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THE IDENTIFICATION OF VARIABLE MASS CONDUCTION CALORIMETRY SYSTEMS

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ABSTRACT

A technique to characterize calorimetric systems which uses a non-linear curve-fitting algorithm to approximate their unit pulse response has been tested satisfactorily and applied to the variable mass case of a calorimeter working with a continuous mixing device.

INTRODUCTION

In order to construct heat conduction calorimeters well suited to different experimental conditions an accurate mathematical description of the experimental system is necessary:

(1) The response of the apparatus to a unit pulse provides a model in the time domain, $h(t)$. The mathematical theory of heat transport in finite, invariable heterogeneous systems shows $h(t)$ to be a sum of exponential functions [1,2].

(2) Given the form of $h(t)$, its Laplace transform, $H(s)$, is a quotient of polynomials whose roots are their zeros and poles [1,2].

(3) The Bode diagram, obtained by considering $H(jw)$, allows the study of the frequency response of the system [2,3].

(4) The Fourier transform, which is now feasible thanks to Fast Fourier Transform algorithms (FFT) and thus can be applied directly to experimental thermograms [4], gives a gain and phase diagram equivalent to the Bode diagram.

Although a theoretical model of a system can always be obtained, the

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determination of its parameters, the time constants, is a tricky affair in practice. This paper presents the results obtained using a technique giving the poles and zeros of the system after approximating $h(t)$ by a least squares non-linear curve-fitting procedure due to Marquardt [5,6]. The method has been tested in almost ideal conditions (high signal-to-noise ratio, constant mass, no stirring, etc.) using resistors introduced into the calorimeter cell to generate heat by the Joule effect. In this way the transfer function $H(s)$ has been obtained in real situations with various contents. The results have been compared with those obtained by applying the FFT to the corresponding thermograms.

THE IDENTIFICATION OF THE SYSTEM

Assuming the experimental device to be a linear, causal, time-invariant system [1–3], its transfer function in terms of the complex variable s is

$$H(s) = k\frac{\prod_{j=1}^{m}(s - c_j)}{\prod_{i=1}^{n}(s - p_i)} \tag{1}$$

where c_j ($j = 1,\ldots,m$) are the zeros of the system, the p_i ($i = 1,\ldots,n$) its poles, and k is a constant. Concerning actual calorimetric systems m must be smaller than n and $p < 0$ (stability condition).

Although a given thermogenesis (instantaneous power released) can usually be well reproduced using an approximation consisting of three or four poles, we have always obtained a model with five poles and up to three zeros. The corresponding unit pulse response is therefore expressed as:

$$h(t) = S\left(\sum_{i=1}^{5} A_i\,\mathrm{e}^{-t/\tau_i}\right) \tag{2}$$

where S is the sensibility of the system, given by

$$S = k\frac{\prod_{i=1}^{5}\tau_i}{\prod_{j=1}^{3}\tau_j^*} \tag{3}$$

and the A_i are coefficients of the form

$$A_i = \tau_i^{n-m-2}\frac{\prod_{j=1}^{m}(\tau_i - \tau_j^*)}{\prod_{k\neq i}^{n}(\tau_i - \tau_k)} \tag{4}$$

The set of variables $\tau_i = -1/p_i$, $\tau_j^* = -1/c_j$ and S thus characterize the calorimetric model.

OBTAINING THE PARAMETERS OF THE MODEL

The parameters of the calorimeter which has been used are experimentally determined from its response to step signals:

$$x(t) = \begin{cases} W & 0 \leqslant t \leqslant t_0 \\ 0 & \text{otherwise} \end{cases} \tag{5}$$

where W is the electrical power dissipated by the Joule effect. The response to this input is given by:

$$y(t) = W\left[e(t) - e(t - t_0)\right] \tag{6}$$

where $e(t)$ is the response to a unit Heaviside function. The sensibility S is calculated from

$$S = \frac{1}{Wt_0} \int_0^\infty y_e(t)\mathrm{d}t \tag{7}$$

where $y_e(t)$ is the thermogram, i.e., the experimental response of the calorimeter.

The remaining parameters are obtained minimizing

$$\chi^2(a_j) = \sum_{i=1}^{N} \left[y_e(t_i) - y_i(a_j) \right] \tag{8}$$

where the a_j are the poles and zeros sought, y_i is the analytical expression of the calorimetric response, and N is the total number of experimental points considered.

