*Journal of Thermal Analysis, Vol. 11 (1977) 431—444*

# AN IMPROVED METHOD FOR THE DETERMINATION OF THE INPUT APPLIED TO A LINEAR SYSTEM BY DECONVOLUTION OF THE OUTPUT. APPLICATION IN THERMOKINETICS

R. POINT, J. L. PETIT* and P. C. GRAVELLE**

* *Département d'Informatique, Institut National des Sciences Appliquées,*

*69621 Villeurbanne; ** Institut de Recherches sur la Catalyse, CNRS, 69626 Villeurbanne, France*

(Received November 20, 1976)

A simplified deconvolution procedure which can be used to remove the distortion, due to thermal lags, from calorimetric data is described and tested. The procedure is based on the state function theory. Noise in the deconvoluted data can be abated by smoothing the experimental data and by a careful choice of the data-sampling frequency. The method is adaptable to on-line processing by means of a microprocessor.

The general deconvolution technique proposed by Brie, Gravelle and Petit [1, 2] allows one to determine the input function applied to a linear system when the output function is known. This technique may be used for the deconvolution of any instrumental data, provided that the instrument behaves as a linear transducer with localized and invariant constants, but it is especially suitable for removing, from calorimetric data, the distortion due to thermal lags in the calorimeter [3].

The different steps of the deconvolution procedure are summarized in the function chart presented in Fig. 1. In the computer program previously used [1, 2]. Part II (determination of the input from a known output) (Fig. 1) was completely automated. However, Part I (model building and identification) (Fig. 1) required a skilled operator to manually adjust parameters when some convergence criteria were fulfilled. This procedure is acceptable in the case of invariant systems since they require a single identification operation, but it is not adapted to the study of linear systems characterized by a variable structure. This is indeed the case in calorimetry since the arrangement of the calorimeter vessel must change with any particular experiment.

In the present article, a simplified deconvolution procedure which has been completely automated is described and tested.

---

** To whom all correspondence concerning this article should be sent

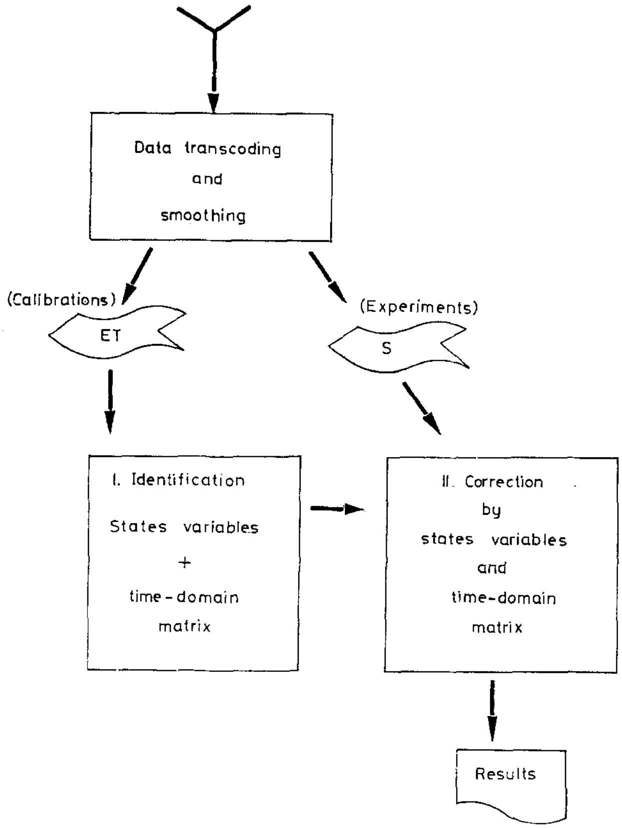

Fig. 1. Schematic representation of the different operations required by the deconvolution procedure

## Description of the simplified identification and deconvolution procedures

The diagram of the new procedure is presented in Fig. 2. The determination of the time-domain matrix (blocks 6, 7 and 8, Fig. 2) is presented in the chart but may be avoided. The different parts of the computer program have been modified in the following way:

### *Identification*

Block 1: The experimental data (e.g. the calorimeter response) recorded in a binary code, e.g. on punched paper tape, are first transcoded. An interpolation program is then used to correct the stray point. Smoothing of the data is finally achieved by means of the following formula:

