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RECENT PROGRESS IN NUMERICAL METHODS FOR THE DETERMINATION OF THERMOKINETICS

RESULTS OF MULTINATIONAL PROGRAMME ON THE COMPARISON OF THE METHODS

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The results of a multinational concerted programme on the determination of thermokinetics are presented. The purpose of the programme was to compare different numerical methods which have been independently proposed for the determination of thermokinetics from experimental calorimetric data. To achieve this end, the same experimental data, obtained from two heat-flow calorimeters, were distributed and successively analyzed by the different methods. Numerical methods based on the state function theory, on Fourier transform analysis, on dynamic optimization and on a simple differentiation of the data were thus critically tested.

During the last few years, dynamic calorimetry has developed significantly. Its function is to determine not only the total heat effect associated with the thermal phenomenon under study, but also the changes of thermal power with time, the "*thermogenesis*" $W(t)$ [1], expressed by

$$W(t) = \frac{dQ(t)}{dt}$$

where Q is the amount of evolved heat and t is the time. Since the reaction progress and the associated heat effects are simultaneous, any calorimetric measurement in which $W(t)$ is correctly determined can be a source of information on the kinetics of the reaction under study.

However, experimental calorimetric data, i.e. directly or indirectly temperature changes *vs.* time $\Theta(t)$, never exactly correspond to $W(t)$. Because of thermal lags in the calorimeter, a distortion always occurs. Hence, in order to reconstruct $W(t)$ from $\Theta(t)$, it is necessary to define a relation between these functions:

$$W(t) = M[\Theta(t)] \tag{1}$$

Several methods [1—5] have been proposed for the determination of thermokinetics, which make use of a 1st-order differential equation. However, these methods are not adapted to the study of rapidly changing heat effects, measured in a calorimeter with a relatively long time-constant [1]. For this reason, a number of other, numerical and analog, methods have recently been proposed. These methods were presented and discussed during the 1st International Colloquy on Thermokinetics, jointly organized by the Institute of Physical Chemistry of the Polish Academy of Sciences and the French Association of Calorimetry and Thermal Analysis (AFCAT), which took place in Nieborów, Poland, in June 1977. As a result of the discussions, the participants recognized the necessity of testing all the methods in the reconstruction of the same experimental, calorimetric data. The results of this concerted programme were discussed during the 2nd International Colloquy on Thermokinetics, jointly organized by the French Association of Calorimetry and Thermal Analysis, the Group of Experimental Thermodynamics of the French Chemical Society and the Institute of Physical Chemistry of the Polish Academy of Sciences, which took place in Cadarache, France, in May 1979. They are summarized in the present article.

Reconstruction methods

Four methods for the reconstruction of thermogenesis from experimental calorimetric data were tested. They are based on Fourier transform analysis, on dynamic optimization, on the theory of state functions and on the simple differentiation of the data.

Fourier transform analysis. This method, first used by Navarro *et al.* [6–8] and then by van Bokhoven [9], takes advantage of the relation which, in the case of a linear system, exists between the Fourier transforms of the input, $W(t)$, and output, $\Theta(t)$, functions (the initial conditions being zero):

$$\Theta(j\omega) = W(j\omega) \cdot H(j\omega) \tag{2}$$

where H is the transfer function of the linear system (the calorimeter) in the frequency domain $\omega(\omega = 2\pi\nu)$.

The transfer function is obtained from calibration experiments which consist in determining the response $\Theta_p(t)$ of the calorimeter to known (Dirac) pulses $P(t)$, generally produced by Joule heating. The quotient of the Fourier transforms of both $\Theta_p(t)$ and $P(t)$ yields, according to Eq. (2), the transfer function of the calorimeter, H. Application of Eq. (2) in the case of any calorimeter response $\Theta(t)$, then allows one to reconstruct the corresponding thermogenesis $W(t)$, provided that the same transfer function characterizes the calorimeter during both calibration and actual experiment [7–10]. It is clear that the last restriction is equally valid in the case of all data-reconstruction methods.

