Thermochimica Acta, 87 (1985) 297–302
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CHARACTERIZATION OF CALORIMETERS USING THE Z TRANSFORM

C. REY, V. PÉREZ VILLAR * and J.R. RODRÍGUEZ

Departamento de Fisica Fundamental, Facultad de Fisica, Universidad de Santiago de Compostela, Santiago de Compostela (Spain)

(Received 12 December 1984)

ABSTRACT

This article presents a new method of characterizing calorimeters based on the Z transform of the system's unit pulse response. Results are presented for various signal-to-noise ratios. As well as giving numerical values for the parameters of the calculator, the method proposed determines the optimal number of such parameters for the description of the system.

INTRODUCTION

Deconvolution techniques currently employed in conduction calorimetry require adequate previous characterization of the calorimeter system. The first attempts at identification [1] started by considering the calorimeter as a set of interconnected physical elements whose number, and the number and nature of whose interconnections, depend on the complexity of the model being used. In spite of the difficulty of determining the large number of parameters involved, this approach is still in use at present [2].

Another way of attacking the problem is to start from the general theory of linear systems. This approach has been intensively developed in recent years [2–6] and in both time and frequency domains has produced the characterization techniques chiefly employed nowadays [7]: least-squares estimation of the unit pulse response of the calorimeter [8,9], identification by Padé approximations [10], the use of modulating functions [11] and identification by Mellin deconvolution [12].

This article describes a new method of determining calorimeter parameters using the Z transform of the unit pulse response of the calorimeter. This method is particularly suitable for processing experimental data collected at equal time intervals, and furthermore allows the optimal number of parameters for the description of the system to be calculated.

* Author for correspondence.

0040-6031/85/$03.30

THEORY

The unit pulse response of a calorimeter may be expressed [8] in the form

$$h(t) = S\left[\sum_{i=1}^{n} A_i \exp(-t/\tau_i)\right] \tag{1}$$

where the τ_i $(i = 1,\ldots,n)$ are the time constants of the calorimeter, S is its sensitivity, and the amplitudes A_i are given by

$$A_i = \tau_i^{n-m-2}\left[\prod_{j=1}^{m}(\tau_i - \tau_j^*)/\prod_{\substack{k=1\\k\neq i}}^{n}(\tau_i - \tau_k)\right] \qquad m \leqslant n-2 \tag{2}$$

where the τ_j^* $(j = 1,\ldots,m)$ are the time constants associated with the zeros of the calorimeter transfer function. The sensitivity S is found by simply integrating the experimental data, for

$$\int_0^\infty h(t)\,dt = S \tag{3}$$

S is therefore the known parameter. In what follows it will be assumed that $S = 1$.

Since after digital sampling our knowledge of the calorimeter response is limited to a succession of values $h[k]$ $(k = 0,\ldots,N)$, each separated from the preceding one by the same time interval T (the sampling period), eqn. (1) is more conveniently expressed in the form

$$h[k] = \sum_{i=1}^{n} A_i \exp(-kT/\tau_i) \qquad k = 0,1,\ldots,N \tag{4}$$

where n, m and the time constants τ_i and τ_j^* (a total of $n+m+2$ parameters) are to be determined.

The Z transform of a succession of values $h[k]$ is defined [13–15] by

$$H(z) = \sum_{k=0}^{\infty} h[k]\,z^{-k} \tag{5}$$

Applying this transform to eqn. (4) yields

$$H(z) = \sum_{k=0}^{\infty}\sum_{i=1}^{n} A_i \exp(-kT/\tau_i)z^{-k} = \sum_{i=1}^{n} A_i \sum_{k=0}^{\infty} p_i^k z^{-k} \tag{6}$$

where $p_i = \exp(-T/\tau_i)$. Since the inner sum on the right-hand side of eqn. (6) is the sum of a geometric progression of ratio $p_i z^{-1}$, $H(z)$ may be written

$$H(z) = \sum_{i=1}^{n} A_i z/(z - p_i) \qquad (z \geqslant 1) \tag{7}$$

Since an experiment of finite duration only yields N values of $h[k]$, the expression given in eqn. (5) for $H(z)$ cannot be calculated, but only

$$H^*(z) = \sum_{k=0}^{N} h[k]\,z^{-k} \tag{8}$$

so that

$$H(z) = H^*(z) + \Delta(z) \tag{9}$$

where

$$\Delta(z) = \sum_{k=N+1}^{\infty} h[k] z^{-k} = \sum_{i=1}^{n} A_i \sum_{k=N+1}^{\infty} p_i^k z^{-k} \tag{10}$$

Note that

$$\Delta(z) = \sum_{i=1}^{n} A_i p_i^{N+1} z^{-N}/(z - p_i) \qquad (z \geqslant 1) \tag{11}$$

Note that calculation of the Z transform of the experimental data involves only a finite summation of easily calculated terms. Other methods of characterization in the frequency domain require calculation of Laplace transforms of the form

$$H(s) = \int_0^{\infty} h(t) \exp(-st) \, dt \tag{12}$$

thereby introducing additional error during the numerical integration.