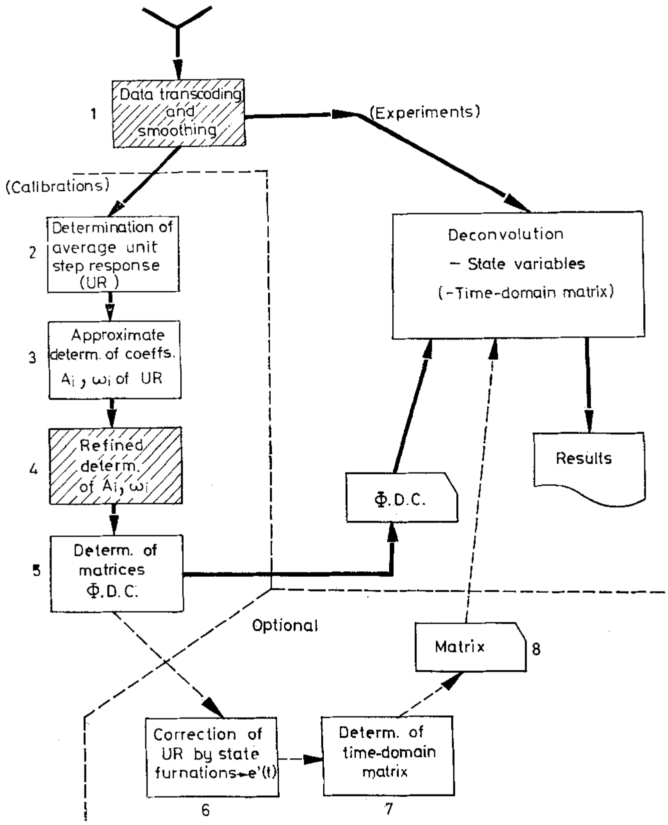

Fig. 2. Diagram of the simplified indentification and deconvolution procedure (shaded blocks are described in the present article; open blocks were described in [3]

$$y_i^* = \frac{1}{429}(18y_{i-5}-45y_{i-4}-10y_{i-3}+60y_{i-2}+120y_{i-1}+143y_i+120y_{i+1}+60y_{i+2}-$$
$$-10y_{i+3}-45y_{i+4}+18y_{i+5})$$

At the initial time, $y_{i-5}, \ldots, y_{i-1}$ are set to 0 and when $y_i = 0$, $y_i^*$ is automatically set to 0.

Blocks 2 and 3: The average unit step response (*UR*) of the system is calculated from the calorimeter responses to thermal steps recorded during *four* identical Joule heatings [1, 2].

The coefficients $A_i$ and $w_i$ are the then deduced from the average unit step response, using the formula:

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

Block 4: The refined determination of coefficients $A_i$ and $w_i$ was previously achieved by means of a non-linear regression routine. This program was often time-consuming and did not appreciably improve the results. A new program, based on the Gradient Method [4], is now used, in which the operator still has to define the variation intervals of the 6 coefficients (in the case of a 3rd-order model) but which thereafter automatically changes the initially defined variation interval and determines the best stepping increments to minimize the total quadratic error, calculated on the total number $N$ of points selected for this procedure.

Although this method may still end in a secondary minimum, it rapidly yields acceptable results. In the case of $N = 100$ points, for instance, the total quadratic error which, before this procedure, was 0.050 decreases to 0.019 after it. The amount of noise in the experimental data being considered, this result is acceptable.

Block 5: The previously described program, which is used to determine the matrices $\phi$, $D$ and $C$ of the following equations:

$$\begin{cases} \overrightarrow{X[k+1)T]} = \phi(T) \cdot \overrightarrow{X[kT]} + D(T) \cdot \overrightarrow{e'(kT)} \\ \overrightarrow{u(kT)} = C \cdot \overrightarrow{X(kT)} \end{cases} \tag{2}$$

(where $T$ is the sampling period and $\vec{X}$, the state vector (phase variable), from the coefficients $A_i$ and $w_i$, has not been modified [1, 2].

Blocks 6, 7 and 8: This part of the former program [1, 2], which used to require a long time in the central processing unit, is now passed over, at least when the calorimeter response is defined by less than 250 points.

To summarize, the improved deconvolution program involves the following operations:

a) determination, from the experimental data, of the theoretical unit step response, according to Eq. (1),

b) determination of the corresponding input $e'(t)$ by means of Eq. (2).

Finally, it is possible, but not always necessary, to determine the elements of the time-domain matrix, $M$:

$$e(t) = M \cdot e'(t) \tag{3}$$

*Deconvolution* (Fig. 2)

This part of the program, which is used to correct the experimental data from instrumental distortion due to thermal lags, once identification of the system has been performed, has not been modified [1, 2]. If needed, a preliminary smoothing of raw data may be achieved according to the following equation:

$$y_i^* = \frac{1}{4}(y_{i-1} + 2y_i + y_{i+1}) \tag{4}$$

The operator may then select a program using state variables only or add to it an additional program involving the use of the time-domain matrix. Deconvoluted data are presented either in numerical tables where input, output and intermediate values are collected, or in diagrams.

## Tests of the simplified deconvolution procedure

### *Simulated tests*

In a first series of tests, the intrinsic efficiency of the method has been determined by means of simulated time series. In these tests, the simulated transfer function of the system is identical to that of an actual TIAN-CALVET calorimeter [5] but the calorimeter response contains no stray points nor noise. Another advantage of these tests is, of course, that any input function may be simulated.