Dynamic optimization method [11]. This method is based on the combination of an input function $x(t)$ to an output function $y(t)$ by the convolution

$$x(t) = \int_0^{t_f} y(t-\tau)H(\tau)\mathrm{d}\tau = \int_0^{t_f} y(t-\tau)\frac{\mathrm{d}h(\tau)}{\mathrm{d}\tau}\mathrm{d}\tau \tag{3}$$

where $H(t)$ is the calorimeter response to a Dirac pulse, $h(t)$ is the calorimeter response to a step function, and τ is the integration variable. Equation (3) supposes that the initial conditions are zero.

The unknown input, the thermogenesis $W(t)$, is obtained by a series of iterations, consisting in testing successive values $j = 0, 1, \ldots, k$ in the function $y^j(t)$, $y^0(t)$ being an arbitrary function. The function $y^k(t)$, which minimizes the integral of the square of the differences between the experimental output $\Theta(t)$ and the output $x(t)$ calculated from Eq. (3) for $y(t) = y^k(t)$, is considered to be the optimum approximation of the input function $W(t)$:

$$q[y(t)] = \int_0^{t_f} [\Theta(t) - x(t)]^2 \mathrm{d}t = \int_0^{t_f} [\Theta(t) - \int_0^{t_f} y(t - \tau)H(\tau)\mathrm{d}\tau]^2 \mathrm{d}t \tag{4}$$

where $<0, t_f>$ is the time interval in which the temperature changes are measured, and $q[y(t)]$ is the criterion which characterizes the fitting of the two output functions, Θ and x. The algorithm of the conjugated gradient was employed for the minimization of this criterion.

Method using the state functions [12, 13]. The first step of the procedure consist in the "identification" of the calorimeter, assumed to be a linear system of 3rd order. This is achieved by means of one, or preferably several, experimental unit step responses, recorded during calibration experiments. They are used to calculate the coefficients A_i and w_i in the equation of the response of a 3rd-order linear system to a unit step:

$$u(t) = Y_0 - \sum_{i=1}^{3} A_i \exp(w_i t)$$

with

$$u(0) = 0 \quad \text{and} \quad Y_0 = \sum_{i=1}^{3} A_i$$

The coefficients A_i and w_i thus defined, allow a description of the response of the calorimeter by means of the following set of two linear equations, referred to as the "state equations":

$$\begin{aligned} \vec{X}_{[(k+1)T]} &= [\Phi_{(T)}] \cdot \vec{X}_{(kT)} + [D_{(T)}] \cdot \vec{W}_{(kT)} \\ \vec{\Theta}_{(kT)} &= [C] \cdot \vec{X}_{(kT)} \end{aligned} \tag{5}$$

where $\vec{X}$ is the column vector with k elements representing the state of the system at time t; $[\Phi]$, $[D]$ and $[C]$ are matrices characterizing the system and calculated from A_i and w_i; T is the data sampling period; and $\vec{W}$ and $\vec{\Theta}$ are the input and output functions, respectively.

In the second step of the procedure, the set of two linear equations, Eq. (5), is inverted, and thus allows reconstruction of the thermogenesis $\vec{W}_{(kT)}$ from any experimental output $\vec{\Theta}_{(kT)}$.

Differentiation method (numerical inverse filters) [14]. The relation between the measured output function $\Theta(t)$ and thermogenesis $W(t)$ may be represented by the following system of linear equations:

$$\begin{aligned} \Theta_1(t) &= \Theta(t) + \tau_1 \frac{\mathrm{d}\Theta(t)}{\mathrm{d}t} \\ \Theta_2(t) &= \Theta_1(t) + \tau_2 \frac{\mathrm{d}\Theta_1(t)}{\mathrm{d}t} \\ &\vdots \\ \Theta_n(t) &= \Theta_{n-1}(t) + \tau_n \frac{\mathrm{d}\Theta_{n-1}(t)}{\mathrm{d}t} \end{aligned} \tag{6}$$

where $W(t) = \lim_{n \to \infty} \Theta_n(t)$ and $\tau_1, \ldots, \tau_n$ are the calorimeter time-constants of successive orders. They can be determined during calibration experiments. In practical cases, a limited number of linear equations is used (1 to 3) and the corresponding calculations are easily performed on a microcomputer.

