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THERMOGENESIS: IDENTIFICATION BY MEANS OF PADE APPROXIMANTS

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ABSTRACT

The paper describes how to obtain an analytic approximation to the transfer function of a conduction calorimeter, namely, a procedure to identify the calorimetric system. In this case Pade approximants are used on the Laplace transform of the thermogram. The feasibility of the method is tested on two models which span the frequency range usually attained by actual calorimeters. The influence of random noise and baseline drift have also been analyzed. The results show that three or four time constants are correctly obtained.

INTRODUCTION

Several techniques which provide for an approach to thermogenesis (power released inside a calorimetric cell as a function of time) are now of widespread use in different fields [1–7]. At the same time, the introduction of relative scales [8] has allowed a systematic analysis of the quality of the resultant thermogenesis in terms of the signal-to-noise ratio of the device and its first time constant [9,10]. The application of such methods and criteria has made it possible to obtain important dynamic results in solid–solid transformations [11,12] and liquid mixtures [12,13].

Generally speaking, two broad categories may be introduced to characterize the deconvolutive methods: whether they use the sampled thermogram corresponding to a Dirac dissipation (or, equivalently, its numeric Fourier Transform) or some sort of approximated transfer function. In the latter case, inverse filters [3,4], methods based on optimal control [5], etc., require a previous model of the system, that is, a mathematical expression for the transfer function of the system or, in other words, the sequence of

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poles and zeros which define it. In fact, for most applications, partial approximations to the transfer function render exceptional results allowing, at the same time, on-line corrections. In this way, such electronic correctors only require two or three time constants which is enough in most cases because the more important part of the spectrum of the signal which is to be deconvoluted lies in low or intermediate frequencies.

Nevertheless, the obtention of an experimental transfer function under conditions equivalent to those existing during the actual experience is extremely difficult [7]. In this way, it is well known that an identification based on Joule calibration may produce not altogether true values of the zeros of the system. What is more, in both cases mentioned (phase transitions and liquid mixtures) the heat capacity of the sample is changing during the experiment so not only do we encounter the classical problems concerning the identification of the system but also the transfer function is changing in time [14]. This means that, whereas there is still a causal relation between input and output signals, the system is no longer time invariant.

Acting on these assumptions, present identification methods aim at finding only the main poles and zeros of the device because it is expected that the resultant analytical model represents the actual transfer function up to a certain frequency not far from the limit imposed by the experimental noise. The procedures used up to date in calorimetry aim, essentially, at fitting the larger time constants and zeros from the last part of the exponential decay of the pulsed transfer function. Successive time constants may then be obtained by iterating this process after having filtered from the transfer function the poles already calculated [3,4]. However, as is easily understood, such a procedure does not lead to a unique solution, but, on the contrary, to a set of solutions which can be obtained by different workers but that are equivalent from the point of view of the method.

Consequently, it would be convenient to consider more systematic methods presenting, simultaneously, their limitations concerning, mainly, the deconvolution to be performed subsequently with the model obtained. In the present work an approximation to the transfer function in Laplace space using Pade approximants is presented. The performance of the method is checked on analytic models chosen in such a way that their spectrum vs. a relative frequency scale cover the whole range attained by actual calorimeters. It is then expected that the results obtained in these models and the analysis which will be carried out subsequently, can be extended to all experimental systems. Finally, the effect of random noise on the transfer function or a slight indetermination in the experimental base line on the performance of the method is also investigated.

APPROXIMATION USING PADE APPROXIMANTS. ALGORITHM

A heat flux calorimeter whose cell contents do not change behaves, within a certain range, as a linear system whose pulsed response may be written as

$$s(t) = \sum_{i=1}^{M} a_i \exp(-t/\tau_i)$$

Taking the Laplace transform the transfer function of the device is

$$L[s(t)] = TF(x) = S\frac{\prod_{i=1}^{N}(\tau_i^* x + 1)}{\prod_{i=1}^{M}(\tau_i x + 1)} \quad (x = \text{Laplace variable})$$

where $S = \Sigma_{i=1}^{M} a_i \tau_i$ is the static gain of the system. The constants τ_i and τ_i^* are commonly referred to as the poles and zeros of the system, respectively.