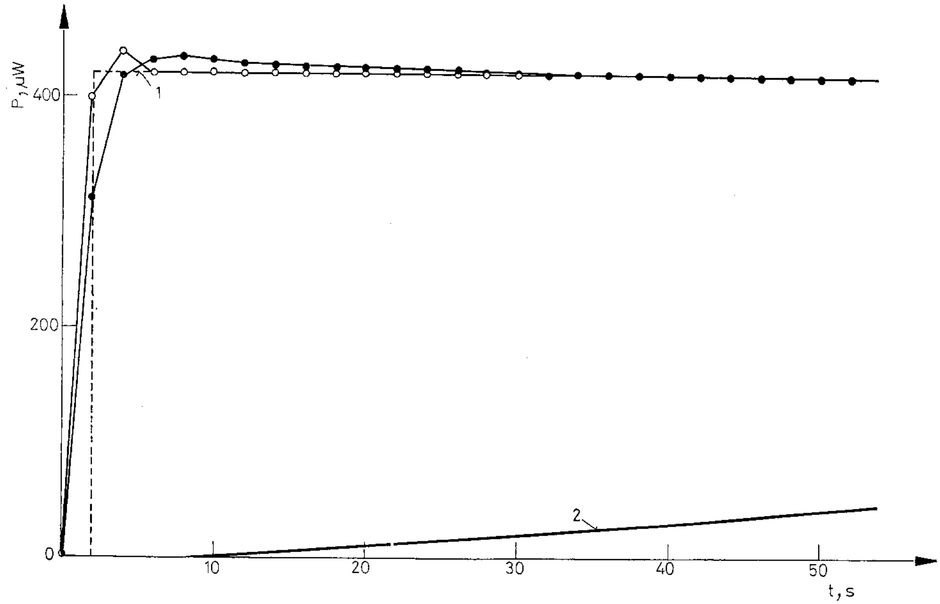

Fig. 3. Correction of simulated calorimetric curves: simulated calorimetric response (curve 2) to a step (curve 1); input reconstructed by the general (●) and simplified (○) deconvolution methods (sampling period: 2 s; thermal power: 423 μW)

Figures 3 to 5 present the input function, the simulated calorimeter response and the reconstructed input function in the case of a step or pulses of different lengths but of a given amplitude. It is clear that the use of the time-domain matrix program in the general deconvolution method does not yield a better reconstruction of the input than the simplified method. These results indicate morever that,

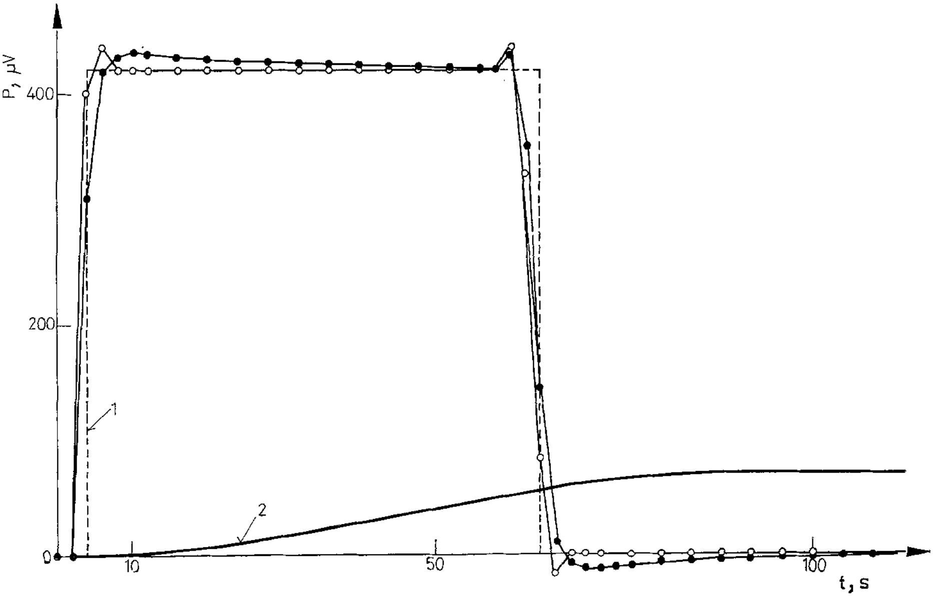

Fig. 4. Correction of simulated calorimetric curves: simulated calorimetric response (curve 2) to a pulse (curve 1, 60 s, 423 µW); input recontructed by the general (●) and simplified (○) deconvolution methods (sampling period: 2 s).

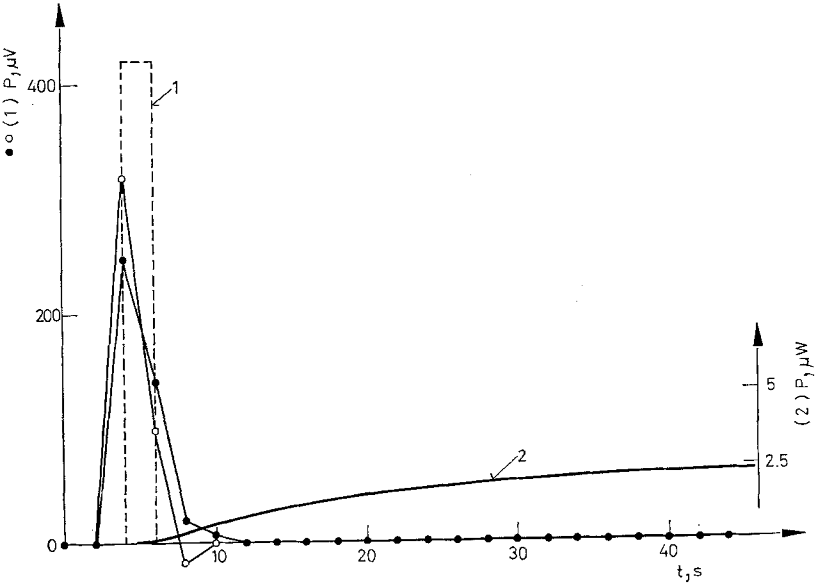

Fig. 5. Correction of simulated calorimetric curves: simulated calorimetric response (curve 2) to a pulse (curve 1, 2 s, 423 µW); input reconstructed by the general (●) and simplified (○) deconvolution methods (sampling period: 2 s)

