mm				Water - 2 mm			
0.3394	-2.3464	2.4913	1.4724	0.3218	−0.8419	0.7528	−0.5216
−2.3464	16.5302	−17.4179	−9.4267	−0.8419	2.4531	−2.0146	2.5528
2.4913	−17.4179	18.4144	10.4120	0.7528	−2.0146	1.7770	−1.3092
1.4724	−9.4267	10.4120	9.7216	−0.5216	2.5528	−1.3092	8.7357
Oil - 0.5 mm				Oil - 2 mm			
0.0649	−0.2870	0.2533	0.1216	0.1920	−0.4540	0.1500	−0.2349
−0.2870	1.3529	−1.1408	−0.4388	−0.4540	1.3544	−0.2825	1.0794
0.2533	−1.1408	0.9958	0.4599	0.1500	−0.2825	0.1413	−0.0219
0.1216	−0.4388	0.4599	0.3979	−0.2349	1.0794	−0.0219	1.4113

Table II. Correlation Matrices

Water - 0.5 mm				Water - 2 mm			
1.0000	−0.9907	0.9966	0.8106	1.0000	−0.9476	0.9954	−0.3111
−0.9907	1.0000	−0.9983	−0.7436	−0.9476	1.0000	−0.9649	0.5514
0.9966	−0.9983	1.0000	0.7782	0.9954	−0.9649	1.0000	−0.3323
0.8106	−0.7436	0.7782	1.0000	−0.3111	0.5514	−0.3323	1.0000
Oil - 0.5 mm				Oil - 2 mm			
1.0000	−0.9685	0.9965	0.7569	1.0000	−0.8903	0.9104	−0.4512
−0.9685	1.0000	−0.9829	−0.5981	−0.8903	1.0000	−0.6457	0.7807
0.9965	−0.9829	1.0000	0.7305	0.9104	−0.6457	1.0000	−0.0491
0.7569	−0.5981	0.7305	1.0000	−0.4512	0.7807	−0.0491	1.0000

Thus, it is possible to estimate a and λ at the same time, if the thickness of the walls is chosen in an optimal way.

One can also notice that the estimation problem is strongly nonlinear since the four studied cases exhibit very different covariance and correlation matrices.

In all cases, it seems difficult to estimate the two parameters β_1 and β_2 simultaneously.

3.1.5. Simplified Study with Two Parameters

With the heat losses being less correlated with the other parameters at short times (until the maximum of the thermogram is reached), let us consider now for simplifying the case without heat loss ($h = 0$) and notice that the results obtained here will be less affected after we would like to take into account the heat transfer coefficient. Indeed, this parameter has few effects on the estimation of the other two parameters of interest β_1 and β_2. To get rid of the influence of the parameter Q/S, a solution consists of working with the reduced thermogram defined by

$$\theta\,(t, \beta_1, \beta_2) = \frac{T\,(t, \beta_1, \beta_2, \beta_3)}{T_{\max}\,(\beta_2, \beta_3)}. \tag{17}$$

Now, the model is only a function of two parameters β_1 and β_2. The results obtained in the case of the four examples considered in the previous section are given in Fig. 7 and Table III.

In some cases, one can notice that the correlation between the parameters β_1 and β_2 is quite large (> 0.99). The first way to improve the estimation is to find if any, a new couple of parameters, which would be less correlated and that could be estimated under better conditions.

