

## A MODEL-BASED STUDY OF DECONVOLUTION IN TIME-VARYING OR INJECTION CALORIMETERS

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### ABSTRACT

A deconvolution algorithm based on time-varying inverse filtering is applied to a calorimetric model. The model is designed to simulate a device in which continuous liquid injection takes place. By means of a proper separation of different contributions to the thermogenesis, classical time-invariant deconvolution routines can be applied even if the model presents zeros in the time-invariant transfer function. The corrections achieved on the thermogenesis are evaluated for two different kinds of thermal power dissipation.

### INTRODUCTION

The development of numerical methods for signal processing and their application to the thermal output signals from calorimetric devices of continuous injection (systems of variable mass) had led to important results in the field of molecular mixtures and of micellar phenomena [1].

In previous works [2–4] we have established the relationships between experimental thermograms and the corresponding energy dissipations, called thermogenesis. We have also set out the numerical and experimental procedures required to obtain the parameters entering the computation of the thermogenesis from the thermogram.

The numerical algorithms developed are based on a time-varying inverse filtering which relates thermogram and thermogenesis by means of an  $N$ -th order linear differential equation with time-varying coefficients. For systems with an invariant transfer function without zero-singularities, it has been shown that invariant methods, the  $z$  transform for example, can be used.

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The purpose of this work is to extend this kind of treatment to systems with zero-singularities in the invariant transfer function.

The thermogenesis is separated into different contributions in such a way that time-invariant deconvolution routines can be applied to every one of them. The relative importance of each contribution in the final thermogenesis is studied. Special attention is paid to the influence, on every correcting term, of the signal-to-noise ratio of the thermogram.

## THE MODEL

In a previous paper [4] we developed a simplified model of a heat-flow calorimeter with time-varying amounts of reactants in the cell. The relationship between the thermal power dissipated  $W(t)$  and the output signal  $s(t)$  is given by a differential equation

$$\sum_{i=0}^K a_i(t) \frac{d^i W(t)}{dt^i} = \sum_{i=0}^N A_i(t) \frac{d^i s(t)}{dt^i} \quad (1)$$

The coefficients  $a_i(t)$  and  $A_i(t)$  can be written in terms of certain parameters  $\tau_i'(t)$ ,  $\tau_i^{*\prime}(t)$  and  $S'(t)$  representing the so called "fictitious" poles; zeros and sensitivity of the system [4]. Assuming a linear temporal variation of these parameters, the coefficients  $A_i(t)$  become polynomials with order  $\leq N + 1$ . If the variability of the system makes  $M$  the maximum power of  $t$ , then

$$A_i(t) = \sum_{j=0}^M A_{ij} t^j \quad (2)$$

and inserting eqn. (2) in the second member of eqn. (1)

$$\sum_{i=0}^N A_i(t) \frac{d^i s(t)}{dt^i} = \sum_{j=0}^M \left( \sum_{i=0}^N A_{ij} \frac{d^i s(t)}{dt^i} \right) t^j$$

To decompose  $W(t)$  we choose a series with  $M$  as a maximum power of  $t$ , as we did in ref. 5, for the system without zero-singularities. In the present case the order chosen for the polynomial is arbitrary and we can choose the same order that would correspond to a system without zero-singularities. Thus

$$W(t) = \sum_{i=0}^M W_i(t) t^i \quad (3)$$

Inserting eqn. (3) in the first member of eqn. (1) and associating homologous powers at each member of the differential equation a system of  $M + 1$  differential equations with constant coefficients is obtained. Every one of these equations can now be solved by the usual deconvolution procedures used for time-invariant systems.

The same model as in ref. 4, consisting of six elements and working in situations 1 and 2, will be used here. In the first situation the power dissipation takes place in the first element, and  $C_1$ ,  $P_{12}$  and  $P_1$  change with time. The change of  $P_{12}$  produces a corresponding change in the sensitivity of the model. In the second situation the dissipation takes place in the second element, and  $C_2$  changes with time.