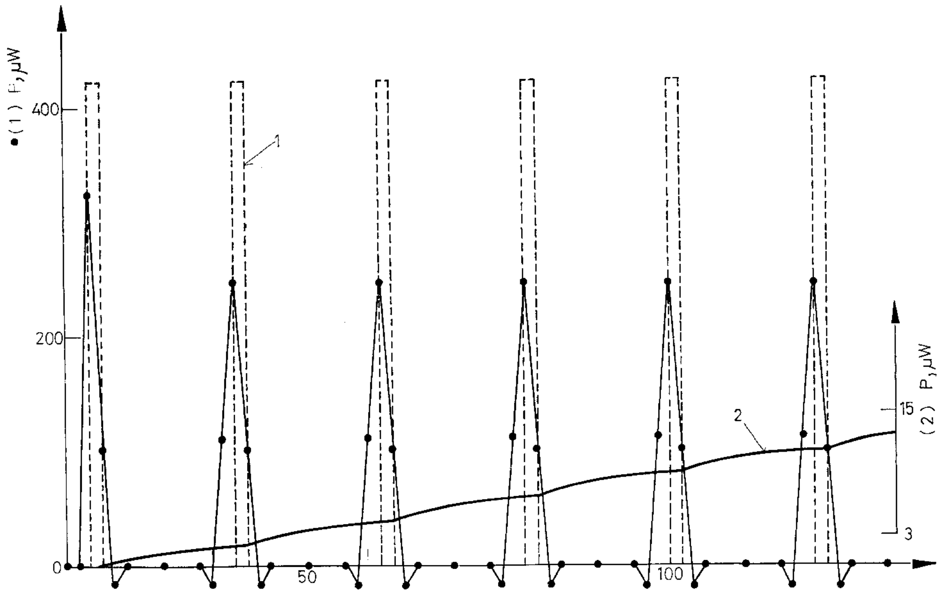

Fig. 6. Correction of simulated calorimetric curves: simulated calorimetric response (curve 2) to a series of pulses (curve 1, 2 s, 423 μW, time interval between pulses: 24 s); input reconstructed by the simplified method (●) (sampling period: 2 s)

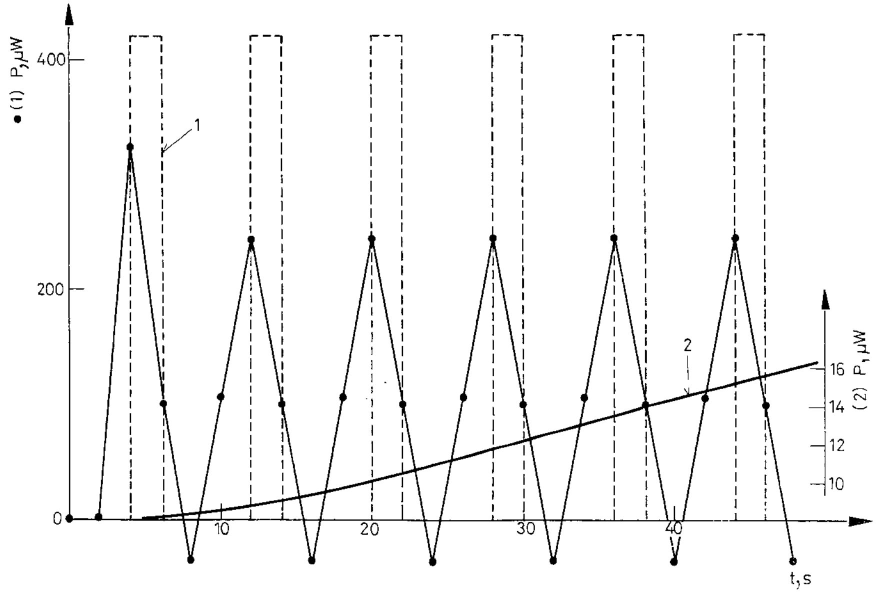

Fig. 7. Correction of simulated calorimetric curves: simulated calorimetric response (curve 2) to a series of pulses (curve 1, 2 s, 423 μW, time interval between pulses: 8 s); input reconstructed by the simplified method (●) (sampling period: 2 s)