Experimental

General conditions of the tests. In order to compare the data-reconstruction methods under identical conditions, it was necessary to eliminate the variation caused by the individual features of the various calorimeters in the different laboratories. Therefore, during the 1st Colloquy on Thermokinetics, it was agreed to distribute to all participants the response of all the calorimeters to normalized series of heat pulses, generated by Joule effect in a heater.

Amplitude, length of the heat pulses, time-interval between pulses and sampling periods were defined in relative units, so that the same tests could eventually be reproduced in any calorimeter.

The value of the sampling period was taken as the time corresponding to 0.002 – 0.003 τ_1, τ_1 being the 1st-order time-constant of the calorimeter (Eq. (6)). The selected period could also be taken as ~1/300 of the half-time of the cooling period.

The length of the heat pulses and the time-interval between them were expressed in multiples of the sampling period.

The amplitude of the pulses was expressed in multiples of the mean amplitude of the random noise in the recorded data (thus originating from *both* the calorimeter and the data acquisition system), when the calorimetric vessel contains a thermally inert object.

Description of the tests. In order to determine the features of the different reconstruction methods unambiguously, 3 normalized tests were porposed (Fig. 1).

test *a:* reconstructions of a short heat pulse of high amplitude;

test *b:* reconstruction of a series of 3 heat pulses of increasing length (2 : 4 : 8) and decreasing amplitude (1000 : 100 : 10); the amplitude "10" of the

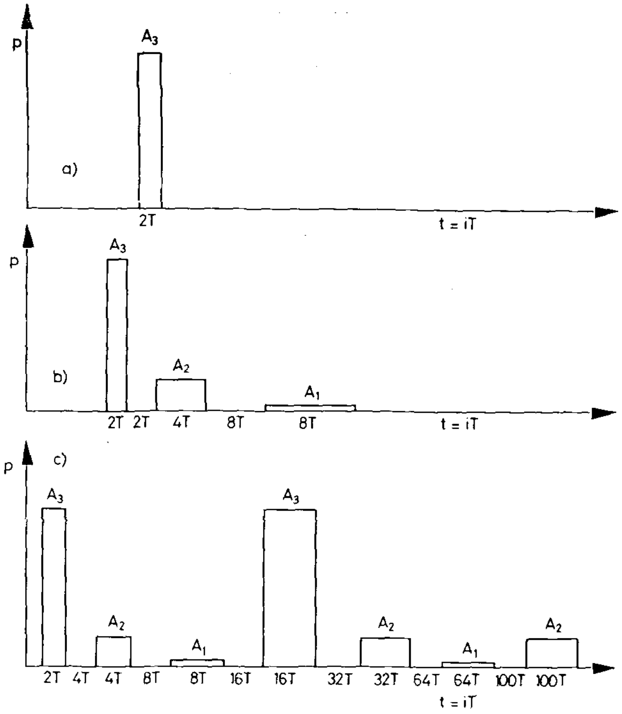

Fig. 1. Schematic representation of the calorimetric tests *a*, *b* and *c* (the ordinates are not drawn to scale)

pulse (or the smallest energy) was determined so that the maximum of the calorimeter response was about 10 times greater than the mean amplitude of the random noises of the system;

test *c*: reconstruction of a series of 7 heat pulses of various lengths and amplitudes.

The actual experiments, whose results in digital form were distributed to all participants, were carried out successively in a BMR-type calorimeter [15] and in a Tian-Calvet calorimeter [1].

The main features of the calorimeters and of the actual tests are summarized in Table 1.

Experimental data given by the BMR calorimeter were reconstructed by application of Fourier transform analysis (E. Cesari, J. Navarro, V. Torra), state functions theory (R. Point, J. L. Petit, P. C. Gravelle), dynamic oprimization (E. Utzig, J. Hatt, J. Gutenbaum, W. Zielenkiewicz) and the differentiation method (R. Point, J. L. Petit, P. C. Gravelle). Data from the Tian-Calvet calorimeter were reconstructed by Fourier transform analysis and differentiation (E. Cesari *et al.)* and dynamic optimization (E. Utzig *et al.*).

