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RECONSTRUCTION OF THERMOKINETICS FROM CALORIMETRIC DATA BY MEANS OF NUMERICAL INVERSE FILTERS

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A simple method for removing the distortion due to thermal lags from calorimetric curves is described and tested. The method is based upon the use of numerical inverse filters. Its results are equivalent to those of the more sophisticated deconvolution methods, using Fourier transform analysis or state function theory. The new method is easily adapted to the on-line reconstruction of calorimetric data by means of a microprocessor.

The calorimetric determination of the kinetics of fast reactions is often hindered by the distortion in the calorimetric curves which is caused by thermal lags in the instrument.

However, several methods are available to correct ("to reconstruct") the calorimetric curves:

(1) a graphical method [1];
(2) (automatic) analog methods [2–7];
(3) numerical methods, based on Fourier transform analysis [8–9] or state function theory [10–12].

The graphical methods is simple and yields acceptable results. However, its application requires long and strenuous work which, moreover, must be accomplished after the calorimetric data have been completely collected ("off-line") [1].

Correction by analog methods can be achieved "on-line". Results are good; however, the instruments performing the reconstruction must be manually adjusted for each calorimeter and even for each new experiment. Moreover, the analog signal should be amplified when a multi-stage correction system is used, with an unavoidable increase of the noise level [2–7].

Numerical methods also yield good results. When Fourier transform analysis is used, the correction must be achieved off-line and, in the case of long experiments, a medium-sized computer (~ 16 Kbytes for 2000 points) must be available [8–9]. The representation of the calorimetric system (calorimeter and data-acquisition line) by state functions and the resulting data reconstruction may be performed on-line [10–12]. The method requires a smaller-sized memory than the method based on Fourier transform analysis. However, both numerical methods are equally sensitive to noise in the data.

An ideal calorimetric data-reconstruction method should be simple to use and adapted to on-line correction. The corrected data should never contain abnormal information (like overshoots, for instance) that could lead to physically meaningless interpretation. The kinetics of the phenomenon under study should be reconstructed precisely and information on heat production should be preserved accurately. The numerical reconstruction method which is described in the first part of this article has been tested with respect to these different criteria. The experimental results of the tests are presented in the second part of the article.

Description of the reconstruction method

The pulse response of a heat-flow calorimeter may be written [13]:

$$h(t) = \sum_{i=1}^{\infty} a_i e^{-t/\tau_i} \quad \text{with} \quad \sum_{i=1}^{\infty} a_i = 0 .$$

The step response, defined as:

$$u(t) = \int_0^{\infty} h(t)\,\mathrm{d}t,$$

may therefore be written:

$$u(t) = \sum_{i=1}^{\infty} a_i \tau_i e^{-t/\tau_i} + K . \tag{1}$$

Since the following boundary conditions must be obeyed:

$$\begin{array}{ll} t \to \infty & u(t) = K \\ t = 0 & u(t) = 0 \end{array}$$

it follows that $\Sigma a_i \tau_i = -K$, and Eq. (1) becomes:

$$u(t) = \sum_{i=1}^{\infty} a_i \tau_i (1 - e^{-t/\tau_i}) . \tag{2}$$

Let us suppose that the calorimeter may be represented by a 1st-order system. Then:

$$h(t) = a e^{-t/\tau}$$

and

$$u(t) = A(1 - e^{-t/\tau}) \qquad \text{with } A = a\tau .$$

The transfer function $H(p)$ of the (linear) system, defined in Laplace coordinates by $S(p) = H(p) \cdot E(p)$, $S(p)$ and $E(p)$ being the Laplace transforms of respectively the calorimeter output and input functions, is identical to the pulse response of the system:

$$H(p) = \frac{a}{p + 1/\tau} .$$

Therefore: $$E(p) = S(p)\cdot 1/H(p) = \frac{1}{a}\left[S(p)\cdot\left(p+\frac{1}{\tau}\right)\right]$$

and $$E(t) = \frac{S(t)}{a\tau} + \frac{\mathrm{d}S(t)}{a\,\mathrm{d}t} = \frac{S(t)}{A} + \tau\frac{\mathrm{d}S(t)}{A\,\mathrm{d}t}.$$

If A is normalized to 1, then:

$$E(t) = S(t) + \tau\frac{\mathrm{d}S(t)}{\mathrm{d}t} \tag{3}$$

Equation (3) is a generalized form of Tian's equation [14]. According to Eq. (3), the reconstruction of the input function, $E(t)$, requires 3 simple operations (a differentiation, a multiplication by a constant factor, and a summation). When the calorimeter is equivalent to a 2nd-order system, the same operations may be repeated a second time, using $E(t)$ from Eq. (3) as the (partially reconstructed) output.

