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THERMOGENESIS: DECONVOLUTION IN NON TIME-INVARIANT CALORIMETRIC SYSTEMS

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ABSTRACT

Most conduction calorimeters do not behave, strictly speaking, as time invariant systems (e.g., calorimeters used to study titrations). In this communication the performance of standard deconvolutive techniques applied on thermograms calculated from discrete variable models is analysed (RC models whose physical parameters change with time). Secondly, two new algorithms are developed which yield the power released inside the calorimetric cell even when the parameters of the system are changing during the experiment. The first algorithm takes advantage of the system of differential equations ruling the time evolution of the discrete model whereas the second deals with inverse filters with variable time constants. In the cases studied, both methods produce equivalent results.

INTRODUCTION

Identification and deconvolution in time invariant calorimetric systems have been thoroughly and extensively analysed during the last few years. These systems are defined, from a physical point of view, by a set of physical parameters, such as heat capacities or thermal conductivities, which are assumed to remain constant during the whole experimental manipulation. In other words, the set of poles and zeros which define their transfer function are constant. However, the introduction of new identification techniques has shown that the time constants of certain systems actually change throughout the measurement. Although the change detected is small, it may be quantitatively evaluated [1–6].

A first estimation of the effects brought about by such a change are analysed in ref. 7, where the most outstanding features encountered are modifications in the static gain of the calorimeter and in the functional dependence of the pulse response of the system.

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In this communication we consider also discrete calorimetric models (RC models) [8–10] where the parameters defining the model may be a function of time. Particularly, we are interested in those cases where the heat capacity of the laboratory cell is changing. In this way, a model whose time constants are roughly equal to those of an ARION-Electronique calorimeter, type BCP [5], has been built up. This calorimeter, used to obtain the excess partial molar enthalpy of liquid mixtures, exhibits a clear evolution of its time constants during the mixing process. This change may reach up to 10% of the main time constant.

Once the parameters of the model are fixed, a variable model allows the calculation of simulated thermograms belonging to a known power input if the time dependence of the parameters defining the model (heat capacity of its different elements and coupling coefficients between them) is also known. Two algorithms are devised which allow the deconvolution of such thermograms. The first one is based on the same differential equations which define the variable model whereas the second one is an extension of an inverse filter by considering variable poles and zeros. Both methods have been tested on thermograms affected by different amounts of noise.

The results clearly show that standard time-invariant deconvolutive techniques produce incorrect power inputs when applied to these thermograms whereas the methods developed, which include the variation in the parameters, yield the correct power input. In the case studied here, the results produced using either the RC differential equations or a time dependent inverse filter are equivalent.

Definition of the model

RC models [8–10] are based upon a discrete representation of the calorimetric system. In each cell or element the temperature is taken to be homogeneous. If we denote C_i as the heat capacity of the ith element, P_{ij} and P_i as the coefficients of Newtonian heat losses towards elements j and to the thermostat, respectively, the energy balance in each element leads to the following system of differential equations:

$$C_i \frac{\mathrm{d}T_i}{\mathrm{d}t} + \sum_{i \neq j} P_{ij}(T_i - T_j) + P_i T_i = W_i(t) \quad i = 1,\ldots,N,\ P_{ij} = P_{ji}$$

where $W_i(t)$ is the instantaneous power released in the ith element.

This formalism allows an easy introduction of variable physical parameters for we only have to consider their explicit time dependence in the equations given above. If all the coefficients are actually constant, the solution to the system of N linear first order differential equations is a series of exponentials where the time constants are functions of the parameters of the model. These time constants are also directly related to the poles of the

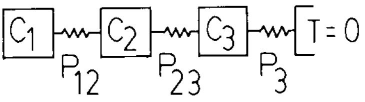

Fig. 1. Schematic representation of the RC model discussed. The values of the different parameters are shown in Table 1.

transfer function of the system. However, if any of these coefficients is a function of time, the solution cannot be obtained any longer except for extremely simple cases [7].

Bearing in mind the experimental situation already described, we have built a simple model consisting of three elements (Fig. 1) in such a way that the power is released in element 1 and the temperature which is experimentally detected is associated to the temperature of element 3. The stirring device of the actual calorimetric system ensures a proper homogenization of the heat dissipation, so we may take element 1 as the laboratory cell. With this choice, the resulting chain-like model is more easily solved; that is, either we may easily calculate the temperature evolution in the different elements once the power released $W_1(t)$ is known or, on the contrary, we may obtain the power released once $T_3(t)$ is given [11,12].

