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DECONVOLUTION IN MICROCALORIMETRY AND AN APPLICATION TO MASS-VARYING SYSTEMS

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ABSTRACT

The behaviour of the calorimetric response in continuous injection devices, which are well suited for measurement of excess partial molar enthalpies at different concentrations, is analysed by means of heat transport models. Signal analysis of the thermal response gives the enthalpy values at very low concentrations. We establish an operating routine for the identification of the time-varying device, and a generalized deconvolution procedure to obtain, with high accuracy, the power released in the calorimeter as a function of time. The main features considered are the changes in sensitivity and dynamic properties of the experimental system due to the injection of one component in the mixture. A formal decomposition of the heat transport equations shows that typically time-invariant methods are able to deal with deconvolution in non-invariant systems.

INTRODUCTION

Heat flux microcalorimetry is a well-established experimental technique for the measurement of small thermal energies [1]. By means of signal analysis it can be extended to the determination of the thermal power released in an experiment at every instant of time. Recently, a great effort has been devoted to equate the identification and deconvolution techniques to the calorimetric problem [2,3,4], and to evaluate their performances. Numerous different calorimeters have been used to test the quality of recovery of the thermal power achieved with the different techniques. On the other hand, calorimeters have also been applied to two different kinds of measurements: the enthalpy involved in solid phase thermoelastic transformations, such as that of the copper/zinc/aluminium alloy [5,6], and the excess partial molar enthalpies of binary mixtures measured by continuous injection of a component [7].

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In the former, the results obtained by deconvolution of the thermograms have highlighted the essentially discontinuous character of the transformation, in accordance with the corresponding acoustic emission.

In the latter, signal analysis has opened up a wider range of minimum molar fractions (from the value of 0.05) in static mixing measurements. In this case, however, the heat capacity of the calorimetric vessel changes with time due to the injection. This fact makes it clear that the classical time-invariant deconvolution techniques are not appropriate for calorimeters with high sensibility and high signal-to-noise ratios; some experimental evidence of the change in the dynamic properties of the system as a function of time has been found [8,9,10]. Additionally, there has been an attempt to extend the time-invariant deconvolution methods, from an experimental point of view, to time-varying systems [11].

In preliminary studies of heat transport models, temporal non-invariancy appears as a result of variation in the heat capacity of the calorimetric vessel with time. This change is due to the injection of a component into the vessel, and as the injection rate is kept constant, the heat capacity variation is supposed to be linear [12,13]. This kind of model reproduces quite well the decrease in the steady-state temperature with injection and, qualitatively, the dependence of such a decrease on the injection rate, the specific heat of the liquid injected and the value of the thermal power released in the process. Appropriate procedures to take these effects into account, paying special attention to experimental feasibility, have already been outlined [14].

However, some continuous injection devices also exhibit a change in their sensibility with time, depending upon the volume of the cell contents; such an effect is impossible to account for with models in which only the heat capacity of the vessel changes with the injection as a function of time.

The purpose of the present paper is two-fold: (1) to generalize the models for continuous injection calorimetric devices in a way that includes not only the change of the steady-state temperature with the injection, but the experimental evidence that the sensibility of the instrument evolves as well; (2) to extend the methods for the identification of the dynamic behaviour of the calorimetric system and subsequent deconvolution of the thermal response to the non-invariant situation, in order to reconstruct the input signal, i.e., the instantaneous thermal power in the mixing process, so that it is free from systematic errors.

MODEL OF THE TIME-VARYING CALORIMETER

For the calorimetric model to be representative of the actual system, its characteristics must depend strongly on the signal-to-noise ratio in the corresponding thermograms. The usual experimental conditions centre around signal-to-noise relations less than or equal to 50 dB, although values

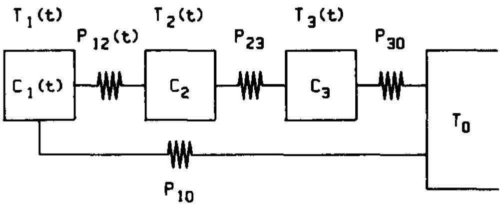

Fig. 1. Schematic representation of the calorimetric model in terms of heat capacities C_i and thermal couplings P_{ij}. The parameters C_1 and P_{12} vary with time due to the injection of liquid into the vessel.