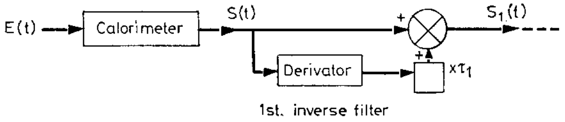

Fig. 1. Schematic representation of the calorimeter and inverse filter system

Let us now consider the system schematically represented in Fig. 1, the pulse response of the calorimeter being:

$$h(t) = \sum_{i=1}^{\infty} a_i e^{-t/\tau},$$

as already indicated. At the output of the first inverse filter, the response becomes:

$$h_1(t) = \sum_{i=1}^{\infty} a_i e^{-t/\tau_i} - k_1\sum_{i=1}^{\infty}\frac{a_i}{\tau_i}e^{-t/\tau_i}.$$

If $k_1 = \tau_1$, the first term in the analytical expression of the pulse response disappears and therefore:

$$h_1(t) = a_2\left(1-\frac{\tau_1}{\tau_2}\right)e^{-t/\tau}\tau_2 + a_3\left(1-\frac{\tau_1}{\tau_3}\right)e^{-t/\tau}\tau_3 + \dots.$$

Distortion of the calorimeter output, due to the 1st-order time constant, has thus been corrected. The second inverse filter could, in turn, correct the data from the distortion caused by the 2nd-order time constant, etc.

This reconstruction method, which, in the present study, has been developed by means of a digital computer, is identical to the method based on the state function theory, in the case of a 1st-order linear system [10]. In the case of 2nd- or 3rd-order systems, this numerical method is equivalent to the previously described, analog methods using RC circuits, amplifiers, etc. [4–7].

Development and testing of the reconstruction method

In the development of the method, two stages may be distinguished: the identification and the correction. Both stages were performed, off-line, by means of a T-2000 computer.

Identification stage: The object of the identification stage is to determine the calorimeter time constants, τ_i, from the response to a unit step. The 1st-order time constant is determined from the recorded response (if A is the maximum amplitude of the response of a 1st-order system to a unit step, the time constant is the time required for the response to attain an amplitude equal to $A[1 - 1/e]$). It is then used to correct the recorded response from 1st-order distortion and, from the partially corrected response, the 2nd-order time constant may be calculated. The same operations may be repeated, if necessary, to determine higher-order time constants. The flow chart summarizing the identification procedure is presented in Fig. 2.

Three methods for the determination of the maximum amplitude A have been tested and compared (Fig. 3), namely (i) the average value of the last 10 points; (ii) the last recorded point; and (iii) Bureau's method [15]. The last method gives excellent results as soon as the number of recorded points corresponds to a time

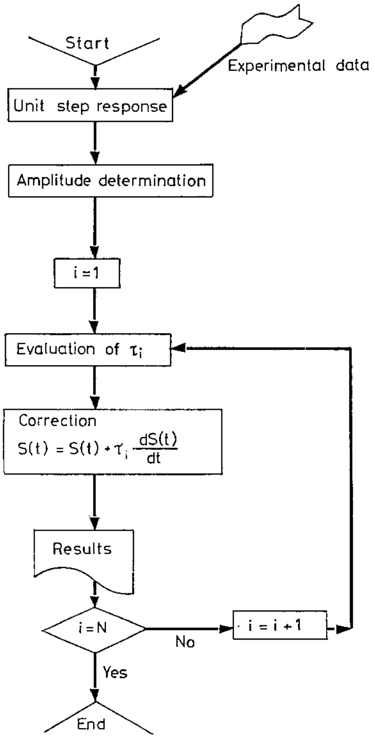

Fig. 2. Flow chart for the determination of the time constants (identification stage)