Table 1

Characteristic parameters of the data-reconstructions tests

Type of calorimeter	Sensitivity, mV · mW^{-1}	1st order time constant, s	Sampling period s	Minimal amplitude A_1 in tests *b* and *c* mW	Signal-noise ratio* in tests *a*, *b* and *c*
BMR	2.14×10^{-2}	860	3.0	*(b)* 7.26 *(c)* 7.26	*(a)* 3×10^2 *(b)* 4×10^2 *(c)* 3×10^3
Tian-Calvet	4.14×10^{-2}	751	2.0	*(b)* 25.5 *(c)* 2.6	*(a)* 1×10^4 *(b)* 2×10^4 *(c)* 2×10^4

* The quotient of the maximum of the calorimeter response and the mean amplitude of the noises.

Results and discussion

The results of the data reconstruction by the different methods are presented in Figs 2–7. In the discussion, it is particularly significant to discuss (i) the exactitude of the reconstructed time-sequence of heat pulses, (ii) the separation of heat pulses, and (iii) the reconstruction of the profile of the heat pulses.

In the case of a single pulse (test *a*, Figs 2 and 3), all methods correctly determine the time when the pulse was generated in the calorimeter. The dynamic optimization method and the method using state functions give better approximations of the pulse amplitude than the other methods, but in all cases a broadening remains in the reconstructed thermogenesis. Consequently, in this case, as in the case of all other tests reported below, the profile of the heat pulse is not reconstructed. This comes, *inter alia*, from the finite value of the sampling period and signal-to-noise ratio, which prevents the reconstruction of nearly vertical slopes such as generated when a Joule heating is switched on or out.

The amplitude of the heat effect under study, compared to that of noise in the data, is of particularly critical importance for the quality of the reconstruction. Data from the Tian-Calvet calorimeter, characterized by a better signal-to-noise ratio (Table 1, column 6) are more exactly reconstructed (Fig. 3) than those given by the BMR calorimeter (Fig. 2).

The first heat pulse in test *b* (Figs. 4 and 5) is reconstructed, by all methods, in a way which is identical to the reconstruction of the isolated heat pulse of test *a* (Figs 2 and 3). The following heat pulse, separated from the 1st one by 2 periods only, is reconstructed in an acceptable manner in Fig. 5 when the signal-to-noise ratio is high. This heat effect is not correctly reconstructed in the case of the BMR calorimeter, since it appears either as a shoulder, when correction is achieved by Fourier transform analysis and state functions, or as a separate heat effect, shifted by 2 sampling periods in the case of dynamic optimization. The differentiation

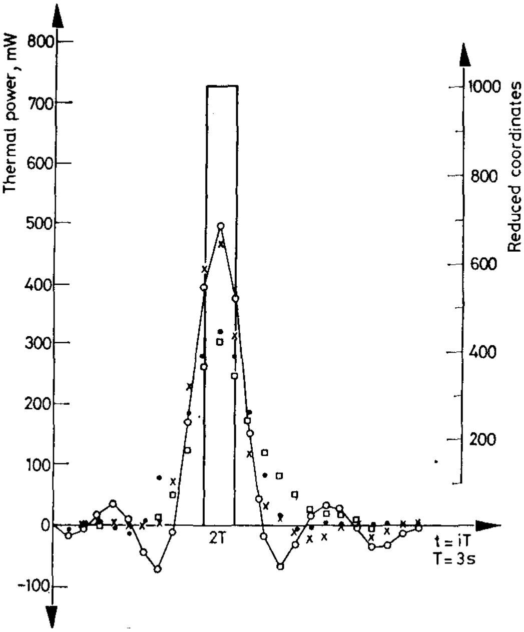

Fig. 2. BMR-type calorimeter, test *a*: reconstruction of a single heat pulse by dynamic optimalization (○), Fourier transform analysis (●), state functions (×) and data-differentiation (□)

