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APPLICATION OF HARMONIC ANALYSIS AND STANDARD INVERSE FILTERING TO A DTA SYSTEM

J. FONT, J. MUNTASELL, J. NAVARRO and J.Ll. TAMARIT

Departament de Física. Universitat Politècnica de Catalunya, Diagonal 647, Barcelona 08028 (Spain)

E. CESARI

Departament de Termologia, Facultat de Física, Universitat de Barcelona, Diagonal 645, Barcelona 08028 (Spain)

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ABSTRACT

We determine the transfer function of a DTA device by means of harmonic analysis. We analyse the evolution of the transfer function for modifications of several experimental conditions and compare it with the evolution of the time constants identified by standard inverse filtering. The frequency limit that makes it possible to reconstruct effects with a good approximation is about 0.02–0.03 Hz. The results obtained corroborate the validity of inverse filtering as an identification technique in DTA systems.

INTRODUCTION

In previous communications [1,2] partial identification of the transfer function of our DTA system using the graphical technique of inverse filtering was carried out. These papers describe the influence of modifications of several experimental conditions (sample mass and compactness) on the values of the two first time constants and analyze the variation of these values with temperature.

We now determine the transfer function using harmonic analysis [3,4]. We analyze the variation of the transfer function's module and phase with change in temperature and the kind of contact between sample and crucible.

We also determine the effect of a correction with two time constants (identified by inverse filtering) on the system's transfer function according to the different configurations and temperatures analyzed. This enables the global transfer function (found by harmonic analysis) to be compared with the approximation that represents the use of two time constants.

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EXPERIMENTAL

Using a constantan wire resistance (diameter 0.05 mm), enclosed in the sample crucible, we generated rectangular signals of duration 10 s by the Joule effect. The measurements were obtained using a furnace having a maximum working temperature of 900 K [1]. This furnace had a feeble thermal coupling between the sample and reference crucibles. We obtained the numerical data on a 0.36 s sampling period. The amplification of the differential signal is 5000 times.

We also included potassium nitrate with a 99% minimum purity in the sample crucible, which enabled us to modify the sample–crucible contact characteristics, by melting the salt before taking some of the measurements.

We took the measurements under isothermal conditions and at many different temperatures between 363 and 573 K; a minimum of 3 measurements was taken for each temperature.

We used two different configurations: configuration 1 corresponds to 19 mg melted KNO_3 and an electric resistance of 148 Ω; configuration 2 corresponds to a resistance of 71 Ω and 41 mg KNO_3 either in power form (grain size 60–100 μm) or previously melted before taking the measurements. In this second configuration, the amount of KNO_3 was increased and the length of the constantan wire was shortened because we wanted to make the effects of change of the sample–crucible contact characteristics (due to salt fusion) more significant. Using configuration 1 we analyzed the influence of the temperature factor.

The approximate value of the generated rectangular signals is 40 mW for configuration 1 and 20 mW for configuration 2.

RESULTS AND DISCUSSION

In Table 1 we include the average values of the time constants determined (by inverse filtering) on the return to the baseline level of the signals generated by the Joule effect, for configuration 1.

