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THERMOGENESIS: IDENTIFICATION AND DECONVOLUTION IN THE UNIPAN MICROCALORIMETER

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ABSTRACT

In this work, different identification methods are applied to the UNIPAN-600 heat conduction microcalorimeter, and the results compared over a range of frequency. The paper shows good correlation between the thermogenesis results obtained with different methods of identification, in spite of the discrepancies between the numerical values of the parameters themselves. The results allow one to have confidence in the deconvolution procedure even under critical experimental conditions (signal/noise ≤ 50 dB).

Moreover, the previous modelization of the UNIPAN-600 is proven, once again, to be a very interesting and valuable tool.

INTRODUCTION

In a previous paper [1] a method for both the identification of calorimetric systems and the determination of thermokinetics was presented. The method follows the N-body theory described in detail in many works [2,3] and is based on the physical parameters of the system. Many other methods to determine the dynamic behaviour of calorimetric systems have been developed. Some of them are based on graphical approaches, e.g., frequential characteristics [4] and inverse filtering [5], while others are essentially numerical, e.g., Padé approximants [6] and modulating functions [7].

In this work the results of applying all these methods in order to determine the dynamic properties of an actual calorimeter will be given. The procedure makes it possible to indicate to what extent each approach to the identification of dynamic systems gives comparable results.

In order to accomplish this objective the identification methods have been verified by frequential characteristics [8], and the thermogeneses obtained on the basis of these identifications have been compared.

EXPERIMENTAL AND RESULTS

The system studied was the microcalorimeter UNIPAN-600. For this microcalorimeter, on the basis of physical parameters, the values for L_k and M_n in the expression of the transmittance

$$Hji(s) = S \prod_{k=1}^{m} (L_k s + 1) / \prod_{n=1}^{N} (M_n s + 1)$$

were obtained [1]. S is the sensibility, $-1/L_k$ are the roots of the transmittance and $-1/M_n$ are the poles of the transmittance. They were subsequently verified by the frequential characteristics method [8]. The values for the constants L_k and M_n obtained were: $L_k = 0$, $M_1 = 531.4$, $M_2 = 20.9$, $M_3 = 16.4$ and $M_4 = 7.3$ s.

Identifications by inverse filtering, modulating functions and Padé approximants have been obtained from impulse responses. A thermal pulse produced by the Joule effect, with power 6.3 W and lasting 2.3 s, was dissipated in an axial resistance of a copper block in the UNIPAN-600 microcalorimeter. The corresponding response was sampled each $\Delta t = 2$ s and stored for a total of 5000 s.

Table 1 presents the identification results obtained by means of inverse filtering (IF), modulating functions (MFM), Padé approximants (PADE) and physical parameters model (MODEL).

Table 1 shows that, because of the method used for identification, from two to four values of M_n (time constants) have been obtained. Only in the case of inverse filtering one zero $L_1 = 2$, which is equal to the value of the sampling period, has been determined. The values presented in Table 1 differ from each other, but as is shown below the differences in the biggest time constants, about 6%, are compensated for when the complete form of the transmittance is used. Graphically this comparison is given in Fig. 1.

TABLE 1

Comparison of identification results obtained by several different methods

	MFM	PADE	IF	MODEL
M_n	567.6	566.6	554.0	531.4
	37.0	32.7	31.0	20.9
			5.0	16.4
				7.3
L_k			2.0	

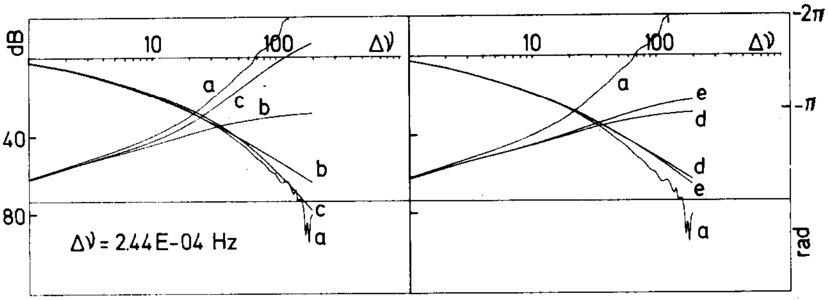

Fig. 1. (a) Modulus and phase of the experimental transfer function obtained by means of the FFT, together with moduli and phases of the transmittances obtained by different identification methods and whose values are shown in Table 1: (b) MFM, (c) MODEL, (d) PADE, (e) IF.

Figure 1 shows the modulus and phase of the Fourier transform, obtained by means of an FFT, of the experimental impulse response together with the transfer functions associated with the identifications performed by the different methods. The figure makes clear the practical coincidence between the different approaches in the low frequency domain ($\nu < 0.033$ Hz). Thus, not only are the sets of parameters obtained rather similar, but the figure also makes it possible to show that the deconvolutive results are not influenced by the identification method selected to determine the transfer function of the system.