In the actual experimental situation, the steady injection of one component into the laboratory cell leads to an increase of its heat capacity [7]. Consequently, the system of differential equations ruling the time evolution of the system turns into a system of linear differential equations with variable coefficients. In a general case, it is difficult to obtain a numeric solution to the system (ten elements or more). However, given that the signal/noise ratio in this system is roughly 60–70 dB, it seems feasible an approximation to the transfer function consisting only of two or three poles or, equivalently, an RC model of two or three elements, at least with respect to the standard case where the parameters do not change with time. The model considered in this case is shown in Fig. 1, and the corresponding set of differential equations is [7]:

$$C_1(t)\frac{dT_1}{dt} + P_{1\,2}(T_1 - T_2) + C_1(t)T_1 = W_1(t)$$

$$C_2\frac{dT_2}{dt} + P_{1\,2}(T_2 - T_1) + P_{2\,3}(T_2 - T_3) = 0$$

$$C_3\frac{dT_3}{dt} + P_{2\,3}(T_3 - T_2) + P_3T_3 = 0$$

where the numerical value of the parameters and the associated time constants may be found in Table 1.

The heat capacity C_1 is taken to depend linearly on time:

$$C_1(t) = C_{10} + C_{1p}T \qquad 0 < t < 2050\text{ s}$$

$$C_1(t) = C_{10} + 2050\, C_{1p} \qquad t > 2050\text{ s}$$

TABLE 1

Heat capacities, coupling coefficients and coefficients of heat losses to the thermostat corresponding to the model of three elements shown in Fig. 1 (the values of the time constants associated to the different C_1 are also shown)

$C_2 = 20$ J K^{-1} $C_3 = 20$ J K^{-1}	$P_{12} = 0.35$ W K^{-1} $P_{23} = 1.25$ W K^{-1}	$P_3 = 0.79$ W K^{-1}

C_1 (J K^{-1})	τ_1 (s)	τ_2 (s)	τ_3 (s)
40	225.3	31.8	6.5
42	235.0	32.0	6.5
44	244.5	32.2	6.5
48	263.9	32.6	6.5

accounting for a steady injection. This system has been numerically solved considering a constant power input of 1 W during 2050 s. The temperature has been recorded during 4100 s to follow its evolution until the final equilibrium state is reached. Three different variable models have been considered, namely total variations in C_1 of 5%, 10% and 20% during the 2050 s of injection. The different values of the time constants associated with these three time-invariant models are also shown in Table 1.

Figure 2 shows the first time constant of the model as a function of the heat capacity C_1. In the case of a non time-invariant model, this may represent the evolution of the time constant of the system vs. time while the injection is taking place. It is to be noted that, strictly speaking, it is meaningless to refer to the time constants of the system because they no longer exist in these kind of models. We may refer to them only in

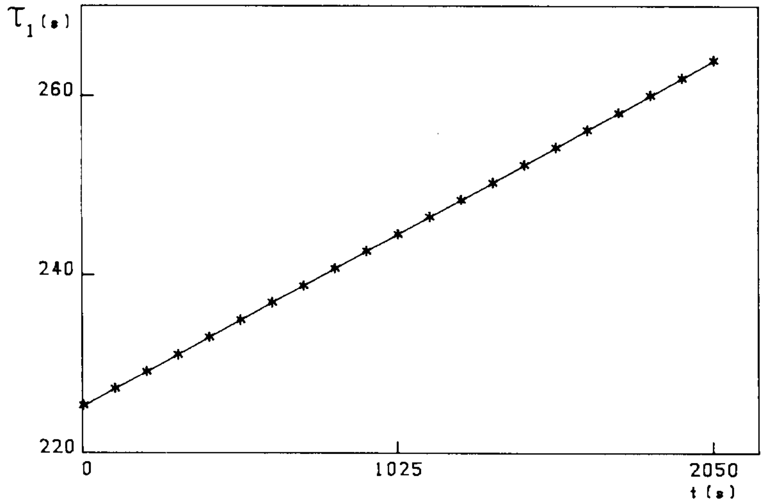

Fig. 2. First time constant vs. time. The values shown are those listed in Table 1. The time scale is defined by considering a steady injection from $C_1 = 40$ to 48 J K^{-1} lasting 2050 s.

association with the instantaneous value of the parameters of the model. In this sense, Fig. 2 shows the first time constant vs. time although they have been calculated considering fixed model parameters whose value corresponds to that particular time. We note a linear behaviour in the particular model chosen.