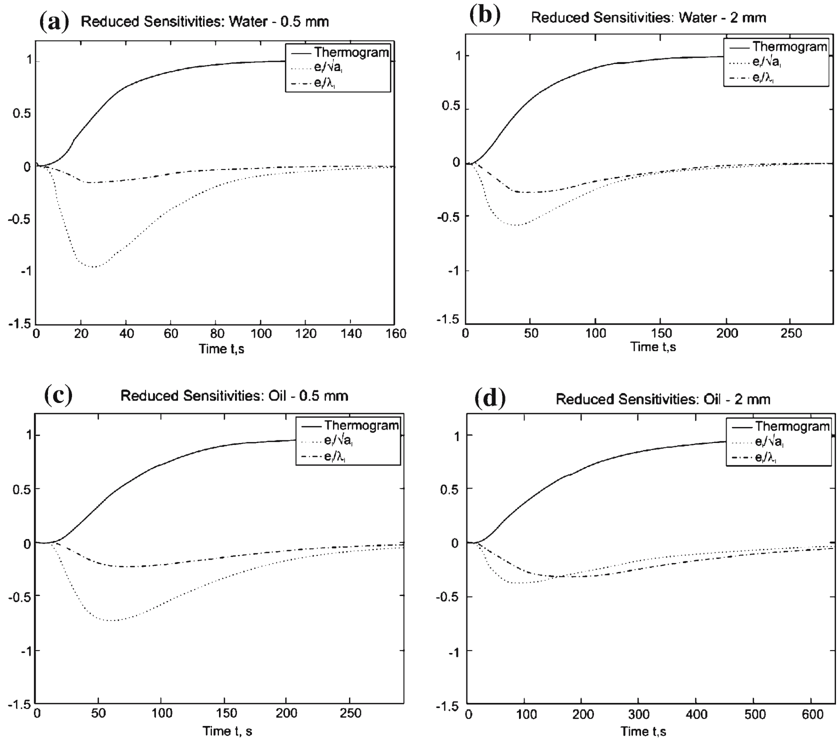


Fig. 7. Reduced thermograms and sensitivity curves for water and oil (0.5 and 2 mm).

Table III. Covariance and Correlation Matrices

Water				Oil			
0.5 mm		2 mm		0.5 mm		2 mm	
Covariance							
0.5007	−3.0373	0.2369	−0.4378	0.1911	−0.5548	0.1977	−0.1851
−3.0373	18.6223	−0.4378	0.8622	−0.5548	1.6662	−0.1851	0.1979
Correlation							
1.0000	−0.9947	1.0000	−0.9688	1.0000	−0.9832	1.0000	−0.9358
−0.9947	1.0000	−0.9688	1.0000	−0.9832	1.0000	−0.9358	1.0000

3.1.6. Parameters Substitution

In the model we have developed, a natural couple of parameters β_1 and β_2 appear. It is then possible, by a change of parameters, to introduce a new set of parameters β_{a} and β_{b}, such as

$$\theta = f\,(t, \beta_1, \beta_2) = g\,(t, \beta_{\mathrm{a}}, \beta_{\mathrm{b}})\,. \tag{18}$$

These new parameters are functions of the previous ones, that is,

$$\beta_{\mathrm{a}} = f_{\mathrm{a}}\,(\beta_1, \beta_2)\,, \tag{19}$$

$$\beta_{\mathrm{b}} = f_{\mathrm{b}}\,(\beta_1, \beta_2)\,. \tag{20}$$

Thus, the sensitivities to the new parameters X_{a} and X_{b} can be written as functions of X_1 and X_2 and the same is also true for the reduced sensitivities, variances, and covariances.
One obtains

- for the sensitivities:

$$X_{\mathrm{ab}} = X_{12} J^{-1}, \tag{21}$$

with

$$J = \begin{bmatrix} \dfrac{\partial f_{\mathrm{a}}}{\partial \beta_1} & \dfrac{\partial f_{\mathrm{a}}}{\partial \beta_2} \\ \dfrac{\partial f_{\mathrm{b}}}{\partial \beta_1} & \dfrac{\partial f_{\mathrm{b}}}{\partial \beta_2} \end{bmatrix} \qquad \begin{matrix} X_{\mathrm{ab}} = \begin{bmatrix} X_{\mathrm{a}} & X_{\mathrm{b}} \end{bmatrix} \\ X_{12} = \begin{bmatrix} X_1 & X_2 \end{bmatrix}. \end{matrix} \tag{22}$$

- for the reduced sensitivities:

$$X^*_{\mathrm{ab}} = X^*_{12} J^{*-1}, \tag{23}$$

with

$$J^* = \begin{bmatrix} \dfrac{\beta_1}{\beta_{\mathrm{a}}} \dfrac{\partial f_{\mathrm{a}}}{\partial \beta_1} & \dfrac{\beta_2}{\beta_{\mathrm{a}}} \dfrac{\partial f_{\mathrm{a}}}{\partial \beta_2} \\ \dfrac{\beta_1}{\beta_{\mathrm{b}}} \dfrac{\partial f_{\mathrm{b}}}{\partial \beta_1} & \dfrac{\beta_2}{\beta_{\mathrm{b}}} \dfrac{\partial f_{\mathrm{b}}}{\partial \beta_2} \end{bmatrix} \qquad \begin{matrix} X^*_{\mathrm{ab}} = \begin{bmatrix} X^*_{\mathrm{a}} & X^*_{\mathrm{b}} \end{bmatrix} \\ X^*_{12} = \begin{bmatrix} X^*_1 & X^*_2 \end{bmatrix}. \end{matrix} \tag{24}$$

- for the covariance matrix:

$$\begin{bmatrix} \mathrm{Var}\,(\beta_{\mathrm{a}}) & \mathrm{Cov}\,(\beta_{\mathrm{a}}, \beta_{\mathrm{b}}) \\ \mathrm{Cov}\,(\beta_{\mathrm{a}}, \beta_{\mathrm{b}}) & \mathrm{Var}\,(\beta_{\mathrm{b}}) \end{bmatrix} = J \begin{bmatrix} \mathrm{Var}\,(\beta_1) & \mathrm{Cov}\,(\beta_1, \beta_2) \\ \mathrm{Cov}\,(\beta_1, \beta_2) & Var\,(\beta_2) \end{bmatrix} J^t. \tag{25}$$

In the same way for the reduced quantities, substitute J for J^*.