METHOD

The first step is to find the calorimeter's sensitivity and divide all the experimental data by the value obtained so as to reduce the sensitivity factor of the unit pulse response to unity.

Secondly, an exponential term of amplitude, A_s, comparable with the expected values of A_i and time constant, τ_s, larger than any value expected for τ_i, is added to the experimental data. This added term will enable the adequacy of each pair of values (n, m) to be estimated. With A_s and τ_s there are now $n + m + 4$ parameters to be determined. The procedure from this point on is as follows.

(1) Calculate $H^*(z_j)$ from eqn. (8) for sufficient values of z_j $(j = 1, \ldots, L)$. Excellent results have been obtained with $L = 20$ and $1 \leqslant z \leqslant 2$.

(2) Since the number of exponentials in the calorimeter's unit pulse response is at least two, and since $m \leqslant n - 2$, the initial values $n = 2$ and $m = 0$ are set up.

(3) Initial estimates for the remaining $n + m + 2$ parameters are set up. For A_s and τ_s the known exact values are, of course, used, and estimates of the others can be found by a "peeling off" procedure [16].

(4) Using the initial values introduced in steps 2 and 3, $H(z_j)$ and $\Delta(z_j)$ are calculated from eqns. (7) and (11) for all z_j $(j = 1, \ldots, L)$.

(5) The squares error sum

$$J = \sum_{j=1}^{L} \left[H(z_j) - H^*(z_j) - \Delta(z_j) \right]^2$$

is minimized with respect to the unknown parameters (including A_s and τ_s but excluding n and m). J has its minimum at values of these parameters which are optimal estimates given the current values of the pair (n, m).

(6) The adequacy of the values of n and m is evaluated by comparing the estimated values of A_s and τ_s calculated in step 5 with their known true values and calculating

$$d(n, m) = 100\left\{\left[\Delta_A(n, m)/A_s\right]^2 + \left[\Delta_\tau(n, m)/\tau_s\right]^2\right\}^{1/2} \quad (13)$$

where $\Delta_A(n, m)$ and $\Delta_\tau(n,m)$ are the differences between the estimated and true values of A_s and τ_s, respectively. If the minimum of $d(n, m)$ appears to have been reached (see examples below) the algorithm may be halted and the corresponding values of n, m and the other parameters taken as optimum estimates.

(7) If the algorithm is not halted in step 6, the pair (n, m) is incremented (following the order (2, 0), (3, 0), (3, 1), (4, 0), (4, 1), (4, 2), etc.) and the algorithm returns to step 3.

EXAMPLES

A Hewlett-Packard HP-9845B computer was used to identify the unit pulse response defined by $\tau_1 = 120$ s, $\tau_2 = 60$ s, $\tau_3 = 10$ s and $\tau_1^* = 20$ s. The procedure was repeated with several different levels of noise added to this signal so as to better simulate a real calorimeter response and to obtain an idea of the effect of noise on the performance of the algorithm. In all cases the sampling period, $T = 1$ s, the number of sample points, $N = 500$, $A_s = 0.01$ and $\tau_s = 250$ s.

TABLE 1

Results of identifying the time constants of a simulated unit pulse response with known true constants $\tau_1 = 120$ s, $\tau_2 = 60$ s, $\tau_3 = 10$ s and $\tau_1^* = 20$ s and a signal-to-noise ratio of 40 dB. The solution is obtained taking $n = 3$ and $m = 1$, since with these numbers the estimated values of A_s and τ_s are closest to their values of 0.01 and 250 s, respectively

	Values of (m, n)					
	(2, 0)	(3, 0)	(3, 1)	(4, 0)	(4, 1)	(4, 2)
τ_1	148.54	114.61	119.44	115.30	119.00	119.46
τ_2	42.13	51.98	60.33	54.87	61.33	60.23
τ_3		0.04	9.78	4.98	7.88	9.72
τ_4				0.02	1.29	4.01
τ_1^*			19.69		19.56	19.54
τ_2^*						4.02
A_s	0.010576	0.009998	0.010001	0.010022	0.010006	0.010001
τ_s	233.8003	249.0481	149.8638	249.5835	249.6801	249.5601

