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THERMAL CURVE INTERPRETATION BY SPECTRAL RESOLUTION INTO A BASIC SET OF RECTANGULAR PULSE CURVES

III. Resolution into other pulse curves

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A generalized spectral resolution method for thermokinetic determination is presented and tested. Any kind and number of identification thermal curves can be used in a single calculation.

There are several interesting solutions to the problem of the determination of quick thermal effects in calorimeters having large time constants [1, 2]. We have proposed a method for thermokinetic determination based on numerical functional analysis [3, 4] and the present paper describes a new improvement in this area.

The problem of thermokinetic determination resolves itself into the numerical analysis of a thermal curve given as a set of experimental points and the reconstruction of the thermal effect from it, by using information about the calorimeter transition function. The transition function could cover everything known about the correlation between the thermal effects and their curves. As one of the forms of the transition function the "Dirac pulse" curve can be taken, which is used in the optimization method [1] and the harmonic method [2] for thermokinetic determination. Of course, broadly speaking, the calorimeter transition is a functional which operates on a thermal pulse curve and produces its thermal curve. In our spectral resolution method the "Dirac pulse" curve was used for thermal effect reconstruction. However, it is possible to use another thermal pulse curve for the purpose of calorimeter identification, as the information about the calorimeter, its "fingerprint", is present in any of its curves.

The aim of the present paper is to generalize the spectral resolution method in the sense of using any kind of identification thermal pulse for determination of the thermokinetics. For several reasons this generalization seems to be interesting and useful. Firstly, we expect that using curves of thermal effects which are much closer to the effect we want to reconstruct for the purpose of calorimeter identification should give much better results. Secondly, the identification of the calorimeter by using only a "Dirac pulse" curve is a serious limitation, because it disregards the possibility for this purpose of the application of many thermochemical reactions for which the thermokinetics have already been determined. In the present paper we describe some examples of the selection of identification thermal effects and show how the results of the spectral resolution method improve on appropriate selection.

Our method creates two different basic sets out of the identification thermal curves. The first is the set of thermal pulses and the second is the set of their thermal curves. They are needed for spectral resolution of the thermal effect under investigation and its curve. The possibility of the best choice of these sets is the reason why the spectral resolution method can be superior to other methods in which the only identification pulse is a "Dirac pulse".

All computations whose results are presented in this paper have been performed for thermal curves which are not experimental but have been created by our computer programme for curve simulation. We decided to use such thermal curves to test our generalized spectral resolution method because by means of the simulation of a certain level of measurement noise we could separate the measurement error from the error of the method in the final results. Further, we had no appropriate set of experimental thermal curves; in the conclusions we propose a calorimetric experiment to obtain a set of curves for a hard test for all the existing methods of thermokinetic determination.

Algorithm of the generalized spectral resolution method

Let us assume that we have to determine the thermokinetics of the thermal pulse E and that its curve $T(i)$, $i = 1, \dots, N$, is given as a set of temperature values obtained from a calorimeter experiment. Let us also assume that at least one identification thermal effect EI with its curve $TI(i)$, $i = 1, \dots, N$, is given and that its measurement period is not shorter than the measurement period of the curve T, the sampling period being identical for the two. We now introduce two basic sets:

1. The identification set of pulses $\{EI_j\}$, $j = 1, \dots, M$. This set can be constructed in several different ways. It could be the scheme proposed by us in the previous paper [4], based on the shifting procedure of the identification thermal pulse by an integral multiple of the sampling period. It could also be a set of different identification pulses selected in such a way as to give a good approximation to the thermal pulse under investigation. Thus for the set $\{EI_j\}$ the following relation should be satisfied:

$$E \cong \sum_{j=1}^{M} c_j \cdot EI_j \tag{1}$$

2. The identification set of thermal curves $\{TI_j\}$, $j = 1, \dots, M$, related to the pulse set $\{EI_j\}$. This set should give a good approximation to the curve T, i.e.:

$$T \cong \sum_{j=1}^{M} c_j \cdot TI_j \tag{2}$$

The aim of the spectral resolution method is to find the coefficients c_j of Eq. 2, for from these we can determine via relation (1) the thermal pulse under investigation. The scheme for the $\{c_j\}$ set determination is as follows:

1. First we transform the curve set $\{TI_j\}$ into the set of orthogonal curves $\{TIN_j\}$:

$$TIN_j = \sum_{k=1}^{M} a_{jk} \cdot TI_k, \qquad j = 1, \ldots, M. \tag{3}$$

The orthogonal condition is:

$$\langle TIN_k \mid TIN_l \rangle = \begin{cases} 0 & k \neq l \\ 1 & k = l \end{cases} \qquad k, l = 1, \ldots, M \tag{4}$$

where for convenience we use the useful Dirac notation $\langle TIN_k \mid TIN_l \rangle$ to represent the sum $\sum_{i=1}^{N} TIN_k(i) \cdot TIN_l(i)$. The realization of transformation (3) is rather difficult, because it is related to the orthogonalization of curves which are very similar to each other. However, there does exist an efficient algorithm based on the Schmidt iteration scheme, which was successfully applied by us to experimental curves [4].