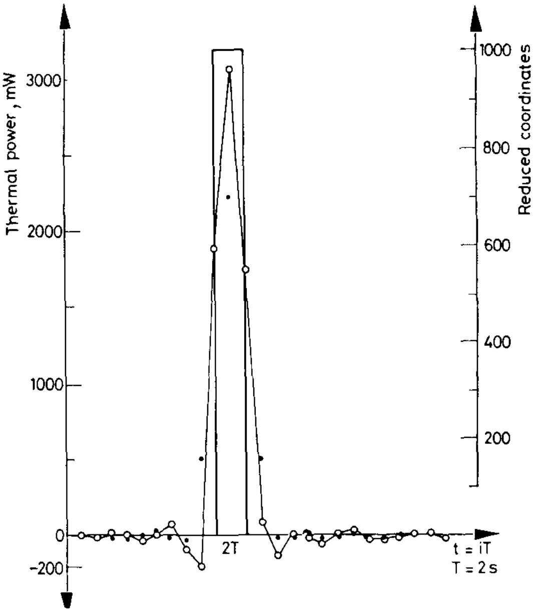

Fig. 3. Tian-Calvet calorimeter, test *a*: reconstruction of a single heat pulse by dynamic optimalization (○) and Fourier transform analysis (●)

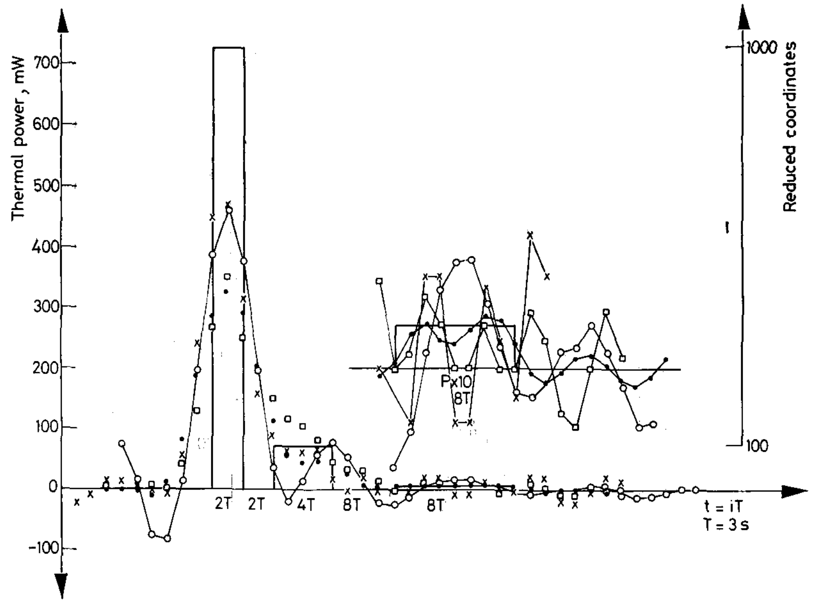

Fig. 4. BMR-type calorimeter, test *b*: reconstruction of a series of 3 heat pulses by dynamic optimalization (●), Fourier transform analysis (●), state functions (×) and data-differentiation (□)