RESULTS

Firstly, we obtain the simulated thermograms corresponding to a known

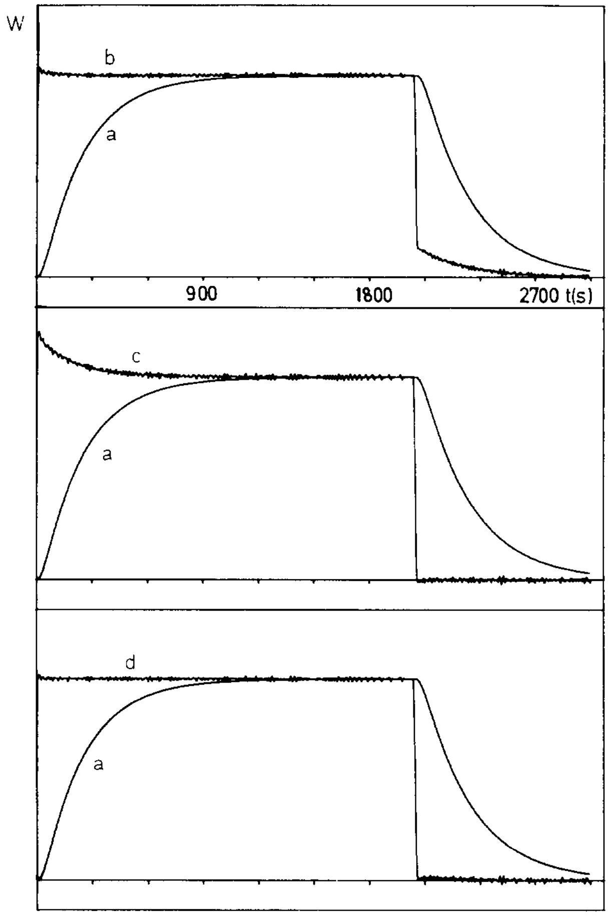

Fig. 3. (a) Thermogram corresponding to a step input ($W = 1$ W) in a system where C_1 changes from 40 to 48 J K^{-1} in 2050 s. After that $W = 0$ W and the parameters are kept constant. The signal/noise ratio is roughly 70 dB. (b) Deconvolution by means of standard inverse filtering. The time constants used correspond to $C_1 = 40$ J K^{-1}. (c) Deconvolution by means of standard inverse filtering. The time constants used correspond to $C_1 = 48$ J K^{-1}. (d) Deconvolution by the system of differential equations defining the model. The correct time evolution of C_1 is explicitely considered.

power input and to the specified functional dependence of the parameters of the model. The power dissipation is defined as follows:

$$W_1(t)=\begin{cases}1\ W & 0<t<2050\ \mathrm{s}\\ 0\ W & t>2050\ \mathrm{s}\end{cases}$$

and $T_3(t)$ is calculated by numerically solving the system of differential equations which define the model. We have used for this purpose the routine DHPCG from the FORTRAN SSP (IBM).

Random signals of different amplitudes also have been superimposed on the thermogram in order to check the performance of the deconvolutive

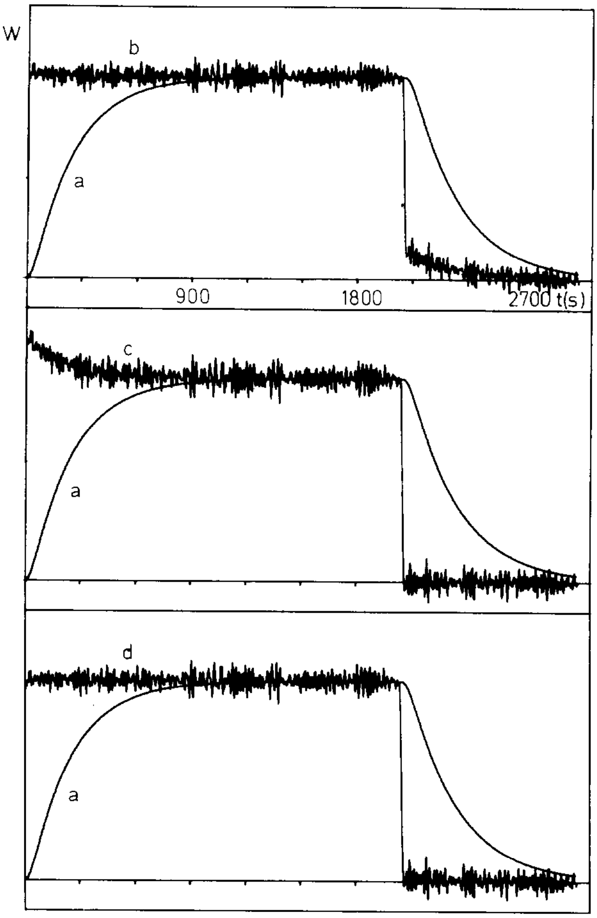

Fig. 4. (a) Thermogram corresponding to a step input ($W=1$ W) in a system where C_1 changes from 40 to 48 J K^{-1} in 2050 s. After that $W=0$ W and the parameters are kept constant. The signal/noise ratio is roughly 50 dB. (b) Deconvolution by means of standard inverse filtering. The time constants used correspond to $C_1 = 40$ J K^{-1}. (c) Deconvolution by means of standard inverse filtering. The time constants used correspond to $C_1 = 48$ J K^{-1}. (d) Deconvolution by the system of differential equations defining the model. The correct time evolution of C_1 is explicitely considered.

methods under different experimental conditions (i.e., under different signal/noise ratios).

