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THERMAL CURVE INTERPRETATION BY SPECTRAL RESOLUTION INTO A BASIC SET OF RECTANGULAR PULSE CURVES.
II. Modification of the algorithm and analysis of the efficiency of the method

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An improvement of the algorithm of the spectral resolution method for the determination of thermokinetics is presented. With the aid of the modified computer program and an experimental thermal curve, an analysis of the method has been performed.

In the previous paper [1] a new method for the determination of thermokinetics has been proposed. It is based on the spectral resolution of a thermal curve into thermal curves of unit rectangular pulses. Our method, as well as the harmonic method [2] and the optimization method [3], is a "black box" method, i.e. information about a calorimeter is used in the calculation in the form of the thermogram of a known rectangular pulse, which has a width of one sampling period. The common name "Dirac pulse" for a pulse of this kind is not very accurate. Different methods make different uses of the "Dirac pulse" for the determination of thermokinetics. For several reasons this determination, which is the identification of a thermal pulse out of the thermal curve, is a complicated procedure. Firstly, each point of the curve contains information about everything that happened in the calorimeter in the past. In particular, at the last point of the thermal curve there is an echo of all thermal pulses which occurred during the experiment. Secondly, each point of the thermal curve could contain an error arising from inaccuracy of measurement and from a certain level of noises which take place in the measurement system. The success of a given method for thermokinetics determination depends on how the method can deal with this problem.

The aim of the present paper is the presentation of a new modification of the algorithm of the spectral resolution method. The modification, which is a change of the orthogonalization procedure of Dirac pulse curves, now permits treating much longer thermal curves and substantially reduces the amount of computer time. A brief account of the spectral resolution method and a description of the new modification are contained in the first part of the present paper. In the second part an analysis of the stability of the results of the spectral resolution method is presented. We have examined the influence of the length of the thermogram and the size of the basic set of the Dirac pulse thermal curves on the quality of the results.

Spectral resolution method and Schmidt orthogonalization procedure of Dirac pulse thermal curves

The spectral resolution method assumes that the thermal pulse under investigation can be approximated by a step function and its thermal curves T by the sum of individual steps, i.e.

$$T(i) \cong \sum_{j=1}^{M} c_j \cdot TD_j(i),\ i = l, \ldots, N\ M \leqslant N \tag{1}$$

where:

- i counts points on the time axis from 1 to N.
- j counts steps, Dirac pulses. The j-th step occurred at the j-th time moment and had a width of one sampling period.
- c_j is the height of the j-th step.
- TD_j(i) is the i-th point of the thermal curve of the j-th unit step pulse.

Now, the essence of the method is the spectral resolution of the thermal curve T into TD_j curves. We do this by the construction of the orthonormal basic set $\{\mathrm{TDN}_j\}$ as a linear combination of TD_j curves, i.e.

$$TDN_j = \sum_{k=1}^{M} a_{jk} \cdot TD_k,\ j = l, \ldots M \tag{2}$$

The orthonormal condition is as follows:

$$\sum_{i=1}^{n} TDN_k\,(i) \cdot TDN_l\,(i) \cdot d = \begin{Bmatrix} 1\ for\ k = \ell \\ 1\ for\ k \neq \ell \end{Bmatrix} \tag{3}$$

where d is a sampling period.

Equation (3) means that TDN curves should be orthonormal in the time interval $[0, N{\cdot}d]$, which has to be the same as the thermal curve T time length. This procedure, in functional analysis language, is the search for an orthogonal basic set for the expanding of a calorimeter response of each thermal step function pulse in the time interval $[0, N{\cdot}d]$. In the previous paper [1] we proposed the construction of the set by the Löwdin orthogonalization procedure. It worked quite well, but because of the necessary diagonalization it was not very convenient. We should mention here that the trouble with the $\{TDN_j\}$ set construction comes from the high overlap of TD curves. This overlap is particularly substantial for neighbouring curves, i.e. the quantity

$\sum_{i=1}^{N} TD_j(i) \cdot TD_{j+1}(i) \cdot d$ is very close to the quanity

$\sum_{i=1}^{N} TD_j(i) \cdot TD_j(i) \cdot d$. The problem of high overlap could be the reason for a loss of the numerical accuracy during the orthogonalization procedure. Indeed, applying the standard version of the Schmidt orthogonalization we had problems. Constructing the set $\{TDN_j\}$ by the Schmidt iteration process as:

$$TDN_j = A\,[TD_j - \sum_{k=1}^{j-1} < TD_j \,/\, TDN_k > TDN_k] \tag{4}$$

where the notation $< TD_j \mid TDN_k >$ stands for the sum $\sum_{i=1}^{N} TD_j(i) \cdot TDN_k(i) \cdot d$ and A is the normalization factor, we were not able to ensure the orthogonality of TDN_j for higher j to the previous curves. We should do this by modifying the orthogonalization scheme. The new procedure is the following. First the TD_j set is normalized, i.e. $TD'_j = A \cdot TD_j$ and $< TD'_j \mid TD'_j > = 1$. The $\{TDN_j\}$ set is then constructed in the following iteration scheme:

$$\begin{aligned}
TDN_1 &= TD'_1 \\
TDN_2 &= A\,[TD'_2 - < TD'_2 \,/\, TDN_1 > TDN_1] \\
TDN_{3,1} &= A\,[TD'_3 - < TD'_3 \,/\, TDN_1 > TDN_1] \\
TDN_3 &= A\,[TDN_{3,1} - < TDN_{3,1} \,/\, TDN_2 > TDN_2] \\
TDN_{4,1} &= A\,[TD'_4 - < TD'_4 \,/\, TDN_1 > TDN_1] \\
TDN_{4,2} &= A\,[TDN_{4,1} - < TDN_{4,1} \,/\, TDN_2 > TDN_2] \\
TDN_4 &= A\,[TDN_{4,2} - < TDN_{4,2} \,/\, TDN_3 > TDN_3]
\end{aligned} \tag{5}$$

and so on, where A means the normalization factor for the object in the square parentheses. Thus, the present scheme differs from the standard procedure in the normalizations of the intermediate shapes of the TDN_j curves.

The advantage of the present procedure for the $\{TDN_j\}$ set generation in comparison with the diagonalization method applied in Ref. [1] comes from the simplification of the algorithm and the possibility of treating thermal curves containing many more experimental points. Now the number of points is not limited by the size of the matrix for the diagonalization.

The further part of the spectral decomposition procedure is identical to that described in Ref. [1]. Thus, cn_j coefficients are calculated as:

$$cn_j = < T \,/\, TDN_j > \tag{6}$$

and finally the coefficients c_j of Eq. (1) are found:

$$c_j = \sum_{k=1}^{M} cn_k \cdot a_{kj}$$

The $\{c_j\}$ set is the step function approximate to the thermal pulse formed in the calorimeter.

The numerical analysis of the method

To examine the efficiency of the spectral resolution method we have taken an experimental thermal curve, made calculations with different variants of the input data and compared the quality of the outputs. The thermal curve for the present calculation is the same as in Ref. [1] and has been done by the authors of Ref. [4] in a Tian-Calvet calorimeter for the calorimetric competition which took place in Nieborów (Poland) in 1977 and was organized for a comparison of the quality of different thermal pulse identification methods. The thermal curve is related to the thermal effect, which consists of three rectangular pulses of increasing length ($2d$, $4d$ and $8d$) and decreasing power in the ratio 100:10:1. Since the entire duration of the thermal effect was $28d$, the minimum number of TD functions should also be 28. The minimum number of points in T and TD thermal curves should be equal to or greater than this number. To examine the stability of results for different choices of the number of points N and the number of TD curves M we have performed calculations for the following pairs of their values:

I.	N=50	M=40
II.	N=150	M=50
III.	N=100	M=90

The results for the reproduction of the twelve points of the thermal effect which cover the period of the first two rectangular pulses are presented in the Table. It is seen that the reproduction of the pulses is satisfactory. Also, it is suprising that there is such a good agreement of the results of all the three cases, and this means that the method is not sensitive to the particular choice of the values of N and M. Furthermore, the spectral resolution method could make use of a relatively small part of the thermal curve to give quite good results.

The fidelity of the thermal pulse reconstruction should be the higher, the smaller the width of the steps in the step approximation of the thermal effect. However, in the case of the thermal effect under the present investigation, we can take as a unit pulse the rectangular pulse of a duration of not just one sampling period but two. This is the maximum unit for an accurate reconstruction of the entire thermal effect. It is not necessary to measure the thermal curve of this unit pulse, because it may be calculated very easily as the sum of the first two terms of the $\{TD_i\}$ set i.e.

Table 1 Experimental thermal pulse reconstruction by using the spectral resolution method with different choices of the numbers of points in the thermal curve, N, and the size of the Dirac pulse basic set, M, used in the calculation. The unit is mW.

Power of the experimental thermal pulse	Its reconstruction		
	N=100 M=50	N=150 M=50	N=100 M=90
0	−15	−17	−13
0	24	27	21
2156	2343	2341	2346
2156	1924	1925	1924
0	475	474	473
0	−179	−179	−177
221	241	242	240
221	301	301	301
221	146	146	146
221	234	235	233
0	74	73	75
0	−40	−40	−40

$\frac{TD_1+TD_2}{2}$. Accordingly, the new TD set is $\left\{\frac{TD_1+TD_2}{2}, \frac{TD_3+TD_4}{2}, \ldots\right\}$.

Using this thermal curve, we have performed the spectral resolution of the thermal curve under investigation. The results are shown in Fig. 1, together with the corresponding results obtained using the resolution into the TD basic set. The reconstruction of the thermal effect is now much better. This means that the best choice for the unit rectangular pulse is the maximum pulse unit which we can use to reconstruct the entire thermal pulse. In this case we could obtain the best cancellation of the noises of the measurement system. Of course, there are not many cases where the choice of the maximum thermal unit is so clear as in the present case and then we should compromise.

