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THERMOGENESIS: UNIVERSAL TRANSFERENCE FUNCTION

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ABSTRACT

The effects introduced by the location of the heat sources upon the transfer function (TF) are systematically analysed in several calorimeters using a reduced representation. In this way a unique approach to the thermogenesis, irrespective of the location of the sources, can be attained within the range 0—30 dB. The pattern of the TF is analysed and two sets of parameters for the analytical form of a Universal Transference Function (UTF) are proposed.

INTRODUCTION

The obtainment of the thermogenesis by means of numeric and/or electronic derivators (one or more steps) proves advantageous due to its simplicity and low cost [1—3]. Several analyses of these techniques, usually limited to one-step filters, have been carried out through the transfer function (TF) of different heat flux calorimeters [4,5].

Experimental measurements [6] and previous theoretical results [7] have shown the effects that the spatial location of the heat sources introduce upon the TF; i.e., the existence of intrinsic frequencial limits when the positions of the sources are unknown. In this case, a simple derivator would not give correct results at high frequencies [5,8].

An experimental approach to a universal transference function (UTF) for heat flux calorimeters, valid within the range of low frequencies (modulus from 0 to 30 dB), together with a reduced frequency representation have been recently proposed [9]. Now, all calorimeters behave in a similar way.

This work presents the TF at relatively low frequencies associated with different locations of the sources. The analysis allows a mathematical expression for the UTF and the selection of two sets of parameters both for high conductivity (HC) and poor conductivity (PC) substances.

In this paper we have incorporated in the analysis three new calorimeters to those described in a previous work (see tables 1 and 2 of ref. 9) following, however, the same experimental recording and numeric techniques.

THE TF AND POSITION OF THE SOURCES

We have analysed the dispersion at low frequencies of the TFs belonging to several calorimeters due to an alteration in the location of the sources. It is then possible to determine the frequencial limits imposed on the TF by this effect. Figure 1 shows the results corresponding to calorimeter B (see table 1 in ref. 9) and G (Table 1). These measurements have been carried out without handling the laboratory cell; otherwise the thermal resistance between the cell and the calorimetric vessel would have been slightly changed [7,10]. so modifying the kinetic analysis of the phenomenon.

Spatial linearity [6] has also been tested in all the calorimeters; i.e., a global response to heat dissipations in different positions is the sum of the responses to each of them alone.

Figure 1 shows a splitting of TFs (in modulus, M) greater than 2 dB at $M \approx -30$ dB as a consequence of a different position of the sources. Obviously, the divergence in PC substances is greater than in HC ones.

In our representation the modulus of the TF is given in dB

$M(\nu) = 20 \log_{10} |\mathrm{FT}|_{\nu}/|\mathrm{FT}|_{\nu=0}$

It starts always at 0 db but there exist relevant changes in the sensibility due to a different location of the sources. The laboratory cell is not completely enclosed by the detector system so there is a direct thermal contact or link between the cell and the ambient. This link is a function of the location of the sources and causes a variation in the sensibility $S = |\mathrm{FT}|_{\nu=0}$ (see Table 2). This variation (less than 5%) depends on the structure of the calorimeter and very strongly on the symmetrical or unsymmetrical position of the detector system (e.g. whether it is cylindrically symmetrical — Tian—

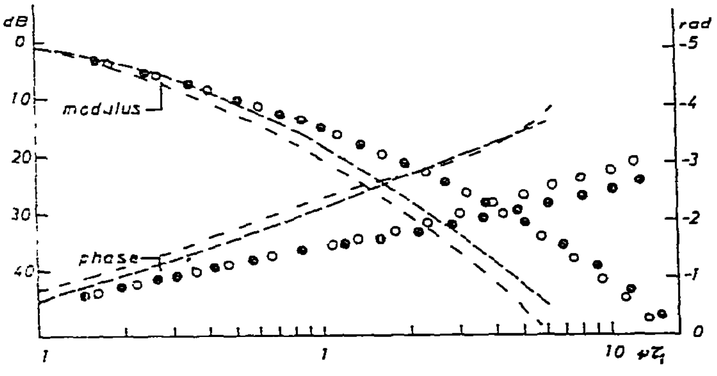

Fig. 1. Experimental transfer functions, TF(jw), showing their different branches associated with the various locations of the sources. ● and ○, calorimeter B (see table 1, ref. 9); (· — · —) and (- - - - - -), calorimeter G

TABLE 1

Dynamic parameters of the calorimeters studied (see ref 9).

