AN EXPERIMENTAL VERIFICATION AND COMPARISON OF THE USE OF PASSIVE AND ACTIVE THERMAL-ELECTRONIC NETWORKS IN DYNAMIC CALORIMETRIC MEASUREMENTS *

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ABSTRACT

An experimental verification and comparison of two dynamic calorimetric methods is presented. One of them is a simple diathermic method with a transfer function corrector, and works on the basis of a passive thermal-electronic network. The other is a feedback compensation method, improved by a transfer function corrector, and works on the basis of a combination of an active and passive thermal-electronic network. The experimental verification has been realized according to recommendations elaborated for comparing dynamic calorimetric methods.

INTRODUCTION

Thermal inertia is one of the main factors limiting the possibilities of dynamic calorimetric measurements. The dynamic properties of a calorimetric vessel are definied by its heat capacity, internal and external heat exchange conditions, as well as by the diffusive character of heat conduction. The influence of the thermal inertia on the calorimetric signal can be considerably reduced in different ways. A number of techniques have been elaborated for this purpose in different laboratories. A review of these techniques has been presented recently [1]. Among these techniques are the analog techniques which can be based on the differentiation or the feedback compensation principles. The aim of this paper is to present an experimental verification and comparison of two such techniques. The first, which is called a diathermic method, with a transfer function corrector, works on the basis of a passive thermal-electronic network. The other, which is called a feedback compensation method, with a transfer function corrector, works on the basis of a combination of an active and passive thermal-electronic network.

DIATHERMIC METHOD WITH A TRANSFER FUNCTION CORRECTOR

Simplified theoretical basis

For simplicity let us assume that the calorimeter is described by a first order differential equation. This means that using Laplacian transforms the relation between a thermal power q_x generated in such a calorimeter (input signal) and recorded calorimetric signal q_r (output signal) is described as follows

$$q_r(s) = \frac{k_c}{1 + \tau_{cal}s} q_x(s) \tag{1}$$

where τ_{cal} is a time constant of the calorimeter and k_{cal} is its static gain. The method of reducing the influence of calorimetric time constant on the recorded calorimetric signal is based on mounting a correction network [2—5] on the output of a measuring amplifier with the transfer function described as follows [6]

$$G_{cor}(s) = \frac{\tau_{cor}s + 1}{\dfrac{\tau_{cor}}{a}s + 1} \tag{2}$$

where τ_{cor} is the time constant of the corrector and a is a constant factor. The transfer function of the total system will be a product of the particular transfer functions. When the time constant of the corrector is adjusted in such a manner that

$$\tau_{cor} = \tau_{cal} \tag{3}$$

the relation between the transforms of the input and output signals is as follows

$$q_r(s) = \frac{k_c}{\dfrac{\tau_{cal}}{a}s + 1} q_x(s) \tag{4}$$

This means that one obtains a response with a time constant a times reduced in comparison to the original time constant of the calorimeter.

Experimental procedure

The basic problem in achieving a sufficient experimental correctness of the method is a proper setting of the time constant of the corrector. As shown above, the value of the corrector time constant depends on the value of the calorimetric time constant. Next, the calorimetric time constant, even in the simplest case when the calorimeter is really a first order system, depends not only on the construction but also on the content of the calorimetric vessel (reaction medium, investigated substances, etc). This means that adjusting the corrector time constant, with the help of a separate calibration vessel, can lead to dynamic errors when performing measurements in a real reaction vessel, unless the former is constructed in such a manner that it