2. We now perform the spectral resolution of the curve T into the $\{TIN_j\}$ curve basic set and obtain expansion coefficient cn_j:

$$cn_j = \langle T \mid TIN_j \rangle, \qquad j = 1, \ldots, M \tag{5}$$

3. Making use of the inverse transformation to transformation (3), we find the set $\{c_j\}$ from the following equation:

$$c_j = \sum_{k=1}^{M} cn_k \cdot a_{kj}, \qquad j = 1, \ldots, M. \tag{6}$$

The computer realization of the above scheme is fairly simple if the orthogonalization step does not cause trouble. The computer programme is written in FORTRAN and is organized in such a way as to keep only one TI curve in the operation memory at a time; hence the calculation can be performed on small computers, even for thermal curves having many experimental points.

Computer generation of thermal curves

To illustrate the job done by the generalized spectral resolution method for the thermokinetic determination, a special computer programme has been written to simulate calorimeter experiments and to produce thermal curves. The programme is based on the linearity of the calorimeter response, makes use of the "Dirac pulse" curve of a real non-isothermic non-adiabatic calorimeter, and produces a curve of a thermal pulse which is a step approximation to an input function $f(t)$. For the present simulation the "Dirac pulse" curve of the Tian—Calvet calorimeter has been taken. The data were kindly made available to us by the authors of Ref. [5]. The width of the step approximation is equal to 0.1 of the Tian—Calvet calorimeter sampling period of 2 s. Thus, in the first step of the procedure, on analogy with the shape of the 2-s rectangular pulse curve for the Tian—Calvet calorimeter, the form of a 0.2-s rectangular pulse curve is assumed with a sampling period of 0.2 s. The program now constructs the curve T of the step approximation to the function $f(t)$ as:

$$T[f(t)] = \sum_{i=1}^{10N} f(\bar{t}_i) \cdot TD_i \tag{7}$$

where TD_i means the rectangular pulse which started at the instant $(i-1) \cdot 0.2$ s and ended at the instant $i \cdot 0.2$ s and $f(\bar{t}_i)$ is the value of $f(t)$ in the middle of this time interval. Now, from the T values we select those related to instants which are integral multiples of the 2-s sampling period, i.e., $T(i \cdot 2\,s)$, $i = 1, \ldots, N$. There is also a simulation of the measurement inaccuracy; this is simply done by cutting the number of figures in the values of T down to six. Accordingly, the resulting level of the measurement noise in our curves is about 1/50 of that in the real Tien—Calvet calorimeter. This reduction of the inaccuracy is necessary to expose the behaviour of the spectral resolution method, which can be better observed on a silent background.