It is then easy to show that if X_1 and X_2 are proportional in a given interval ($X_1 = K X_2$), then X_{a} and X_{b} are also correlated on this same interval $\left(X_{\mathrm{a}} = K' X_{\mathrm{b}}\right)$.

Thus, the interest of introducing a new set of parameters is not to try to estimate the two parameters simultaneously but to determine the more sensitive parameter of the system by nullifying the sensitivity to the second parameter. Theoretically, it is possible to find a couple of parameters (β_a, β_b), which allow us to reach this result. Nevertheless, in practice, this parameter must have a physical meaning and does not have to depend on the nominal values of the parameters. The estimation problem being nonlinear, one can show that the optimum parameter is not unique and varies according to the liquid we consider.

One can also notice that the sensitivity to a parameter varies according to the choice of the second parameter, which would let one think (if the parameters are not completely correlated) that it is possible to improve the estimation of a given parameter by associating it with a particular parameter. In fact, if we compute the variance of a parameter that represents the error made in the estimated value of this parameter, we can show that this error is independent of the choice of the second parameter (the demonstration of this general result is quite long and is not given here).

Thus, the estimation of the values of a new couple of parameters from a model that is a function of these new parameters is equivalent to calculating the values of these parameters directly from the estimated values obtained for the parameters of the previous couple. This shows that the choice of the parameters has no effect on the quality of the estimation.

In practice, the only interest in a change of parameters to appear in the theoretical model, involves a quantity that can be evaluated independently (for instance, through another experiment) and that can be fixed to a nominal value in the model, which is equivalent to removing a parameter in the estimation.

3.1.7. Choice of Model and Parameters

Let us apply the preceding remarks to the four thermograms in Fig. 7 and find a new set of parameters with the form:

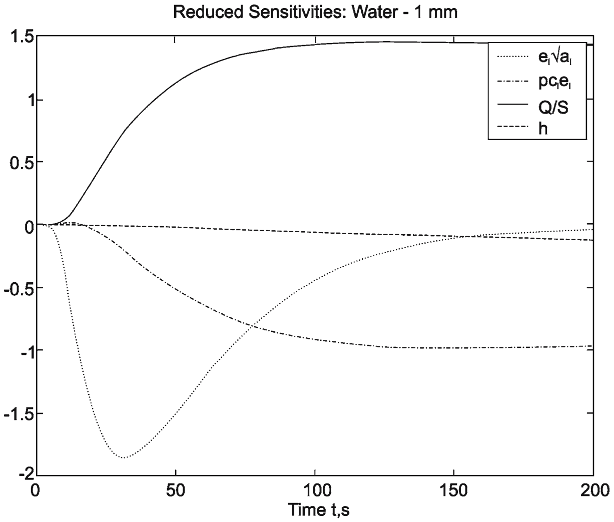
$$\begin{cases} \beta_a = \beta_1^m \beta_2^n \\ \beta_b = \beta_2. \end{cases} \tag{26}$$

One obtains (for the reduced sensitivities)

$$J^* = \begin{bmatrix} m & n \\ 0 & 1 \end{bmatrix}. \tag{27}$$

The new sensitivities are given by

$$\begin{cases} X_a^* = \frac{1}{m} X_1^* \\ X_b^* = X_2^* - \frac{n}{m} X_1^*. \end{cases} \tag{28}$$



Fluid (Water) [$e_f = 4.5$ mm, $\lambda_f = 0.597$ W·m^{-1}·K^{-1}, $a_l = 1.43\times10^{-7}$ m^2·s^{-1}, $\rho c_l = 4.17\times10^6$ J·m^{-3}·K^{-1}]
Walls (Copper) [$e_w = 1$ mm, $\lambda_w = 395$ W·m^{-1}·K^{-1}, $a_w = 1.15\times10^{-4}$ m^2·s^{-1}, $\rho c_w = 3.43\times10^6$ J·m^{-3}·K^{-1}]
$h = 5$ W·m^{-2}·K^{-1}, $Q/S = 4\times10^4$ J·m^{-2}

Fig. 8. Sensitivity curves.

One has to choose n/m in such a way that $X_b^* \simeq 0$.

Let us use the maximum of the sensitivity curves to choose n/m. From Fig. 7a, one finds $n/m \simeq 1/6$ and from Fig. 7c, $n/m \simeq 1/3$. The values depend strongly on the nature of the fluid. Thus, it is impossible to find only one solution for β_a. In practice, if two parameters are maintained, it will be necessary to fix the nominal value of β_b (or β_2) because the sensitivity will be never exactly equal to zero (parameters not being fully correlated).