The values of heat capacities and thermal conductivities considered are the values given in Tables 1 and 2 of ref. 4, and the values corresponding to the parameters  $\tau_i$ ,  $\tau_i^*$ ,  $\tau_i'$ ,  $\tau_i^{*}$ ,  $S_i$  and  $S_i'$  can be found in Tables 3 and 4 from the same reference. In both situations (1 and 2) the thermogram is the difference between the temperatures  $T_5$  and  $T_6$ .

In order to test the deconvolution procedure, two kinds of dissipations resembling two typical experimental runs in calorimetry of liquid mixtures have been simulated: on the one hand, a mixture of cyclohexane and benzene; on the other hand, this same dissipation, showing however a sudden discontinuity to simulate a phase separation.

For the injection of cyclohexane into benzene the dissipation reads

$$W(t) = h_1^E \cdot \dot{n}_1$$

where  $\dot{n}_1$  is the injection rate ( $\dot{n}_1 = 5.8546E - 06 \text{ mol s}^{-1}$ ), and  $h_1^E$  the excess partial molar enthalpy of the injected component. The latter is given by ref. 6

$$h^E = x_2^2(3518.1 - 2082.2x_1 + 2866.8x_1^2 - 1253.6x_1^3)$$

where  $x_1$  and  $x_2$  represent the molar fractions of cyclohexane and benzene, respectively. In agreement with actual experimental runs, the simulated injection takes place during one hour, from  $t = 100 \text{ s}$  to  $t = 3700 \text{ s}$ . During this interval the system changes with time, but at  $t = 3700 \text{ s}$  it becomes a time-invariant system.

The second kind of dissipation is equivalent to the previous one from  $t = 100 \text{ s}$  to  $t = 2400 \text{ s}$ . For  $t > 2400 \text{ s}$  the dissipation reads

$$W(t) = (h_1^E \cdot \dot{n}_1)/4$$

simulating a process of mixture separation. This produces a discontinuity in  $t = 2400 \text{ s}$ .

For every dissipation, the calorimetric model has been used to compute two thermograms: the first thermogram presents a signal/noise  $> 100 \text{ dB}$ , the only source of noise being the numeric round-off of the computer during the calculations. Additional white noise has been added to the second thermogram, to get a signal/noise =  $60 \text{ dB}$ , a value that is around that found in actual experimental thermograms.

The sampling period used to compute the thermograms is  $\Delta t = 1 \text{ s}$ , selected by the criterion  $\Delta t = \tau_1/300$ .

## RESULTS

In the first model, a linear variation of the two larger time constants and of the sensitivity has been considered; in the second, a linear variation of the three larger time constants. As detailed above, the time-variability of both models leads to  $M = 3$ .

In what follows, the system of differential equations which applies for each one of the models is detailed. The solution starts by solving the last equation, which is not difficult because the coefficients in the equation are constant. Once  $W_3(t)$  is obtained, it can be used in the second equation to obtain  $W_2(t)$  and from it, in a recursive way,  $W_1(t)$ . Thus all the correcting terms are determined and hence  $W(t)$ .

*Dissipation in element 1*

$$\begin{aligned}
 W_0 + b_0 W_0' + b_0 W_1 &= \sum_{i=0}^6 A_{0i} \frac{d^i s(t)}{dt^i} \\
 W_1 + b_0 W_1' + 2b_0 W_2 &= \sum_{i=0}^6 A_{1i} \frac{d^i s(t)}{dt^i} \\
 W_2 + b_0 W_2' + 3b_0 W_3 &= \sum_{i=0}^6 A_{2i} \frac{d^i s(t)}{dt^i} \\
 W_3 + b_0 W_3' &= \sum_{i=0}^6 A_{3i} \frac{d^i s(t)}{dt^i}
 \end{aligned} \tag{4}$$