Since y_i is a non-linear function of the a_j, then χ^2 is too. Nevertheless, if y_i is replaced by its first order Taylor series approximation in the neighbourhood of the initial values a_j^0 of the a_j, eqn. (8) becomes

$$\chi^2 = \sum_{i=1}^{N} \left[y_e(t_i) - y_i\left(a_j^0\right) - \sum_{j=1}^{n+m} \left(\frac{\partial y_i}{\partial a_j} \right)_{a_j = a_j^0} \delta a_j \right]^2 \tag{9}$$

which is linear with respect to the increments δa_j. At the minimum of χ^2, and for $k = 1, \ldots, n + m$ gives

$$-2 \sum_{i=1}^{N} \left\{ \left[y_e(t_i) - y_i\left(a_j^0\right) - \sum_{j=1}^{n+m} \left(\frac{\partial y_i}{\partial a_j} \right)_{a_j = a_j^0} \delta a_j \right] \left(\frac{\partial y_i}{\partial a_k} \right)_{a_k = a_k^0} \right\} = 0 \tag{10}$$

or, in matrix form,

$$\beta = \alpha \cdot \delta a \tag{11}$$

where β and the curvature matrix α are defined by

$$\beta_k = \sum_{i=1}^{N} \left[y_e(t_i) - y_i(a_j^0) \right] \left(\frac{\partial y_i}{\partial a_k} \right)_{a_k = a_k^0}$$

$$\alpha_{kj} = \sum_{i=1}^{N} \left(\frac{\partial y_i}{\partial a_j} \right)_{a_j = a_j^0} \left(\frac{\partial y_i}{\partial a_k} \right)_{a_k = a_k^0}$$

The values of δa sought are therefore given by

$$\delta a = \alpha^{-1} \beta \tag{13}$$

In practice, the algorithm described by Marquardt [6] uses a modified form of the curvature matrix, α', in which

$$\alpha'_{ij} = \begin{cases} \alpha_{ij}(1 + \lambda) & i = j \\ \alpha_{ij} & i \neq j \end{cases} \tag{14}$$

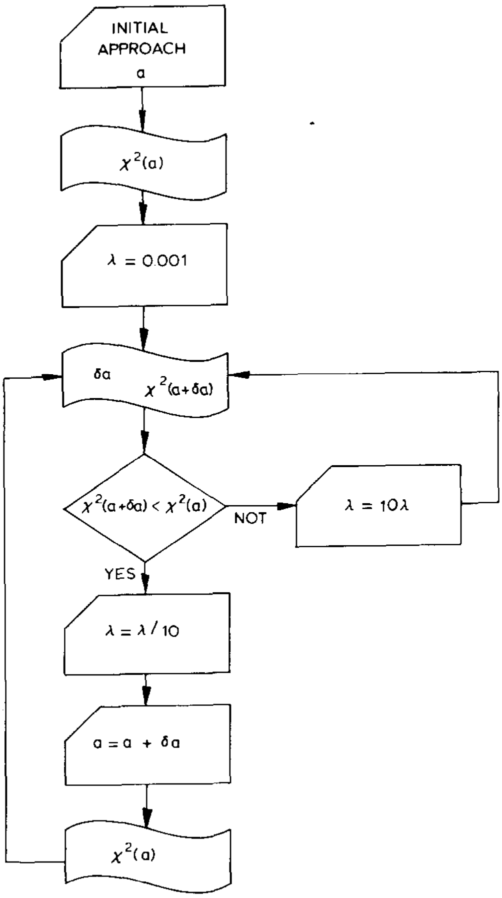

Fig. 1. Flowchart of the algorithm used to calculate λ.

TABLE 1

Time constants of the model transfer function for the lower limit of average calorimeter behaviour (fitted with 5 poles). L88. Values of model used. A. Without deformation of the simulated output signal. B. with a 50 dB signal to noise ratio. C. Like B, but with positive baseline drift, roughly 1/400 of the peak signal. D. Like C, but with negative drift

	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8
L88	192	49	18	4	2	1.2	0.4	0.3
A	191.69	49.54	17.01	4.17	4.32	–	–	–
B	191.71	49.54	17.02	4.25	4.24	–	–	–
C	196.12.	47.16	18.55	3.99	3.98	–	–	–
D	187.24	51.85	14.55	4.55	4.54	–	–	–

where λ is a variable parameter used to control the progress of the algorithm and improve the rate of convergence. Figure 1 shows how λ was chosen.

