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THERMOGENESIS: EXPERIMENTAL APPROACH TO A REDUCED TRANSFERENCE FUNCTION

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ABSTRACT

The dynamic treatment of conduction microcalorimeters must be accomplished through their transference function (TF). A systematic analysis of experimental TFs belonging to calorimeters whose dynamic characteristics are quite different (the first time constants ratio is roughly 16) shows:

(a) in order to verify the relative dynamic characteristics it is convenient to use a reduced representation of modulus (dB) and phase (rad) against a reduced scale $\nu\tau_1$. Such a representation between 0 and 30 dB does not depend on the laboratory cell and the kind of detector;

(b) in this representation, TFs associated with materials of high conductivity coincide within the range $0 < \nu\tau_1 < 4$. For materials of low conductivity, the TFs group in the range $0 < \nu\tau_1 < 1$. It seems feasible, then, to use a reduced TF irrespective of the type of calorimeter.

INTRODUCTION

Several numerical and/or electronic techniques applied to the thermogram produced by conduction calorimeters allow a good approximation of the thermogenesis or heat power dissipated as a function of time. Harmonic analysis [1—4] and optimalization [5—7] are two successful approaches. One- or two-step inverse filters [8—10] are operative via electronic devices which are now available.

All the techniques previously mentioned use part of or the whole TF of the calorimetric system. Several analyses have been carried out on both experimental [11,12] and theoretical [13,14] TFs. We have studied, in particular, the effects introduced by the handling of the calorimetric cell, noise (noise/signal ratio) and spatial localization of heat sources.

Given the important divergences which show the various calorimeters used, the introduction of relative sampling periods to systematize the results

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TABLE 1

Dynamic parameters of the calorimeters studied

		Tian-Calvet [a]		ARION-BCP	JLM-E1 [b]	JLM-E4 [b]	Tib [b]
		A	B	C	D	E	F
Volume	V (cm^3)	15	80	39	10	3	15
First time constant	τ_1 (s)	231.7	704.5	506.0	186.5	43.9	106.3
Sampling period	Δt (s)	1	2	2	0.5	0.5	0.5
Cell contents	Material	Hg	Al	Mineral oil	Cu	Brass	Hg
Sensibility	S (mV s J^{-1})	65	41	51	62	25	77
Noise frequency	ν_n (Hz)	0.20	0.10	0.04	0.40	0.50	0.45
Inverse filter limit	$\nu_{if} 10^3$ (Hz)	15	8	1	21	30	50
	$\nu_{if}\tau_1$	3.5	5.3	0.7	4.0	1.3	5.3

[a] Mylar or PVC insulating materials.

[b] Semiconductor thermoelements.

has been proposed [15]. The basic problem associated with calorimetric systems lies in their dynamic characteristics and in the particular structure of the physical phenomenon which is being studied [16]. The TF of the system, then, is not clearly determined: there exist as many TFs as dissipation places [12—14] and, consequently, the TF connected to an actual phenomenon is a combination of local TFs. Furthermore, for a certain type of effect, the TF changes in time. Consequently, any analysis of an experimental system is handicapped by two sets of effects: the type of calorimeter and the characteristics of the phenomenon under study.

In this study we analyze whether it is possible to attain a systematization of the dynamic characteristics of the calorimeters. To this purpose, we propose reduced time-scales and frequency. Moreover, this systematic analysis allows the clarification of the limitations of inverse filters to provide a correct approximation of the thermogenesis.

EXPERIMENTAL

To carry out the systematic analysis six microcalorimeters were used (Table 1) whose static and dynamic characteristics are different (the extreme value for the relation τ_i/τ_j is 16) and whose sensibilities range between 25 and 77 mV s J^{-1}. A digital system was always used to store the calorimeter outputs. The sampling period was selected in agreement with the present recommendations [15]. To obtain the TF, rectangular pulses of width $u < \Delta t \approx \tau_1/300$ were generated. However, to calculate the TF in the frequencial space, the transform of the thermogram was divided by the transform of the pulse.

RESULTS AND DISCUSSION

The representation of TF(t) in absolute units (mV J^{-1}) against a relative time-scale (t/τ_1) shows the various kinetic sensibilities of the devices studied (Fig. 1).

The TF in the frequencial space was calculated via the Fourier Transform of the thermogram and that of the pulse (see, for example, ref. 2) using, concerning the thermogram, the Fast Fourier Transform (FFT). The transform of the rectangular pulse is elementary.

The results are plotted in Fig. 2 using a reduced scale of frequencies (modulus in dB and phase in rad vs. the product $\nu\tau_1$). The representation shows that all the calorimeters behave in a similar way in the range 0—30 dB provided that the materials contained in the calorimetric cell are high conductors (HC). Within this range, the TF adopts a common pattern for all the calorimeters which depends only on S and τ_1.