where  $b_0 = \tau_1^*$

*Dissipation in element 2*

$$\begin{aligned}
 W_0 + b_0 W_0' + a_0 W_0'' + b_0 W_1 + 2a_0 W_1' + 2a_0 W_2 &= \sum_{i=0}^6 A_{0i} \frac{d^i s(t)}{dt^i} \\
 W_1 + b_0 W_1' + a_0 W_1'' + 2b_0 W_2 + 4a_0 W_2' + 6a_0 W_3 &= \sum_{i=0}^6 A_{0i} \frac{d^i s(t)}{dt^i} \\
 W_2 + b_0 W_2' + a_0 W_2'' + 3b_0 W_3 + 6a_0 W_3' &= \sum_{i=0}^6 A_{0i} \frac{d^i s(t)}{dt^i} \\
 W_3 + b_0 W_3' + a_0 W_3'' &= \sum_{i=0}^6 A_{0i} \frac{d^i s(t)}{dt^i}
 \end{aligned}$$

where  $a_0 = \tau_1^* \cdot \tau_2^*$ ,  $b_0 = \tau_1^* + \tau_2^*$  and for both systems

$$W_i = W_i(t)$$

$$W_i' = dW_i(t)/dt$$

$$W_i'' = d^2W_i(t)/dt^2$$

$$W(t) = W_0(t) + W_1(t) \cdot t + W_2(t) \cdot t^2 + W_3(t) \cdot t^3$$

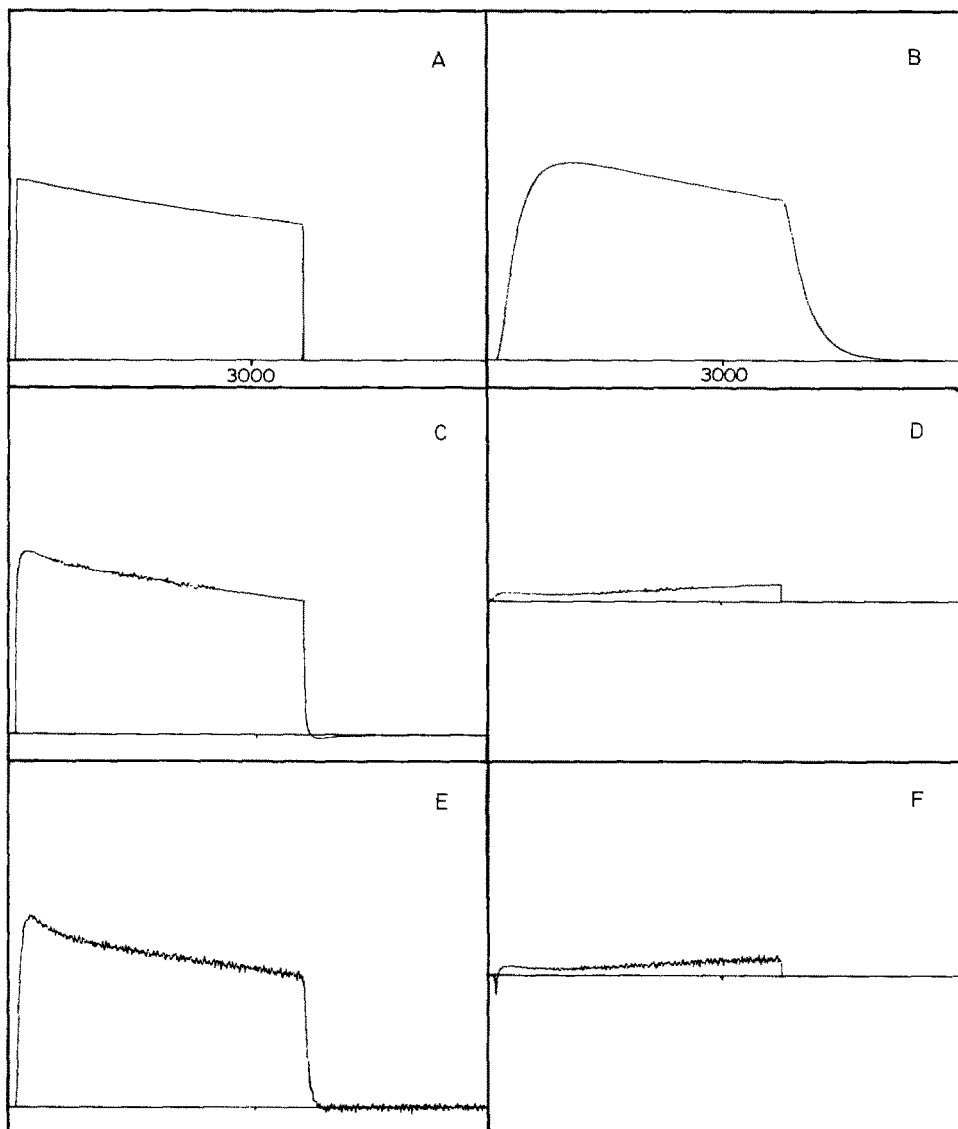


Fig. 1. Corresponds to situation 1 in the text. The vertical scale is in arbitrary units, time is in seconds. A, simulated thermogenesis; B, corresponding thermogram; C, thermogenesis computed from the thermogram without addition of noise; D, correcting term  $10W_1(t) \cdot t$ , corresponding to C; E, thermogenesis computed from a thermogram with additional noise resulting in a signal-to-noise ratio = 60 dB; F, correcting term  $10W_1(t) \cdot t$ , corresponding to E.