However, there is a physical limitation with this theoretical approach. The parameter $\beta_b = e_l/\lambda_l$ is unknown since it is a quantity that one finds to measure. Then, it seems to be more relevant to introduce a parameter than can be measured in an additional experiment, for instance, $\rho c_l e_l$. As it is impossible in all cases to eliminate a parameter and knowing that the parameters substitution does not have any influence on the quality of the estimation (if one keeps the same number of parameters), one chooses next:

$$\beta_1 = e_l/\sqrt{a_l} \quad \text{and} \quad \beta_2 = \rho c_l e_l.$$

In difficult cases, one will have to fix β_2 to its nominal value (as the standard deviation for β_2 is too large).

Figure 8 gives an example of sensitivity curves obtained from the four-parameter ($e_l/\sqrt{a_l}$, $\rho c_l e_l$, Q/s, and h) and the three-parameter model (β_2 is fixed in this case).

Table IV. Covariance and Correlation Matrices

Water - 1 mm						
4 Parameters: $e_1/\sqrt{a_1}$, $\rho c_1 e_1$, Q/s, and h				3 Parameters ($\rho c_1 e_1$ fixed): $e_1/\sqrt{a_1}$, Q/s, and h		
Covariance						
0.2567	1.5697	1.0776	0.0993	0.0057	0.0094	0.1353
1.5697	9.8171	6.6809	−0.2249	0.0094	0.0208	0.3121
1.0776	6.6809	4.5673	0.1590	0.1353	0.3121	4.8955
0.0993	−0.2249	0.1590	4.9007			
Correlation						
1.0000	0.9888	0.9952	0.0886	1.0000	0.8596	0.8074
0.9888	1.0000	0.9977	−0.0324	0.8596	1.0000	0.9777
0.9952	0.9977	1.0000	0.0336	0.8074	0.9777	1.0000
0.0886	−0.0324	0.0336	1.0000			

Table IV gives the corresponding covariance and correlation matrices. One can observe that the variances and the correlations are strongly improved when β_2 is fixed.

3.2. Optimization of the Wall Thickness

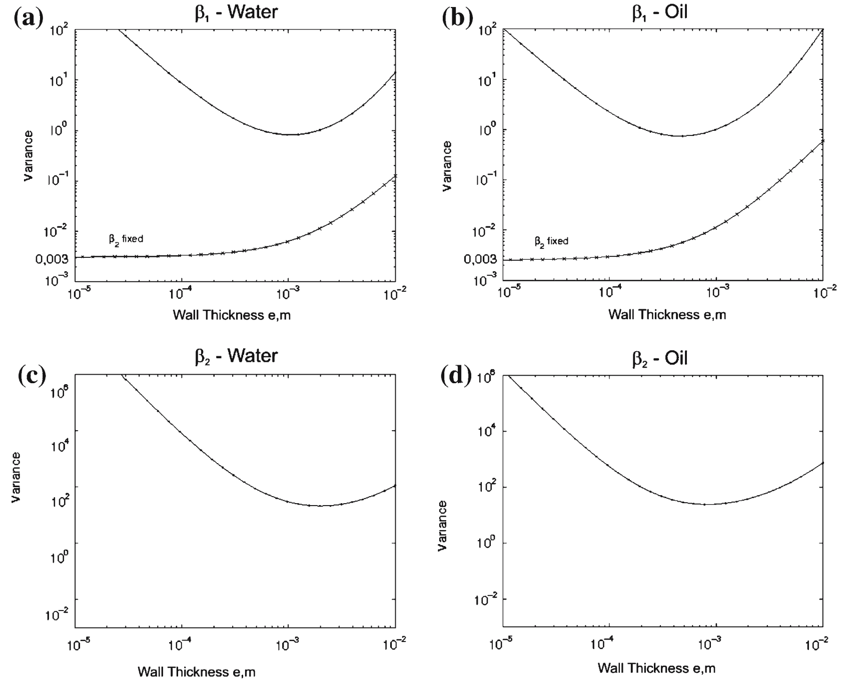
The problem being nonlinear, the estimation of β_1 and β_2 can be improved by choosing a thickness for the walls that minimizes the variance of the parameters by taking into account the increase of the signal/noise ratio as the wall thickness is decreased (keeping the measurement noise constant, the amplitude of the measured temperature decreases with an increase of the wall thickness).

The study is made on the reduced thermograms with the three-parameter model:

$$\theta = f\,(t, \beta_1, \beta_2, h)\,. \tag{29}$$

The results are given in Fig. 9 for water and oil. At first sight, the results are quite surprising. Contrary to what one could imagine, the variances are larger for small wall thicknesses.