Generally speaking, a Pade approximant is a rational function $P_N(x)/Q_M(x)$ where $P_N(x)$ and $Q_M(x)$ are polynomials in x of degrees N and M, respectively, and it is symbolically denoted by $[M,N]$. The rational function $[M,N]$ is said to be a Pade approximant of a given function f(x) if, and only if, the power series expansion of $[M,N]$ is identical to that of f(x) up to order x^{M+N} [15]. Let the approximant be

$$\frac{P_N(x)}{Q_M(x)} = \frac{\sum_{n=0}^{N} p_n x^n}{\sum_{n=0}^{M} q_n x^n} \quad (q_0 = 1) \tag{1}$$

The requirement that the series expansion of the approximant and of f(x) coincide up to x^{N+M} leads to a set of linear equations whose solutions are the coefficients $\{p_n\}$ and $\{q_n\}$. It is obvious that the functional dependence of TF(x) and $[M,N](x)$ is identical, so once the coefficients $\{p_n\}$ and $\{q_n\}$ are known, the roots of the corresponding polynomials are simply related to the zeros and poles of the system, respectively.

It should be pointed out here that the Pade approximation technique, or equivalently, the continued fractions method, may produce unstable reduced models even if the system were stable [16]. These problems usually come out when the system step response has a large overshoot at the beginning due to the presence of large poles [17]. However, this will not be of much concern here because such an overshoot never appears in actual calorimetric thermograms and, even though low order models we have obtained by this method are actually unstable, the instability usually disappears after increasing the order of the model. Moreover, there exist general methods to obtain stable reduced models which will not be discussed here [17].

The actual procedure used to obtain the coefficients $\{p_n\}$, $\{q_n\}$ is not based on the series expansion of f(x), but on a least-squares fit on the Laplace transform of the true response by a rational function of the form (1). We first calculate the transfer function of the system from its sampled pulse response by calculating numerically (trapezoidal rule) the integral

$$\mathrm{TF}(x) = \int_0^{\infty} \mathrm{s}(t)\, \mathrm{e}^{-xt}\, \mathrm{d}t$$

for a given set of values of the variable x. The method requires the values of the function $\mathrm{TF}(x_i) \pm \delta(x_i)$, where $\delta(x_i)$ is a certain error assigned to each point. The following functional is minimized

$$\begin{aligned} \chi^2 &= \sum_{i=1}^{\mu} \left\{ \left[\mathrm{TF}(x_i) - \frac{P(x_i)}{Q(x_i)} \right] / \delta(x_i) \right\}^2 \\ &= \sum_{i=1}^{\mu} \frac{1}{[Q(x_i)\delta(x_i)]^2} \left[\sum_{n=0}^{M} q_n x_i^n \mathrm{TF}(x_i) - \sum_{n=0}^{N} p_n x_i^n \right]^2 \end{aligned}$$

where μ is the total number of points considered in the approximation. The $N+M+1$ parameters $\{p_n\}$, $n = 0, \dots, N$; $\{q_n\}$, $n = 1, \dots, M$ are in this case the unknowns. If the functional is minimized with respect to this set of parameters—assuming that $Q(x_i)$ is known—the following system of $N+M+1$ linear equations is obtained

$$0 = \sum_{i=1}^{\mu} \frac{x_i^m}{[Q(x_i)\delta(x_i)]^2} \left[\sum_{n=0}^{M} q_n x_i^n \mathrm{TF}(x_i) - \sum_{n=0}^{N} p_n x_i^n \right] \qquad m = 0, \dots, N$$

$$0 = \sum_{i=1}^{\mu} \frac{x_i^m \mathrm{TF}(x_i)}{[Q(x_i)\delta(x_i)]^2} \left[\sum_{n=0}^{M} q_n x_i^n \mathrm{TF}(x_i) - \sum_{n=0}^{N} p_n x_i^n \right] \qquad n = 1, \dots, M$$