TESTING THE METHOD BY SIMULATION

To evaluate the method of characterization described above, the upper and lower boundaries of the average behaviour of conduction calorimeters in a relative frequency scale were simulated in a computer using the unit pulse response functions L88 and L89, whose time constants are shown in Tables 1 and 2, respectively (see refs. 7–9). In different runs the simulated output also included various conditions of noise and drift. In all cases the time constants calculated by applying our method of characterization, which are also shown in Tables 1 and 2, agree well with the true values.

TABLE 2

Time constants of the theoretical transfer function for the upper limit of average calorimetric behaviour (fitted with 5 poles and 2 zeros). L89. Values of model used. A. Without deformation of the simulated output signal. B. With a 56 dB signal to noise ratio. C. Like B, but with positive baseline drift, roughly 1/400 of the peak signal. D. Like C, but with negative drift

	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_1^*	τ_2^*
L89	192	49	9	4	1.2	0.4	0.3	64	6
A	192.87	48.89	12.11	3.14	3.17	–	–	64.98	9.11
B	192.87	48.89	12.11	3.18	3.15	–	–	64.98	9.11
C	196.55	48.58	12.93	3.19	3.16	–	–	65.89	9.72
D	187.00	41.65	13.28	3.30	3.04	–	–	55.60	9.79

TABLE 3

Details of the experiments carried out. The number of the record (thermogram) analysed is given together with the sampling period T (s), the initial and final points where the Joule dissipation or the injection take place (N_0 and N_f), the total number of experimental points used (N_T) and the mass and volume of the calorimetric cell

Measurement		T	N_0	N_f	N_T	Cell contents	
Type	Number					m (g)	V (cm^3)
Joule	DUB 125	1.5	50	130	3000	10.477	11.9
Injection	DUB 126	3.0	50	2800	4100		
Joule	DUB 127	1.5	50	130	3000	14.542	17.1
Joule	DUB 128	1.5	50	130	3000	20.525	12.0
Injection	DUB 129	1.5	50	2800	4100		
Joule	DUB 130	1.5	50	130	3000	12.557	14.6
Injection	DUB 131	1.5	50	2800	4100		
Joule	DUB 132	1.5	50	130	3000	14.589	17.2

EXPERIMENTAL RESULTS

Table 3 shows the details of two groups of continuous mixing experiments in which cyclohexane was injected into a calorimetric cell containing benzene [10]. In the first group a Joule dissipation takes place before and after injection so as to characterize the apparatus with different cell contents. In the second group injection was done in two steps, with a third Joule dissipation between them. The results of the identification are shown in Table 4 together with those obtained from the thermogram decay after stopping the injection. In this case the output is considered to be the decay from a Heaviside function. Figure 2 shows the variation of the transfer function of the calorimeter with the heat capacity of the cell.

TABLE 4

Time constants of the system obtained from the thermogram corresponding either to the Joule dissipation or after stopping the injection (see Table 3)

Thermogram number	τ_1	τ_2	τ_3	τ_4	τ_5	τ_1^*
DUB 125	223	36	15	3.0	2.9	17
DUB 126	245	21	21	2.5	2.5	10
DUB 127	242	33	16	3.5	3.3	17
DUB 128	216	47	19	12	0.02	36
DUB 129	229	24	24	9.4	0.62	21
DUB 130	227	34	25	4.0	2.3	28
DUB 131	236	24	23	0.02	0.02	15
DUB 132	237	44	16	4.3	3.4	25

