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DECONVOLUTIVE PROCEDURES IN NON-INVARIANT SYSTEMS: AN APPROACH TO AN EXTENDED TRANSFER FUNCTION IN MICROCALORIMETRY

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ABSTRACT

This article analyses the problem of applying deconvolution techniques to conduction calorimeters with the continuous injection of a liquid. An efficient working procedure is described which characterizes the calorimeter system by means of three different transfer functions obtained using a simple localized constants model. In this way the problem is transferred to the field of invariant systems. An example with a signal-to-noise ratio of 80 dB is discussed.

INTRODUCTION

In recent years the field of application of conduction calorimetry has been extended to embrace dynamic measurements to the introduction of deconvolution techniques. This has permitted research into systems such as oscillating reactions [1] and martensitic phase transformations [2,3]. Accurate measurements of liquid mixtures [4–6] are hard to obtain owing to the fact that the heat capacity of the calorimeter cell, and with it the transfer function of the calorimeter system, changes during the continuous injection of the second component, thus preventing treatment on the same lines as that of invariant systems. Nevertheless, by defining various transfer functions instead of a single one, these systems can also be simply and systematically handled.

THE EQUATIONS OF THE MODEL

The localized constants model [7] is illustrated in Fig. 1. The temperatures, ξ_i, of the elements (three in this case) are naturally functions of the time, t.

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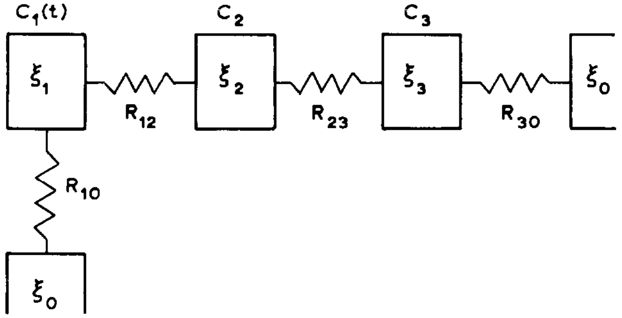

Fig. 1. The three-element model. $\xi_i(t)$ $(i=1,2,3)$ are the temperatures of the elements of the calorimeter, ξ_0 is that of the thermostat, C_i are heat capacities and R_{ij} are thermal resistances.

The temperature of the thermostat, ξ_0, is constant, as are the thermal coupling $P_{ij} = 1/R_{ij}$ and the heat capacities C_2 and C_3. The heat capacity of the first element varies with time

$$C_1(t) = C_1^0 + vC_1^1 t \tag{1}$$

where v is the rate of injection of the second component and C_1^1 is its specific heat. Assuming that it is only in the first element that heat is dissipated, the energy balance of this system in terms of the variables, $\theta_{\mathrm{i}} = \xi_{\mathrm{i}} - \xi_0$, is given by the differential equations

$$\begin{aligned} w_1(t) &= C_1(t)\frac{\mathrm{d}\theta_1}{\mathrm{d}t} + \left(vC_1^1 + P_{10} + P_{12}\right)\theta_1 - P_{12}\theta_2 \\ 0 &= C_2\frac{\mathrm{d}\theta_2}{\mathrm{d}t} - P_{12}\theta_1 + (P_{12} + P_{13})\theta_2 - P_{23}\theta_3 \\ 0 &= C_3\frac{\mathrm{d}\theta_3}{\mathrm{d}t} - P_{23}\theta_2 + (P_{30} + P_{23})\theta_3 \end{aligned} \tag{2}$$

The variable measured directly as the output of the calorimeter in the experimental thermogram is θ_3. The second and third of the above equations may readily be solved for θ_1 and θ_2 in terms of this variable

$$\begin{aligned} \theta_1 &= \sum_{i=0}^{2} a_{1i}\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \\ \theta_2 &= \sum_{i=0}^{1} a_{2i}\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \end{aligned} \tag{3}$$

where a_{ij} are constants whose full expressions are given in the Appendix. Substitution of these expressions for θ_1 and θ_2 in the first of eqns. (2) yields

$$w_1(t) = \sum_{i=0}^{3} A_i(t)\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} + vC_1^1\sum_{i=0}^{2} a_{1i}\frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \tag{4}$$

A_i in eqn. (4) depends linearly on time

$$A_i(t) = A_{i0} + A_{i1}t \qquad (5)$$

where A_{ij} are constants whose full expressions are given in the Appendix. Equation (4) may thus be broken down in the form

$$w_1(t) = w_1^1(t) + tw_1^2(t) + w_1^2(t) \qquad (6)$$

where

$$\begin{aligned} w_1^1(t) &= \sum_{i=0}^{3} A_{i0} \frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \\ w_1^2(t) &= \sum_{i=1}^{3} A_{i1} \frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} \\ w_1^3(t) &= \upsilon C_1^1 \sum_{i=0}^{2} a_{1i} \frac{\mathrm{d}^i\theta_3}{\mathrm{d}t^i} = \sum_{i=1}^{3} A_{i1} \frac{\mathrm{d}^{i-1}\theta_3}{\mathrm{d}t^{i-1}} \end{aligned} \qquad (7)$$

note that $w_1^2(t) = \mathrm{d}w_1^3(t)/\mathrm{d}t$.