of 70 dB or higher could be attainable in some special devices. In these particularly favourable conditions, the effects of injection become increasingly important. Furthermore, there is a modification in the thermal balance of the calorimeter because the injected liquid enters the vessel at the temperature of the external thermostat. Generally, a third-order model is detailed enough to describe these main features, however, it can be readily generalized to higher orders when necessitated by the quality of the thermal signals. The model, schematically shown in Fig. 1, is described in terms of localized constants [15] by the following system of equations

$$W_1(t) = C_1(t)\dot{T}_1 + P_{12}(t)[T_1 - T_2] + [\dot{C}_1(t) + P_{10}][T_1 - T_0] \tag{1a}$$

$$0 = C_2\dot{T}_2 + P_{12}(t)[T_2 - T_1] + P_{23}[T_2 - T_3] \tag{1b}$$

$$0 = C_3\dot{T}_3 + P_{23}[T_3 - T_2] + P_{30}[T_3 - T_0] \tag{1c}$$

where $C_1(t)$ represents the heat capacity of the vessel, in which the heat dissipation $W_1(t)$ takes place, and $P_{12}(t)$ represents the thermal coupling between the vessel and the rest of the calorimeter. Both parameters change with time as a consequence of the change in vessel contents during the injection. The thermal response is given by the temperature difference $(T_3 - T_0)$.

Assuming $\theta_i = T_i - T_0$, where T_0 stands for the constant temperature of the thermostat, the system (1) can be rewritten in the form

$$W_{10}(t) = W_1(t) - W_{11}(t) - W_{12}(t) = \sum_{i=0}^{3} D_i(t)\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \tag{2a}$$

$$W_{11}(t) = \dot{C}_1(t)\sum_{i=0}^{2} E_i(t)\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \tag{2b}$$

$$W_{12}(t) = -\dot{P}_{12}(t)\sum_{i=0}^{2} F_i(t)\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \tag{2c}$$

System (2) can, in turn, be converted into one linear differential equation

$$W_1(t) = \sum_{i=0}^{3} D_i\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \tag{3}$$