The reduced TFs are grouped when $\nu\tau_1$ goes from 0 to 4 and coincide with a simple filter (see Fig. 2 and Table 1) for $0 < \nu\tau_1 < 1$. Then, for all frequencies $\nu < 1/\tau_1$ a simple derivative would provide a correct thermogenesis (modulus and phase). Table 1 also gives the values for ν_{if} (upper limit for a

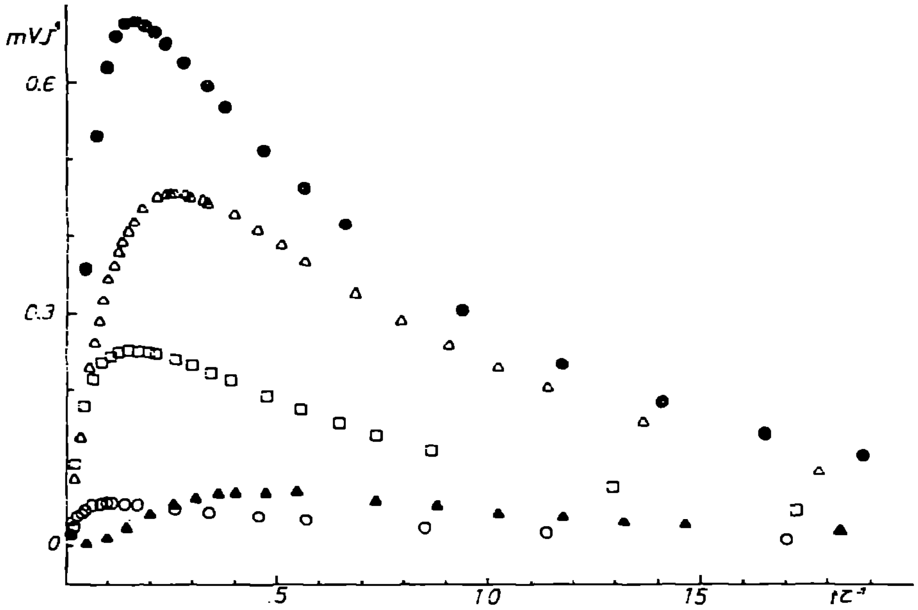

Fig. 1. TF(t) in absolute units (mV J^{-1}) vs. t/τ_1. □, ○, ▲, △, ● represent calorimeters A, B, C, E and F, respectively. The heights show the relative dynamic performances; the content of the cell is also important. (see Table 1).

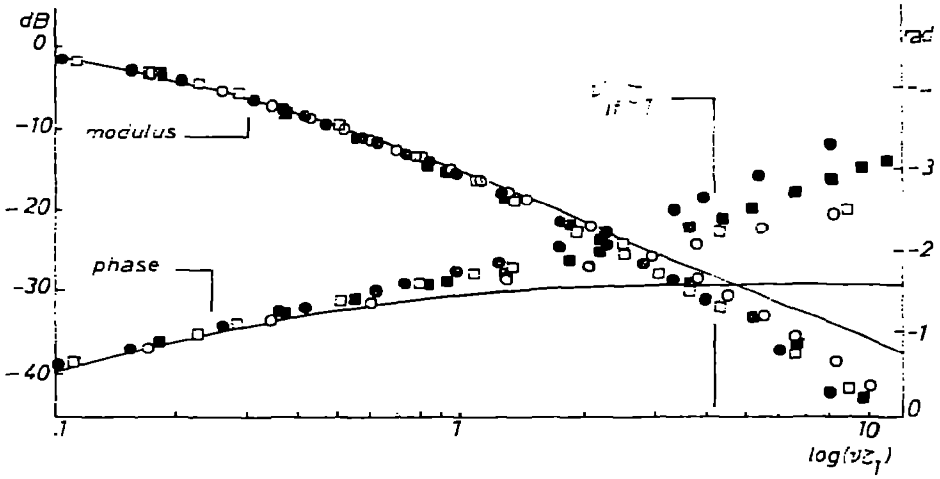

Fig. 2. TF(jω) (in Fourier space) for low frequencies corresponding to several high conductivity materials. Modulus (dB) and phase (rad) vs. a reduced scale of frequency [log($\nu\tau_1$)]. □, ○, ■, ● represent calorimeters A, B, D and F, respectively. The continuous lines represent the modulus and phase of an inverse one-step filter.