Application of the Laplace transformation to eqn. (7) now yields three different equations for T_3, the Laplace transform of θ_3

$$T_3(s) = H_i(s)W_1^i(s); \quad i = 1, 2, 3 \qquad (8)$$

where W_1^i is the Laplace transform of w_1^i and H_i are three invariant transfer functions given by

$$\begin{aligned} H_1(s) &= 1/\left(A_0 + A_{10}s + A_{20}s^2 + A_{30}s^3\right) \\ H_2(s) &= \frac{1}{s}H_3(s) = 1/s\left(A_{11} + A_{21}s + A_{31}s^2\right) \end{aligned} \qquad (9)$$

Once these transfer functions are known, the problem of reconstructing $w_1(t)$ to give the experimental thermogram output is solved by simply carrying out three deconvolutions of the invariant type for which satisfactory procedures already exist [8–11].

IDENTIFICATION

In order to obtain the A_{ij} coefficients and, hence, the transfer functions H_i, no more is required than to fit straight lines to measurements of $A_i(t)$ for various values of t. If injection of the injected substance is halted at time t_k, then from that moment on the heat capacity C_1 has the constant value $C_1^0 + \upsilon C_1^1 t_k$ (eqn. 1) and eqn. (4) shows that the transfer function of the calorimeter is given by

$$H(s, t_k) = 1/\left[A_0 + A_1(t_k)s + A_2(t_k)s^2 + A_3(t_k)s^3\right] \qquad (10)$$

This constant transfer function may be identified by any of the standard methods [8,12,13] from the decay curve after injection is interrupted or by using Joule effects. The values of $A_i(t_k)$ in terms of the corresponding time constants, $\tau_i(t_k)$, and sensitivity, S, are given by

$$\begin{aligned} A_0 &= 1/S \\ A_1(t_k) &= [\tau_1(t_k) + \tau_2(t_k) + \tau_3(t_k)]/S \\ A_2(t_k) &= [\tau_1(t_k)\tau_2(t_k) + \tau_1(t_k)\tau_3(t_k) + \tau_2(t_k)\tau_3(t_k)]/S \\ A_3(t_k) &= \tau_1(t_k)\tau_2(t_k)\tau_3(t_k)/S \end{aligned} \tag{11}$$

After a few "partial" characterizations of this type for different times, t_k, a straight line can be fitted to $A_i(t_k)$ so, for each i, values of the A_{ij} can be obtained and, hence, the complete specification of the transfer functions (eqn. 9).

EXAMPLE

The model illustrated in Fig. 1 was simulated on an HP-9845B computer using the values $R_{10} = R_{30} = 0.07$, $R_{12} = R_{23} = 0.14$, $C_2 = 11$, $C_3 = 12$, $C_1^0 = C_1^1 = 5$ and $v = 6.6667 \times 10^{-4}$. The heat capacity of the first element thus varies linearly from 5 to 10 during the 1500-s injection period. The input signal employed was

$$w_1(t) = \begin{cases} 1\text{–}3 \times 10^{-4}t - 3 \times 10^{-8}t^2 & 0 \leqslant t \leqslant 1500 \\ 0 & \text{otherwise} \end{cases} \tag{12}$$

which, qualitatively, is of the type expected in continuous mixing processes. The sampling period, T, of the output signal (the thermogram) was 1 s. Figure 2 shows the true input signal together with the simulated response, in which simulated noise was included to give a signal-to-noise ratio of 80 dB.

Partial characterizations carried out for different injection times using simulated Joule effects [8] produced the values shown in Table 1 for $\tau_i(t_k)$ and S, and (by eqn. 11) the values of $A_i(t_k)$ are shown in Table 2. Fitting straight lines to these values produced the results

$$\begin{aligned} A_0 &= 0.21 \\ A_1 &= 58.7498 + 6.66662 \times 10^{-3}t \\ A_2 &= 2860.71 + 0.964301t \\ A_3 &= 33673.1 + 22.4500t \end{aligned} \tag{13}$$

These expressions are of course valid only for $0 \leqslant t \leqslant 1500$ s, after which A_i values maintain the fixed values $A_i(1500)$.