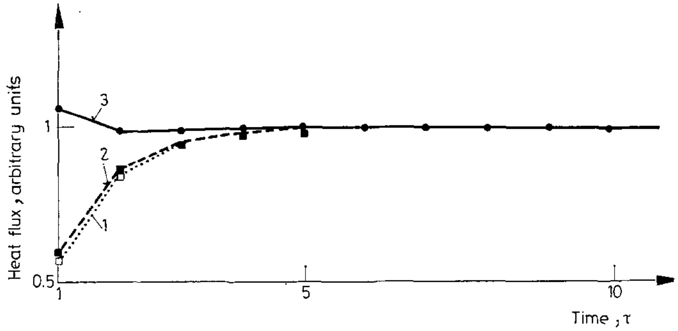

Fig. 3. Determination of the maximum amplitude A: 1 — average value of the last 10 recorded points; 2 — last recorded point; 3 — application of Bureau's method [15]

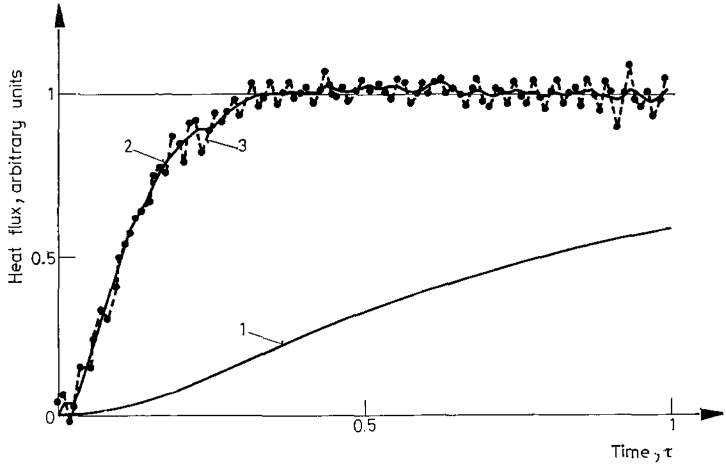

Fig. 4. Tests of derivation sub-programmes: 1 — experimental unit step response; 2 — correction after application of SP_1; 3 — correction after application of SP_2 (see text)

exceeding twice the time constant, i.e. this method does not require, as the methods mentioned in (i) and (ii), the complete record of the calorimeter response. It is moreover insensitive to noise, and independent of the value of the sampling frequency. For these reasons, Bureau's method was selected, in the following experiments, when the determination of A was required.

The numerical derivation which is required (Eq. (13), Fig. 2) inevitably leads to some increase of the noise level. Two sub-programmes of derivation were tested:

$$SP_1, \quad \text{where } \frac{d\gamma(3)}{dt} = \frac{1}{8T}\,[\gamma(5) - \gamma(1) + 2\gamma(4) - 2\gamma(2)]$$

$$SP_2, \quad \text{where } \frac{d\gamma(3)}{dt} = \frac{1}{12T}\,[\gamma(1) - 8\gamma(2) + 8\gamma(4) - \gamma(5)].$$

T is the sampling period. The results in the case of the 1st-order correction of an experimental unit step are presented in Fig. 4; SP_1, which gives the best results, was used thereafter.

Correction stage: The object of the correction stage is to apply Eq. (3) to each experimental point, first with τ_1, then with higher-order time constants. Figure 5 shows the results in the case of the correction of the response of a Calvet type calorimeter to a unit step. Oscillations appear in the corrected data when a 2nd-

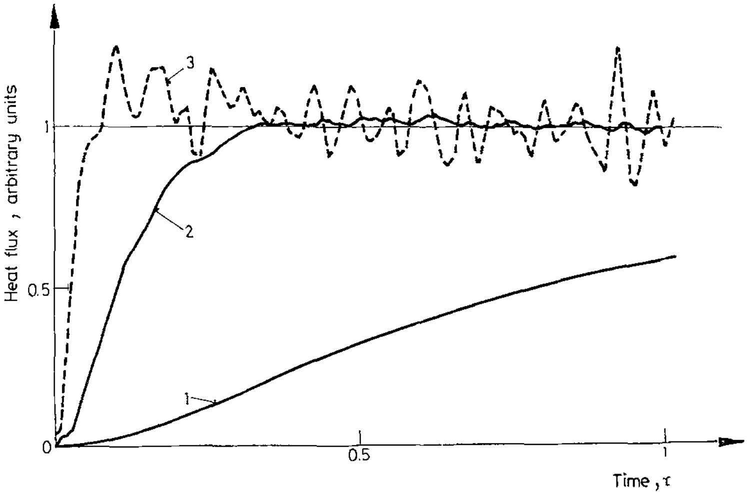

Fig. 5. Reconstruction of a unit step by means of numerical inverse filters: 1 — experimental unit step response; 2 — 1st-order correction; 3 — 2nd-order correction