has the same properties as the real reaction vessel. This requirement can be compared to requirements of 'equivalence of sources', widely accepted conditions of correctness for isoperibol calorimeters [7,8]. But, while in the isoperibol calorimeters only the energy equivalent must have an identical value in a real experiment and in the comparison calibration experiment, in dynamic measurements, the time and space dependent parameters must also have identical values. For example, in a calorimeter with a given constant heat capacity and given well-defined external heat exchange conditions, the same heat effect, located in the same geometrical position, can cause slightly different dynamic responses only when changing internal heat exchange conditions [1]. In these experiments the energy equivalent of the calorimeter and the final temperature rise remained uncharged. This suggests that for correct dynamic measurements special requirements must be fulfilled. These requirements can be called 'dynamic equivalence of sources'. A practical fulfilment of such conditions is very difficult to realize in separate experimental mountings of calorimetric vessels. To facilitate the realization of such an aim we have constructed calorimetric vessels [9] in which the calibration heater is located inside the reaction space of the vessel. A schematic diagram of an example of such a vessel located inside a cylindrical calorimetric detector is shown in Fig. 1. The calibration heater (1) is made of a constantan wire placed in a thin stainless steel capillary, soldered in the bottom of reaction vessel (2) and connected to two electrodes (3) mounted on the vessel. The other pair of electrodes (4) is mounted on the calorimetric detector (5).
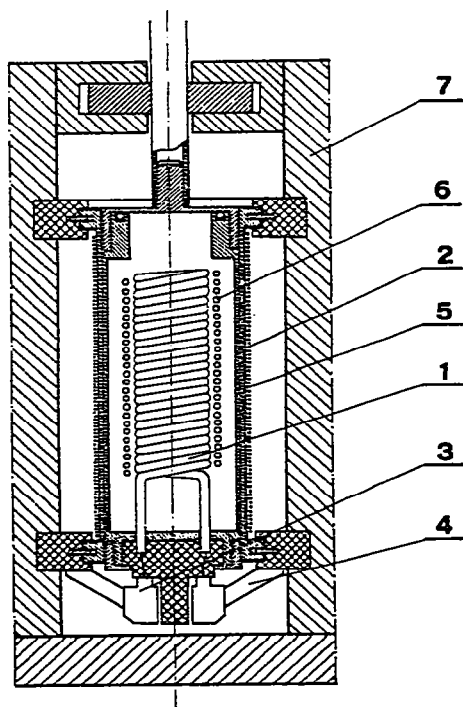

Fig. 1. A schematic diagram of the calorimetric vessel: 1, calibration heater; 2, reaction vessel; 3, 4, electric connection electrodes; 5, calorimetric detector; 6, electrical heater for simulation of thermal effects; 7, calorimetric block.

When the vessel is introduced into the calorimeteric detector then the calibration heater is automatically connected to an electronic unit with the help of these electrodes. During the reported measurements the reaction space was filled with a copper powder. Adjustment of the corrector time constant values was performed by check and try method, using power square pulses until the corrected response was the most rapid and still no overshoots appeared. A simulation of real heat effects in the reaction space was realized with the help of a separate electrical heater (6) located in the copper powder.

Results

An experimental verification of the method in dynamic measurements was performed in a prototype of Microcalorimeter Unipan type 600 [5] (Unipan Scientific Instruments, ul. KRN 51/53, 00-818 Warsaw, Poland) according to recommendations elaborated during the first thermokinetic meeting in Nieborów n/Warsaw. These recommendations suggest the checking and comparison of possibilities of dynamic calorimetric methods by performing two sets of impulse input pulses with given power and energy ratios. A separation in time of these pulses depends on the value of the original time constant of a
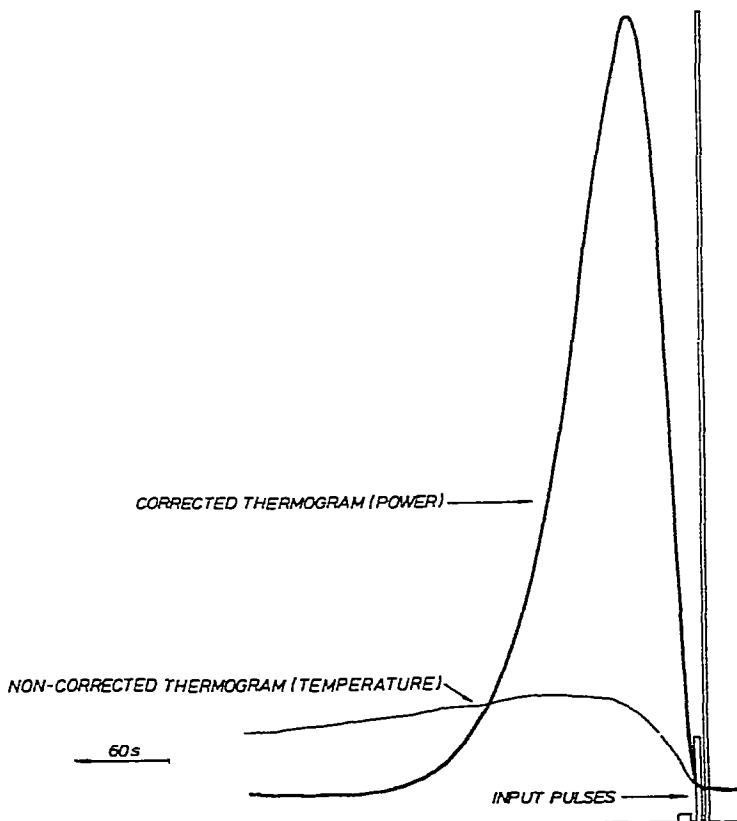