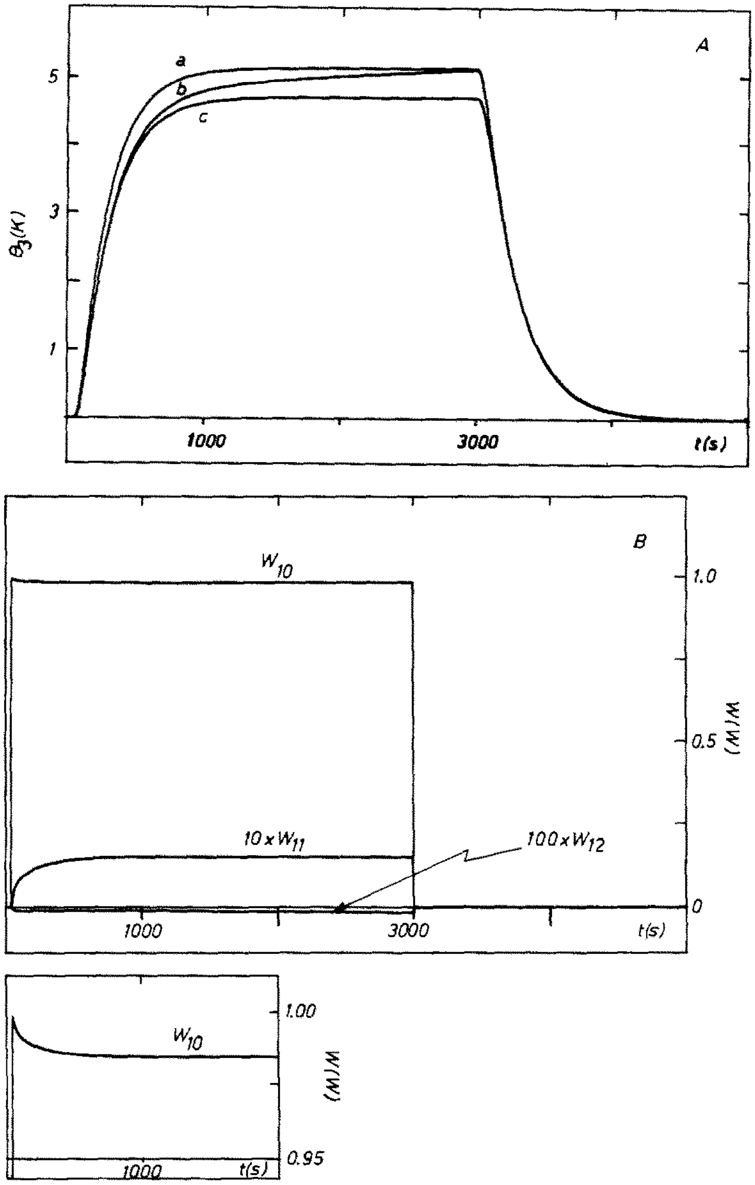

Fig. 2. A. Thermal curves θ_3 (K) obtained from the model for a constant dissipation $W_1 = 1$ W between $t = 50$ s and $t = 3000$ s. Curve (a) corresponds to a constant coupling $P_{12} = 0.28$ W K^{-1}, curve (c) to a constant coupling $P_{12} = 0.14$ W K^{-1} and curve (b) to a coupling P_{12} that varies linearly from 0.14 to 0.28 W K^{-1} during the power dissipation. In the three cases, the heat capacity varies from 5 to 10 J K^{-1}, and the other parameters are kept constant. B. The three components in which the thermal power W_1 has been separated. W_{11} carries all the dependency on $\dot{C}_1$, while W_{12} carries all the dependency on $\dot{P}_{12}$. In the picture below, the initial part of W_{10} is shown with a greater magnification.

The formal analogy between eqns. (2a) and (3) should be noted. The coefficients $D_i(t)$ in eqn. (2a), considered at $t = t_k$, coincide with those of a time-invariant system that has the same level of liquid in the cell as the general variable model has at $t = t_k$. The impulse response of such an invariant system is defined by a certain area S and a set of time constants $\{\tau_i\}$ verifying

$$D_3 = (\tau_1\tau_2\tau_3)/S \tag{4a}$$

$$D_2 = (\tau_1\tau_2 + \tau_1\tau_3 + \tau_2\tau_3)/S \tag{4b}$$

$$D_1 = (\tau_1 + \tau_2 + \tau_3)/S \tag{4c}$$

$$D_0 = 1/S \tag{4d}$$

where all the values are supposed to be taken at $t = t_k$. By formal analogy with the time-invariant situation, we may rewrite the preceding equations for the coefficients D_i' in differential eqn. (3) by substituting the parameters $\tau_i(t)$ and $S(t)$ by certain other parameters $\tau_i'(t)$ and $S'(t)$.

Figure 2A shows the response of the model to a constant input power in three different cases: one with a linear evolution of the coupling $P_{12}(t)$ during the interval of dissipation and two others with two extreme constant values of P_{12}. The variation of the coupling is responsible for the change in sensibility with time. In contrast, Fig. 2B shows the three different terms in which the thermal input power $W_1(t)$ has been decomposed in eqns. (2). It is clear that the major contribution to $W_1(t)$ is given by $W_{10}(t)$, which might be obtained directly from the values of $\tau_i(t)$ and $S(t)$. However, neglecting the two other terms, which carry the dependence on $\dot{C}_1(t)$ and $\dot{P}_{12}(t)$, would represent a systematic error on the determination of $W_1(t)$, especially in those cases where it is possible to obtain high-quality thermograms.

SYSTEM IDENTIFICATION

Identification of the parameters $\tau_i(t)$ in eqns. (4) may be performed by stopping the injection, and consequently the dissipation, at different times t_k, considering the decay to zero of the thermogram as the response to a stepped input, and applying classical time-invariant methods of identification [16]. Through eqns. (4), the coefficients $D_i(t)$ in eqn. (2a) are determined, except for the value of the sensibility $S(t)$. The latter may be obtained from calibration by means of the Joule effect.