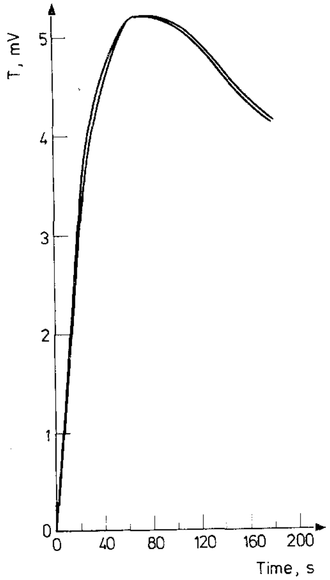


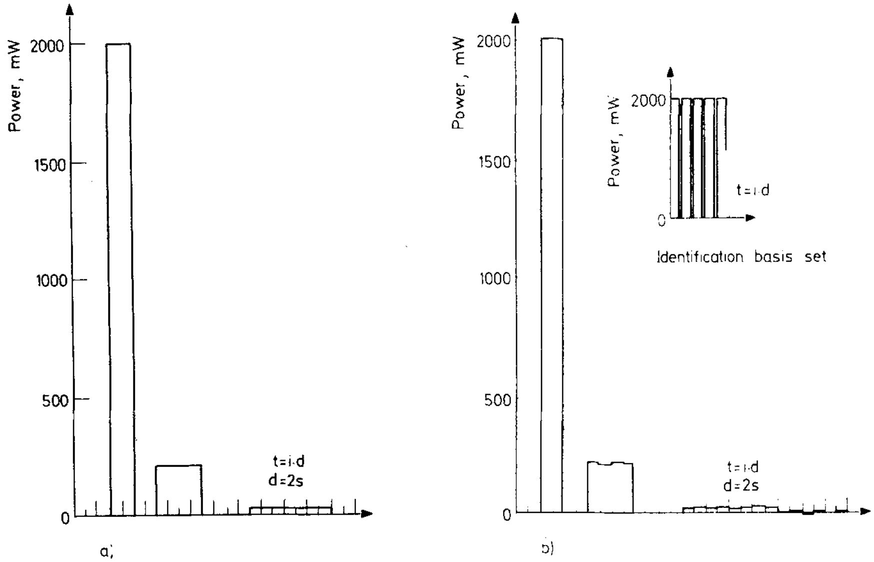
Fig. 1 Comparison of the experimental Tian—Calvet curves with a 2-s rectangular pulse with the curve obtained by our computer simulation procedure

Figure 1 shows the comparison of two 2-s rectangular pulse curves obtained in the Tian–Calvet calorimeter and in our computer calorimeter and illustrates the similarity of the two.

Numerical results

The first calorimeter curve which we created was a curve of a series of three rectangular pulses (see Fig. 2*a*) identical with those of the calorimetric competition in Nieborów (Poland) in 1977, organized for a comparison of the quality of different thermal pulse identification methods [5]. This thermal effect is accurately decomposed into rectangular pulses with a width of one sampling period, and so its reconstruction by using this pulse for the calorimeter identification in the spectral resolution method is nearly accurate, as is shown in Fig. 2*b*. For the same reason it is clear that the optimization method and the harmonic method gave such good results for the experimental curve in competition [5] because both performed indirectly a spectral decomposition of the curve under investigation.

The situation is different for the thermal effect of Fig. 3*a*, which, as before, is a series of similar pulses, but of the form of a sine function. For this case the spectral resolution method using the rectangular "Dirac pulse" for the identification did not work correctly (see Fig. 3*b*). The same behaviour could be expected in the case of



a)

b)

Fig. 2 Thermal effect proposed by the authors of Ref. [5] for the calorimetric competition (*a*) and its reconstruction by the spectral resolution method from the curve simulated by our computer programme (*b*)