Fig. 2. The first set of thermal pulses and responses obtained by the diathermic method. Energy ratios, 1 : 4.7 : 26; power ratios, 1 : 9.5 : 104; time constant reduction, ~10.
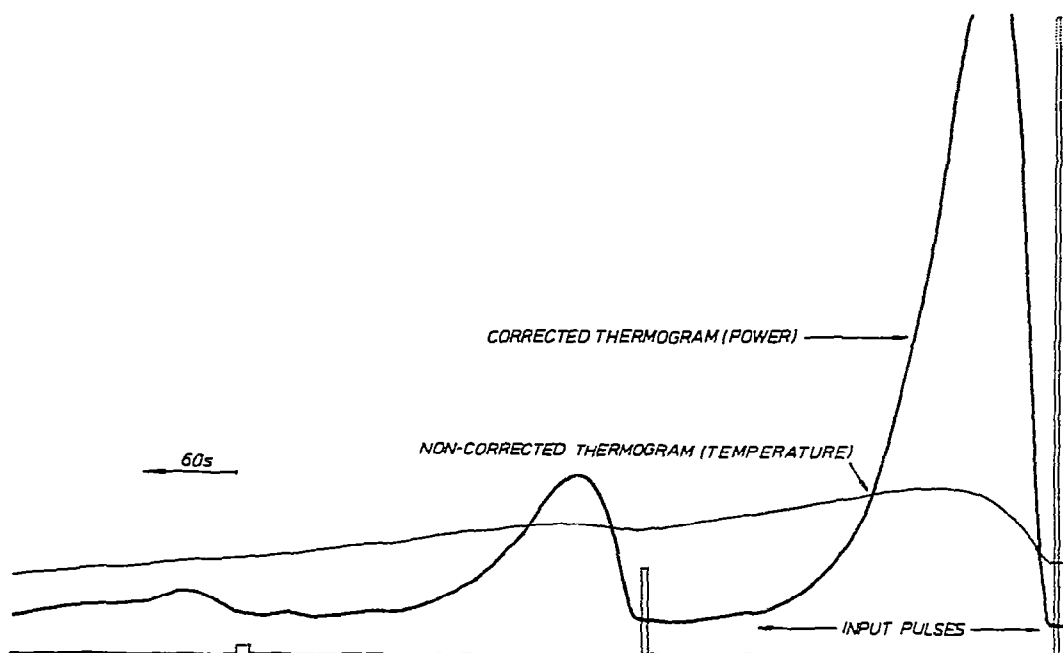
Fig. 3. The first set of thermal pulses, separated infinitely in time, and responses obtained by the diathermic method. Energy ratios, 1 : 4.7 : 26; power ratios, 1 : 9.5 : 104; time constant reduction, ~10.
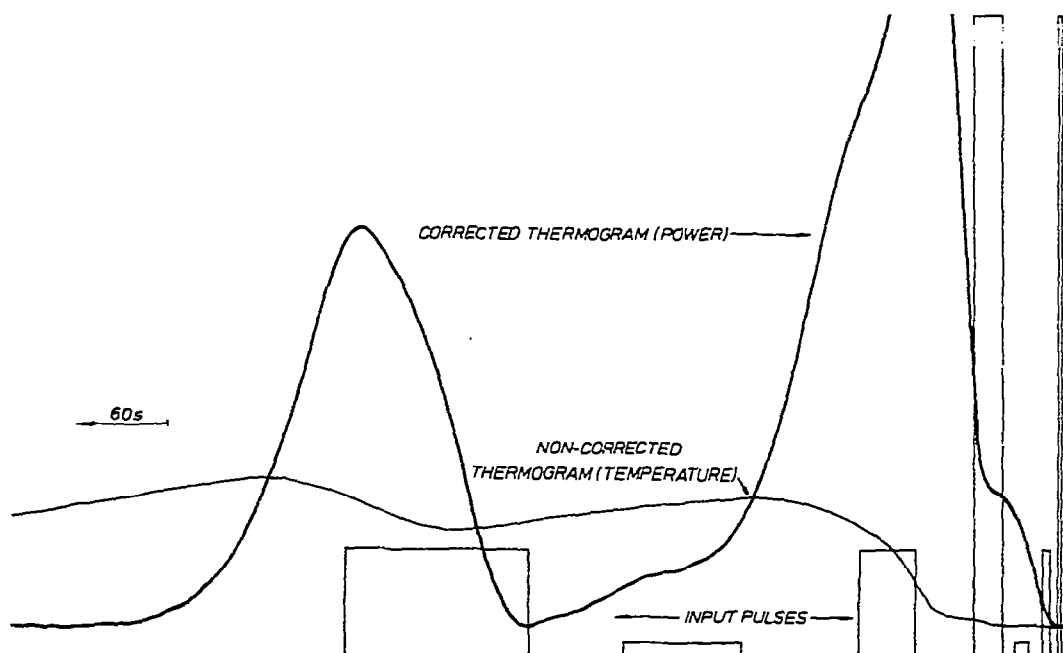