Unfortunately, the remaining terms $W_{11}(t)$ and $W_{12}(t)$ cannot be calculated directly from the thermogram and the coefficients $D_i(t)$. An alternative approach consists of considering the whole of eqn. (3) and the symbolic expression of its coefficients $D_i'(t)$ in terms of parameters $\tau_i'(t)$ and $S'(t)$. Numeric simulations for different models described by eqns. (1) show that these parameters have the same functional dependence on time as the

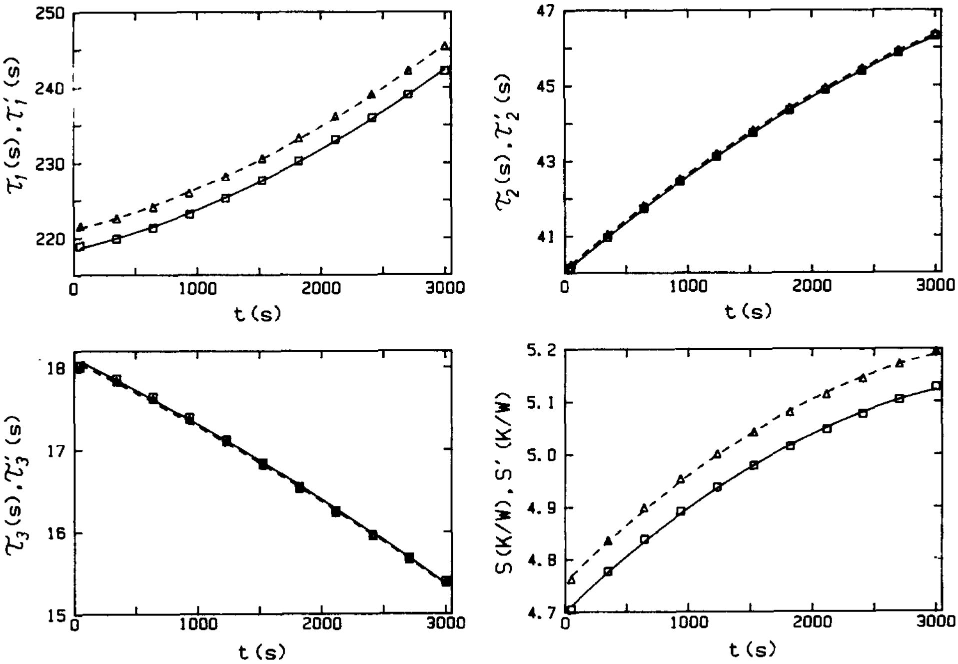

Fig. 3. Dynamic parameters and sensibility of the model as a function of time. Δ represents the unprimed parameters; □ represents the primed parameters. Least-squares fits to second-degree polynomials are also shown.

corresponding $\tau_i(t)$ and $S(t)$, and are only shifted from them by certain constant values $\Delta\tau_i$ and ΔS, as shown in Fig. 3. The shift can be evaluated at two different times, e.g., at the beginning and at the end of the injection, by determining the corresponding $\tau_i'(t)$ and $S'(t)$ by means of a generalized identification method. The method is based on inverse filtering and τ_i' play the role of the time constants to be identified, in the form

$$\tau_i'(t) = \tau_i(t) + \Delta\tau_i \qquad (5)$$

The time dependency is centred on $\tau_i(t)$, which are known from time-invariant identification as described above, and the increments $\Delta\tau_i$ are determined by optimizing the result of inverse filtering. $S'(t)$ is obtained by comparing the reconstructed thermal power (in arbitrary units) obtained from a standard mixture with the corresponding tabulated values of the partial molar enthalpies of the mixture at different concentrations.

From an experimental point of view, the whole identification procedure can be summarized as follows.

(i) The parameters $\tau_i(t_k)$ are identified, by means of invariant methods, from the thermogram decays corresponding to halts in the injection at $t = t_k$. This is done for every different binary liquid mixture studied.