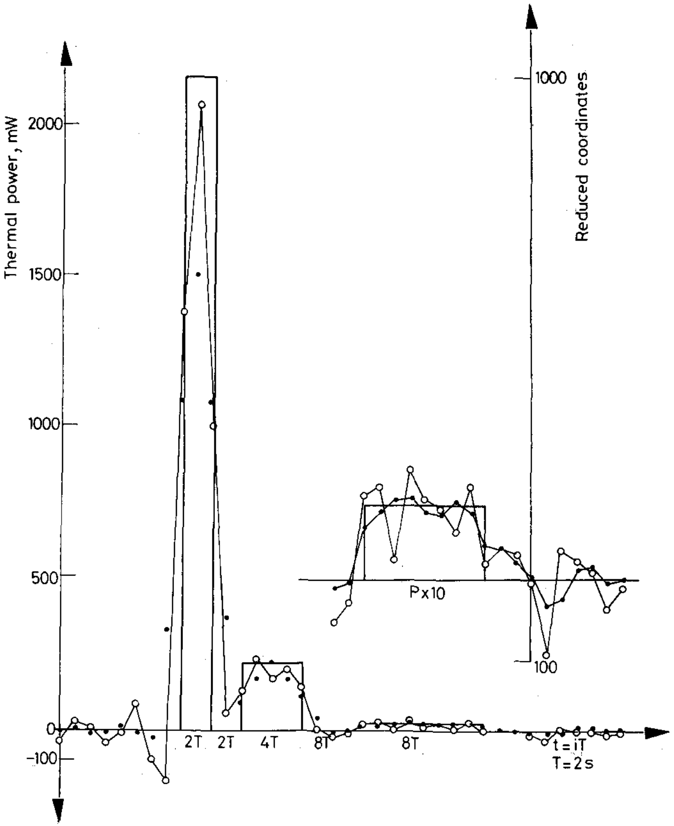

Fig. 5. Tian-Calvet calorimeter, test *b*: reconstruction of a series of 3 heat pulses by dynamic optimalization (o) and Fourier transform analysis (●)

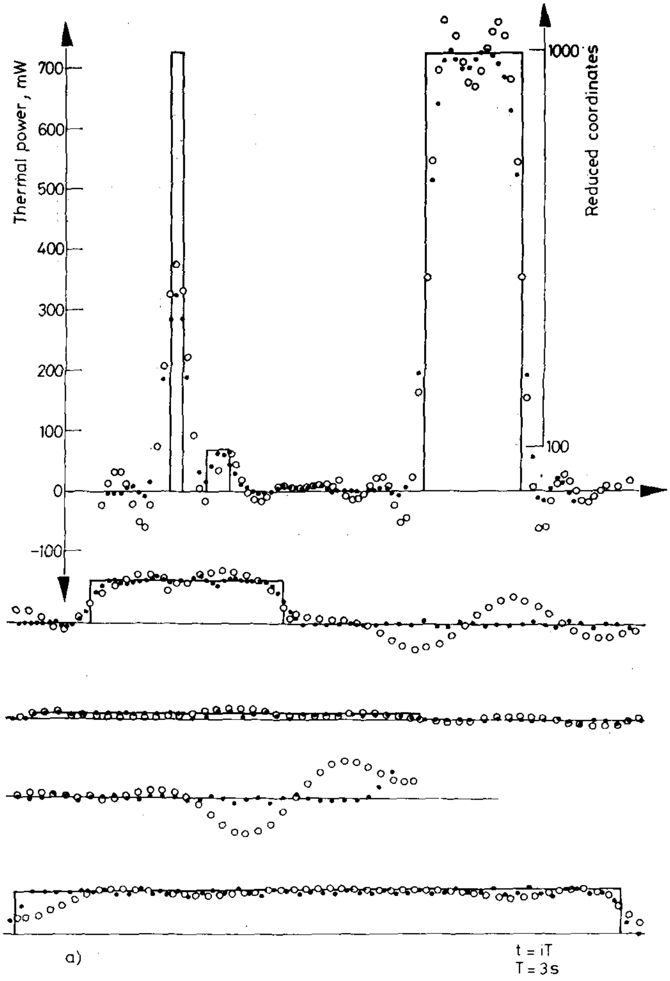

Fig. 6

method, which in these experiments was limited to the correction of the 1st-order time constant (τ_1), shows the poorest resolution. These results indeed confirm and amplify previous experiments [13] showing that the reconstruction method based on state functions can not resolve kinetics phenomena separated by a time interval smaller than 3 sampling periods.

The third impulse, of small amplitude, in test *b* was not reconstructed (but may be by Fourier transform analysis) in the case of BMR-calorimetric data (Fig. 4). Reconstruction is satisfactory in the case of the Tian-Calvet calorimeter (Fig. 5) as a consequence of the good signal-to-noise ratio.