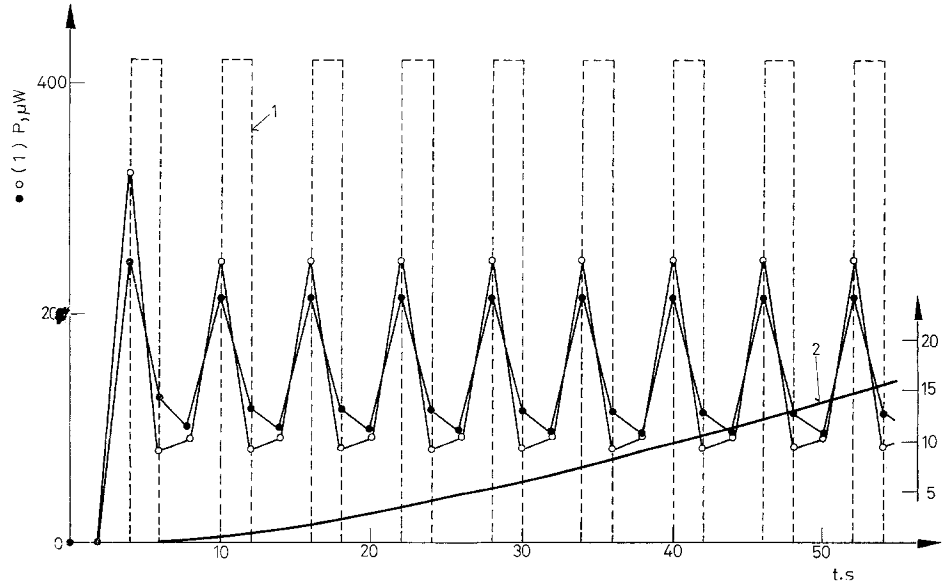

Fig. 8. Correction of simulated calorimetric curves: simulated calorimetric reponse (curve 2) to a series of pulses (curve 1, 2 s, 423 μW, time interval between pulses: 6 s); input reconstructed by the general (●) and simplified (○) methods (sampling period: 2 s)

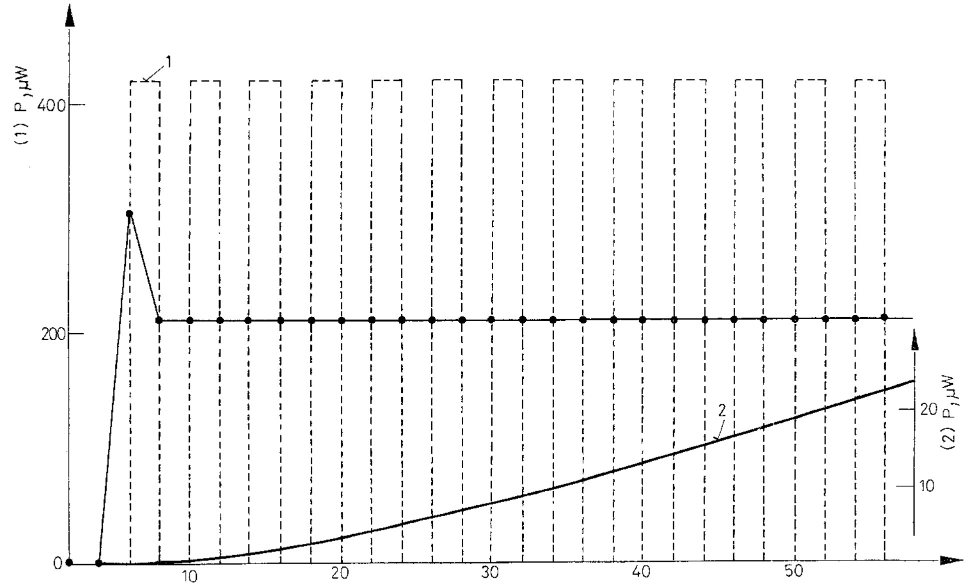

Fig. 9. Correction of simulated calorimetric curves: simulated calorimetric response (curve 2) to a series of pulses (curve 1, 2 s, 423 μW, time interval between pulses: 4 s); input reconstructed by the simplified deconvolution method (●) (sampling period: 2 s)

although the input function is correctly reconstructed when a step or a long pulse are simulated, the reconstruction is less accurate when the length of the pulse corresponds to 1 sampling period (Fig. 5). It appears, however, that, even in this extreme case, significant kinetic information is obtained. For these reasons, we have used such narrow pulses to study the resolution of the deconvolution procedure.

Figures 6 to 9 report the result of a series of tests during which the gap between pulses was varied. When the pulse frequency, $f$, is smaller than $1/3T$ ($T$: sampling period), the kinetics of the simulated pulses and their resolution are correctly reconstructed (Figs 6 and 7). The proposed deconvolution procedure therefore allows one to resolve kinetic phenomena separated by a time interval larger than 3 sampling periods.

### *Experimental tests*

The main object of this series of tests was to determine the influence of noise on the quality of the deconvolution. The data acquisition and recording line is schematically presented in Fig. 10. It includes a galvanometric amplifier A (output voltage: $S = 10^4E - 2\times10^5I$; $E$: input voltage; $I$: current in the external generator for zero shifting), an analog recorder, a digital voltmeter which performs the following functions: analog-to-digital converter, *BCD* coding processor and numerical display, an interface to pilot the punch, an 8-channel paper-tape punch and a data-entry keyboard.

This line was connected to a TIAN-CALVET type calorimeter [5]. The experimental arrangement to generate Joule heatings in the calorimeter vessel has been described elsewhere [2]. It has been used to produce steps (400 $\mu$ W), long pulses (24 s, 750 $\mu$ W) and short pulses (2 s, $\sim$ 9 mW).

The influence of the value of the sampling period is presented in Fig. 11. Three sampling periods (2, 4 and 8 s) were used. The experimental data were not smoothed before processing. It appears that a short sampling period is not recommended when noise is present in the experimental data. In agreement whith Shannon's theorem [6], the sampling frequency ($F_e$) must be equal to or larger than twice the highest frequency ($F_M$) in the spectrum. A practical relation which takes into account the tolerated error ($\varepsilon$) in the deconvoluted signal and the power contribution ($a$) of $F_M$ is given by:

$$F_e \geq aF_M \frac{2 \cdot 2}{\sqrt{\varepsilon}}$$

In the case where $F_M$ contributes 1% ($a = \sqrt{0.01} = 0.1$) and where $\varepsilon = 1\%$, one obtains $F_e \geq 2.2\ F_M$. When a 4 s sampling period ($F_e = 0.25\ H$) is selected, it is therefore assumed that $F_M \simeq 0.1\ H$. In the case of the calorimeter used in this work, $F_M$ has been estimated equal to 0.5 $H$. In the case of a 4 s period, $F_M$ is therefore slightly underevaluated and a larger sampling frequency (a shorter sampling period) would seem preferable. However, Fig. 11 indicates that the amount of noise increases when the sampling frequency increases. This is expected since an increased sampling frequency implies a larger band pass width and the signal, though correctly deconvoluted, still contains noise.