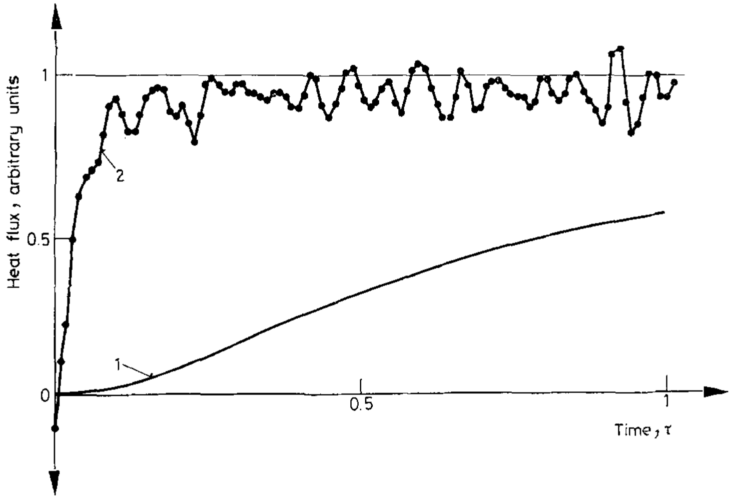

Fig. 6. Reconstruction of a unit step by application of the method based on state functions [10]; 1 — experimental response; 2 — reconstructed step

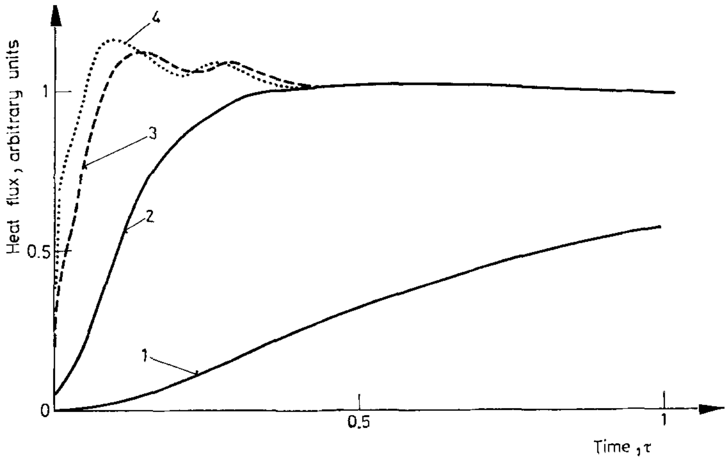

Fig. 7. Influence of data-smoothing before correction: 1 — experimental unit step response; 2 — 1st-order correction; 3 — 2nd-order correction; 4 — 3rd-order correction

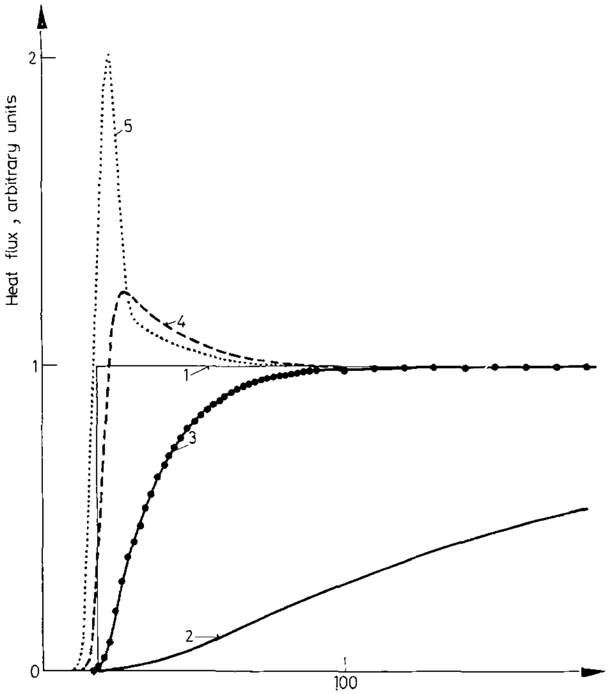

Fig. 8. Reconstruction of a unit step by means of numerical inverse filters: 1 — simulated input; 2 — simulated unit step response; 3 — 1st-order correction; 4 — 2nd-order correction; 5 — 3rd-order correction ($\tau_1 = 190$ s, $\tau_2 = 36$ s, $\tau_3 = 18$ s)

order correction is applied; a 1st-order correction, however, leaves some residual distortion, as expected (for comparison purposes, the same data, corrected by application of the state function theory [12], are presented in Fig. 6).