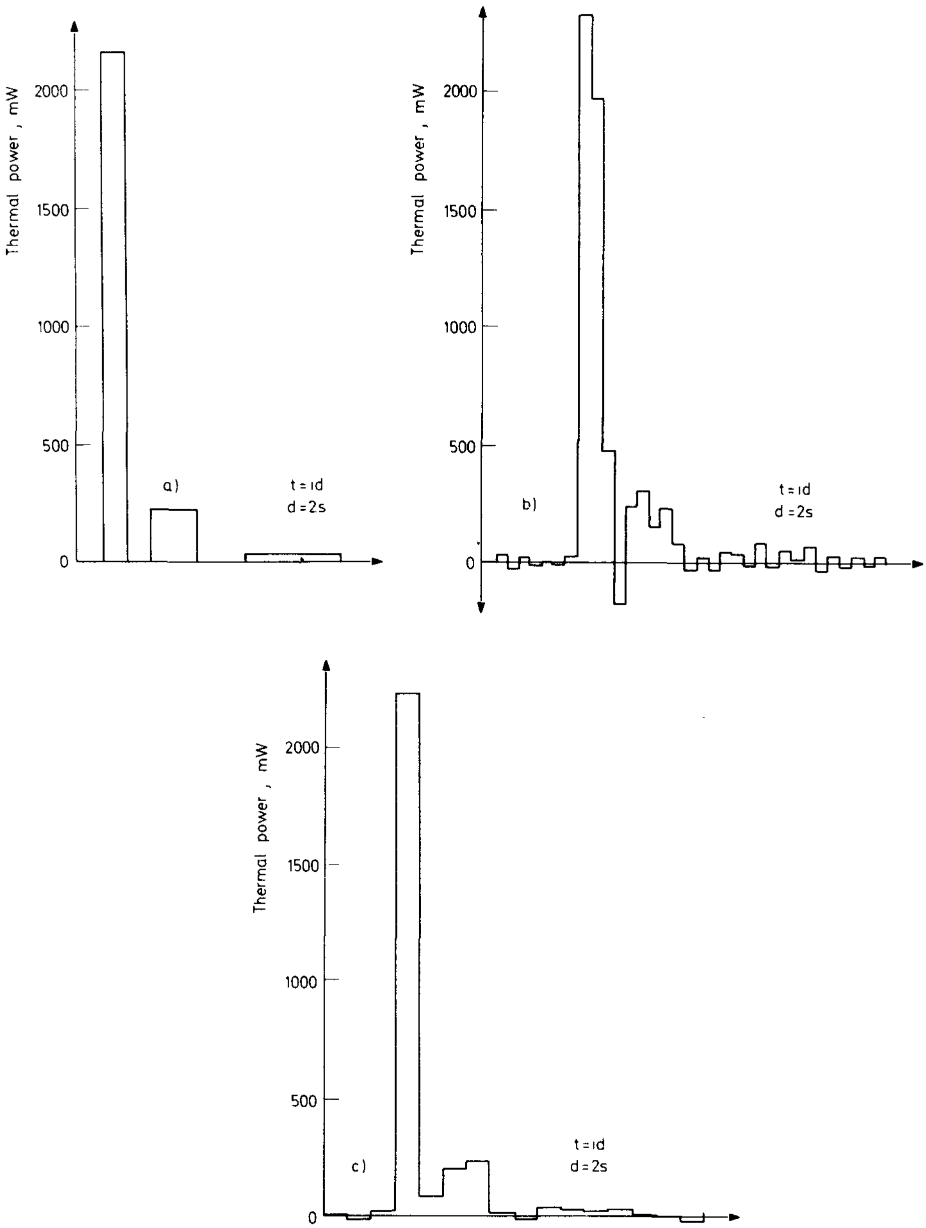

Fig. 1 Experimental pulse (part a) reconstruction by using the spectral resolution method. Part b: the curve was obtained by using the Dirac pulse of width *Id*. Part c: the Dirac pulse had width 2*d*.

Summary

For the method of thermal curve interpretation by spectral resolution into the basic set of rectangular pulse curves, a modified algorithm is proposed. The modification is related to the orthogonalization of the rectangular pulse basic set and it is important for the efficiency of calculations. It is also shown, by using an experimental example, that the method is not sensitive to change in the number of points in the thermal curve used in the calculation or to the size of the basic set of rectangular pulse curves, but it is sensitive to the choice of the size of the basic set ractangular pulses.

References

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Zusammenfassung — Der Algorithmus der *Spektrenauflösungsmethode* zur Bestimmung der Thermokinetik wird verbessert. Mit Hilfe des modifizierten Computerprogramms wird eine experimentelle thermische Kurve analysiert.

Резюме — Представлен улучшенный алгоритм для метода спекрального разрешения при определении термокинетических параметров. С помощью измененной вычислительной программы и экспериментальной термической кривой проведен анализ этого метода.