These are solved by iteration using the well-known weighted minimax algorithm, i.e. if the $Q(x_i)$ were actually known, the solution to this system of equations would yield the coefficients $\{p_n\}$, $\{q_n\}$. Nevertheless, we make an initial guess concerning the parameters $\{q_n\}$ and iteratively solve the set of equations till the assumed and obtained $\{q_n\}$ converge. Such an iterative procedure is most conveniently expressed in terms of matrices. Let us re-write the set of equations as

$$AC = B$$

where

$$C_s = p_{s-1} \qquad s = 1, \dots, N-1$$

$$C_s = q_{s-(N+1)} \qquad s = N+2, \dots, N+M+1$$

The matrix A, whose dimension is $(N+M+1)(N+M+1)$, is defined as

$$A_{st} = \sum_{i=1}^{\mu} x_i^{s+t-2}/Z \qquad s,t = 1,\ldots,N+1$$

$$A_{st} = \sum_{i=1}^{\mu} -x_i^{s+t-N-2}\mathrm{TF}(x_i)/Z \qquad \left.\begin{array}{l} s = N+2,\ldots,N+M+1 \\ t = 1,\ldots,N+1 \end{array}\right\}$$

$$A_{ts} = -A_{st}$$

$$A_{st} = \sum_{i=1}^{\mu} -x_i^{s+t-2N-2}\mathrm{TF}^2(x_i)/Z \qquad s,t = N+2,\ldots,N+M+1$$

and the vector $\mathbf{B}$

$$\mathbf{B}_s = \sum_{i=1}^{\mu} x_i^{s-1}\mathrm{TF}(x_i)/Z \qquad s = 1,\ldots,N+1$$

$$\mathbf{B}_s = \sum_{i=1}^{\mu} x_i^{s-N-1}\mathrm{TF}^2(x_i)/Z \qquad s = N+2,\ldots,N+M+1$$

and $Z = [Q(x_i)\delta(x_i)]^2$. The iteration is now defined as

$$C^{(k+1)} = \left[A^{(k)}\right]^{-1}\mathbf{B}^{(k)}$$

where the matrix $A^{(k)}$ is calculated from the polynomial $Q_N^{(k)}(x)$ obtained in the previous iteration. $C^{(0)}$ is defined arbitrarily *.

RESULTS

The performance of the method has been tested on two analytic models chosen in such a way that they span all the frequency range attained by actual conduction calorimeters. These models have been defined as

M8			M9		
τ_i	τ_i^*	a_i	τ_i	τ_i^*	a_i
192.0		0.4866×10^6	192.0	64.0	0.2957×10^6
49.0		-0.7895×10^6	49.0	6.0	0.1577×10^6
18.0		0.3254×10^6	9.0		-0.3407×10^6
4.0		-0.2805×10^5	4.0		-0.2945×10^6
2.0		0.6227×10^4	1.2		0.2197×10^6
1.2		-0.7310×10^3	0.4		-0.5979×10^5
0.4		0.3281×10^1	0.3		0.2193×10^5
0.3		-0.4715×10^0			
$s(t)_{\max} = 192680.0$			$s(t)_{\max} = 333571.0$		

Their sensibility is $S = \sum_{i=1}^{M} a_i\tau_i = 0.605 \times 10^8$ in arbitrary units. The models

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* Flow diagram and source listing are available on request.

TABLE 1

χ^2, poles and zeros given by the routine in successive iterations
The model approximated is M9 whereas the routine is searching six poles and three zeros.

Iteration	1	2	3	4	5
χ^2	0.18E-11	0.63E-13	0.21E-14	0.11E-13	0.72E-13
Poles	193.41	192.01	192.00	192.00	192.00
	53.66	49.07	49.06	49.06	49.06
	7.18	8.70	8.70	8.71	8.71
	−0.12	3.00	2.98	3.01	3.00
	Complex	1.78	1.79	1.78	1.78
	Complex	−0.44	−0.40	−0.41	−0.41
Zeros	69.29	64.06	64.05	64.05	64.05
	1.39	5.09	5.08	5.11	5.10
	−0.05	−0.43	−0.39	−0.40	−0.40

roughly simulate the transfer function—corresponding to two different locations of the heat sources—of the calorimeter JLM-E1 (see ref. 9). In this case the thermogram units would be nV. Random noise and baseline drift have also been added to both models in order to reproduce better the usual experimental conditions. The various models are denoted as

M8 (resp. M9) + 50 N: random noise ranging ± 50 units (signal/noise ≃ 70 dB);

M8 (resp. M9) + 50 D: linear drift where the last ordinate is shifted by + 50 units;

M8 (resp. M9) + 50 N + 50 D: random noise plus baseline drift.