The deconvolution of these records has been performed in three different ways: standard (time invariant) inverse filtering, putting them back into the system of differential equations and solving for $W_1(t)$ and, finally, considering an inverse filter whose time constants are function of time.

In the first case, we have considered two different filters, namely, those corresponding to the time constants before and after the injection. Figures 3 and 4 show the results obtained concerning signal/noise ratios of roughly 100 and 60 dB, respectively. The fluctuations observed in Fig. 4 are mainly due to the third-order derivative required to filter three time constants. Also, this derivative is multiplied by the product $\tau_1\tau_2\tau_3$ which leads to a decrease in the effective signal/noise ratio.

Both examples are affected by overcorrections at the beginning of the injection when considering the time constants corresponding to the end and vice versa. In order to avoid this problem, we have devised an algorithm based on the system of differential equations where the change in the parameters may be taken into account in a natural way. The algorithm is the generalization of its time invariant counterpart which may be found in ref. 11. The results obtained, concerning both signal/noise ratios, are also shown in Figs. 3 and 4. The thermogenesis obtained is no longer affected by over- or undercorrections.

Finally, given that in our model the first time constant is found to depend linearly on the heat capacity (i.e., on time, see Fig. 2), a generalization of a standard filter has been also applied to the aforementioned thermograms. In this case, the time constants defining the filter are assumed to depend linearly on time. For instance, a one step filter is defined as follows:

$$T_3^{(1)}(t) = T_3(t) + \tau_1(t)\frac{\mathrm{d}T_3(t)}{\mathrm{d}t} \qquad \tau_1(t) = \tau_{10} + \tau_{1p}t$$

Strictly speaking, it is meaningless to consider a time constant dependent on time because the pulse response of the system is no longer, in the variable case, a series of exponentials. This filter is to be interpreted only as a local approximation if the change in the physical parameters of the system is slow enough in the time scale of the measurement. Only in this case we may consider, as a first approximation, that, locally, the system may be represented by a set of time constants.

The result given by this method in the case of the lowest signal/noise ratio is shown in Fig. 5. Concerning the particular model chosen the same power input is given by the two variable methods described. This fact suggests that it is feasible to consider an inverse filter with variable time constants in those cases where the physical parameters of the system do not change appreciably in the time scale of the measurement. Nevertheless, in

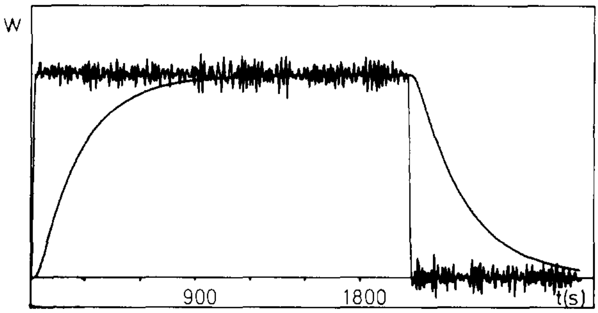

Fig. 5. Deconvolution by means of variable inverse filtering of the thermogram shown in Fig. 4. The time constants used change linearly from their value at $C_1 = 40$ J K^{-1} to the value at $C_1 = 48$ J K^{-1}.

this case, a proper identification of the system before and after the injection is essential.

CONCLUSIONS

Even though non time-invariant calorimetric systems cannot be handled analytically, it is feasible to attempt to perform the deconvolution of the experimental records. A simple algorithm has been built up for when the values of the heat capacities and coupling coefficients defining the RC model associated to a particular device are known; this produces the correct instantaneous power released inside the laboratory cell. The method is based on physical arguments; i.e., the increase in the mass of the laboratory cell is explicitly contained in the deconvolutive procedure. The method is affected as much by the experimental noise as is standard inverse filtering.

It is also feasible to introduce a time dependent inverse filter where the poles and zeros considered are functions of time provided that the change in the physical parameters of the system is slow enough; otherwise, this local approximation does not make sense. In this case, a correct identification of the system at the beginning and at the end of the experiment is essential.

In the particular model studied, the time constants are found to change linearly vs. time. Inverse filtering including this linear behaviour leads to the same result as the one given by the previous method (which incorporates the explicit variation of the heat capacity).

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