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VERIFICATION OF CALORIMETRIC MODELS BASED ON PHYSICAL PARAMETERS BY FREQUENTIAL CHARACTERISTICS

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ABSTRACT

Quantitative criteria to ascertain the quality of calorimetric models based on physical parameters are presented. These include not only a comparison between model and experimental pulse responses, especially for the larger time constants, but also an analysis of their spectra up to the frequential limit brought about by the experimental noise.

A calorimetric model based on the physical parameters of a Unipan 600 calorimeter is used to reconstruct a given power dissipation. The results are then compared to those given by other methods, i.e. dynamic optimization, inverse filtering and harmonic analysis.

INTRODUCTION

In a previous paper [1], a method of determination of thermokinetics based on the physical parameters of a calorimetric system was described. This method was shown to be convenient for the determination of thermokinetics and because of its simplicity can be easily applied on-line to a system. It is evident that the results concerning the reconstruction of thermokinetics using this kind of calorimetric model depends on the quality of the determination of the model parameters. This means that the criteria of accordance of the model with the calorimetric system are of great importance.

In work [2,3] concerning the determination of the models, the criteria of accordance proposed were: (1) between the values of the first time constants, experimental and calculated from the model; (2) between the values of their

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corresponding amplitudes; (3) between the thermograms of the response to a Dirac pulse of the calorimetric system and that calculated from the model.

As a test of a proper determination of a given model, the results concerning the reconstruction of known heat pulses were also examined. The whole procedure enables us to deduce the conclusions, which were the basis for the acceptance of the elaborated models. The search for more accurate criteria (not only qualitative but also quantitative) for the determination of the quality of a model is the main purpose of this work. We are also interested in comparing the thermokinetics given by several methods.

It should be pointed out that, although this paper concerns time-invariant systems, models based on time-dependent physical parameters of the system could allow the deconvolution of those processes which are associated with a change in the thermal parameters of the system (e.g. solid–solid phase transformations or liquid mixtures).

METHOD

The description of calorimetric systems in order to verify the elaborated model based in physical parameters of the calorimetric system is carried out in frequency space. This proposed verification includes the following steps after the model (time constants and pre-exponential coefficients) and the thermograms are compared: (1) the calculus by means of the Fast Fourier Transform (FFT) of the experimental transfer function (modulus and phase for the Bode diagram) and comparison with the model; (2) determination of kinetic and frequential limits [4] of the calorimetric system; (3) examination of how the experimental transfer function is successively corrected by filtering the poles and zeros of the model transfer function.

This approach enables us to verify not only the agreement of the main time constants but also the whole model transfer function up to the limit imposed by the existence of experimental noise, including the values of the zeros of this transfer function. In this way, analysis of the dynamic properties of a calorimetric model, determined on the basis of physical parameters, follows the same lines as those used in the deconvolution methods based on the black box notion [5]. This means that, for all deconvolution methods of calorimetric signals, the same criteria of verification can be used.

EXPERIMENTAL AND RESULTS

In order to determine the usefulness of the multi-body method based on physical parameters, the results given by this method are compared with the results of other methods, i.e. harmonic analysis, dynamic optimalization and inverse filtering.