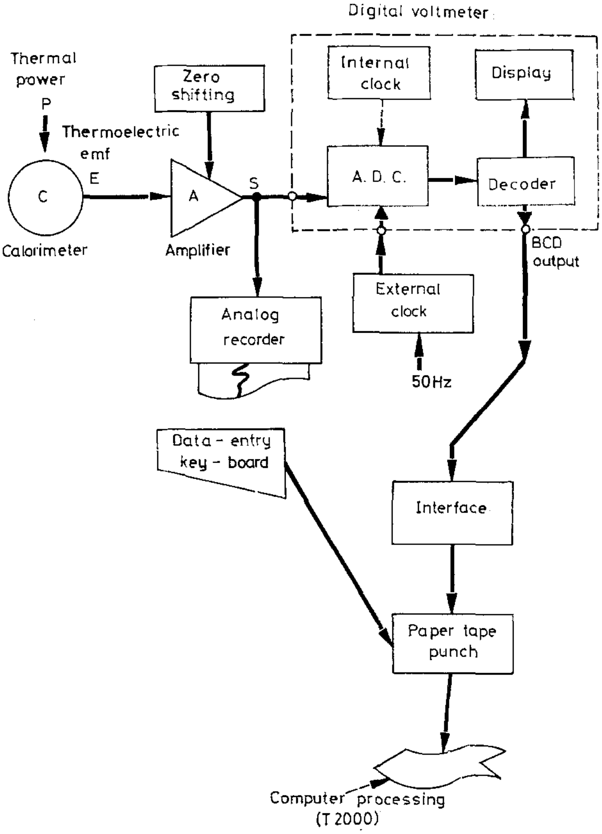

Fig. 10. Schematic representation of the amplification and data acquisition line

The proposed correction method being sensitive to noise, low sampling frequencies ($T = 4$ or 8 s, $F_e = 0.25$ or 0.125 $H$) must be selected and $F_M$ must be purposely underevaluated. This means that the contribution to the total power of the frequencies between $F_e$ and $F_M$ must be neglected. A consequence of this choice is that the total amplitude of a narrow pulse is not completely reconstructed.

For a given sampling period, it is possible, however, to improve the quality of the reconstruction by smoothing raw experimental data. Figure 12 shows, in the case of a 240 s pulse, the influence of 1 or 9 smoothing processings.

In order to illustrate the method, two applications are presented:

a) The calorimeter response to a narrow and intense electrical pulse (2 s, 9 mW) and the deconvoluted input are presented in Fig. 13.

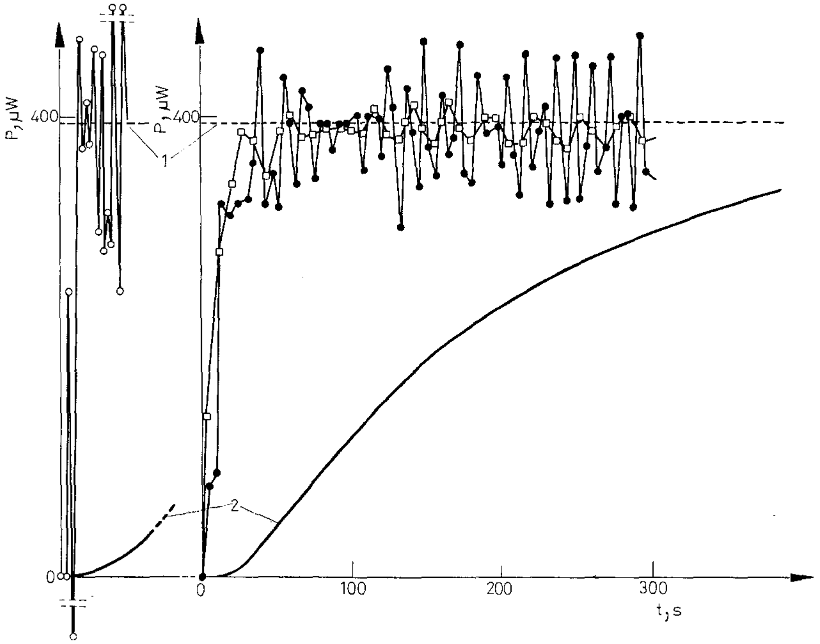

Fig. 11. Correction of experimental calorimetric curves: experimental calorimetric response (curve 2) to a step (curve 1, 394 μW); reconstructed inputs: sampling period: 2 s (○), 4 s (●), 8 s (□)