The routine has always handled 30 points (not equally spaced); the variable step has been chosen to be $\Delta p = 0.3065 \times 10^{-2}$. The domain in p-space covered in the approximation was (0, 350 Δp) in the case of model M8 and related variants, and(0, 700 Δp) in model M9. These values give the

TABLE 2

Change in χ^2 with the order of the model which is approximated to M9 + 50 N + 50 D
The value shown always corresponds to the sixth iteration. M and N are the number of poles and zeros, respectively. Note how this table belongs to one of the most unfavorable cases, namely, a model with random noise and baseline drift.

N	M					
	4	5	6	7	8	9
0	0.26E-05	0.76E-06	0.64E-06	0.47E-06	0.24E-06	0.11E-06
1	0.47E-09	0.25E-09	0.59E-10	0.17E-10	0.29E-11	0.73E-12
2	0.27E-09	0.69E-09	0.45E-12	0.85E-13	0.32E-13	0.13E-12
3	0.79E-10	0.62E-12	0.14E-12	0.27E-12	0.80E-11	0.90E-05

TABLE 3

Final values of the poles and zeros selected in the different models studied

	Model							
	M8	M8 + 50N	M8 + 50D	M8 + 50N + 50D	M9	M9 + 50N	M9 + 50D	M9 + 50N + 50D
Poles	192.00	191.99	191.62	191.62	192.01	192.00	191.69	191.68
	49.00	49.03	49.68	49.68	49.10	49.04	48.45	48.56
	18.00	17.84	16.35	16.13	8.76	8.91	9.23	8.68
	3.99	5.67	7.59	8.41	3.47	3.84	4.18	2.95
	2.12				1.47	1.27	1.13	1.71
					0.25	0.43	0.57	0.18
Zeros					64.09	64.04	63.33	63.39
					5.39	5.80	6.35	4.97