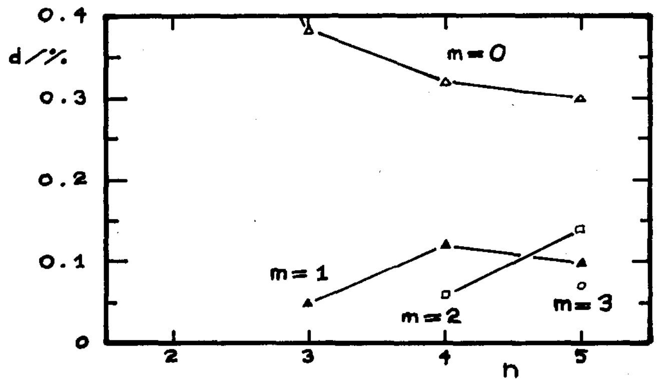

Fig. 1. Values of the error function d(n, m) for various values of the arguments. The spurious solutions at $n = 4$, $m = 2$ and $n = 5$, $m = 3$ simply repeat the solution at $n = 3$, $m = 1$, the extra poles being cancelled out by extra zeros of equal value.

Table 1 and Fig. 1 show the results obtained when the noise added gave a signal-to-noise ratio of 40 dB. The optimal estimates of n and m indicated by the minimum of d(n, m) are the correct values $n = 3$ and $m = 1$, and these values also gave the best estimates of A_s and τ_s independently of each other. The near-optimal values of n and m that are greater than the true value ((4, 2) and (5, 3)) may be considered as spurious solutions: the extra A_i introduced by raising n proves to allow near-optimal estimation only if it is reduced to zero by the extra τ_i values being offset by an extra τ_j^* of equal value (e.g., τ_4 and τ_2^* in Table 1).

Table 2 shows the results obtained for the various noisy signals employed (in each case values of $n = 3$ and $m = 1$ were used). The accuracy of the estimated values naturally increases with the signal-to-noise ratio, but even with a ratio as low as 40 dB the error in the determination of the first time constant is less than 1%.

TABLE 2

Results of characterizing the signal of Table 1 when different levels of noise are present. With a signal-to-noise ratio of 100 dB the values calculated agree with the true values to 5 significant figures

S/N (dB)	Time constants			
	τ_1	τ_2	τ_3	τ_1^*
40	119.44	60.33	9.78	19.69
60	119.94	60.01	9.95	19.93
80	119.99	60.00	9.99	19.99
100	120.00	60.00	10.00	20.00

CONCLUSIONS

The Z transform is particularly suitable for processing digital calorimeter data with a uniform sampling period. The use of this transform after addition of a known exponential term to the experimental data allows the optimal number of parameters for describing a given system to be obtained, as well as the values of these parameters. For the typical 3-pole, 1-zero response simulated in the present article, the accuracy of these values has been shown to be excellent even with signal-to-noise ratios as low as 40 dB.

REFERENCES

1 J.L. Macqueron, J. Navarro and V. Torra, An. Fis., 73 (1977) 163.
2 J. Hatt, E. Margas and W. Zielenkiewicz, Thermochim. Acta, 64 (1983) 305.
3 E. Cesari, J. Navarro, V. Torra, J.L. Macqueron, J.P. Dubes and H. Tachoire, Thermochim. Acta, 39 (1980) 73.
4 E. Cesari, J. Ortín, V. Torra, J. Viñals, J.L. Macqueron, J.P. Dubes and H. Tachoire, Thermochim. Acta, 40 (1980) 269.
5 E. Cesari, J. Ortín, V. Torra, J. Viñals, J.L. Macqueron, J.P. Dubes and H. Tachoire, Thermochim. Acta, 43 (1980) 305.
6 E. Cesari, J. Ortín, P. Pascual, V. Torra, J. Viñals, J.L. Macqueron, J.P. Dubes and H. Tachoire, Thermochim. Acta, 48 (1981) 367.
7 L.S. Shied, C.F. Chen and J.C. Huang, Int. J. Control, 13 (1971) 1027.
8 C. Rey, J.R. Rodríguez and V. Pérez-Villar, Thermochim. Acta, 61 (1983) 1.
9 R. Kechavarz, J.P. Dubes and H. Tachoire, Thermochim. Acta, 79 (1984) 15.
10 J. Ortín, V. Torra, J. Viñals and E. Cesari, Thermochim. Acta, 70 (1983) 113.
11 J. Ortín, V. Torra, T. Castán and E. Cesari, Thermochim. Acta, 70 (1983) 123.
12 R. Prost and R. Goutte, Int. J. Control, 13 (1971) 1027.
13 J. Szamosi and Z.A. Schelly, J. Phys. Chem., 88 (1984) 3197.
14 I.M. Sneddon, The Use of Integral Transforms, McGraw-Hill, New York, 1972.
15 W.H. Beyer (Ed.), CRC Standard Mathematical Tables, 26th edn., CRC Press, Boca Raton, FL, 1981.
16 C.F. Bernasconi, Relaxation Kinetics, Academic Press, New York, 1976.