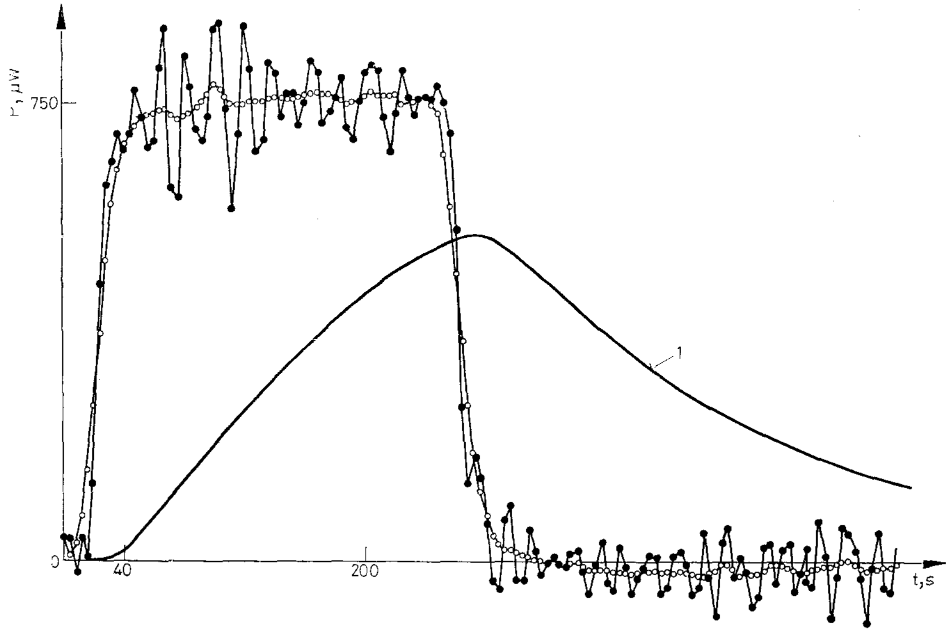

Fig. 12. Correction of experimental calorimetric curves: experimental calorimetric response (curve 1) to a pulse (240 s, 750 μW); reconstructed input: after 1 smoothing operation (●), after 9 smoothing operations (○) (sampling period: 4 s)

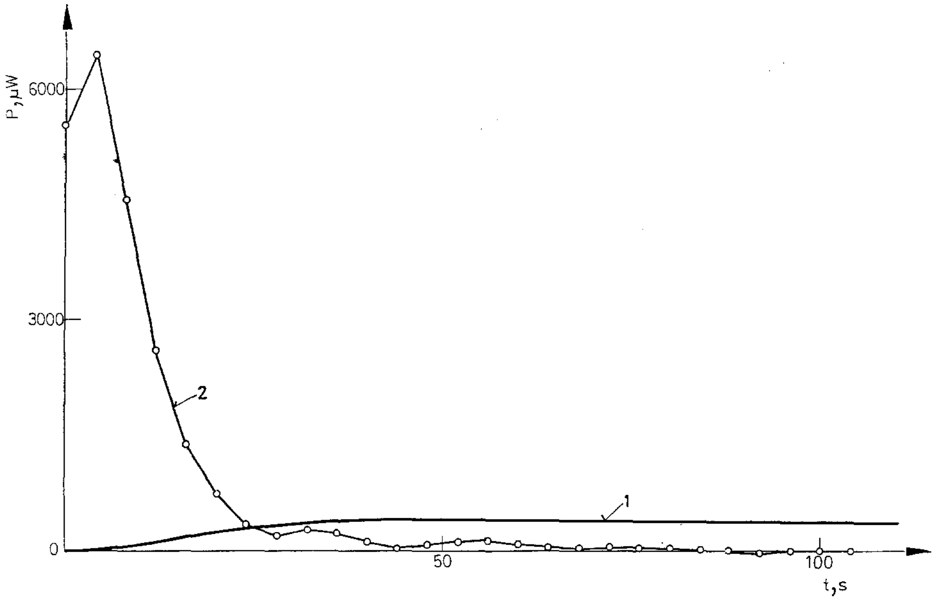

Fig. 13. Correction of experimental calorimetric curves: experimental calorimetric response (curve 1) to a pulse (2 s, 9000 μW); reconstructed input (curve 2) (sampling period: 2 s, 1 data smoothing)

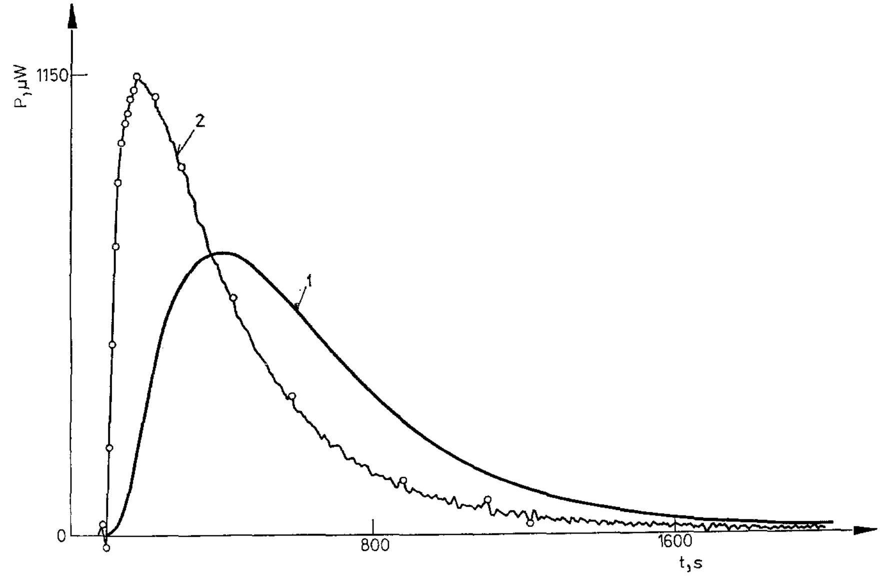

Fig. 14. Correction of experimental calorimetric curves: experimental calorimetric curve recorded during the catalytic decomposition of a dose of nitrous oxide over a nickel oxide catalyst at 473 K (curve 1); reconstructed calorimetric curve (curve 2) (sampling period: 8 s, 1 data smooting)