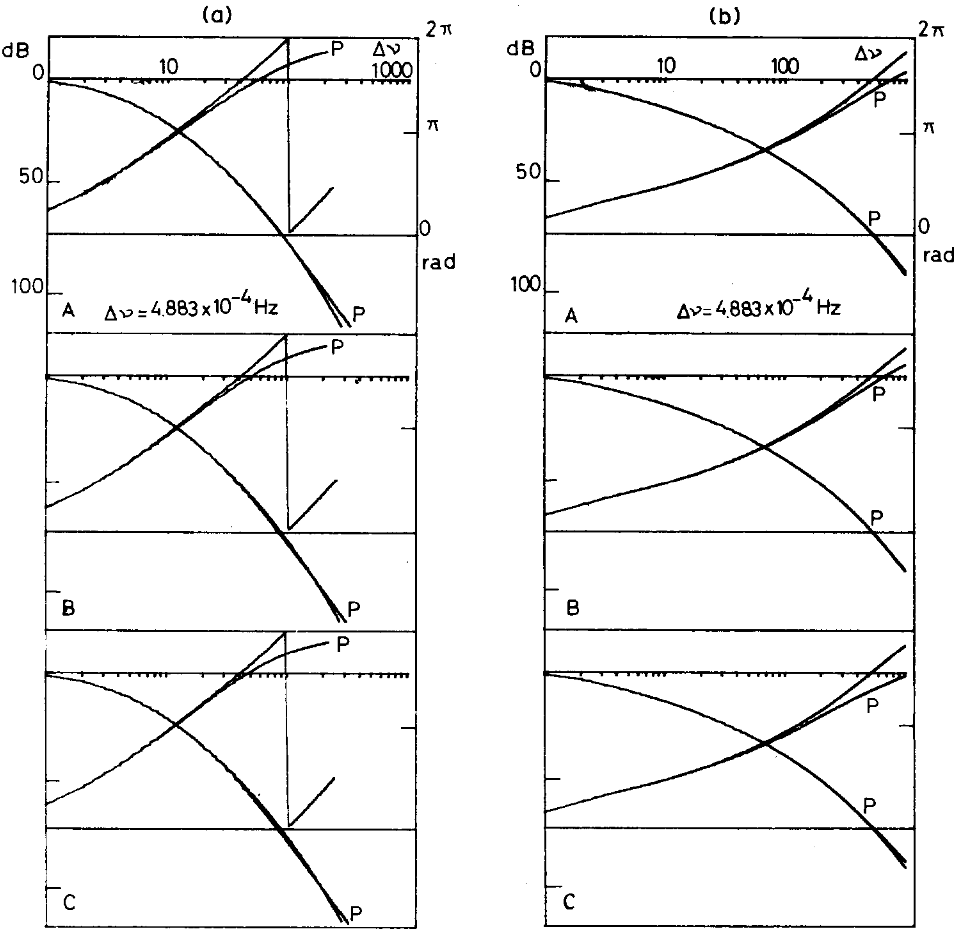

Fig. 1. Transfer function of the models (a) M8 and (b) M9 together with A, transfer function of the approximation given by the Pade algorithm (P) to models M8 + 50 N (a) and M9 + 50 N (b); B, transfer function of the approximation given by the Pade algorithm (P) to models M8 + 50 D (a) and M9 + 50 N (b); C, transfer function of the approximation given by the Pade algorithm (P) to models M8 + 50 N + 50 D (a) and M9 + 50 N + 50 D (b). The poles and zeros which define the approximation are given in Table 3.

ratios

$$\frac{\mathrm{TF}(350\Delta p)}{\mathrm{TF}(p=0)} = 70\ \mathrm{dB}, \quad \frac{\mathrm{TF}(700\Delta p)}{\mathrm{TF}(p=0)} = 85\ \mathrm{dB}$$

The first item to be dealt with is the order of the transfer function which is to be approximated, that is, the number of poles and zeros desired. Once this number is fixed, $C^{(k)}$ converges in seven or eight iterations, that is, χ^2 continually decreases towards a nearly stationary minimum and the coefficients $\{p_n\}$ and $\{q_n\}$ remain unchanged (Table 1). The poles and zeros thus obtained may be real or complex numbers. The occurrence of complex poles is interpreted to be a consequence of having approximated too low an order model. As a general criterium only the real poles and zeros have been kept, provided that those of the modulus of the complex were small.

We next obtain χ^2 to successively higher order models. Its value is seen to decrease with increasing order whereas, simultaneously, the complex poles and zeros either disappear or are considerably reduced. The crucial feature is that the main poles and zeros remain constant throughout the different approximations (from a certain minimum order upwards). Table 2 shows the evolution of χ^2 under a change in the number of poles and zeros given by the routine. It is seen there how a stationary value is attained. Further increase in the order of the model leads to an increase in χ^2. The poles and zeros which remain unchanged, being χ^2 near its minimum, are regarded as the best approximation to the transfer function given by the present method.

Finally, Table 3 presents the poles and zeros obtained in all the models considered. They have been obtained following the criteria mentioned earlier. Figure 1 shows the frequency spectrum of the models and their approximations.

CONCLUSIONS

Details of the calculations can be summarized as follows: double precision —16 digits—has been used throughout the routine. The numeric Laplace transform uses 4100 points of the thermogram sampled with $\Delta t = 0.5$ s. The transform has been calculated each $\Delta p = 0.3065 \times 10^{-2}$ s^{-1}. The least-squares approximation handles 30 points not equally spaced in order to cover $350\Delta p$ in the case of model M8 and $700\Delta p$ in model M9. In all cases only six or seven iterations have been performed.

The algorithm which has been presented succeeds in finding the more relevant poles and zeros of the transfer function of an analytic model previously calculated. The algorithm needs the sampled transfer function of the device given in Laplace space and the order of the model which is to be approximated.

The method has proved to be not especially sensitive to disturbances on the model. Thus the existence of random noise ($s/n \simeq 70$ dB) and baseline drift do not considerably affect the values of the poles and zeros obtained. Obviously, the worse the experimental conditions—larger noise or drift—the higher the uncertainty in the time constants. Nevertheless, three time constants are easily found.

The results suggest that the method gives enough time constants—poles and zeros—so as to have an adequate representation of the transfer function of an actual calorimeter up to its frequential limit imposed by the existence of experimental noise or due to a certain indetermination in the location of the heat sources.

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