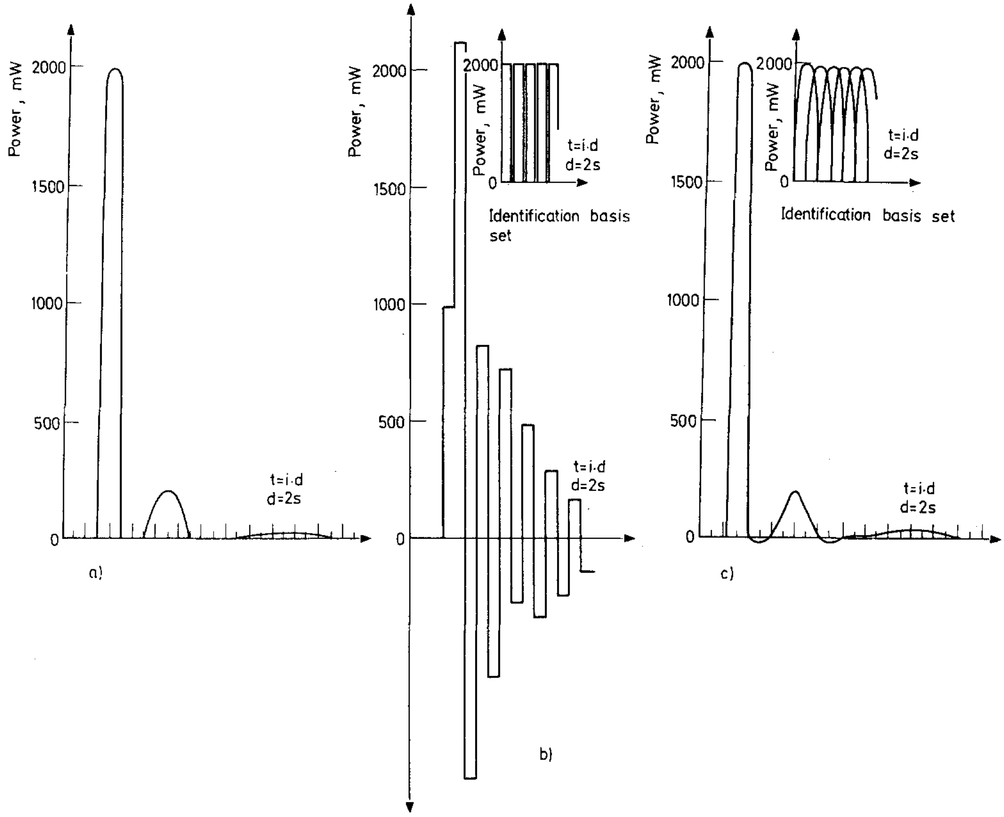


Fig. 3 Series of sine pulses (*a*) and its reconstruction by using a rectangular pulse (*b*) and sine pulse (*c*) for identification of the calorimeter

the optimization and harmonic methods. However, when the rectangular identification pulse was replaced by a sine pulse with a width of 4 s which was close to the shape of the thermal effect under investigation, and the scheme of the generalized spectral resolution method was applied, the accuracy of the thermokinetic reconstruction increased substantially (see Fig. 3*a*). The thermal pulse basic set $\{EI_j\}$ was generated by the shifting procedure and the first few curves are indicated in Fig. 3*c*. Of course, the same procedure was also applied to the construction of the thermal curve basic set $\{TI_j\}$. This numerical experiment shows how important for the thermal effect determination is the proper choice of the identification pulses in the spectral resolution method. There are many cases where the choice is not so simple, however, and trouble is caused by the appearance of pulses of different shapes in one thermal effect. For instance, the thermal pulse of Fig. 4*a* was of that type, and the spectral resolution of its curve into a basic set of rectangular pulse curve produced an incorrect reconstruction of the thermokinetics (see Fig. 4*b*). However, if the identification set

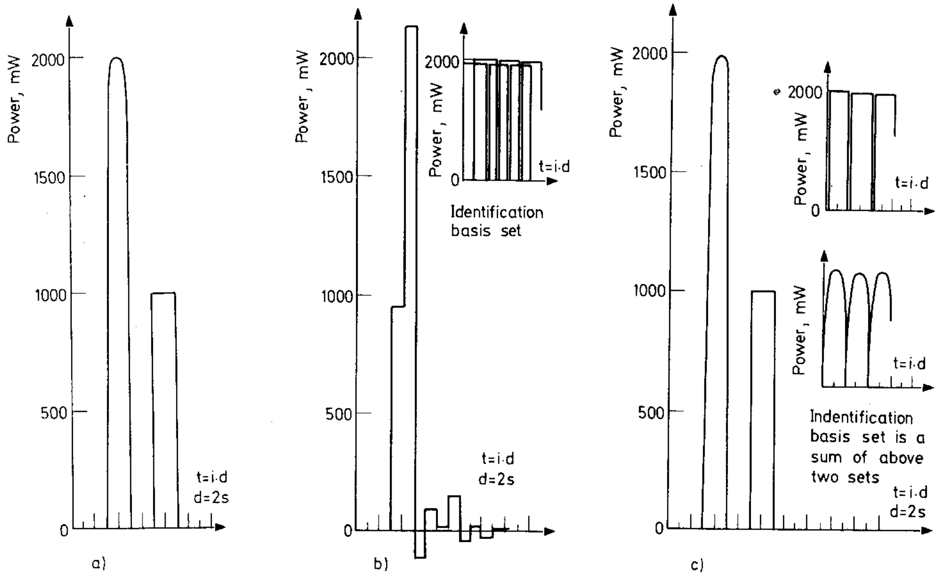


Fig. 4 Thermal effect of two pulses of different characters (*a*) and its reconstruction by spectral resolution into rectangular pulse basic set (*c*)

was constructed as the sum of two sets obtained by the shifting procedure applied to the rectangular "Dirac pulse" and the sine pulse, the result was excellent (see Fig. 4*c*).

It could be expected that the application of the optimization method and the harmonic method to the curve of the thermal effect of Fig. 4*a* would be ineffective because of the use of only one identification pulse. It is clear that the possibility of the application of two or even more identification curves in the generalized spectral resolution method is a real advantage and in particular cases becomes the only chance to reconstruct the thermokinetics.