Fig. 4. The second set of thermal pulses and responses obtained by the diathermic method. Energy ratios, 1 : 1.2 : 3.8 : 8 : 13.5 : 30 : 106; power ratios, 1 : 7.5 : 53.3; time constant reduction, ~10.

calorimeter. In a way suggested by the recommendations the possibilities of dynamic methods can be compared and not the calorimeters themselves, which can be large and heavy, small and rapid, depending on their own mechanical construction.

The first set of pulses and obtained responses are shown in Fig. 2. It can be seen that in this case there is no influence of the separated input pulses, neither on the original non-corrected thermogram, nor on the thermogram corrected by the electronic network with a carefully adjusted value of its time constant; however, the time constant of the total corrected system is 10 times smaller than the original time constant of the calorimeter. The same set of pulses, as far as the power ratios are concerned, but practically infinitely separated in time, is shown in Fig. 3. It is evident that in this case the dynamic correction is helpful and it is possible not only to distinguish but even measure the input pulses with the corrected response, while the original non-corrected thermogram is almost uninfluenced by the smaller pulses. The second set of pulses according to the recommendations mentioned above and obtained responses are shown in Fig. 4. This time the power and energy ratios and time separations of pulses are more favourable for dynamic measurements and for this reason there are slight traces of input pulses on the corrected responses.