The expressions (13) fully determine the transfer functions (eqn. 9), and

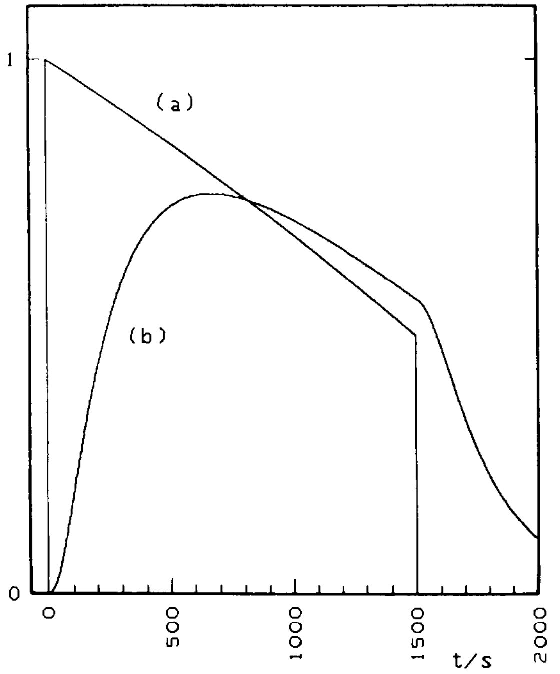

Fig. 2. Input power (a) and output thermograms (b) simulated using the model of Fig. 1.

standard deconvolution techniques using the Z transform [8] yield the three input power terms of the decomposition (eqn. 6). These are shown in Fig. 3, and their sum perfectly reproduces the true input signal (eqn. 12).

TABLE 1

Partial characterization parameters obtained for different injection times

Time (s)	S	τ_1	τ_2	τ_3
0	4.7619	221.54	40.233	17.990
500	4.7619	230.63	43.870	21.131
1000	4.7619	240.35	47.982	23.174
1500	4.7619	250.66	52.220	24.501

TABLE 2

Values of A_i for different injection times

Time (s)	A_0	A_1	A_2	A_3
0	0.210000	58.7502	2860.73	33673.3
500	0.210000	62.0825	3342.82	44897.6
1000	0.210000	65.4163	3825.01	56123.3
1500	0.210000	68.7501	4307.17	67348.1

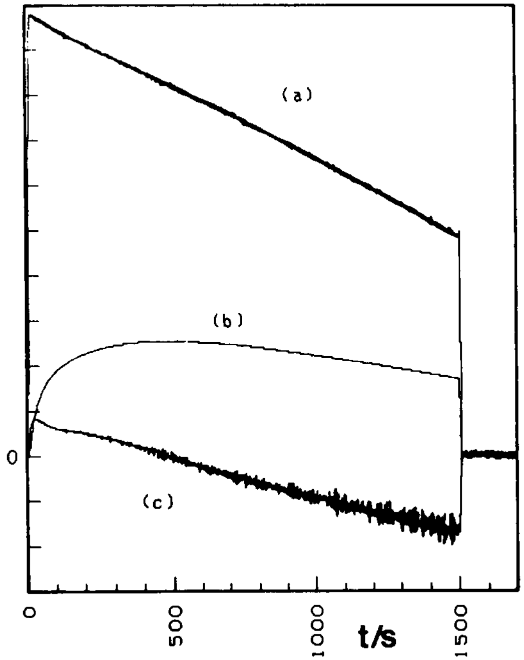

Fig. 3. The three individual terms of the deconvoluted signal: (a) $w_1^1(t)$, (b) $10 \times t w_1^2(t)$ and (c) $10 \times w_1^3(t)$, whose sum is the total deconvoluted signal.

CONCLUSIONS

By using three different transfer functions it is possible to establish a satisfactory working procedure for the deconvolution of thermograms obtained in simple continuous injection conduction calorimeters lending themselves to localized constants models. These transfer functions are readily calculated by conventional characterization methods. The deconvolution of signals obtained from non-invariant systems is thus reduced to three deconvolutions of invariant type. In spite of the simplicity of the procedure, the results are highly satisfactory, and the nature of the technique suggests that it may be successfully generalized to more complicated systems with more elements and zeros in their transfer functions.

APPENDIX

The a_{ij} constants of eqn. (3) are given by

$$a_{10} = \frac{1}{P_{12}P_{23}}\left[(P_{12} + P_{23})(P_{30} + P_{23}) - P_{23}^2\right]$$

$$a_{11} = \frac{1}{P_{12}P_{23}}\left[C_2(P_{30} + P_{23}) + C_3(P_{12} + P_{23})\right]$$

$$a_{12} = C_2C_3/P_{12}P_{23}$$

$$a_{20} = (P_{30} + P_{23})/P_{23};a_{21} = C_3/P_{23}$$

The A_{ij} constants of eqn. (5) are given by

$$A_0 = A_{00} = -a_{20}P_{12} + a_{10}(P_{10} + P_{12});A_{01} = 0$$

$$A_{10} = a_{10}C_1^0 + a_{11}(P_{10} + P_{12}) - a_{21}P_{12};A_{11} = a_{10}vC_1^1$$

$$A_{20} = a_{11}C_1^0 + a_{12}(P_{10} + P_{12});A_{21} = a_{11}vC_1^1$$

$$A_{30} = a_{12}C_1^0;A_{31} = a_{12}vC_1^1$$

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