TABLE 1

Time constants determined by inverse filtering for configuration 1

T (K)	τ_1 (s)	τ_2 (s)
363	27	4
393	25	4
413	24	4
473	23	4
523	22	4
573	19	4

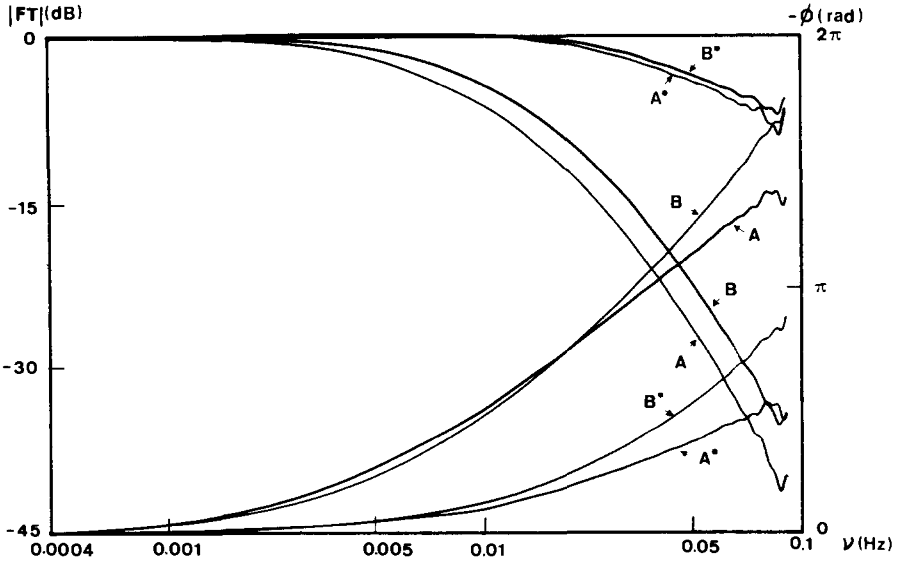

Fig. 1. Module and phase of the transfer function for two different temperatures (A, 363 K; B, 573 K). Module and phase of the transfer function corrected with the time constants found by inverse filtering for these two temperatures (A*, 363 K; B*, 573 K) are also given.

These values confirm the almost linear decrease of the principal time constant, with the increase in temperature which has already been determined [1].

Thanks to the measurements realized at 393 and 413 K, temperatures which are close to those of the KNO_3 II → I transition (400 K), we have verified the concordance, (previously checked [2]), among the time constants associated with the transition peak and those that correspond to Joule effect dissipation at temperatures close to that of the real process. This concordance justifies the validity of the time constants on the real thermogram.

In Fig. 1 we show the module and phase of the transfer function, for two measurements that correspond to the two extreme temperatures studied: 363 and 573 K. We also show the transfer function after correction using values of τ_1 and τ_2, determined by inverse filtering.

Figure 1 reveals that at higher temperatures the module of the transfer function decreases more slowly when the frequency increases. We have verified that this course persists in the entire temperature interval studied, since the rest of the graphics that correspond to the module are found between those drawn in Fig. 1, and follow the same arrangement with temperature. This fact shows that the system has a faster response at higher temperatures and that it agrees with the evolution of the time constants determined by inverse filtering.

If, in Fig. 1, we analyze the module of the corrected transfer function, we may affirm that these corrections are adequate up to frequencies close to

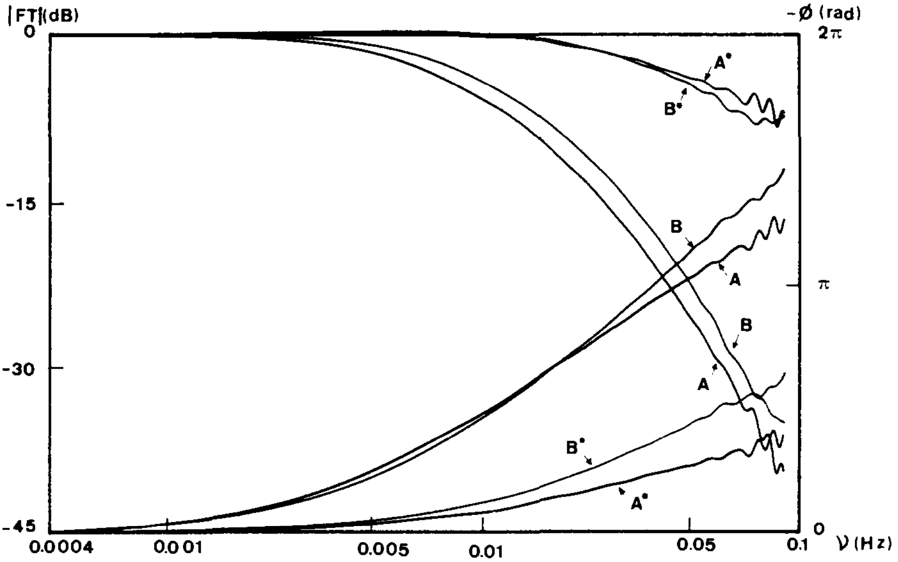

Fig. 2. Module and phase of the transfer function for 413 K and KNO_3 (A, not melted; B, melted). Module and phase of the transfer function corrected with the time constants found by inverse filtering (A*, not melted KNO_3; B*, melted KNO_3) are also given.