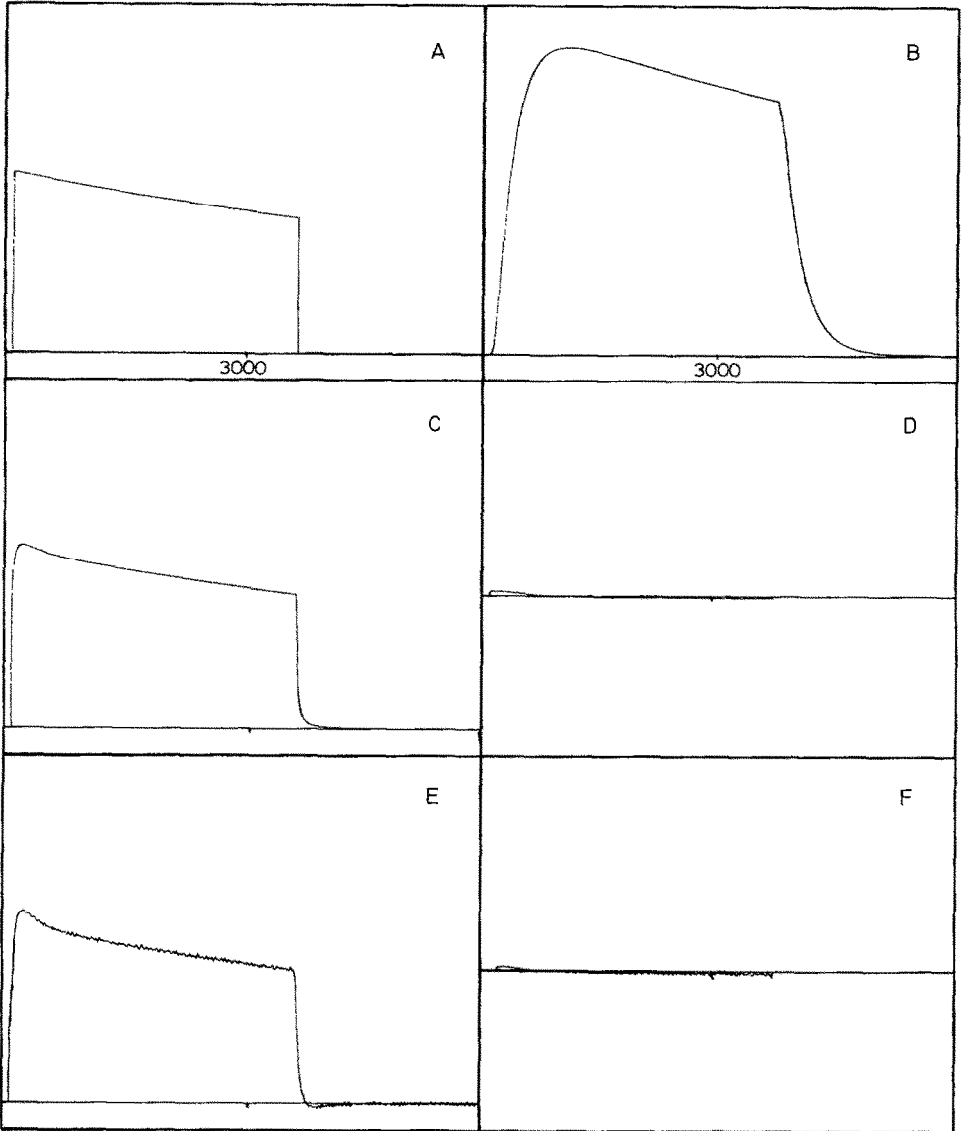


Fig. 2. Corresponds to situation 2 in the text. The vertical scale is in arbitrary units, time is in seconds. A, simulated thermogenesis; B, corresponding thermogram; C, thermogenesis computed from the thermogram without addition of noise; D, correcting term  $10W_1(t) \cdot t$ , corresponding to C; E, thermogenesis computed from a thermogram with additional noise resulting in a signal-to-noise ratio = 60 dB; F, correcting term  $10W_1(t) \cdot t$  corresponding to E.

The contributions  $W_3$ ,  $W_2$ ,  $W_1$  and  $W_0$  have been computed from the simulated thermograms. The results are shown in Figs. 1, 2, 3 and 4.

Figure 1 shows the simulated thermograms and the thermogenesis corresponding to an ordinary mixture (situation 1). A variable correction  $W_1(t) \cdot t$  comes into play. The different pattern obtained when the signal-to-noise