In order to study the correlations between the thermogeneses, a series of Joule effect dissipations, with different durations and amplitudes, has been generated inside the cell, following the same configuration used for the identification. Figure 2 represents the dissipation and the corresponding experimental thermogram. The sampling period has been chosen to be $\Delta t = 2$ s. The durations of the rectangular dissipations have been selected, a priori, in such a way that they impose limiting conditions on the separation (in the case of those of 30 s) and the full reconstruction (in the case of those of 90 s) of elementary pulses [4]. It is not difficult to see this: the frequential limits imposed by the experimental noise on the UNIPAN-600 are ν_n(2

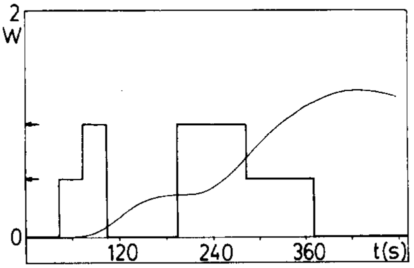

Fig. 2. Schematic representation of the actual thermal power dissipated in the UNIPAN-600 by means of the Joule effect, and the corresponding thermal response of the instrument in arbitrary units, as a function of time.

dB) = 0.033 Hz and ν_n(10 dB) = 0.073 Hz (see ref. 8). Considering the more restrictive case, i.e., ν_n(2 dB) = 0.033 Hz, the complete separation of power pulses is achieved for a minimum interval of $T = 3/(2\nu_n) = 46$ s between pulses, and the shape reconstruction for a duration of $T = 9/(2\nu_n) = 140$ s. At the widest limit, i.e., ν_n(10 dB) = 0.073 Hz, these values would be $T = 21$ s for the separation and $T = 63$ s for the shape reconstruction. The time intervals between the dissipations in Fig. 2 lie between the values corresponding to the two limiting frequencies ν_n. This choice makes it possible, on deconvolution, to evaluate the influence of the different identifications over the entire frequency range attainable with the experimental device.

The parameters from each of the identification methods have been used to perform the deconvolution of the thermogram in Fig. 2. The deconvolution has been carried out by numeric inverse filtering and, also, by an analogic filtering (one stage) which can be performed on-line in the UNIPAN-600.

Figure 3 presents the results obtained in each situation. Although the different correction in the phase of the TF (Fig. 1) leads to small delays in the appearance of the peaks, the figure shows clearly, in what concerns the kinetics of the process, the equivalence of the calculated thermogenesis. In particular, the preceding results confirm the value of carrying out a physical modelization of calorimeters and its later validation by comparison of the dynamic characteristics of the device with those of the model. The values of poles and zeros that result from the model are, as it has been shown, well suited for the deconvolution of the thermogram. On the other hand, it is known and has recently been emphasized that a very simple model of

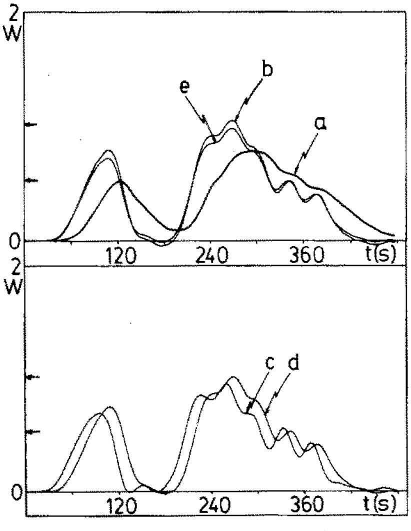

Fig. 3. Thermogenesis obtained by inverse filtering of the thermogram in Fig. 2. The values considered as the poles and zeros of the transmittance correspond to those of Table 1, for the different identification methods, namely: (b) MFM, (c) MODEL, (d) PADE, (e) IF. The deconvolution obtained by analogic filtering with $M_1 = 528$ s is also shown (a).

calorimetric system gives one the chance of studying new phenomena with great accuracy. Examples could be the influence of a change in the cell contents (from copper to water, for instance) and the effects of time-varying in the continuous injection devices [9,10,11,12].

CONCLUSIONS

(1) Different methods of identification, whether numeric as the modulating functions and the Padé approximants, or essentially graphic as inverse filtering, or starting from a modelization of the calorimeter, are fully operative nowadays and have been applied to the UNIPAN-600 calorimeter with a copper-block vessel. The dynamical parameters sets thus obtained, though not strictly identical (especially under conditions of 50 or 60 dB of signal/noise ratio), exhibit frequency properties in modulus and phase that are practically equivalent.

(2) The different identifications are all equivalent when applied to obtain the thermogenesis, i.e., the power dissipated inside the calorimetric cell. The deconvolution is performed by inverse filtering of the thermogram in an identical manner for all the examples. The results show, on the one hand, the convergence and thus the performance of the different identification methods. On the other hand, they guarantee the deconvolution results even in cases where, due to the importance of the experimental noise, it seemed to be difficult to identify the system with great accuracy.

(3) The preceding conclusions serve as a verification of the model of physical parameters representing the UNIPAN-600. The time constants obtained from the modelization are adequate to perform the deconvolution. Moreover, the modelization enables one to study new experimental situations easily.

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