(ii) Consider experiments in which a constant thermal power is released by means of the Joule effect and, simultaneously, liquid A is injected into a vessel already partially filled with liquid A. From the thermogram obtained after stopping the heating, but not the injection, and by means of variable inverse filtering, the increments $\Delta\tau_l$ may be determined. It is not difficult to see that, in this case; $\dot{C}_1(t) \neq 0$ and $\dot{P}_{12}(t) \neq 0$.

(iii) The time-varying sensibility $S'(t)$ is determined by calibration with standard binary mixtures.

THERMAL POWER DECONVOLUTION

Given the values of $\tau_l'(t)$ and $S'(t)$, the coefficients $D_l'(t)$ in eqn. (3) can be obtained immediately. The thermal power released in a certain experiment is then obtained, through eqn. (3), by numerically calculating the three first derivatives of the corresponding thermogram $\theta_3(t)$, weighting them with the coefficients $D_l'(t)$ at every instant of time, and adding the resulting four terms. This procedure is, in fact, a generalization to the time-varying case of the well-known inverse filtering.

It is not necessary to carry out a new identification for every binary system under study. Considering different initial values of the heat capacity $C_1(t)$, computer simulations of the calorimetric model described by eqns. (1) show that the shift values $\Delta\tau_l$ and ΔS depend essentially upon the product ρc (density × specific heat) of the liquid injected into the calorimetric vessel

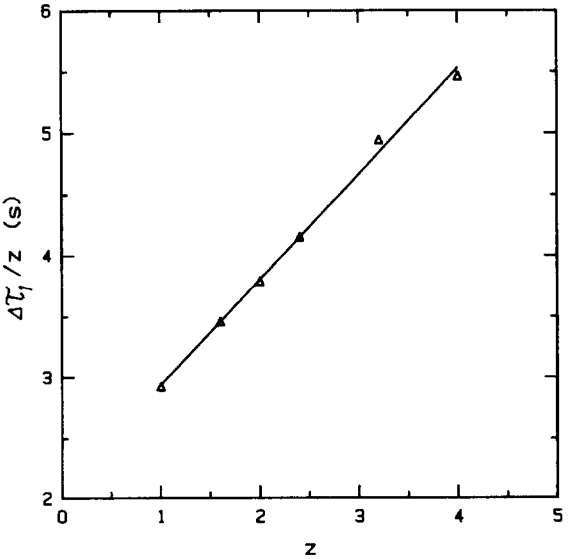

Fig. 4. The shift in the parameter τ_1, divided by z, versus z. The variable z stands for the values ρc corresponding to different liquids, referred to a certain initial value $\rho_0 c_0$ corresponding to the choice of C_1 in our model.

(Fig. 4). Generally, the values of interest for the product ρc fall in a certain limited range. The experimental procedure should be as follows:

(i) To perform calibrations using two different liquids whose values of ρc represent the actual limits for the mixtures of interest: $\rho_1 c_1 < \rho c < \rho_2 c_2$. To calculate their corresponding shifts $\Delta p(1)$ and $\Delta p(2)$ in the parameters, where p represents either τ_i or S. This is done following the steps outlined in the preceding section.

(ii) To take the linear dependence between $\Delta p/\rho c$ and the product ρc for every injection rate. The change $\Delta p(x)$ for the parameter p with the liquid x is then given by

$$\frac{\Delta p(x)}{\rho_x c_x} = \frac{\Delta p(1)}{\rho_1 c_1} + \frac{\Delta p(2)/\rho_2 c_2 - \Delta p(1)/\rho_1 c_1}{\rho_2 c_2 - \rho_1 c_1} \left\{ \frac{\Delta p(x)}{\rho_x c_x} - \frac{\Delta p(1)}{\rho_1 c_1} \right\} \tag{6}$$

Remark

Once the values of the coefficients $D'_i(t)$ in eqn. (3) have been determined, it is possible to apply any time-invariant deconvolution method to obtain the input $W_1(t)$. The problem of deconvolution in a time-varying system has been reduced to a multiplicity of time-invariant deconvolution problems. The coefficients $D'_i(t)$ in eqn. (3) may be fitted against polynomials of the variable t. The degree n of the polynomials should be chosen according to the required precision and the number of invariant identifications performed. Then, the coefficients read

$$D'_i(t) = \sum_{j=0}^{n} D'_{ij} t^j \tag{7}$$

and

$$W_1(t) = \sum_{j=0}^{n} W'_{1j} t^j = \sum_{i=0}^{3} \sum_{j=0}^{n} D'_{ij} t^j \frac{\mathrm{d}^i \theta_3}{\mathrm{d}t^i} \tag{8}$$