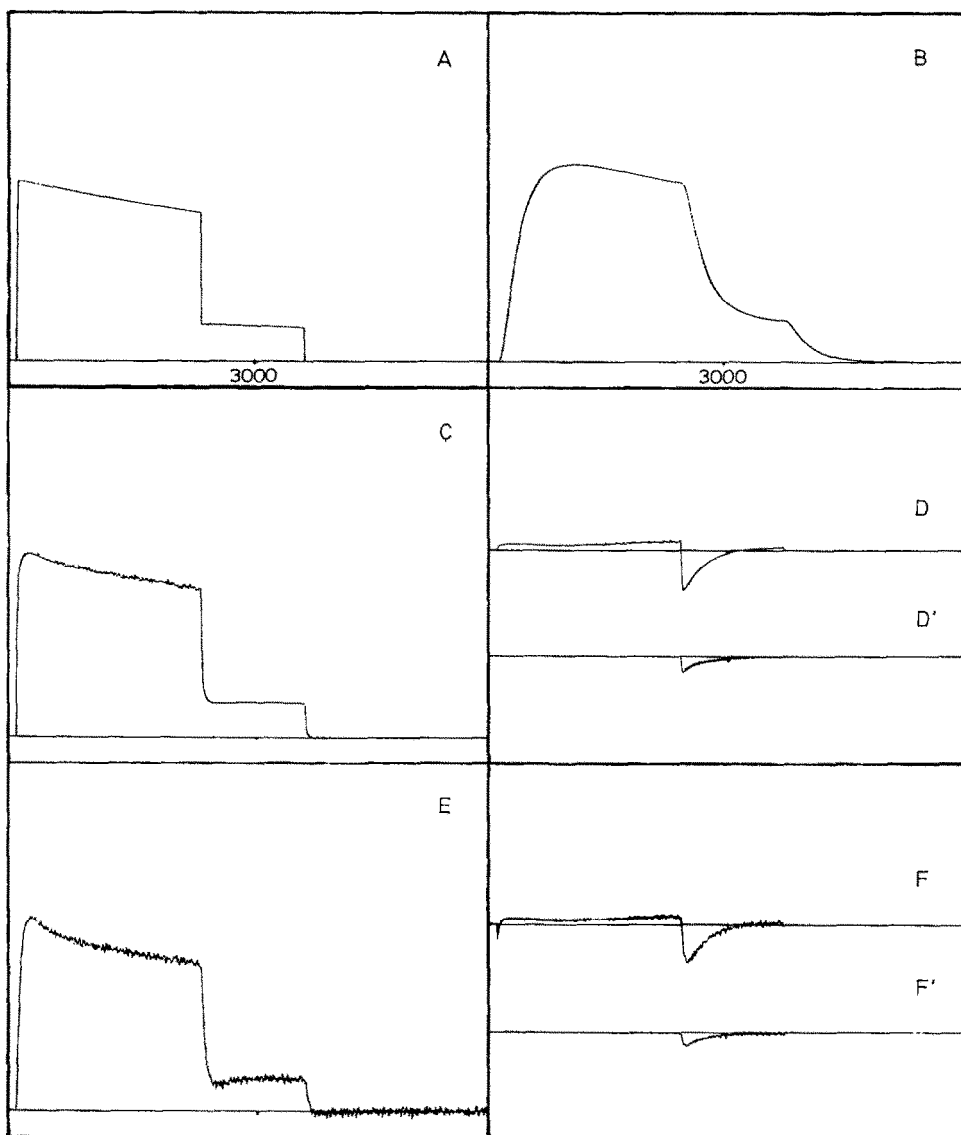


Fig. 3. Corresponds to situation 1 in the text. The vertical scale is in arbitrary units, time is in seconds. A, simulated thermogenesis; B, corresponding thermogram; C, thermogenesis computed from the thermogram without addition of noise; D, correcting term  $10W_1(t) \cdot t$ , corresponding to C; D', correcting term  $100W_2(t) \cdot t^2$ , corresponding to C; E, thermogenesis computed from a thermogram with additional noise resulting in a signal-to-noise ratio = 60 dB; F, correcting term  $10W_1(t) \cdot t$ , corresponding to E; F', correcting term  $100W_2(t) \cdot t^2$  corresponding to E.

ratio is reduced to 60 dB should be noted. In Fig. 2, corresponding to situation 2, the correction  $W_1(t) \cdot t$  becomes irrelevant.

Figures 3 and 4 correspond to the simulation of a mixture separation. The influence of  $W_1(t) \cdot t$  is relatively important (23%) in the region of mixture