0.02–0.03 Hz. We may also notice on the figure that from a frequency close to 0.07 Hz forward, there are fluctuations in the module and the phase of the transfer functions; these fluctuations are understandable if we think of the existence of an experimental noise that corresponds to a signal/noise relation of the order of 40 dB. This level of noise limits to two the number of time constants that it is possible to identify by inverse filtering [5].

By this analysis of the influence of temperature on the response of the system we have also been able to check that changes of the temperature in the 50–70 K range give perceptible variations in the curve of the module of the transfer function, bearing in mind the repetitive nature of our system.

For configuration 2 we obtained as average values, $\tau_1 = 24$ s and $\tau_2 = 5$ s, when we used unmelted KNO_3 and $\tau_1 = 21$ s and $\tau_2 = 5$ s when we used previously melted KNO_3, both corresponding to a Joule effect at 413 K.

In Fig. 2 we present the transfer functions corresponding to a measurement with melted KNO_3 and another with unmelted KNO_3. We also include the functions corrected with time constants found by inverse filtering.

We may observe in Fig. 2 that for the measurement with melted KNO_3, the module of the transfer function decreases more slowly with the frequency. The use of melted salt makes the contact between sample and crucibles better, and the system's response is faster. This result agrees with the decrease of the time constant obtained by inverse filtering for the measurement with melted KNO_3.

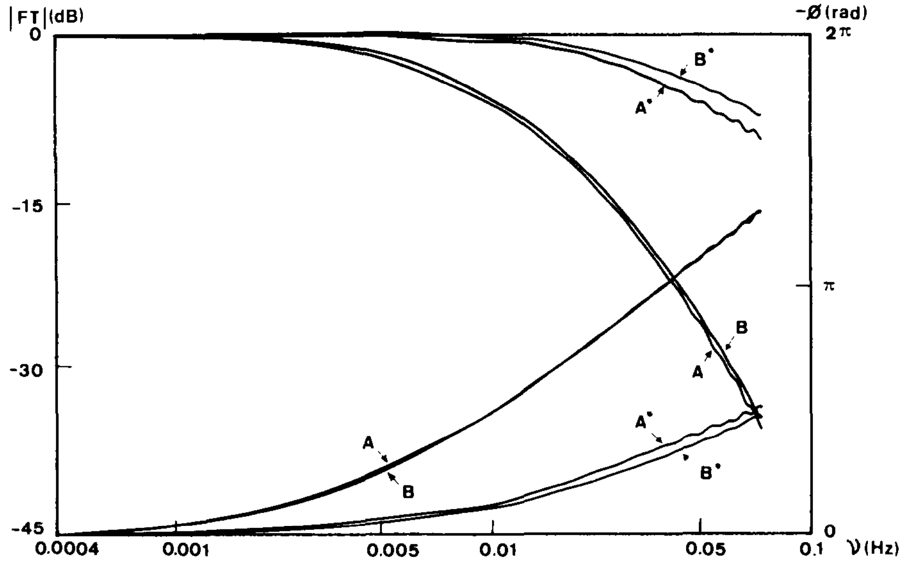

Fig. 3. Module and phase of the transfer function for two measurements under equal experimental conditions (A and B) and module and phase of the transfer function corrected with the time constants determined by inverse filtering (A* and B*).

We have checked that the effect of the kind of contact between sample and crucible on the values of the time constants decreases when the temperature increases. The difference among the values of τ_1 obtained at 523 K, with KNO_3 both melted and unmelted, is 1 s. This value is almost the resolution limit estimated for the identification by inverse filtering of the signals given by our DTA system [1]. This decrease of the effect of fusion with increase of temperature, may also be observed on the transfer function determined by harmonic analysis. This fact, and also the decrease of the transfer function module with frequency at higher temperatures, happens because the radiation effects are more significant at higher temperatures.

In Fig. 3 we represent the transfer functions that correspond to two measurements carried out under equal experimental conditions (393 K, configuration 1). We also include the module and the phase of the transfer function once it has been corrected with the time constants determined by inverse filtering on each of these measurements ($\tau_1 = 25$ s, $\tau_2 = 4$ s for measurement A and $\tau_1 = 24$ s, $\tau_2 = 5$ s for measurement B).

Figure 3 shows how the system's repetition affects the shape of the curve that corresponds to the module and the phase. This figure also enables us to analyze the influence of the resolution limit of inverse filtering ($\simeq 1$ s) upon the corrected transfer function.