Indeed, for small wall thicknesses, we should find the behavior of a monolayer material, with a variance of 0.003 for β_1 but this value can only be obtained when β_2 is fixed to its nominal value. Thus, contrary to what one could imagine, the use of thin walls does not improve the parameters estimation, except if those are so small that they can be neglected (this case



Fluid (Water) [$e_f = 4.5$ mm, $\lambda_f = 0.597$ W·m^{-1}·K^{-1}, $a_l = 1.43\times10^{-7}$ m^2·s^{-1}, $\rho c_l = 4.17\times10^6$ J·m^{-3}·K^{-1}]
Fluid (Oil) [$e_f = 4.5$ mm, $\lambda_f = 0.132$ W·m^{-1}·K^{-1}, $a_l = 7.33\times10^{-7}$ m^2·s^{-1}, $\rho c_l = 1.8\times10^6$ J·m^{-3}·K^{-1}]
Walls (Copper) [$\lambda_w = 395$ W·m^{-1}·K^{-1}, $a_w = 1.15\times10^{-4}$ m^2·s^{-1}, $\rho c_w = 3.43\times10^6$ J·m^{-3}·K^{-1}]
$h = 5$ W·m^{-2}·K^{-1}, $Q/S = 4\times10^4$ J·m^{-2}

Fig. 9. Optimization of the walls thickness (water and oil).

is not very convenient in practice because it corresponds to very thin walls). So, according to the wall thickness, we can consider three different cases:

1. Less than a few microns, one is in the presence of a monolayer of fluid.
2. Between a few microns and hundreds of microns, one is in the presence of a homogeneous system, i.e., the response is the response of a homogeneous medium but with an apparent diffusivity that can differ from the real fluid diffusivity.

$$a_{ap} = \frac{\lambda_{ap}}{\rho c_{ap}}, \tag{30}$$

$$\text{with} \quad \lambda_{ap} = (e_l + 2e_w) \Big/ \left(\frac{e_l}{\lambda_l} + \frac{2e_w}{\lambda_w} \right)$$

$$\text{and} \quad \rho c_{ap} = (\rho c_l e_l + 2\rho c_w e_w) \big/ (e_l + 2e_w).$$

3. Above hundreds of microns, one is in the presence of a non-homogeneous three-layer material.

From this, two strategies can be defined:

1. For case 2, one can estimate an apparent diffusivity by a classical flash model (model with three parameters: a, h, and Q) that must be then corrected knowing the characteristics of the wall and the specific heat of the fluid.
2. For case 3, there exists an optimum between 1 and 2 mm for the wall thickness; one has to use a more detailed model with four parameters allowing estimate of a and ρc of the liquid if β_1 and β_2 are uncorrelated and with a knowledge of the characteristics of the wall.

For practical reasons, particularly the hardness of the walls required to obtain a good centering of the cylinders, we made the choice to work with case 3.

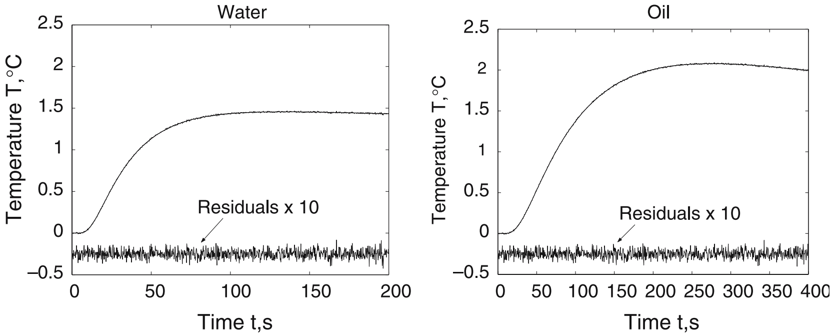
3.3. Inverse Problem

At first, the efficiency of our approach has been tested on simulated thermograms. From the quadrupole model, one computes the theoretical temperature response of the system and adds noise to obtain a simulated thermogram on which the estimation will be carried out. Let us notice that the noise added on the signal has a standard deviation of ±0.005°C that is of the same order of magnitude as those observed on experimental thermograms.

The estimation program uses the Levenberg–Marquardt [22] algorithm. The objective function depends on four parameters:

- $\beta_1 = e_l / \sqrt{a_l}$ (square root of the characteristic time of the fluid)
- $\beta_2 = \rho c_l e_l$ (heat capacity of the fluid)
- Q/S (energy per unit of area absorbed by the system)
- h (convective heat transfer coefficient between the walls and the surroundings)

We plotted in Fig. 10 the simulated and theoretical curves obtained from the estimated parameters, as well as the residuals (difference between theoretical and simulated curves). We also calculated (See Table V) the covariance matrix as well as the standard deviations of the estimators. Results are given for water and oil.