The calorimeter is then represented by $n + 1$ transfer functions which, in the Laplace space, read

$$H_j(s) = \frac{T_3(s)}{W'_{1j}(s)} = 1 \Bigg/ \left(\sum_{i=0}^{3} D'_{ij} s^i \right) \tag{9}$$

$T_3(s)$ and $W'_{1j}(s)$ are the Laplace transforms of $\theta_3(t)$ and $W'_{1j}(t)$, respectively. From the knowledge of the transfer functions $H_j(s)$, time-invariant deconvolution methods lead to the values of $W'_{1j}(t)$ and therefore to the power input $W_1(t)$.

EXAMPLES OF APPLICATION

A third-order calorimetric model, described by eqns. (1), has been considered. The parameters for this model have been arbitrarily chosen to obtain a

TABLE 1

Values of the heat capacities C_i and thermal couplings P_{ij} for the calorimetric model in Fig. 1

C_2 (J K^{-1})	C_3 (J K^{-1})	P_{10} (W K^{-1})	P_{30} (W K^{-1})	P_{23} (W K^{-1})
11	12	0.07	0.07	0.14

t (s)	$C_1(t)$ (J K^{-1})	$P_{12}(t)$ (W K^{-1})
$0 \leqslant t < 50$	5	0.14
$50 \leqslant t < 3000$	$5+(t-50)/590$	$0.14+0.07(t-50)/1475$
$3000 \leqslant t$	10	0.28

set of time constants with the same order of magnitude as in actual continuous injection calorimeters, and are given in Table 1.

Figure 3 shows the values of $\tau_1(t_k)$ and $S(t_k)$ for this model, calculated from eqns. (4). They correspond to the parameters that would be obtained, by means of time-invariant identifications, from the decays to zero of the experimental thermograms when the injection is halted to stop at $t = t_k$. A least-squares fit to second-degree polynomials, also shown in Fig. 3, leads to

$$\tau_1 = 221.26 + 4.31E - 3t + 1.34E - 6t^2 \quad \text{(s)} \tag{10a}$$

$$\tau_2 = 40.24 + 2.76E - 3t - 2.34E - 7t^2 \quad \text{(s)} \tag{10b}$$

$$\tau_3 = 18.04 - 7.39E - 4t - 5.86E - 8t^2 \quad \text{(s)} \tag{10c}$$

$$S = 4.77 + 2.29E - 4t - 2.93E - 8t^2 \quad \text{(K W}^{-1}\text{)} \tag{10d}$$

The values of $\tau_i'(t)$ and $S'(t)$ are also presented in Fig. 3. They have been obtained from the coefficients $D_i'(t)$ of the complete variable model. Least-squares fits give

$$\tau_1' = 218.65 + 4.11E - 3t + 1.34E - 6t^2 \quad \text{(s)} \tag{11a}$$

$$\tau_2' = 40.16 + 2.77E - 3t - 2.35E - 7t^2 \quad \text{(s)} \tag{11b}$$

$$\tau_3' = 18.07 - 7.46E - 4t - 5.81E - 8t^2 \quad \text{(s)} \tag{11c}$$

$$S' = 4.71 + 2.24E - 4t - 2.86E - 8t^2 \quad \text{(K W}^{-1}\text{)} \tag{11d}$$

It is clear from the figure that the temporal behaviour of the primed and unprimed parameters follows a regular pattern, which is reinforced by the similarity between the coefficients on t and t^2 for the corresponding parameters in eqns. (10) and (11). The mean shifts between the primed and unprimed parameters are given by

$$\Delta\tau_1 = -2.922 \text{ s} \tag{12a}$$

$$\Delta\tau_2 = -0.066 \text{ s} \tag{12b}$$

$$\Delta\tau_3 = 0.024 \text{ s} \tag{12c}$$

$$\Delta S = -0.063 \text{ K W}^{-1} \tag{12d}$$

These shifts can be obtained from $\tau_i'(t)$ and $S'(t)$ identified at two different