	G	H	B'
Volume $V(\mathrm{cm}^3)$	80 *	15	80
First time constant τ_1(s)	1222.0	263.9	609.0
Sampling period Δt(s)	2	2	2
Cell content Material	H_2O	Aniline	Hg
Sensibility $S(\mathrm{mVsJ}^{-1})$	44.7	15	42
Noise frequency ν_n(Hz)	0.012	0.10	0.10
Inverse filter limit $\nu_{if}10^3$(Hz)	1	2	17
$\nu_{if}\tau_1$	1.0	0.5	10

* Effective volume 30 cm^3 inside a pyrex flask

Calvet calorimeter — whose change is ≤1.5% or those calorimeters whose detector system is distributed over a lateral surface, ≤3%). According to the divergences between the sensibilities there is an initial divergence ranging from 0 to even 0.5 dB.

Concerning the approach to thermogenesis via derivator devices [4], the dispersions associated with the sensibility is not relevant because they only eliminate pole after pole from the TF without affecting the static gain. However, systems which require either the whole TF, or any analytic approximation to it, need the appropriate value of their sensibility. That approach to a real thermogenesis, where there is an evolution in the position of the sources, is clearly an unsolved problem.

The effect which the calculation itself has on the phase of the TF should also be noted. The FFT (Fast Fourier Transform) forces it to reach zero for $\nu_{\mathrm{Sh}} = 1/2\Delta t$. Consequently, the experimental phase (always negative) continuously decreases, whereas the calculated one undergoes a severe deformation [10]. This fact implies that an analytic approach to a calculated TF by means of the FFT does not give strictly correct values of phase at intermediate and high frequencies. Its real values are only attainable through the experimental delay between a sinusoidal heat power input and the corresponding output thermogram.

TABLE 2

Change in sensibility (mVW^{-1}) vs. vertical position of the resistance *

	Up		Middle		Bottom	
	a	b	a	b	a	b
B'	65.4	65.3	65.8	65.5	65.6	65.2
F	78 2	78.2	77.6	76.6	74.1	70.2
G	44.3		44.7		43.9	

* (a) Represents a spherical resistance placed in the symmetry axis of the system, and (b) an "O-ring" resistance in a coaxial position near the cell walls of the calorimetric vessel.

A previous paper [9] showed that the analysis of the TF in a reduced scale between 0 and 30 dB led to the consideration of a common transference function with two sets of values associated with HC and PC substances, respectively. In order to approximate experimental TFs within the aforesaid domain, we propose the following expression for the Universal Transference Function (UTF) in Laplace space

$$\mathrm{UTF} = S\,\frac{1}{(\tau_1 p + 1)(\alpha p + 1)(\beta p + 1)}$$

(in Fourier space: $p = j2\pi\nu$). The set of values, common to all calorimeters studied, gives

$$\text{HC: } \tau_1/\alpha = 40 \pm 2 \qquad \tau_1/\beta = 100 \pm 10$$

$$\text{PC: } \tau_1/\alpha = 7 \pm 2 \qquad \tau_1/\beta = 12 \pm 3$$

In a relative frequency scale their validity is restricted to

HC: $0 < \nu\tau_1 < 4$ (modulus at $\simeq$30 dB)

PC: $0 < \nu\tau_1 < 1$

Table 3 shows the deviations of the UTF from the experimental TFs. Specific values for two calorimeters (B and C from ref. 9) are shown in Table 4. Within the range 0—30 dB there are very many sets of values which adjust equally well the experimental TF, so obviously there is a considerable dispersion affecting α and β. This fact shows that the parameters α and β need not coincide with the actual values of τ_2 and τ_3. Figure 2 shows the dispersion in modulus and phase of the UTF associated to values within the uncertainties in α and β mentioned above.