Fluid (Water) [$e_f = 4.5$ mm, $\lambda_f = 0.597$ W·m^{-1}·K^{-1}, $a_l = 1.43\times10^{-7}$ m^2·s^{-1}, $\rho c_l = 4.17\times10^6$ J·m^{-3}·K^{-1}]
Fluid (Oil) [$e_f = 4.5$ mm, $\lambda_f = 0.132$ W·m^{-1}·K^{-1}, $a_l = 7.33\times10^{-7}$ m^2·s^{-1}, $\rho c_l = 1.8\times10^6$ J·m^{-3}·K^{-1}]
Walls (Copper) [$e_w = 1$ mm, $\lambda_w = 395$ W·m^{-1}·K^{-1}, $a_w = 1.15\times10^{-4}$ m^2·s^{-1}, $\rho c_w = 3.43\times10^6$ J·m^{-3}·K^{-1}]
$h = 5$ W·m^{-2}·K^{-1}, $Q/S = 4\times10^4$ J·m^{-2}

Fig. 10. Estimation on simulated thermograms by an ordinary least-squares (OLS) method.

We can observe that the estimations of the thermal diffusivities are good (for water $a = 1.417\times10^{-7}\,\mathrm{m^2{\cdot}s^{-1}}$ and $\sigma_a^* = \pm0.5\%$, for oil $a = 7.284\times10^{-8}\,\mathrm{m^2{\cdot}s^{-1}}$ and $\sigma_a^* = \pm0.3\%$). Also, the heat capacities are estimated with a large uncertainty as given by the covariance matrices. The comparison of the estimation obtained for each fluid allows us to confirm that the estimation for water is slightly less precise than for oil.

The results obtained when the value of the parameter β_2 is fixed are given in Table VI. In this case, one finds a more precise estimation for β_1 and thus for the thermal diffusivity.

4. IMPLEMENTATION

4.1. Experimental Bench

The previous study allows us to define the optimal characteristics for the measuring cell (Fig.11):

- Walls in copper or stainless steel (1-mm thick)
- Thickness of the fluid (3 mm/4.5 mm)
- Height of the cell (100 mm)
- Inner diameter (24 mm)

The tubes constituting the walls are embedded in two pieces in Teflon not only to ensure the concentricity and the sealing of the cell, but also the

Table V. Estimated Values, Covariance, and Correlation Matrices (four parameters)

4 parameters: $e_1/\sqrt{a_1}$, $\rho c_1 e_1$, Q/s, and h							
Water				Oil			
Parameters				Parameters			
Nominal $a_l = 1.43 \times 10^{-7}$ m^2·s^{-1} $\rho c_l = 4.17 \times 10^6$ J·m^{-3}·K^{-1} $h = 5$ W·m^{-2}·K^{-1} $Q/S = 4 \times 10^4$ J·m^{-2}		Estimated $a_l = 1.417 \times 10^{-7}$ m^2·s^{-1} $\rho c_l = 4.276 \times 10^6$ J·m^{-3}·K^{-1} $h = 5.083$ W·m^{-2}·K^{-1} $Q/S = 4.071 \times 10^4$ J·m^{-2}		Nominal $a_l = 7.33 \times 10^{-7}$ m^2·s^{-1} $\rho c_l = 1.8 \times 10^6$ J·m^{-3}·K^{-1} $h = 5$ W·m^{-2}·K^{-1} $Q/S = 4 \times 10^4$ J·m^{-2}		Estimated $a_l = 7.284 \times 10^{-7}$ m^2·s^{-1} $\rho c_l = 1.827 \times 10^6$ J·m^{-3}·K^{-1} $h = 5.014$ W·m^{-2}·K^{-1} $Q/S = 4.026 \times 10^4$ J·m^{-2}	
Covariance							
0.2604	1.6099	1.1144	0.1305	0.0885	0.4597	0.1814	−0.0129
1.6099	10.1769	6.9852	−0.0272	0.4597	2.5109	0.9409	−0.2640
1.1144	6.9852	4.8152	0.2932	0.1814	0.9409	0.3747	−0.0099
0.1305	−0.0272	0.2932	4.8916	−0.0129	−0.2640	−0.0099	0.3976
Correlation							
1.0000	0.9890	0.9952	0.1156	1.0000	0.9753	0.9962	−0.0686
0.9890	1.0000	0.9978	−0.0038	0.9753	1.0000	0.9700	−0.2642
0.9952	0.9978	1.0000	0.0604	0.9962	0.9700	1.0000	−0.0257
0.1156	−0.0038	0.0604	1.0000	−0.0686	−0.2642	−0.0257	1.0000