In the case of tests *c* (Figs 6 and 7), all the methods separate and correctly locate the successive heat pulses. The differentiation method, again limited to a 1st-order

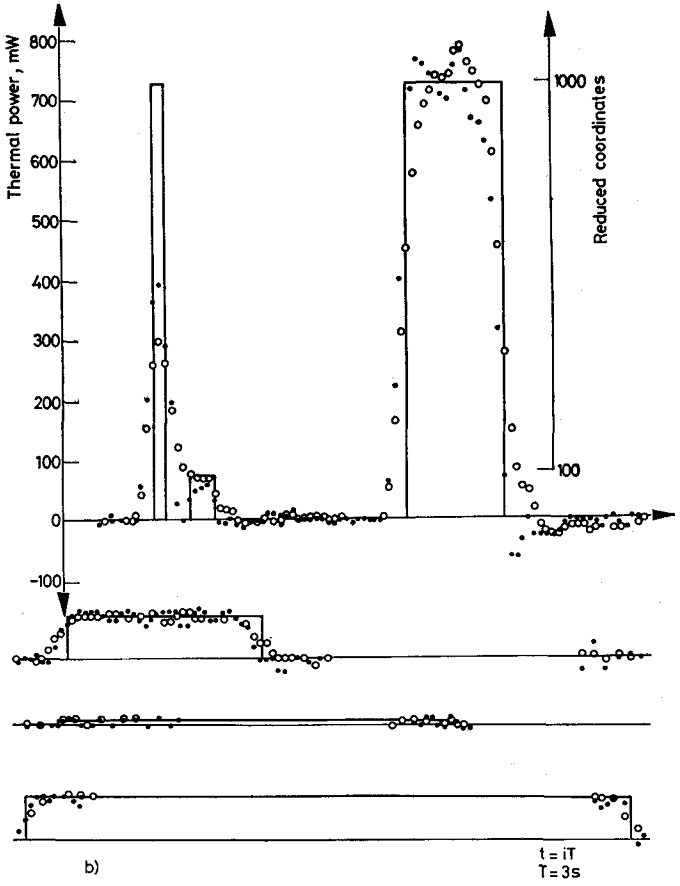

Fig. 6. BMR-type calorimeter, test *c*: reconstruction of series of 7 heat pulses by (Fig. 6a) dynamic optimalization (○), Fourier transform analysis (●) and (Fig. 6b) state functions (×), data-differentiation (□)

correction, is unable to resolve the two heat pulses separated by only 4T (Fig. 6b). Fourier transform analysis and state functions give very comparable results. However, the dynamic optimization method appears to be less adapted than the preceding methods in the reconstruction of long time-series of data: as already indicated, in this method reconstruction is achieved by the minimization of a function which has as many variables as samples in the experimental data series. When the number of points increases, the convergence of the minimization algorithm decreases.