The difference between A* and B* is not typical of that associated with the uncertainty for the determination of τ_1 and τ_2, for experimentally identical transfer functions. In this case, the difference between the used

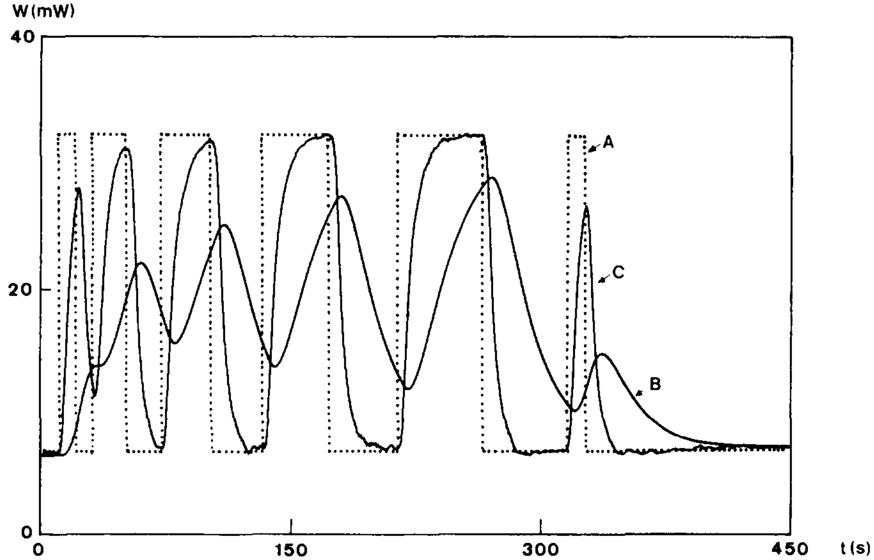

Fig. 4. Generated signal (A), system's response signal (B), and deconvoluted thermogram (C) that correspond to several Joule effects of different duration.

time constants in A* and B* represents the limit of resolution for the inverse filtering method.

To give an example, we analyzed the reconstruction capacity of the effects of many different durations for configuration 2 using KNO_3 melted at 393 K. To do this, we employed inverse filtering with the two time constants identified for our system. In Fig. 4 we represent the signal obtained by the system, and the deconvoluted registration (deconvoluted with $\tau_1 = 22$ s and $\tau_2 = 4$ s), of several Joule effects for time periods in the 10–50 s range.

The conversion to power units was achieved thanks to the use of the system's calibration factor at the former temperature ($K = 4.3$ mV W^{-1}).

The Joule effects were generated with a power of the same order as that corresponding to the peak crest of the II → I transition of a KNO_3 mass close to 40 mg.

Figure 4 shows the kinetic limits of our system [6,7]. We also remark that when we correct the thermogram with two time constants, we may distinguish two effects, separated by 10 s. When the separation is about 20 s, the deconvoluted signal regains the level of the baseline. On the other side, by means of the deconvolution, we are able to reconstruct, truthfully, signals of a duration 30–50 s.

CONCLUSIONS

In this work we have studied by means of harmonic analysis the influence that variations of the experimental conditions (temperature and nature of contact between sample and crucible) have on the shape of our experimental system's transfer function. We have also seen (always bearing in mind the repetitive nature of our system) how the transfer function may be affected by temperature changes (50–70 K) and by changes in the characteristics of the thermal contact between sample and crucible.

This study enables us to verify the concordance between the evolution of the time constants, identified by inverse filtering, and the evolution of the transfer function determined by harmonic analysis, obtained by modifying the experimental conditions or changing the temperature at which the effect develops.

By means of the harmonic analysis, we have checked that, up to a frequency in the 0.02–0.03 Hz range, good concordance exists between the experimental transfer function and that obtained by means of the time constants, identified by inverse filtering, for the entire temperature domain and the configurations studied.

This frequency limit corresponds to a time period in the 30–50 s range, which corroborates that found when filtering two time constants; it is possible to reconstruct effects of this time period, to a good approximation. We have also checked that the deconvolution enables us to distinguish thermal effects of 10–20 s duration.

The results obtained in this work corroborate the validity of inverse filtering as an identification technique of easy application to DTA systems.

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