Table VI. Estimated Values, Covariance, and Correlation Matrices (three parameters)

3 Parameters ($\rho c_l e_l$ fixed) : $e_l/\sqrt{a_l}$, Q/s, and h						
	Water			Oil		
	Parameters ($\rho c_l = 4.17 \times 10^6$ J·m^{-3}·K^{-1})			Parameters ($\rho c_l = 1.8 \times 10^6$ J·m^{-3}·K^{-1})		
	Nominal $a_l = 1.43 \times 10^{-7}$ m^2·s^{-1} $h = 5$ W·m^{-2}·K^{-1} $Q/S = 4 \times 10^4$ J·m^{-2}	Estimated $a_l = 1.428 \times 10^{-7}$ m^2·s^{-1} $h = 5.084$ W·m^{-2}·K^{-1} $Q/S = 4.005 \times 10^4$ J·m^{-2}		Nominal $a_l = 7.33 \times 10^{-7}$ m^2·s^{-1} $h = 5$ W·m^{-2}·K^{-1} $Q/S = 4 \times 10^4$ J·m^{-2}	Estimated $a_l = 7.323 \times 10^{-7}$ m^2·s^{-1} $h = 5.022$ W·m^{-2}·K^{-1} $Q/S = 4.005 \times 10^4$ J·m^{-2}	
Covariance						
	0.0058	0.0095	0.1347	0.0044	0.0092	0.0354
	0.0095	0.0211	0.3117	0.0092	0.0223	0.0888
	0.1347	0.3117	4.8196	0.0354	0.0888	0.3651
Correlation						
	1.0000	0.8609	0.8089	1.0000	0.9339	0.8879
	0.8609	1.0000	0.9779	0.9339	1.0000	0.9840
	0.8089	0.9779	1.0000	0.8879	0.9840	1.0000

(for water $a = 1.428 \times 10^{-7}$ m^2·s^{-1} and $\sigma_a^* = \pm 0.08\%$, for oil $a = 7.323 \times 10^{-7}$ m^2·s^{-1} and $\sigma_a^* = \pm 0.06\%$).

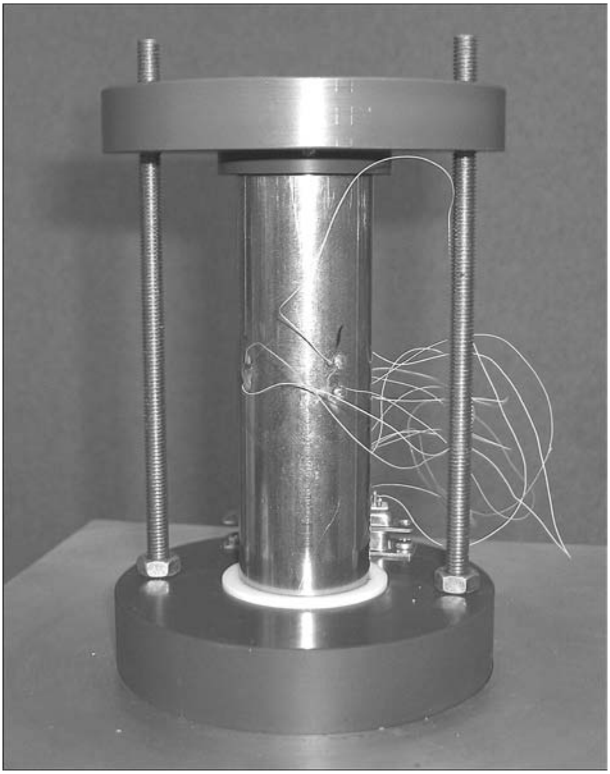


Fig. 11. Measuring cell.

insulation between the inner and outer cylinders. The cell is placed on a frame surrounded by a metallic shield and an insulated bell to limit the heat exchange by convection and radiation with the surroundings.

The pulse stimulation is produced by a moving flashlamp, which can take place inside the measuring cell for the stimulation. The time length of the pulse is a few milliseconds and its power is about 1000 J. To avoid any heat release to the cell after the flash, the lamp is removed by an automatic and motorized system after the stimulation. The temperature evolution is measurement via welded chromel-alumel thermocouples (120-μm diameter) with separated contacts. The acquisition system is composed of an analog or digital acquisition card and a conditioning module and computer that allows automated treatment of the thermogram (See Fig. 12).

Fig. 12. Experimental device.