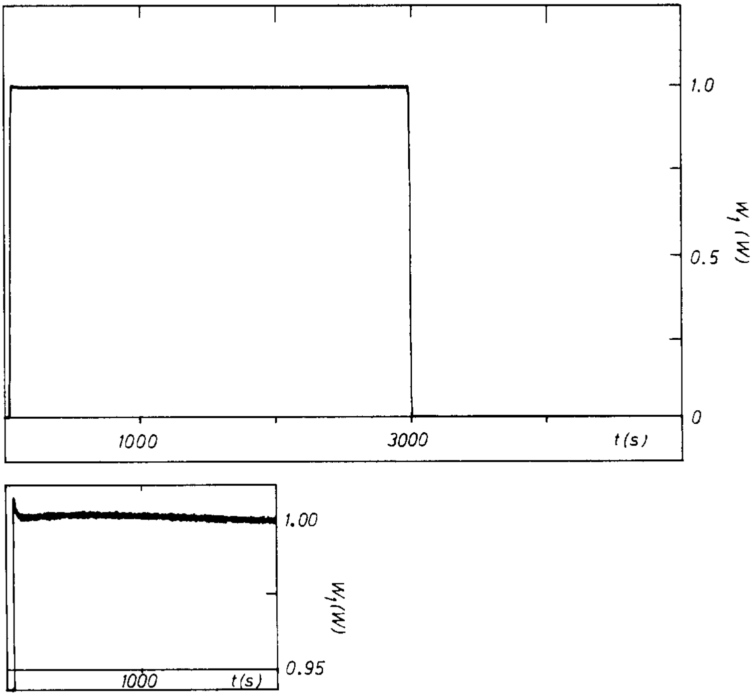

Fig. 5. Reconstruction of the thermal power $W_1(t)$ from the thermogram $\theta_3(t)$ by means of time-varying inverse filtering. In the picture below, for comparison with Fig. 2B, the thermal power is shown with a greater magnification.

times. The identification, as mentioned above, is performed by means of a variable inverse filtering where the dependence on t is taken from that of $\tau_i(t)$ and $S(t)$.

Figure 4 shows the values of $\Delta\tau_1$ for different volumic heat capacities ρc or, in other words, for different liquids that may be injected. They have been simulated with different initial values of the heat capacity $C_1(t)$ in the model described above (Table 1) while keeping the other parameters at their original values. The result is fitted to a straight line which represents eqn. (6).

Finally, Fig. 5 presents the resulting thermal power input after a deconvolution of the thermograms in Fig. 1. The deconvolution has been performed by means of a variable inverse filtering, using the values of $\tau_i'(t)$ and $S'(t)$ given by eqns. (11). The recovery of the power is shown to be highly accurate even at the initial times of the dissipation. In a mixing experiment, these initial times could correspond to very low concentrations of the injected liquid in the mixture.

CONCLUSIONS

(1) Microcalorimetric devices with continuous injection, as those used for the study of liquid mixtures, present a variation of their sensibility and

inertial properties with time. If the quality of the thermal signal is considerable (signal/noise greater than 50 dB), then neglecting this variation results in systematic errors on the thermal power recovered.

(2) By means of several classical time-invariant identifications performed in every experiment, the invariant parameters $\tau_i(t)$ and $S(t)$ are evaluated. They are only shifted by a constant value from the $\tau_i'(t)$ and $S'(t)$ values, which completely describe the calorimeter.

(3) A variable identification gives the shifts in the invariant parameters $\tau_i(t)$ and $S(t)$, from which the corresponding variable parameters are deduced. This identification has only to be performed for two different liquids corresponding to extreme values of the product ρc (density × specific heat of the liquid). The correcting shifts for other substances are calculated from a linear interpolation.

(4) The thermal power released in the experiment can be determined, as a function of time, either by time-varying inverse filtering or by any classical time-invariant method of deconvolution using a hierarchy of transfer functions.

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