TABLE 2

Dynamic parameters for a Tian-Calvet calorimeter with an insulation of mica

Cell contents	Material	Sulphur	H_2O	Benzene	Hg	Cu
Sensibility	S (mV s J^{-1})	16	16	15	16	16
First time constant	τ_1 (s)	196.6	270.7	222.1	183.4	226.9
Inverse filter limit	$\nu_{if}10^3$ (Hz)	3	3	2	33	18
	$\nu_{if}\tau_1$	0.6	0.9	0.5	6.0	4.7

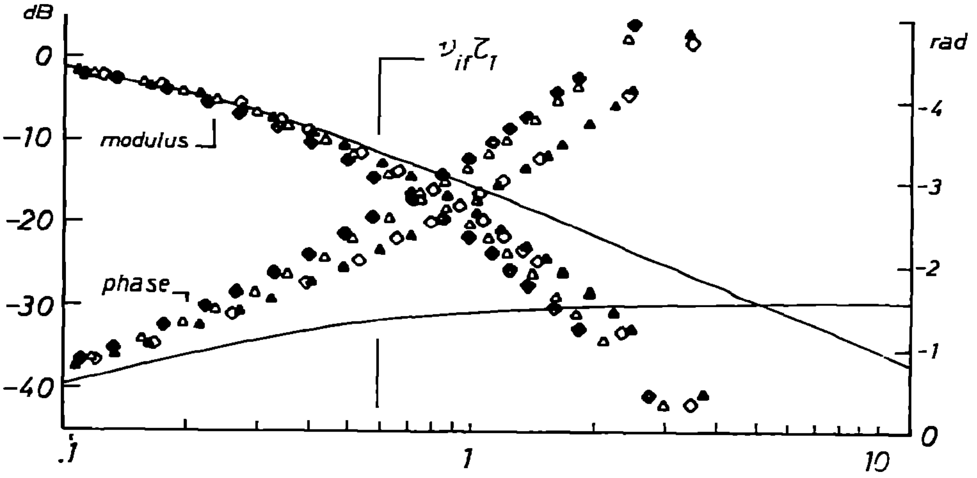

Fig. 3. TF(jω) for poor conductors against a reduced scale. ◇ represents an ARION-BCP calorimeter; △, ▲, ◆ represent a standard Tian-Calvet containing sulphur, water and benzene, respectively. The continuous lines represent the modulus and phase of an inverse one-step filter.

one-step filter) and ν_n [10]. When the material contained in the cell exhibits a poor conductivity (PC), e.g. water or other liquids, the TF diverges considerably from those of HC materials, although the corresponding curves have a similar pattern. The ARION-BCP calorimeter together with a standard Tian-Calvet containing PC substances (Table 2) are represented in Fig. 3. The curves are also remarkably grouped within 0—30 dB ($0 < \nu\tau_1 < 2$) though, now, the phase of the inverse filter diverges considerably from $\nu\tau_1 > 0.2$. The evolution of the modulus and the phase of TF from HC to PC can be interpreted in terms of the relation τ_2/τ_1.

Tables 1 and 2 show that the average value of the product $\nu_{if}\tau_1 \cdot \nu_{if}$ corresponds to a divergence of ±2 dB between the modulus of the TF and that of an inverse filter [10]. This filter introduces a considerable deformation on the actual thermogenesis for frequencies above ν_{if}.

CONCLUSIONS

(1) The representation of thermograms associated with a rectangular pulse $\Delta t \approx \tau_1/300$ (Δt is the sampling period for digital systems) using a reduced scale t/τ_1 provides a simple visualization of the relative sensibilities of the calorimeters.

(2) The selection of a reduced scale of frequencies (modulus in dB and phase in rad vs. the product $\nu\tau_1$) allows a considerable grouping of the TFs. The coincidence is remarkable within the range 0—30 dB when considering calorimeters containing similar substances (HC or PC). The result does not practically depend on the volume of the laboratory cell and the kind of detector.

(3) The extreme values for the product $\nu\tau_1$ group around 4 in HC materials and around 0.6 in those of PC. This divergence affects the values of

ν_{if}, which are the frequency limits for an inverse one-step filter. The shift associated with $\nu_{if}\tau_1$ corresponding to the transition from HC to PC comes from the remaining time constants of TF(t) and mainly from the ratio τ_2/τ_1.

(4) The efficiency of an inverse filter to reproduce a thermogenesis is limited by ν_{if}. In our representation, ν_{if} for HC is $4/\tau_1$ and $0.6/\tau_1$ for PC. In both cases, the phase of the filter diverges quicker than the modulus. If one wishes to include it within the experimental dispersion, ν_{if} would be reduced by a factor of ~4.

(5) The results suggest the feasibility of introducing a reduced pattern for the TF which could be adapted to experimental ones within the range 0—30 dB. Such reduced functions would not depend on the type of calorimeter and the volume of the laboratory cell, admitting, though, two versions corresponding to HC or PC materials. A "universal function" UF could then be introduced concerning reduced corrections between 0 and 30 dB. In order to transform it to the proper units of the calorimeter, the parameters S and τ_1 would be required. Obviously, within this range the effects due to the spatial localization are not relevant.

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