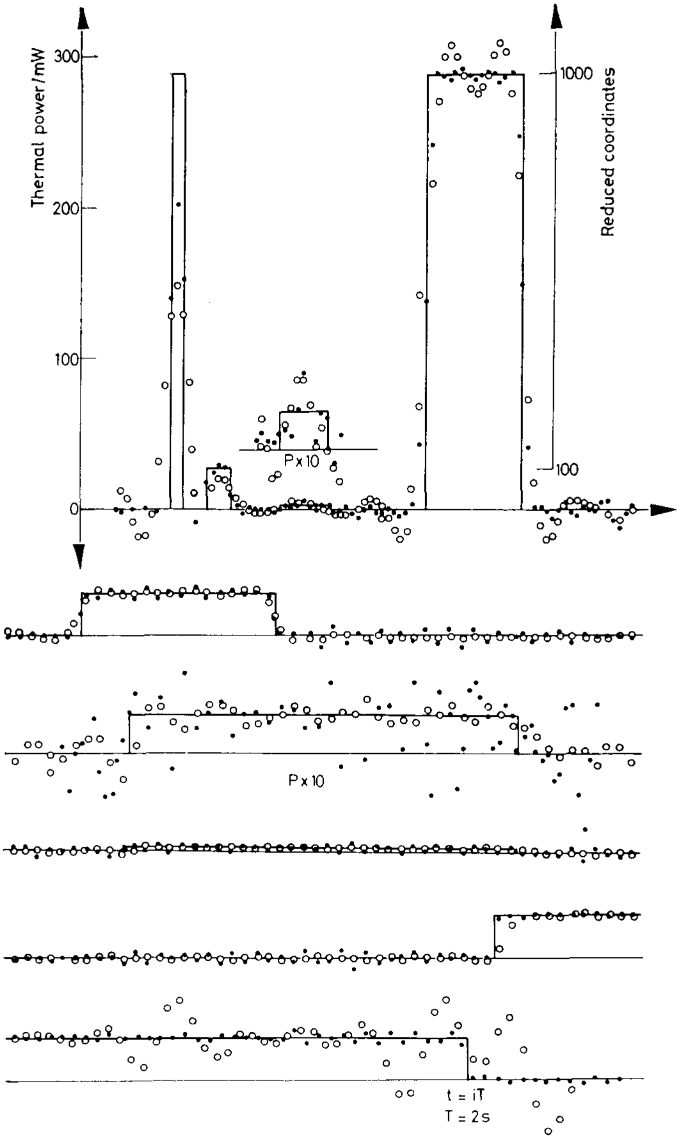

Fig. 7. Tian-Calvet calorimeter, test *c*: reconstruction of a series of 7 heat pulses by dynamic optimalization (○) and Fourier transform analysis (●)

Conclusions

At the end of the concerted programme on the reconstruction methods, it is not possible to recommend specifically the usage of one of the methods, nor even to propose a quantitative estimate on the quality of the different methods. A few remarks, however, may be made.

I. The presented results indicate that the applied numerical methods show a considerable progress in the reconstruction of thermogenesis. It is clear that the objective is not the complete reconstruction of thermogenesis for kinetic studies, but rather the decrease of the influence of thermal lags in the calorimetric data; thus, after reconstruction, the residual time-constant which appears in the data is ~200 times smaller than the actual 1st-order time-constant of the instrument used.

II. It appeared that the general conditions of the experiments proposed to compare the data reconstruction methods were useful, viz. multiples of the 1st-order time-constant for the time-scale and multiples of the noise level for the thermal power.

III. All methods are equally sensitive to noise in the data, which limits the quality of the reconstruction and especially its resolution. Data-smoothing procedures and sampling periods selected with particular care [13, 17] would be advisable.

IV. The ranges of application of the presented methods are different. The optimization method shows its advantage especially in cases when the number of experimental data need not be greater than 100–150. The Fourier transform analysis, state function method and numerical inverse filter are not influenced by such limits and may freely be applied for the reconstruction of effects requiring a great number of data.

V. The presented numerical methods have to be carried out by using computers or minicomputers. In the case of tests *a*, *b* and *c*, the following memory space of the computer was used consequently: for state functions 8 Kwords, for Fourier transform analysis 30 Kwords, for dynamic optimization 3.5, 4.4 or 8.8 Kwords, and for the 1st-order differentiation method 8 Kwords.

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RÉSUMÉ — Les résultats d'un programme de recherches concerté multinational sur la détermination des données thermocinétiques sont présentés. Le but du programme était de comparer différentes méthodes numériques proposées indépendamment pour la détermination des données thermocinétiques à partir des mesures calorimétriques expérimentales. Pour celà, les mêmes données expérimentales fournies par deux calorimètres à flux de chaleur ont été distribuées et analysées successivement par 4 méthodes: utilisation des variables d'état, analyse de la transformée de Fourier, optimalisation dynamique et simple différentiation des données.

ZUSAMMENFASSUNG — Es wurden die Ergebnisse der gemeinsamen Arbeiten über die Bestimmung der Thermokinetik mit 4 numerischen Methoden (dynamische Optimalisierung, Methode der Zustandfunktionen, harmonische Analyse und umgekehrte Korrektion) vorgestellt. Die experimentellen Daten wurden mit Hilfe von 2 Kalorimetern mit einer konstanten Temperatur des Isoliermantels ermittelt. Die Durchführung der Versuche ermöglichte ein Vergleich der angewandten Methoden.

Резюме — Представлены результаты определения термокинетических параметров согласно международной программы. Основной целью программы являлось сопоставление различных численных методов, независимо представленных для определения термокинетических данных из экспериментальных калориметрических измерений. С этой целью одни и теже экспериментальные данные, полученные от двух теплопоточных калориметров, были классифицированы и последовательно проанализированы различными методами. Критически проведены численные методы, основанные на теории функций, Фурье анализе, динамической оптимализации и простом дифференцировании данных.