In order to decrease the oscillations, the same data were smoothed before the 1st-, 2nd- and 3rd-order corrections. The results presented in Fig. 7 show that data-smoothing has very little influence on the 1st-order correction, but that it

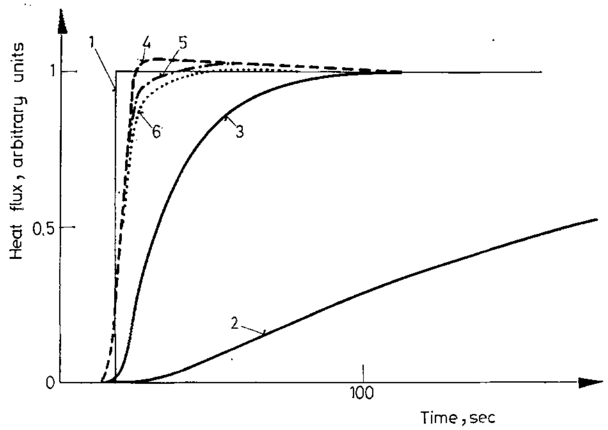

Fig. 9. Influence of a damping coefficient: 1 — simulated input; 2 — simulated unit step response; 3 — 1st-order correction; 4 — 2nd-order correction with $k_2 = 0.50$; 5 — 2nd-order correction with $k_2 = 0.45$; 6 — 2nd-order correction with $k_2 = 0.40$

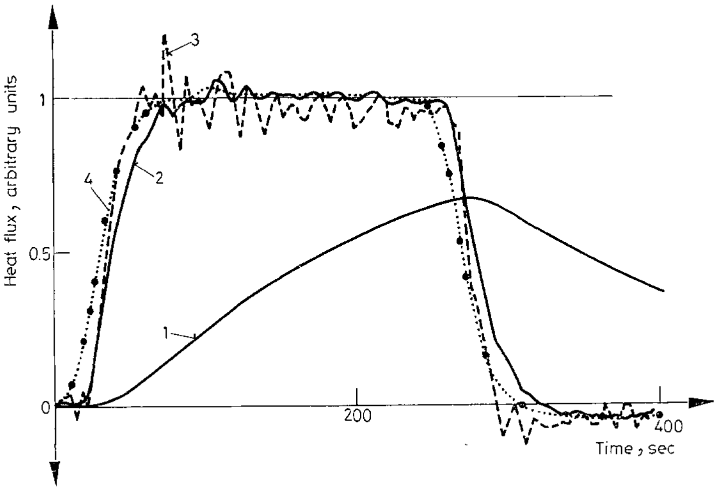

Fig. 10. Reconstruction of a square signal produced by Joule heating (240 s, 795 μW): 1 — experimental calorimetric curve; 2 — correction by a numerical inverse filter (1st-order); 3 — correction by application of the state functions [12]; 4 — correction by numerical inverse filters (2nd-order and a damping coefficient)

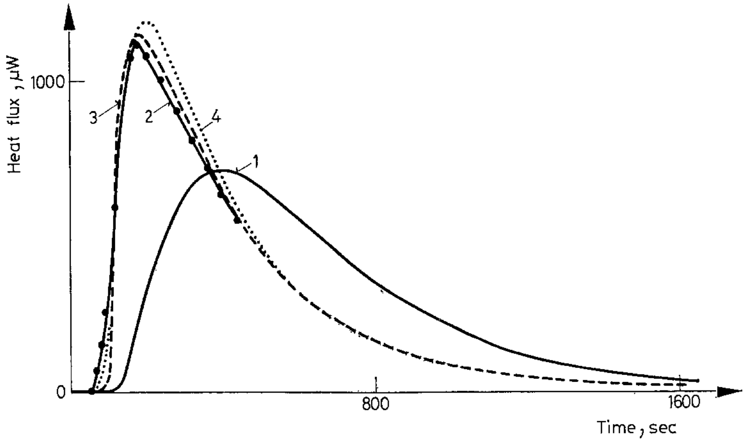

Fig. 11. Reconstruction of a calorimetric curve produced by the decomposition of a dose of nitrous oxide on a sample of nickel oxide at 473 K [16]: 1 — experimental calorimetric curve; 2 — correction by application of Fourier transform analysis [9]; 3 — correction by application of the state functions [12]; 4 — correction by numerical inverse filters ($\tau_1 = 202$ s, $\tau_2 = 10$ s, $k_2 = 0.40$)

does indeed abate noise in the case of a 2nd-order or even 3rd-order correction. However, overshoots clearly remain, which ought to be removed since they could lead to erroneous interpretations. The origin of overshoots has been traced to the derivation procedure which is used, and not to noise in the experimental data. For instance, Fig. 8 shows that, even in the case of a simulated calorimeter response to a unit step, free therefore from noise, high-order corrections (2nd- and 5th-order) still exhibit overshoots.