POWER COMPENSATION METHOD WITH A TRANSFER FUNCTION CORRECTOR

Simplified theoretical basis

In power compensation calorimeters there is a compensation of thermal effects, simultaneously with their generation, so that the temperature of the calorimetric vessel should remain unchanged. The compensation is usually performed by an electronic feedback loop. Such a thermal-electronic system is called an active system [10]. In such active systems the relation between the transforms of the input signal $q_x(s)$ and recorded signal $q_r(s)$ is as follows

$$q_r(s) = \frac{1}{1 + \frac{\tau_{cal}}{K}s} q_x(s) \tag{5}$$

where K is the total gain of the compensation feedback loop. For simplicity it was assumed that the calorimeter is a first order system. Relation (5) is valid only under the basic condition that the investigated substance or the reaction medium developing the power q_x is located inside the feedback loop. The statement and analysis of this condition were given by Randzio and Sunner [11]. This condition of correctness for compensated calorimeters is equivalent to the conditions of dynamic equivalence of sources for passive thermal-electronic systems, and to the conditions of equivalence of sources for isoperibol calorimeters. It can be concluded from eqn. (5) that the time constant of the compensated calorimeter is reduced K times in comparison to the original time constant of the calorimeter. Unfortunately, in real systems K can have rather low values, because with higher values insta-

bilities or overshoots can appear. In this case, it is possible to increase the reduction of the time constant by applying a corrector with the transfer function described by eqn. (2) on the output of the compensated system. When the time constant of the corrector is adjusted in such a manner that

$$\tau_{cor} = \frac{\tau_{cal}}{K} \tag{6}$$

the relation between the transforms of the input and output signals is as follows

$$q_r(s) = \frac{1}{\dfrac{\tau_{cal}}{Ka}s + 1} q_x(s) \tag{7}$$

This means that in this case one obtains a response with time constant Ka times reduced in comparison to the original time constant of the calorimeter.

Experimental procedure

The experiments were performed in the same vessel as presented before in Fig. 1. The simulation of real heat effects (pulses according to recommenda-
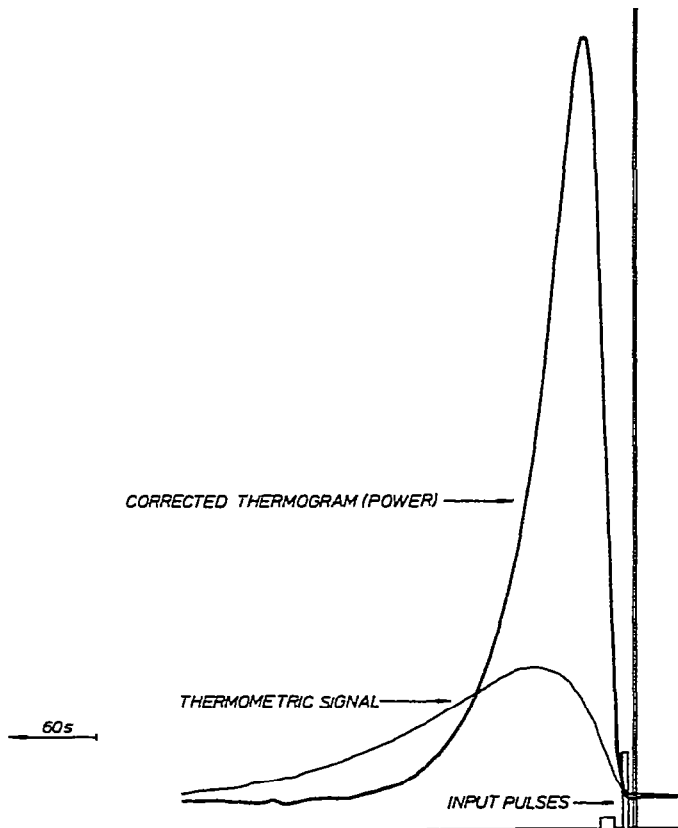

