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THERMOGENESIS: DETERMINATION OF THERMOKINETIC PARAMETERS

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ABSTRACT

This work analyses the performance of the method of obtaining the time constant (rate reaction constant) defining a first-order process after the deconvolution of the experimental record given by a heat conduction calorimeter. The analysis is carried out for different signal/noise ratios and the results given in relative time and frequency scales.

INTRODUCTION

Investigations of thermogenesis—the function describing heat power released inside the calorimetric cell vs. time—in the case of certain types of solid–solid transitions (e.g., martensitic transformations in shape memory alloys) [1–4], in many types of chemical reactions (e.g., clathration of aromatic guest compounds by a Werner MeX_2A_4 type complex; hydration of minerals) [5–7], and in liquid mixtures [2–4,8] have shown several remarkable results concerning, in the former cases, the determination of their kinetic behaviour and, in the latter case, the evaluation of the excess molar enthalpy down to very low solute concentrations.

Among the present techniques for the deconvolution of the experimental records, are for example, harmonic analysis [9,10], dynamic optimization [11], inverse filters, either numeric or electronic [5,12–15], multi-body method [16,17], spectral resolution method [18], and methods based on optimal control [19,20]. Most of the methods require a previous identification of the system, i.e., the obtention of the sequence of poles and zeros which define

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the transfer function of the device. A preliminary analysis of the various identification methods at hand [21–24] has been carried out in order to ascertain how different methods, and consequently different values of the main poles and zeros of the system, could affect the resultant thermogenesis [25].

What is more, given that in many cases either the mass or the heat capacity of the sample change during the experiment, we have begun an analysis of the models based on heat transport equations whose parameters change in time [26] and, on experimental grounds, of the change in the transfer function measured at different times along the experiment [24,25,27].

Nevertheless, concerning the determination of the kinetic parameters which define the process under study, further analysis is still necessary. The most simple case to be analysed is related to the obtention of rate constant, k, in a first-order reaction (k corresponds to τ in this paper) [5,28]. Thus, the performance of recovering the time constant after the deconvolution has taken place, for different signal/noise ratios, is studied in this communication. The results may be readily systematized in a relative frequency scale.

COMPUTATIONAL SCHEME

The output signal in linear, time invariant systems, may be obtained as a convolution of the corresponding input signal

$$\mathrm{s}(t)=\mathrm{TF}(t)*\mathrm{e}(t) \text{ or } \mathrm{s}(t)=\int_0^t \mathrm{e}(x)\mathrm{TF}(t-x)\mathrm{d}x$$

where TF(t) is the transfer function of the system. Consequently, the obtention of the thermogenesis associated with a given experimental thermogram, s(t), may be obtained by inverting this integral equation. The exact transfer function of the system is never known, so if we denote by $\mathrm{TF}^+(t)$ the approximate transfer function actually used, the corresponding approximation to e(t) is given by

$$\mathrm{e}^+(t)=[\mathrm{TF}^+(t)]^{-1}*\mathrm{s(t)}=[\mathrm{TF}^+(\mathrm{t})]^{-1}*[\mathrm{TF}(t)*\mathrm{e}(t)]$$

In the case where $\mathrm{TF}^+(t)\equiv\mathrm{TF}(t)$, the deconvolution would yield the exact e(t) value because the action of both transfer functions cancel each other out. However, neither have we the exact transfer function nor the deconvolutive technique, which implicitly handles discrete functions, can use the whole frequency spectrum of the signal. In the latter case, the available part of the spectrum is limited theoretically by the Shannon frequency, and practically by the signal/noise ratio.

It is assumed that, as a first approximation, the exact transfer function is known, and that the deconvolutive technique is exact. The only limitation thus remaining is the cut-off frequency brought about by the experimental noise. Acting on these assumptions the Fourier Transform (through the FFT routine) of e(t) can be calculated, and the corresponding approximation to the thermogenesis may be calculated by considering a finite inverse Fourier Transform. The cut-off frequency is chosen according to different signal/noise ratios belonging to actual calorimetric systems. Therefore, within this approximation, the transfer function is simply not taken into account.

Another alternative way to include the influence of experimental noise is the convolution of e(t) with a given transfer function leading to a certain thermogram. A random signal may then be added to simulate an actual thermogram. The deconvolution is then performed in the usual fashion; that is, dividing the transform of the thermogram by TF(ω) which is the Fourier Transform of the function used to perform the forward convolution. A cut-off frequency must also be considered, for the noise waveform superimposed on the thermogram affects primarily high frequencies. This frequency is defined to correspond to the most favourable signal/noise ratio of the thermogram [29,30]. Nevertheless, a useful first approximation is, as mentioned above, simply to perform a finite inverse transform of F[e(t)] where the cut-off frequencies are those chosen from given signal/noise ratios in actual thermograms.