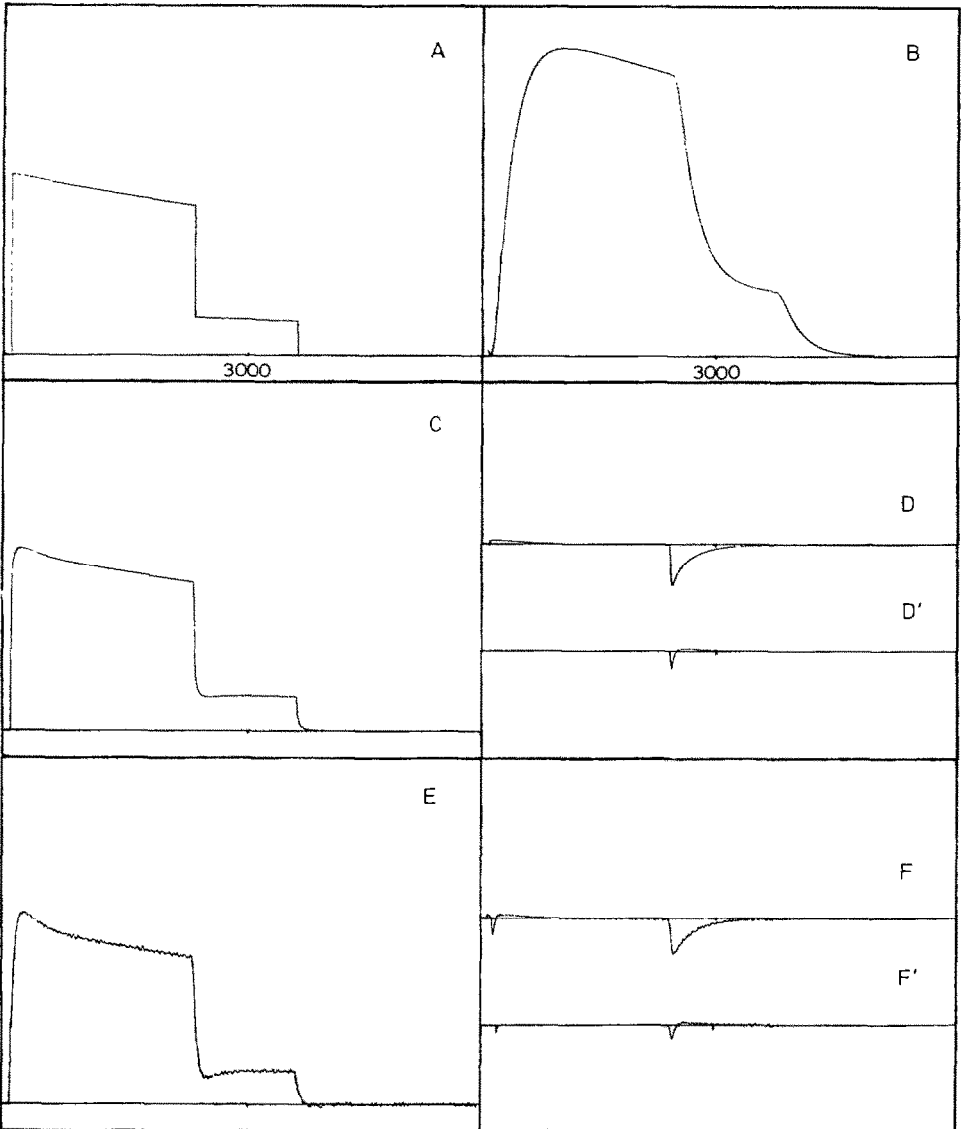


Fig. 4. Corresponds to situation 2 in the text. The vertical scale is in arbitrary units, time is in seconds. A, simulated thermogenesis; B, corresponding thermogram; C, thermogenesis computed from the thermogram without addition of noise; D, correcting term  $10W_1(t) \cdot t$ , corresponding to C; D', correcting term  $100W_2(t) \cdot t^2$  corresponding to C; E, thermogenesis computed from a thermogram with additional noise resulting in a signal-to-noise ratio = 60 dB; F, correcting term  $10W_1(t) \cdot t$ , corresponding to E; F', correcting term  $100W_2(t) \cdot t^2$ , corresponding to E.

separation, and even  $W_2(t) \cdot t^2$  becomes relevant (2%). It is worth noting that any increase in the injection rate would result in an amplification of all the correcting terms.



## CONCLUSIONS

The contribution  $W_0(t)$  is the most relevant one in the global thermogenesis. The remaining terms in the series expansion only contribute significantly in the discontinuities of the thermal power dissipation.

Even for relatively low signal-to-noise ratio, the corrective terms are significant for an accurate determination of the concentrations at which separation of the mixture takes place.

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