Concerning calorimeters where the dissipation takes place near the detec-

TABLE 3

Deviations of the UTF from experimental TFs (Δm = |UTF| — $|\mathrm{TF_{exp}}|$ in dB and Δp = arg(UTF) — arg($\mathrm{TF_{exp}}$) in rad) [The values of α and β selected are $\tau_1/\alpha = 40$, $\tau_1/\beta = 100$ (HC) and $\tau_1/\alpha = 7$, $\tau_1/\beta = 12$ (PC)]. L has S; M, H_2O; N, C_6H_6; J, Hg; and K, Cu (ref. 9).

Calorimeters (HC)		A	B	F	B′	J	K
20 dB	Δm	0.26	−1.32	−0.05	−1.93	−2.04	−1.14
	Δp	−0.05	0.13	−0.16	0.26	−0.03	−0.12
30 dB	Δm	1.39	−1.38	1.18	−2.82	−2.79	0.02
	Δp	0.09	0.29	−0.30	0.53	−0.27	0.24
Calorimeters (PC)		C	G	H	L	M	N
20 dB	Δm	1.71	−2.44	1.62	−1.14	−1.95	−0.22
	Δp	−0.40	0.45	−0.78	−0.42	−0 09	−0.43
30 dB	Δm	2.18	−5.15	2.50	−1.29	−3.69	−0.39
	Δp	−0.59	0.57	−1.06	−0.74	−0.38	−0.79

TABLE 4

Specific values of the parameters α, β and α, β, γ for the analytic expression of the UTF and UTF* respectively. (Note how important variations in the parameters produce essentially the same results. In this case Δm and Δp are always less than 0.5 dB and 0.5 rad up to $M \simeq -30$ dB.)

Calorimeter B	τ_1/α	τ_1/β	τ_1/γ	Calorimeter C	τ_1/α	τ_1/β	τ_1/γ
UTF	>25	>55		UTF	5 ± 2	20 ± 10	
UTF*	35 ± 15	80 ± 60	20 ± 10	UTF*	5 ± 2	15 ± 8	—65 ± 35

tor system (especially when the cell content is an HC substance) the experimental modulus surpasses that of a simple filter [5] (see Fig. 3). Then, any combination of products of simple poles always remains under the experimental modulus even though they intercept afterwards.

In PC substances the experimental phase decreases quicker than that of a product of three simple poles, soon reaching 4 rad (corresponding to a decrease in modulus $\simeq$30 dB, $\nu\tau_1 \simeq 2$) which is approximately the maximum value provided by a UTF consisting of three poles (1.5π rad at $\nu\tau_1 > 10$).

In order to have an expression including these two behaviours, one could add a term $(\gamma p + 1)$ in the numerator of the UTF

$$\mathrm{UTF}^* = S\,\frac{(\gamma p + 1)}{(\tau_1 p + 1)(\alpha p + 1)(\beta p + 1)}$$

If $\gamma > 0$ and $1 < \tau_1/\gamma < \tau_1/\alpha$, it provides an adequate deformation of the modulus in HC substances. When $\gamma < 0$ and $\tau_1/\beta < \tau_1/|\gamma|$, it gives an important decrease in the phase without excessively distorting the modulus. In this case the system reduces, to some extent, to a TF whose modulus is equivalent to two simple poles and phase to four.

The average values for the UTF* are

HC: $\tau_1/\alpha = 6 \pm 0.5$ $\quad\tau_1/\beta = 25 \pm 3$ $\quad\tau_1/\gamma = 4 \pm 0.5$

PC: $\tau_1/\alpha = 7 \pm 2$ $\quad\tau_1/\beta = 12 \pm 4$ $\quad\tau_1/\gamma = -40 \pm 10$

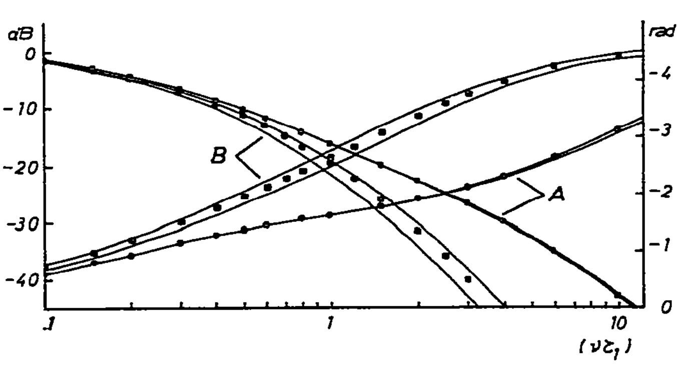

Fig. 2. Dispersion of the UTF. A and B correspond to HC and PC substances, respectively.