Fig. 5. The first set of pulses and responses obtained by the compensation method with a transfer function corrector. Energy ratios, 1 : 5.2 : 19.2; power ratios, 1 : 10.3 : 76.7; time constant reduction, ∼13.
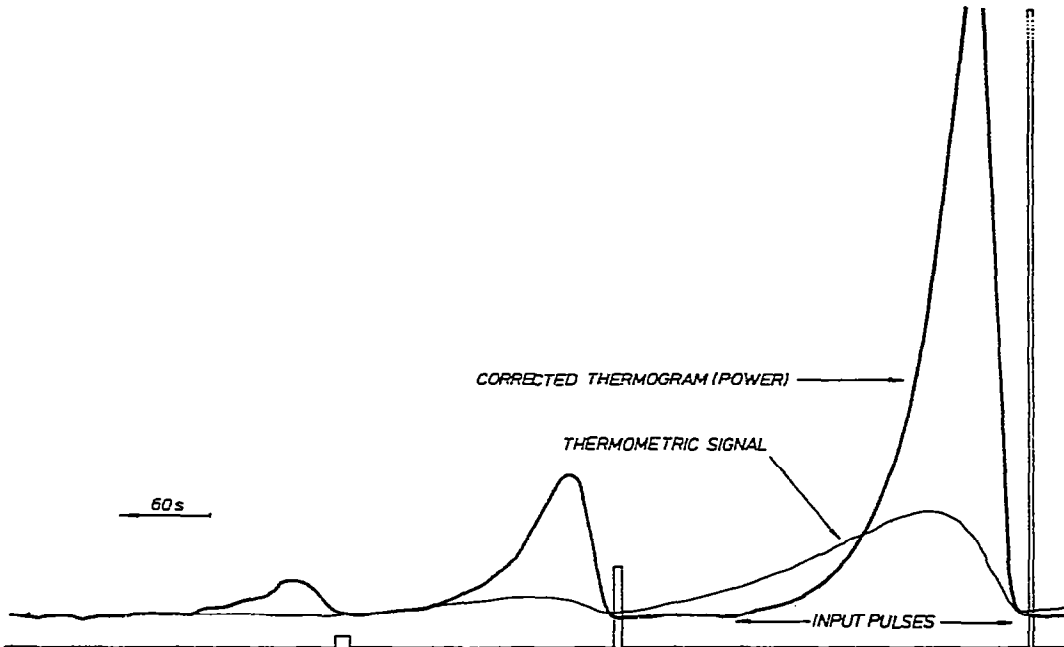
Fig. 6. The first set of thermal pulses, separated infinitely in time, and responses obtained by the compensation method with a transfer function corrector. Energy ratios, 1 : 5.2 : 19.2; power ratios, 1 : 10.3 : 76.7; time constant reduction, ~13.
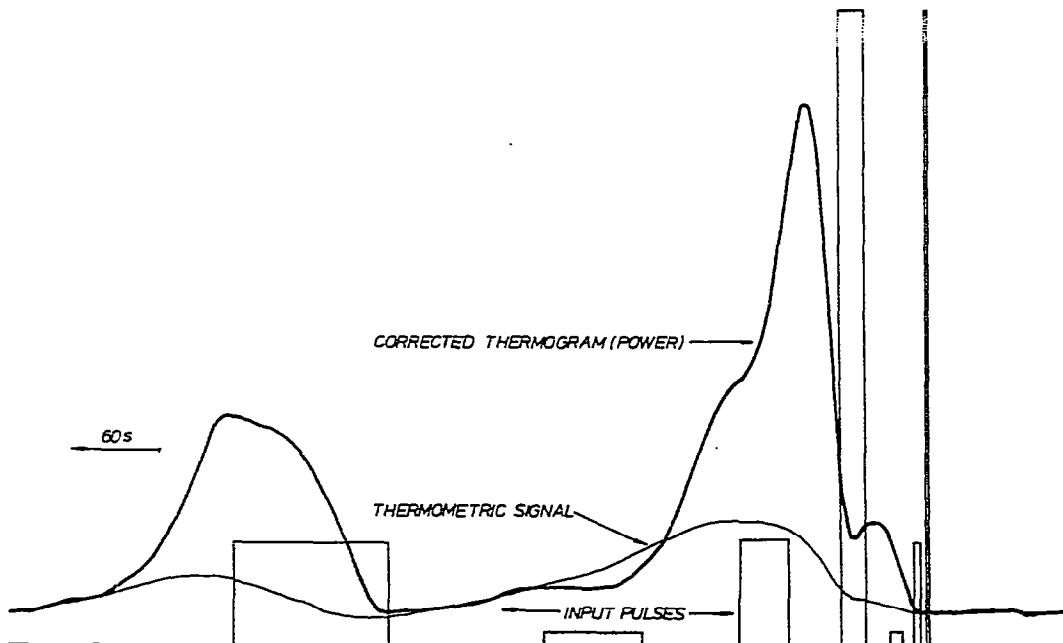