The thermograms and the elaborated dynamic model of the Unipan 600 microcalorimeter, described previously [1], were taken into account. The transfer function of this model was described by seven poles: $M_1 = 537.94$ s, $M_2 = 29.52$ s, $M_3 = 25.42$ s, $M_4 = 15.45$ s, $M_5 = 11.32$ s, $M_6 = 8.63$ s, $M_7 = 7.56$ s and three zeros: $L_1 = 29.65$ s, $L_2 = 12.04$ s, $L_3 = 7.63$ s. The comparison of the larger time constants (experimental and calculated) [1] agreed fairly well. A good agreement between the experimental and calculated thermogram was also achieved [1]. This accordance enabled us to carry out the next verification steps. The experimental transfer function of the calorimetric system in modulus and phase was calculated using the FFT routine (Fig. 1). The value of the Shannon frequency was determined; it corresponds to $\nu_{Sh} = 1/\Delta t = 0.333$ Hz, where $\Delta t = 3$ s is the sampling period used in the experiment. The corresponding frequency scale is also discrete, being $\Delta\nu = 1.627 \times 10^{-4}$ Hz. The number of points handled by the FFT routine is $N = 2048$. The existence of experimental noise produces another frequential limit, ν_n. If this frequency is defined to be that frequency where the modulus of the transfer function fluctuates by ± 2 dB, we get [10] $\nu_n = 200\ \Delta\nu = 0.033$ Hz, or when it fluctuates by ± 10 dB, $\nu_n = 450\ \Delta\nu = 0.073$ Hz. Figure 1 also gives us information about the width of a pulse which can be properly reconstructed, knowing the value of the maximum frequency for calculations, $\nu_c < \nu_n$ which can be given by [4] $T^* = 3/(2\nu_c) = 20.5$ s ($\nu_c = 450\ \Delta\nu$).

Figure 1 also shows that the transfer function of the seven-body model properly corrects the modulus of the experimental transfer function up to the noise frequency, ν_n, giving a little shift in the phase correction. The expression of the transfer function indicates that three poles can be cancelled by three zeros; thus a transfer function of only four poles can be proposed. A four-body model based on the seven-body model was elaborated. Figure 2 shows the block diagram of this model. In the four-body model we have kept

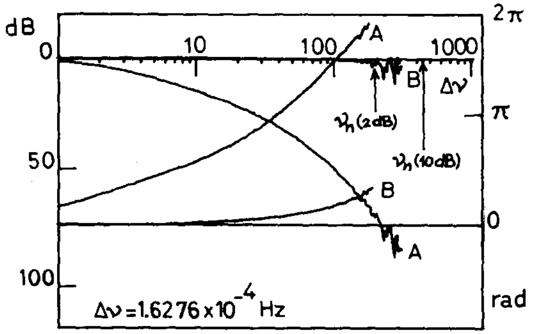

Fig. 1. A, Modulus (dB) and phase (rad) vs. a frequency scale in units of $\Delta\nu = 1.6276 \times 10^{-4}$ Hz of the experimental transfer function of the Unipan 600 microcalorimeter obtained by means of the FFT; B, correction achieved by filtering of the seven poles and three zeros. Frequential limits corresponding to a noise amplitude of 2 dB and 10 dB are also presented.

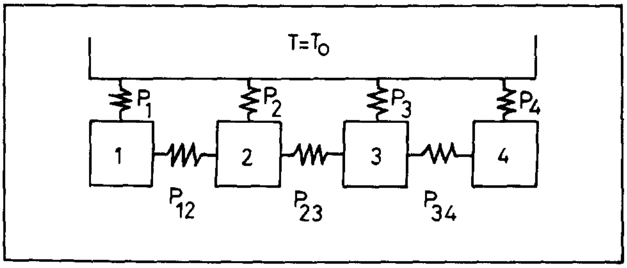

Fig. 2. Block diagram of the four-body model of the Unipan 600 microcalorimeter. The values of the heat capacities and heat-loss coefficients in SI units are: $C_1 = 2.253$, $C_2 = 32.26$, $C_3 = 18.265$, $C_4 = 1.578$, $P_{12} = 0.13$, $P_{23} = 1.5$, $P_{34} = 0.055$, $P_{01} = 0.0025$, $P_{02} = 0.00089$, $P_{03} = 0.085$, $P_{04} = 0.021$. The P_{ij} are interaction coefficients [9].