b) Figure 14 gives an example of application of the method in the field of heterogeneous catalysis. The calorimeter response was recorded during the catalytic decomposition at 473 K of a small dose of nitrous oxide on the surface of nickel oxide. Analysis of the deconvoluted calorimetric curve indicated that the reaction follows a 1st-order kinetic law (Fig. 15).

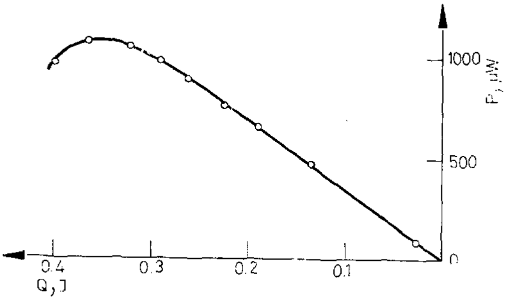

Fig. 15. Transform of curve 2 in Fig. 14. according to 1st-order kinetics.

A more detailed analysis of the calorimetric study of this system is presented elsewhere [7].

## Conclusions

The simplified deconvolution method, based on the state function theory, which has been described in the present article, yields results which are kinetically significant. It is necessary, in many cases, to refine the deconvolution by means of a time-domain matrix. Integration of the output and reconstructed input functions, for the determination of energies, yields similar results (maximum deviation: 4%). The method, moreover, may be readily adapted to any linear system and allows the on-line deconvolution of the data by means of a microprocessor.

The tests which have been described, however, indicate that the accuracy of the results may be decreased by noise in the experimental data. In the case of calorimetric experiments, noise is mainly generated by the amplification and acquisition line. In order to effectively curtail its effects, it is recommended (i) to smooth the experimental data, before correction (smoothing the reconstructed input results in a loss of kinetically significant information), and (ii) to carefully select the sampling period.

*

The authors gratefully acknowledge the assistance of Dr. J. Van Bokhoven, Chemisch Laboratorium TNO, Rijswyk, the Netherlands, during the experimental part of this work.

## References

1. C. Brie, M. Guivarch and J. L. Petit, Proc. 1st Intern. Conf. on Calorimetry and Thermodynamics, Warsaw, Pol. Sci. Pub., 1971, p. 73; C. Brie, PhD Thesis, Lyons, N° 44, 1971.
2. C. Brie, J. L. Petit and P. C. Gravelle, J. Chim. Phys., 70 (1973) 1107 and 1115.
3. C. Brie, J. L. Petit and P. C. Gravelle, J. Chim. Phys., 70 (1973) 1123.
4. V. W. Eveleigh, Adaptative control and optimization techniques, McGraw-Hill Book Company, New York, 1967.
5. E. Calvet and H. Prat, Microcalorimétrie, applications physico chimiques et biologiques, Masson, Paris, 1956; E. Calvet, H. Prat and H. A. Skinner, Recent Progress in Microcalorimetry, Pergamon, New York, 1963.
6. J. Max, Méthodes et techniques de traitement du signal et applications aux mesures physiques, Masson, Paris, 1 (1972).
7. R. Point, J. L. Petit and P. C. Gravelle, J. Catalysis (in the press).

Résumé — Une procédure simplifiée de déconvolution qui peut être utilisée pour éliminer des courbes calorimétriques, la distorsion causée par l'inertie thermique du calorimètre, est décrite et testée. La procédure est basée sur la théorie des variables d'état. Le bruit de fond des courbes corrigées peut être diminué par le lissage des données expérimentales et par le choix d'une fréquence d'échantillonnage appropriée. La méthode peut être adaptée au traitement en ligne des données au moyen d'un microprocesseur.

Zusammenfassung — Ein vereinfachtes Dekonvolutionsverfahren, das sich zur Behebung von infolge thermischer Lag-Erscheinungen auftretenden Zerrungen kalorimetrischer Daten eignet, wird beschrieben und getestet. Das Verfahren beruht auf der Theorie der Zustandsfunktion. Geräusche der Dekonvolutionsdaten können durch Ausgleichen der Versuchsdaten und durch sorgfältige Wahl der Datennahme-Frequenz gedämpft werden. Die Methode kann mittels eines Mikro-Verarbeiters zur on-line Verarbeitung eingesetzt werden.

Резюме — Описан и проверен метод развертки, который может быть использован для удаления из калориметрических данных искажения, обусловленного термическими запаздываниями. Метод основан на теории функций состояния. Шум в данных развертки может быть уменьшен сглаживанием эксперименталных данных и тщательным выбором частоты данных отбора проб. Этот метод легко приспосабливаем посредством микропроцессора к режиму работы "on-line".