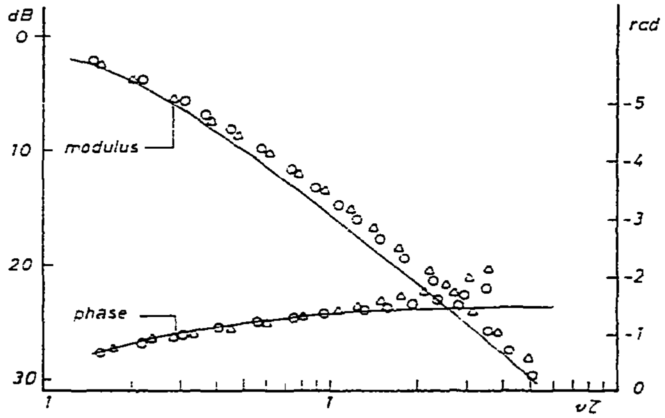

Fig. 3. Continuous lines represent a one-step filter, and ○ calorimeter B′ whose cell content is a HC substance It is clearly seen that the experimental modulus surpasses that of the filter A term ($\gamma p + 1$) may account for this fact, representing Δ the analytical form of the UTF* proposed.

Divergences in the UTF* from experimental values are presented in Table 5. A remarkable coincidence between the UTF* (HC substances) and the TF of calorimeter I is shown in Fig. 3.

A preliminary kinetic analysis of the UTF and UTF* for HC substances indicates a better behaviour of the latter when applied to heat productions distributed inside the calorimetric cell (e.g. liquid mixtures).

CONCLUSIONS

(1) The dispersion in the TF because of different positions of the sources is not relevant at low frequencies $\nu\tau_1 \lesssim 4$ (HC) or $\nu\tau_1 \lesssim 1$ (PC). Within these

TABLE 5

Deviations of the UTF* from experimental TFs (Δm = |UTF*| — $|\mathrm{TF_{exp}}|$ in dB and $\Delta p = \arg\{\mathrm{UTF^*}\} - \arg\{\mathrm{UTF_{exp}}\}$ in rad) [The values of α, β and γ selected are $\tau_1/\alpha = 6, \tau_1/\beta = 25, \tau_1/\gamma = 4$ (HC) and $\tau_1/\alpha = 7, \tau_1/\beta = 12, \tau_1/\gamma = -40$ (PC)]

Calorimeters (HC)		A	B	F	B′	J	K
20 dB	Δm	2 75	1.22	2.38	0.62	0.51	1 39
	Δp	—0.18	0.023	—0.30	0.16	—0.14	—0.23
30 dB	Δm	3.57	0 49	3.32	—1.01	—1.15	1.83
	Δp	0.00	0.17	—0.39	0.40	—1.40	—0.37
Calorimeters (PC)		C	G	H	L	M	N
20 dB	Δm	1 85	—2.29	1.72	—1.00	—1.81	—0.10
	Δp	—0.23	0.63	—0.63	—0.24	0.09	—0.27
30 dB	Δm	2.52	—4.58	2.72	—0.89	—3.20	—0.02
	Δp	—0 31	0.93	—0.83	—0.44	—0.05	—0 44

domains, a universal transference function (UTF) can be achieved either in a simplified form (product of three poles) or in slightly modified form (adding a zero in the numerator).

(2) In the present state of art, the parameters α and β from the UTF have no precise meaning; i.e., they are not to be taken as the real time constants (τ_2, τ_3, ...) of the calorimeter. Moreover, the parameters α and β are highly undetermined even for a given calorimeter, providing all of them with a remarkable coincidence with the experimental TF within the range 0—30 dB.

(3) The transfer function of the global system: calorimeter—UTF—corrector has remarkable dynamic properties. There is no damping in the modulus or delay in the phase up to $\nu\tau_1 \lesssim 4$ (HC) and $\nu\tau_1 \lesssim 1$ (PC). The positions of the sources and the effects introduced by the handling of the laboratory cell are not relevant within this domain. Some atention must be paid to calorimeters whose sensibilities change appreciably against the position of the sources.

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