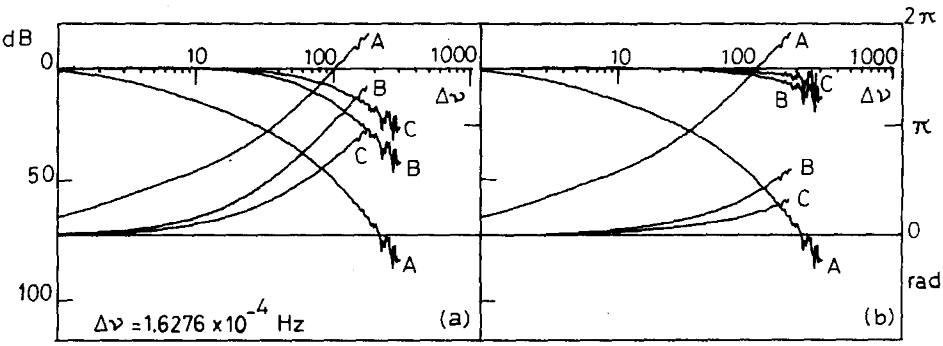

Fig. 3. (a) A, Modulus (dB) and phase (rad) vs. a frequency scale of the experimental transfer function of the Unipan 600 microcalorimeter; B, correction of the modulus and phase using $M_1 = 531.4$ s; C, correction using M_1 and $M_2 = 20.94$ s. (b) A, Experimental; B, correction using M_1, M_2 and $M_3 = 16.43$ s; C, correction using M_1, M_2, M_3 and $M_4 = 7.309$ s.

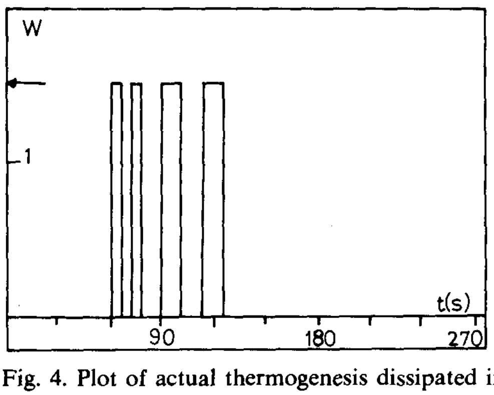

Fig. 4. Plot of actual thermogenesis dissipated inside the laboratory cell. It corresponds to a sequence of two rectangular impulses of width 6 s, followed by two others of width 12 s. The arrow on the power scale indicates the maximum of the power released, $W = 1.52$ W.

the values of the capacities of the four first elements of the seven-body model, however, the most uncertain couplings have been changed. The choice of the latter parameters enables us to obtain the transfer function given by

$$\mathrm{TF}(\omega)=\frac{S}{(531.4i\omega+1)(20.94i\omega+1)(16.43i\omega+1)(7.31i\omega+1)}$$

Figure 3 shows the successive corrections on the modulus and phase of the experimental transfer function given by the four poles of the model, giving the same result as Fig. 1. This indicates that the four-body model can also be used to describe this calorimetric system.

This model was used to perform the deconvolution of a sequence of pulses as shown in Fig. 4, by the multi-body method [1]. This result was compared with the results given by harmonic analysis [6], dynamic optimalization [7] and inverse filtering [8]. Figure 5 presents the results obtained by application of these methods to the thermogenesis shown in Fig. 4.