Fig. 7. The second set of thermal pulses and responses obtained by the compensation method with a transfer function corrector. Energy ratios, 1 : 1.2 : 3.8 : 8 : 13.5 : 30 : 106; power ratios, 1 : 7.5 : 53.3; time constant reduction, ~13.

tions) was realized with the help of the heater located in the copper powder. The compensation of these pulses was realized in the calibration heater connected to the electronic system of the calorimeter.

Results

The thermograms obtained with the first set of pulses are presented in Fig. 5. The same pulses, but separated infinitely in time, are presented in Fig. 6. The thermograms obtained with the second set of pulses are presented in Fig. 7. When comparing the two methods one can find two advantages of the compensation method: (1) the reduction of the time constant is larger than in the diathermic method, (2) the temperature of the calorimetric vessel in the compensation method always returns to the initial value, while in the diathermic method temperature deviates, which can cause supplementary disadvantages.

CONCLUSIONS

The experimental verification of the two dynamic calorimetric methods, has shown that both methods have comparable possibilities in dynamic measurements. The reduction of the original calorimetric time constant by a factor of 10, easily realizable, is sufficient for numerous laboratory experiments. The compensation method improved by an external transfer function corrector is technically a little more complicated but gives a greater reduction of the time constant and maintains the calorimetric vessel almost at constant temperature. Both methods also facilitate measurements of small and rapid heat effects, which remain almost invisible on the original thermogram when no dynamic method is applied. The diathermic method gives correct results under the condition that the adjusting of corrector values is done in a vessel fulfilling the requirements of 'dynamic equivalence of sources'. The compensation method gives correct results providing the reaction medium or the investigated substance is placed inside the compensation feedback loop.

LIST OF SYMBOLS

a = constant factor;
G_{cor} = transfer function of electronic corrector;
K = total gain of feedback loop;
k_c = static gain of calorimeter;
q_r = recorded calorimetric signal (W);
q_x = input signal (W);
s = Laplacian operator;
τ_{cal} = time constant of calorimeter (s);
τ_{cor} = time constant of electronic corrector (s).

REFERENCES

1 S.L. Randzio and J. Suurkuusk, in A. Beezer (Ed.), Biological Microcalorimetry, Academic Press, London, 1980, p. 311.
2 E. Calvet and F.M. Camia, J. Chim. Phys., 55 (1958) 818.
3 Y. Touvenin, C. Hinnen and A. Rousseau, in Microcalorimétrie et Thermogenèse, CNRS, Paris, 1967, p. 65.
4 J.P. Dubes, M. Barres and H. Tachoire, Thermochim. Acta, 19 (1977) 101.
5 M. Lewandowski and S. Randzio, Apar. Nauk. Dyd., 4 (6) (1978) 45.
6 V.E. Shukshunov, Correction Circuits in Instruments Measuring Non-stationary Temperatures, Energia, Moscow, 1970.
7 E.D. West and K.L. Churney, J. Appl. Phys., 41 (1970) 2705.
8 C. Mosselman and K.L. Churney, in S. Sunner and M. Mansson (Eds.), Combustion Calorimetry, Pergamon Press, Oxford, 1979, p. 35.
9 S. Randzio, B. Piasecki and T. Strzelecki, Polish Pat. 101, 975.
10 H. Weber, Thermochim. Acta, 9 (1974) 29.
11 S. Randzio and S. Sunner, Anal. Chem., 50 (1978) 704.