4.2. Example of Experimental Results

As shown previously, water is a good test fluid because it exhibits the most unfavorable thermophysical properties for this kind of measurement. In practice, the magnification factor K of the experimental device (sensitivity of the thermocouples, amplifier, oscilloscope), which consists of multiplying the measured signal (temperature) to obtain a potential that can be measured through an oscilloscope is ill-known. Thus, the parameter Q/S is replaced by KQ/S in the theoretical model. For practical reasons (estimation with three parameters, for instance), the experimental thermogram is normalized with respect to its apparent maximum $U_{\max}$. Thus, the estimated parameter in the four-parameter model is: $KQ/SU_{\max}$. Figure 13

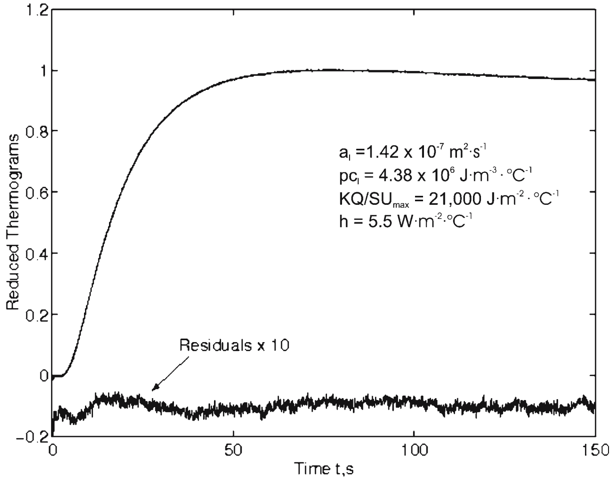


Fig. 13. Estimation for an experimental thermogram (water) — four parameters model.

Table VII. Covariance and Correlation Matrices

Water						
4 Parameters: $e_1/\sqrt{a_1}$, $\rho c_1 e_1$, Q/s, and h				3 Parameters ($\rho c_1 e_1$ fixed): $e_1/\sqrt{a_1}$, Q/s, and h		
Covariance						
0.1453	0.6414	0.3682	0.0941	0.0039	0.0039	0.0557
0.6414	2.9094	1.6528	0.1704	0.0039	0.0064	0.0959
0.3682	1.6528	0.9452	0.1949	0.0557	0.0959	1.5606
0.0941	0.1704	0.1949	1.6610			
Correlation						
1.0000	0.9866	0.9936	0.1915	1.0000	0.7734	0.7111
0.9866	1.0000	0.9967	0.0775	0.7734	1.0000	0.9612
0.9936	0.9967	1.0000	0.1556	0.7111	0.9612	1.0000
0.1915	0.0775	0.1556	1.0000			

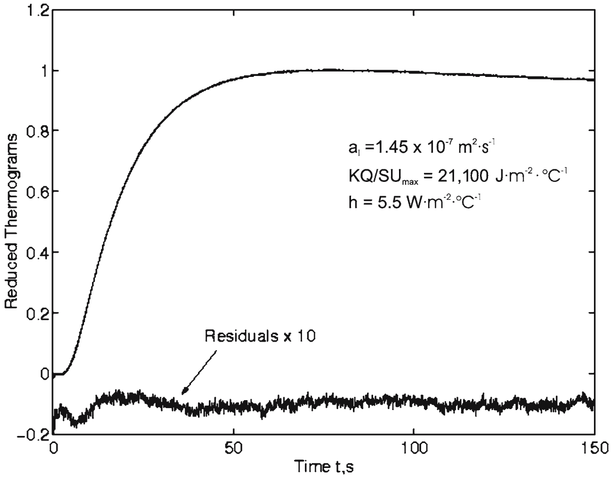


Fig. 14. Estimation for an experimental thermogram (water) — three parameters model.

gives the results we obtained from the four-parameter model and the corresponding variances are given in Table VII. As expected from the theoretical study, one can observe that the estimation of the specific heat (ρc) is not good. Figure 14 gives the results obtained from the three-parameter model (i.e., ρc is fixed to its nominal value of $4.18 \times 10^6\ \mathrm{J \cdot m^{-3} \cdot K^{-1}}$) and in Table VII are given the corresponding variances.

One can note that the variances are much smaller than for the case of four parameters, which characterizes a better estimation, especially for the thermal diffusivity.

5. CONCLUSION

We described the different steps to develop an adapted device and model for the estimation of the thermophysical properties of liquids. A sensitivity study on the parameters enabled us to define an optimum wall thickness for the measuring cell. A complete study on the estimation problem shows that for most liquids, it is possible to measure by this method two main properties of the fluid (a and ρc). Lastly, an experimental design was implemented. This method looks very interesting because it is a transient and low time-consuming technique that allows us to measure several properties of the fluid by only one experiment and without any calibration of the device (only the thermal properties of walls are required). The first measurements obtained on water showed the relevance of the theoretical study.

ACKNOWLEDGMENT

We would like to thank the Bureau National de Métrologie (Paris) for its financial support (Contract BNM-INPL No. 023001).

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