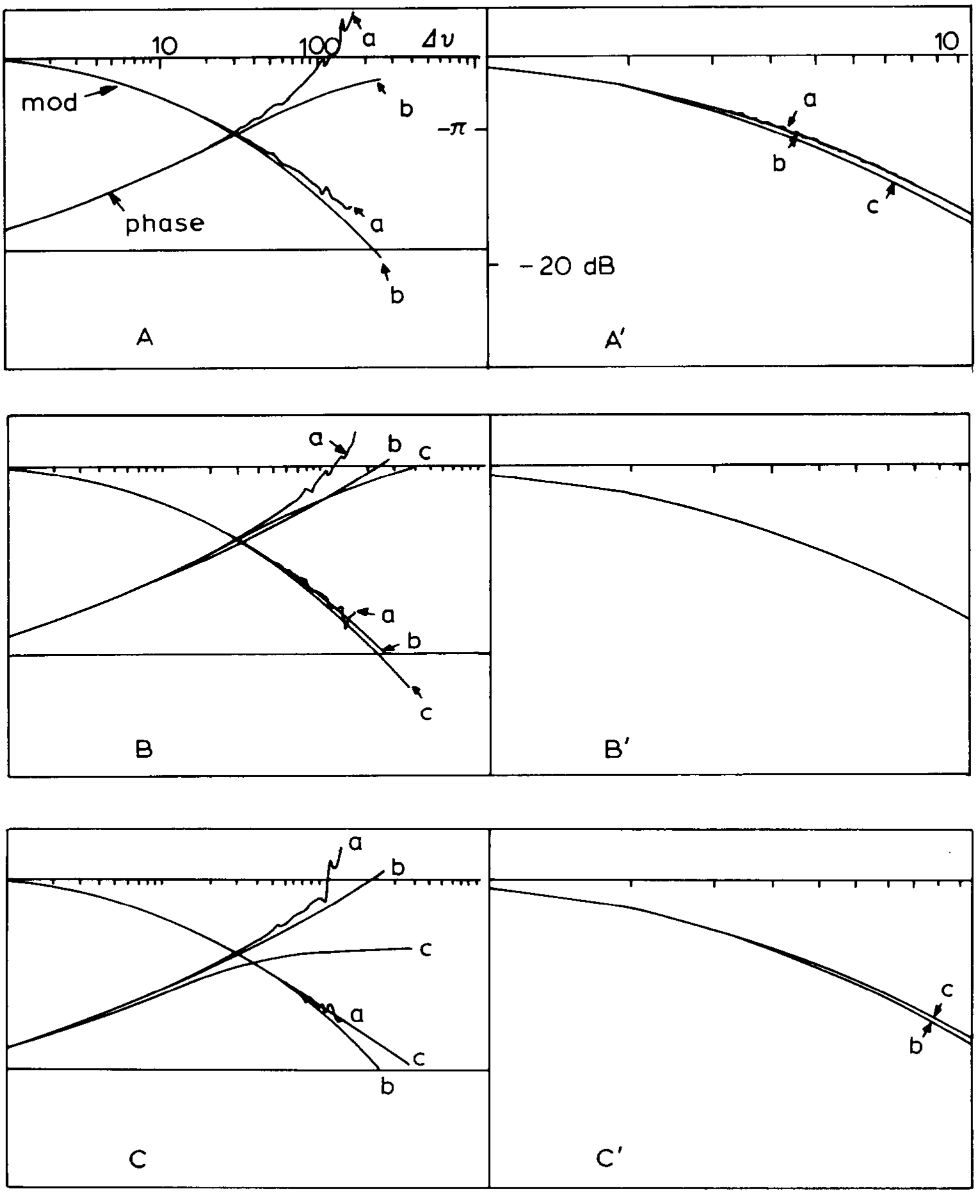

Fig. 2. *A* and *A'* measurement DUB 128. *A*, modulus and phase of the frequency response of the calorimeter. (a) Experimental (by FFT), (b) model-fitted. *A'* Models fitted (expansion of low frequencies region) at measurements DUB 128 (a), DUB 130 (b), and DUB 132 (c). *B* and *B'* measurement DUB 130. *B*, modulus and phase of the frequency response of the calorimeter. (a) Experimental (FFT), (b) model-fitted, (c) model-fitted at DUB 129 after stopping the injection. *B'* Expansion of the low frequency region (no difference between them). *C* and *C'* measurement DUB 132. *C*, modulus and phase of the frequency response of the calorimeter. (a) Experimental, (b) model-fitted, (c) model-fitted at DUB 131. *C'* Expansion of the low frequency region. The sampling frequency is $\Delta\nu = 0.0003255$ Hz.

CONCLUSIONS

Table 4 shows the change of the time constants of the system with the mass of the calorimetric cell contents. The variation of the first time constant is consistent with the mathematical results obtained by means of the heat transfer theory [11].

The values obtained for the time constants of the simulated theoretical system (Tables 1 and 2) show that the identification algorithm used is effective even when applied to noisy signals with drifting baselines.

Although on-line correction of calorimetric output signals is useful as a first approximation to the true thermogenesis, off-line analysis is necessary if optimal quantitative results are required.

The results of Tables 3 and 4 show that the identification by the Joule effect agrees with that obtained from the thermograms after stopping the injection. Even when it is not possible to introduce a resistor into the calorimetric cell, a sufficient approximation may therefore be obtained from the latter.

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