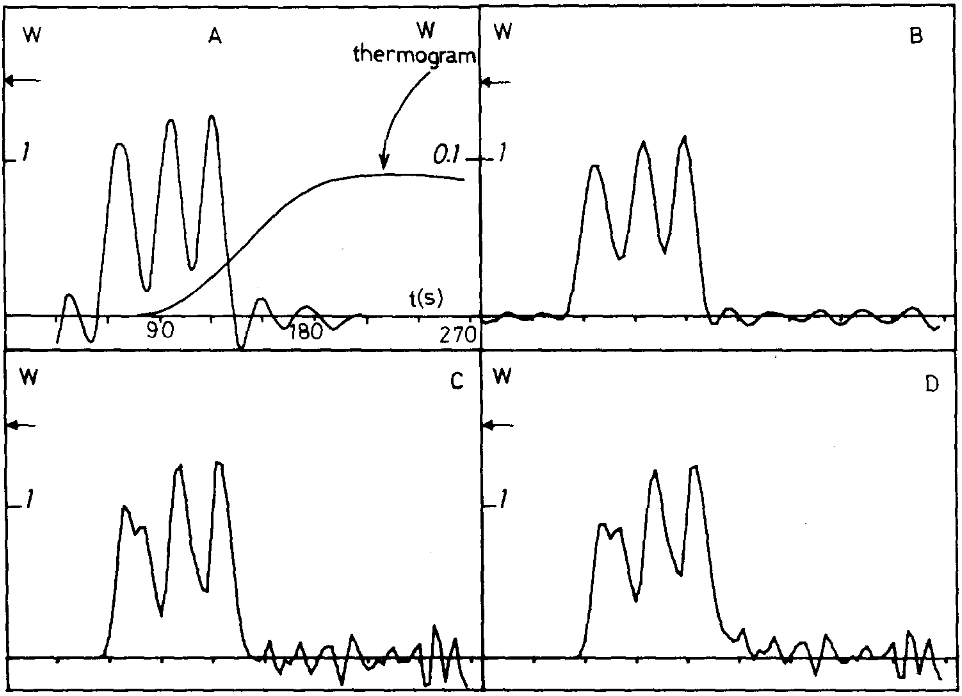

Fig. 5. Comparison of the performances of four deconvolution methods in approaching the same well-known thermogenesis, i.e. that corresponding to Fig. 4. (A) Optimization method; the thermogram, referred to the correct scales is also presented: (B) harmonic analysis using a cut-off frequency, $\nu_c = 411\ \Delta\nu$: (C) inverse filtering; the maximum step used in derivations was $2\Delta t$: (D) multi-body method; again the step in derivations was $2\Delta t$. The arrows in the left-hand scales indicate the actual power released in the laboratory cell.

With regard to harmonic analysis, the cut-off frequency selected was $\nu_c = 411\Delta\nu < \nu_n(10 \text{ dB})$ and $L = 2$ (see ref. 4), the number of points handled in the calculations was 2048 (the whole thermogram). In the dynamic optimalization method, 34 iterations were made using 60 points. In the multi-body method, the parameters of the four-body model were used in the heat balance equations. In inverse filtering we used the values of poles obtained by the multi-body method (corresponding to the four-body model). The multi-body method and inverse filtering only require the number of points which correspond to the time interval where the dissipation takes place. All methods fail to reconstruct the pulses, because the signal–noise ratio is not high enough for such sharp pulses. In fact, we should require up to $\nu_n = 0.250$ Hz $= 1536\ \Delta\nu$ in order to reconstruct pulses lasting 6 s, and $\nu_n = 0.125$ Hz $= 768\ \Delta\nu$ for pulses lasting 12 s. These two values are bigger than the $\nu_n = 450\ \Delta\nu$ associated with our system. The frequential representation can predict the probable quality of the reconstruction. The shift in phase which is not corrected indicates that the result of the deconvolution given by the multi-body method and inverse filtering will give a shift in time of the pulses. This result is not due to the methods themselves but is caused by the fact that the model chosen does not completely compensate the phase of the transfer function of the calorimetric system. The result obtained by harmonic analysis and dynamic optimalization is not shifted, but compared with the result based on the model, these two methods fail to separate the first two pulses, whereas in the multi-body method and inverse filtering the separation of the first pulses is evident (Fig. 5).

CONCLUSIONS

(1) Analysis of frequential characteristics is an adequate method to verify calorimetric models based on physical parameters. An especially important advantage is the information about the system, such as kinetic limits and the performance that the deconvolutive method can achieve.

(2) The efficiency of four deconvolutive methods has been tested on the same thermogenesis, giving approximately the same results.

(3) A shift in time in the results given by the multi-body method and inverse filtering is observed because the model transfer function fails to compensate the phase of the experimental transfer function, but it is not a property of the method itself.

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