Finally, we would like to present one more example of a calculation in which several different identification pulses were used. The calculation was performed for the reconstruction of the thermokinetics of a first-order thermochemical reaction with a time constant of 0.1 s^{-1} (see Fig. 5*a*), first by using an ordinary identification basic set of rectangular thermal pulses. The thermal effect reconstruction was inadequate (see Fig. 5*b*), particularly for the first part of the curve, where the slope is large. The result improved substantially when five different exponential thermal curves with time constants of 1/4 s^{-1}, 1/8 s^{-1}, 1/12 s^{-1}, 1/16 s^{-1} and 1/20 s^{-1} were taken for the identification (see Fig. 5c).

The examples of identification basic set selections described in the present paper naturally do not cover all cases, but give an idea of how to make this selection. However, each particular thermokinetics needs a separate analysis.

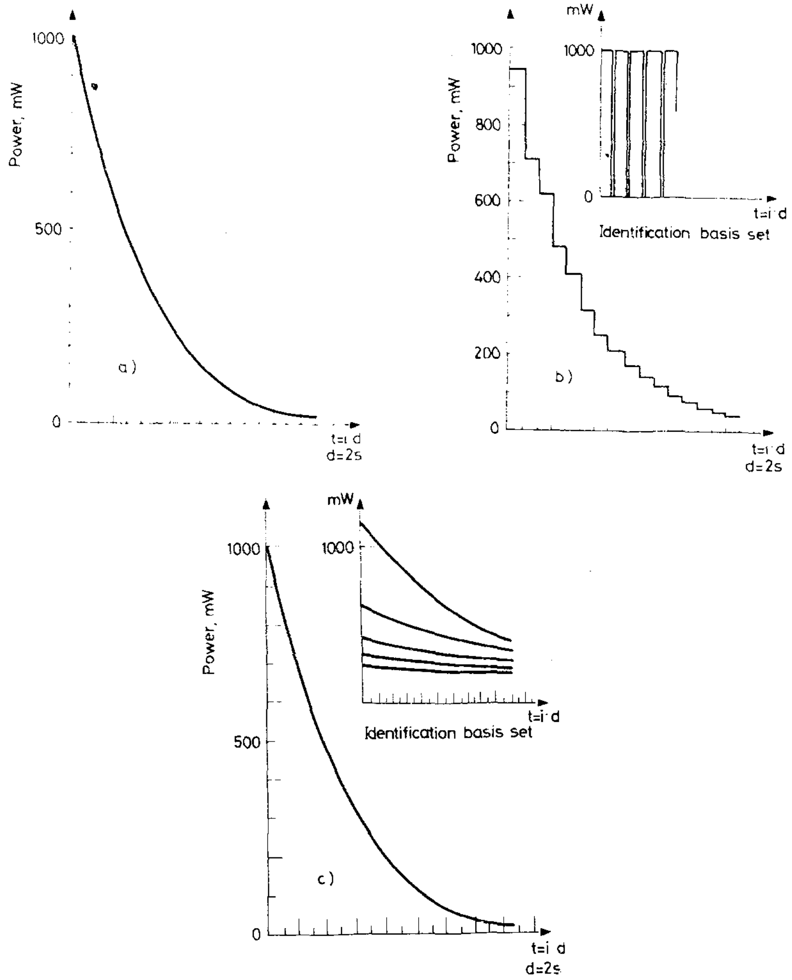


Fig. 5 Reconstruction of first-order thermochemical reaction (*a*) by spectral resolution into rectangular pulse basic set (*b*) and basic set of five different exponential functions (*c*)

Conclusions

The spectral resolution method does not restrict the number or kind of identification thermal curves for the thermokinetic determination. The selection of the set of these curves depends on the expected form of the thermal pulse under investigation; the choice should give a good approximation to this pulse.

It is difficult to compare our generalized spectral resolution method with other methods, because the only set of curves for which comparative results exist is related to the series of rectangular pulses with the identification pulse also rectangular in form [5]. The selection of this set could obscure the possibility of bad behaviour of the optimization and harmonic methods in the case where the thermal effect under investigation cannot be accurately reconstructed from shifted rectangular pulses. Accordingly, we would like to propose for a future calorimetric competition a thermal effect which contains the same pulses as in the previous competition [5], but where each rectangular pulse is followed by an additional sine pulse of the same length and the same power. Our experience shows that this could be a very hard test for every method of thermokinetic reconstruction.

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Zusammenfassung — Eine verallgemeinerte Spektralauflösungsmethode für thermokinetische Bestimmungen wurde dargelegt und getestet. Die Identifizierung von thermischen Kurven beliebiger Art und Anzahl kann mit nur einer Berechnung erfolgen.

Резюме — Представлен и проверен обобщенный метод спектрального разрешения для термоаналитических определений. В единственном расчете может быть использован какой-либо тип термических кривых и их число опознания.