Finally, if reduced frequency scales are taken into account, the selection of

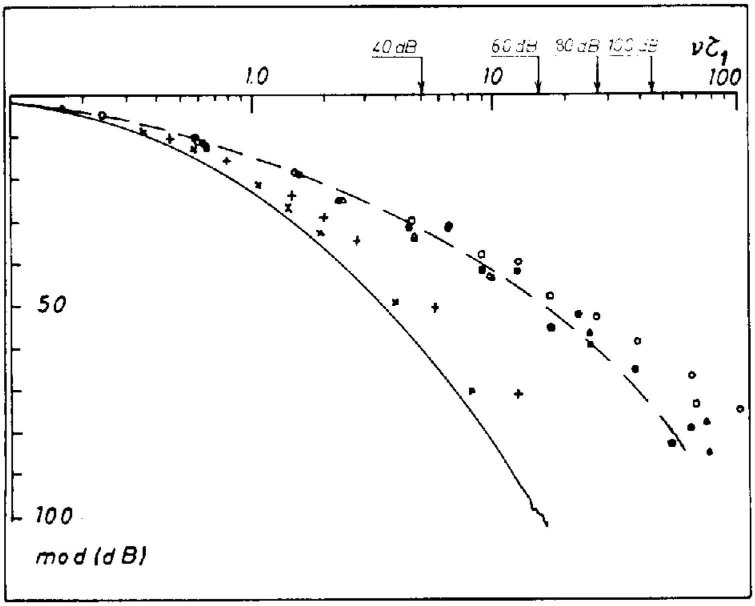

Fig. 1. Modulus (dB) vs. a reduced frequency scale ($\nu\tau_1$) of several calorimeters. The figure spans, from bottom to top, the transition between the PC to the HC regime (see ref. 31). The arrows show the various frequencies associated to signal/noise ratios ranging from 40 to 100 dB.

such frequential limits may be taken in a systematic way. Every signal/noise ratio is related to a definite frequency range in this representation irrespective of the actual calorimetric system considered (Fig. 1).

RESULTS

Given that a fair number of interesting physicochemical processes may be described as first- or second-order processes, the influence of a frequency cut-off on the reconstruction of an exponential-like input signal is analysed.

The results obtained are to be considered as first approximations or, better, as upper bounds to the quality of the reconstructed input signal. In any case, the procedure may easily be generalized to more general power dissipations, in particular, to higher order reactions.

The input signal considered is defined as follows

$$e(t)=\begin{cases}0 & t<t_0\\ \exp(-(t-t_0)/\tau) & t\geqslant t_0\end{cases}$$

The values of τ chosen are $\tau = 384$, 96, 48, 19.2 and 9.6 s. This choice has been taken according to a hypothetical first time constant of the calorimetric device of $\tau_1 = 192$ s which is the main time constant of the models discussed in refs. 21 and 22. Nevertheless, the results obtained will be independent of the particular choice of τ_1. The only significant quantity is the ratio τ_1/τ. In this way, the relative time and frequency scales will allow the expression of the results only in terms of this ratio which, in this case, ranges from 0.5 to 20. The sampling period used is $\Delta t = 1$ s, consistent with the requirement that $\Delta t \approx \tau_1/300$.

The Fourier Transform (FFT) of the various exponential input signals defined is calculated. The cut-off introduced in the inverse transform corresponds to different signal/noise ratios (40, 60, 80 and 100 dB). In a relative frequency scale each signal/noise ratio automatically gives the frequency range (in $\Delta\nu$ units) which may be attained irrespective of the calorimeter considered. Three cut-offs have been used in practice for every ratio, namely those associated with the average and both extreme behaviours (high (HC) or low (PC) conductivity cell contents). These values are given in Table 1 and ref. 31. Once the cut-off is known, the finite inverse transform yields the approximation $e^+(t)$. This curve is then smoothed following standard techniques [31] which partially suppress the extra ripple introduced by the finite inverse transform.

Once $e^+(t)$ or the smoothed $e^+(t)$ are known, a least-squares fit gives the time constant and the amplitude of the exponential. The complete procedure is shown schematically in Fig. 2. Figure 3 shows four different reconstructions also including the most favourable and unfavourable cases studied. The

TABLE 1

Amplitudes and time constants given by the least-squares routine in the different cases analysed. In all cases the fit has been performed on the smoothed curve. Cut-off associated to the average behaviour (a), to the PC limit (b) and to the HC limit (c). (d) Actual values of the amplitude and time constant. N_c is the cut-off selected in $\Delta\nu$ units [31]