The relative importance of the overshoot can be decreased by applying a damping coefficient to the calculated high-order time constants. In Fig. 9, different values of the damping coefficient, k_2, have been tested in the 2nd-order correction of a simulated unit step response. In these experiments, the 2nd-order time constant was taken equal to $k_2\tau_2$. When $k_2 = 0.40$, the overshoot disappears almost completely and the reconstruction of the unit step is then correct. This value of the damping coefficient was therefore used in the case of the reconstruction of the experimental calorimetric curves presented in Figs 10 and 11, since the time-constants selected for the simulated experiments were purposely similar to those determined for the real calorimeter.

In the case of the reconstruction of a square signal produced by the Joule effect in a heater (Fig. 10), or in the case of the reconstruction of the calorimetric curve produced by the decomposition of nitrous oxide on a sample of nickel oxide at 473 K (Fig. 11) [16], the correction by means of a numerical inverse filter yields results which are equivalent to those obtained by means of the previously published reconstruction methods. In particular, the activity constants which may be calculated [16] from the descending branches of the corrected calorimetric curves (Fig. 11), when different reconstruction methods are used, are constant to within 5%, i.e. within the expected incertitude of the chemical experiment. For its application, however, the present method requires much less time and computer memory space than the preceding ones.

Conclusions

The reconstruction method described in this article, based on the application of a numerical inverse filter, though very simple, yields results which are equivalent to those of more sophisticated methods [8–12]. Compared to (automatic) analog correction methods [4–7], the present method offers two advantages: (i) manual adjustments are avoided since the identification of the calorimeter system is numerically achieved, and (ii) no additional amplification of the calorimeter output signal is needed when high-order correction is applied. Because of its simplicity, this new method is well adapted to the on-line correction of calorimetric data by means of a microprocessor. Such a data-acquisition and correction system, making use of a Z80 microprocessor, has indeed been constructed and tested [17].

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15. Bureau's method: when s(t) is an exponential function: $s(t) = A(1-e^{-t/\tau})$, it is possible to calculate A from a set of 3 points S_1, S_2, S_3, separated by identical time-intervals, by means of the formula:

$$A = \frac{S_2^2 - S_1S_3}{2S_2 - (S_1 + S_3)}$$

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Résumé — Une méthode simple pour la correction de la distorsion des courbes calorimétriques, amenée par l'inertie thermique, est décrite et éprouvée. La méthode est basée sur l'emploi de filtres numériques inverses. Les résultats obtenus sont équivalents à ceux fournis par des méthodes plus complexes de déconvolution, utilisant l'analyse harmonique ou la théorie des variables d'état. La nouvelle méthode peut être facilement adaptée à la correction simultanée des courbes calorimétriques au moyen d'un microprocesseur.

Zusammenfassung — Eine einfache Methode zur Beseitigung der infolge thermischer Hysterese-Effekte entstandenen Verzerrungen kalorimetrischer Kurven wurde beschrieben und geprüft. Die Methode beruht auf der Anwendung numerischer Inversfilter. Die Ergebnisse sind den durch verfeinertere Dekonvolutionsmethoden unter Einsatz der Analyse durch Fouriertransformation oder durch die Zustandsfunktionstheorie erhaltenen gleichwertig. Die neue Methode läßt sich der on-line Erfassung kalorimetrischer Daten durch einen Mikroprocessor leicht anpassen.

Резюме — Описан и проверен простой метод для удаления нарушения из калориметрических кривых, которое вызвано термическими запаздываниями. Метод основан на использовании численных обратных фильтров. Результаты этого метода эквивалентны результатам, полученным более усложненными деконволюционными методами при использовании Фурье- преобразования и теории функций. Новый метод легко адаптируется к перестройке на линии связи с ЭВМ калориметрических данных с помощью микропроцессора.