Signal/noise (dB)		$\tau_1/\tau = 0.5$		2		4		10		20		N_c
		A	τ	A	τ	A	τ	A	τ	A	τ	
40	a	1.000	384.95	1.005	96.097	1.024	48.067	1.309	18.610	0.182	15.853	54
	b	1.011	374.63	1.045	94.890	1.158	47.261	5.349	14.914	4.628	11.471	27
	c	1.000	383.81	1.002	95.980	1.007	47.986	1.058	19.118	1.318	9.366	109
60	a	1.000	383.93	1.001	95.994	1.004	47.997	1.023	19.209	0.753	10.290	147
	b	1.001	383.49	1.006	95.942	1.024	47.967	1.056	19.685	1.919	10.759	60
	c	1.000	384.00	1.000	96.000	1.001	48.000	1.005	19.198	0.972	9.668	342
80	a	1.000	384.00	1.000	96.000	1.001	48.001	1.010	19.192	1.176	9.409	257
	b	1.000	383.81	1.002	95.980	1.007	47.986	1.058	19.118	1.318	9.366	109
	c	1.000	384.00	1.000	96.000	1.000	48.000	1.001	19.199	1.050	9.536	684
100	a	1.000	384.00	1.000	96.000	1.000	48.000	1.002	19.201	0.992	9.623	513
	b	1.000	383.98	1.000	95.998	1.001	48.000	1.008	19.207	0.931	9.747	229
	c	1.000	384.00	1.000	96.000	1.000	48.000	1.001	19.200	1.002	9.601	1025
	d	1.000	384.00	1.000	96.000	1.000	48.000	1.000	19.200	1.000	9.600	

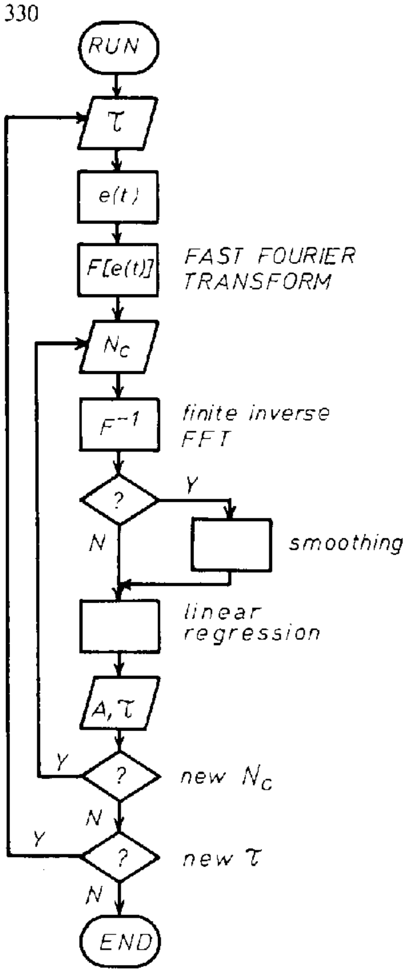

Fig. 2. Calculation scheme.

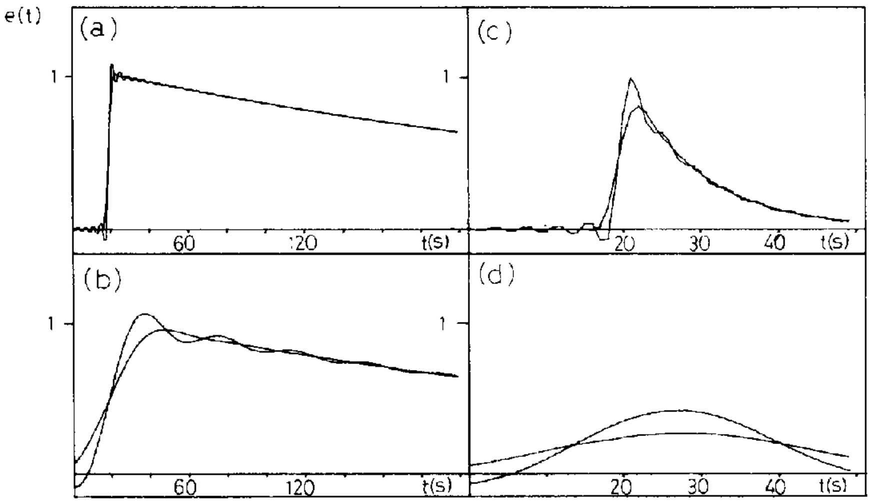

Fig. 3. Results obtained after the finite inverse transform for four different cases. The curves obtained after smoothing are also shown. (a) $\tau = 394$ s, signal/noise = 100 dB; (b) $\tau = 394$ s, signal/noise = 40 dB; (c) $\tau = 9.6$ s, signal/noise = 100 dB; (d) $\tau = 9.6$ s, signal/noise = 40 dB.

amplitudes and time constants obtained are summarized in Table 1.

It is to be noted that the cut-off simulates the effect of experimental noise whereas that part of the spectrum included in the calculations is assumed to be exact. Consequently, the results obtained are to be considered as the optimum performance of recovering the time constant of a given first order process.

CONCLUSIONS

Heat conduction calorimeters allow the rate constant of the process studied to be obtained with a high accuracy. This accuracy depends on the τ_1/τ and signal/noise ratios. For example, in the case of $\tau_1/\tau = 0.5$ and signal/noise ratio = 100 dB, the accuracy is $> 0.003\%$. When $\tau_1/\tau \sim 10$ and the signal/noise ratio is near 40 dB, the rate constant can be determined with an accuracy of $> 5\%$. These results show that to a large extent the precise determination of the rate constant depends on the experimental conditions, expressed by the τ_1/τ and signal/noise ratios (Table 1).

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