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

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A new numerical method for the determination of thermokinetics is proposed. This is based on the spectral resolution of a thermal curve into the basic set of unit rectangular pulse curves orthogonalized by Löwdin's transformation. A numerical example shows that the present method can be successfully applied to experimental curves.

The search for a method of interpreting the readings of temperature from a calorimeter, i.e. of re-creating from them the thermal effects formed in the calorimeter, is still an open problem. On the whole, the best results are ensured at present by two methods: the optimization method proposed by Utzig [1] and the harmonic analysis method of Navarro [2]. The first of these methods assumes that the effect formed can be approximated by a step function (each step has the width of one sampling period). The optimization method utilizes the principle of the linear dependence of temperature on the magnitude of the thermal pulse formed in the calorimeter and approximates the thermal curve (T) under investigation by the sum of the curves of individual rectangular impulses (TD) of unit energy:

$$T(i) \cong T'(i) = \sum_{j=1}^{M} c_j TD_j(i), \quad i = 1, \ldots, N, \quad M \leq N \tag{1}$$

where i denotes the successive points in the curve and $TD_j(i)$ is the i-th point in the curve which corresponds to a single unit pulse formed in the calorimeter at the j-th moment of time. The coefficients c_j arise from the minimalization of the difference between curves T and T'. In the summation in Eq. (1) the number of components can be equal to or smaller than the number of points in curve T, and in principle it should contain as many functions TD as would ensure that the rectangular pulses corresponding to them would permit full approximation of the thermal effect. The weakness of the optimization method is the difficulty of minimalizing a function of many parameters.

The method of harmonic analysis gives results comparable to those obtained by the optimization method and consists in transforming T and TD by the Fourier transform into a frequency representation. In this representation a convolution of functions is transformed into an ordinary product. This permits the calculation of the Fourier transform of the effect formed in the calorimeter as a quotient of the corresponding transforms, and thus also of the effect itself. The main disadvantage of this method is the necessity of measuring the curve up to the return of the thermal equilibrium state in the calorimeter.

The present paper proposes a new method of identifying the thermal effect in the calorimeter, which uses approximation (1) and replaces the process of optimization of the coefficient c_j by a spectral decomposition into orthogonalized functions TD_j. This decomposition resembles decomposition of a thermal curve into trigonometric functions in the harmonic method and in a certain sense constitutes a generalization of that method.

Description of the method

Let us assume that we have a curve $T(\mathrm{i})$ ($i = 1, \ldots, N$) of the thermal effect and a curve $TD(\mathrm{i})$ ($i = 1, \ldots, N$) of a unit rectangular pulse. Having TD, we generate the set $\{TD_j\}$ ($j = 1, \ldots, m$) by adding j-1 additional initial zero points and subtracting the same number of final points. We then apply an orthogonalization and normalization of the set of functions $\{TD_j\}$ over the interval (0, Nd) (d being the sampling period) and obtain a new set of functions $\{TDN_j\}$, the orthogonality condition being as follows:

$$\sum_{i=1}^{N} TDN_k(i) \cdot TDN_l(i) \cdot d = \begin{cases} 1 & k = l, \\ 0 & k \neq l \end{cases}, k, l = 1, \ldots, M \tag{2}$$

The sum (2) corresponds to the integral $\int_0^{Nd} TDN_k(t) \cdot TDN_l(t)dt$ which is the scalar product of the Hilbert space spanned by the set of functions $\{TDN_j\}$.

We can obtain the set of orthogonal functions $\{TDN_j\}$ from the set $\{TD_j\}$ in many different ways. However, the procedure proposed by Löwdin [3] and often applied in quantum chemistry calculations is particularly useful in the present method, since it gives at set of orthogonal functions which maximally resembles the set of orthogonalized functions, i.e. the quantity

$$\sum_{j=1}^{M} \left(\int_0^{Nd} TDN_j(t) \cdot TD_j(t)dt \right) \cong \sum_{j=1}^{M} \left(\sum_{i=1}^{N} TDN_j(i) \cdot TD_j(i) \cdot d \right)$$

reaches its maximum.

The scheme of Löwdin's method is as follows: We form a matrix S which, by a quantum analogy, we can call the matrix of overlap integrals. The element S_{kl} of the matrix is defined as follows:

$$(S)_{kl} = \sum_{i=1}^{N} TD_k(i) \cdot TD_l(i) \cdot d. \tag{3}$$

We diagonalize the matrix S:

$$C^T \cdot S \cdot C = V \tag{4}$$

where the matrix C is the matrix of eigenvectors, C^T is the transposition of C, and the matrix V is the diagonal matrix of the eigenvalues.

We then calculate the matrix $S^{-\frac{1}{2}}$ defined as follows:

$$S^{-\frac{1}{2}} = C^T \cdot V^{-\frac{1}{2}} \cdot C \tag{5}$$

where $V^{-\frac{1}{2}}$ is the diagonal matrix obtained from matrix V by replacing each eigenvalue by the square root of its inverse, i.e.

$$(V^{-\frac{1}{2}})_{jj} = \frac{1}{\sqrt{(V)_{jj}}}. \tag{6}$$

The matrix $S^{-\frac{1}{2}}$ is the required matrix of the coefficients of the expansions of the set of functions $\{TDN_j\}$ into functions from the set $\{TD_j\}$, i.e.

$$TDN_j = \sum_{k=1}^{M} (S^{-\frac{1}{2}})_{kj} \cdot TD_k . \tag{7}$$

The fulfilment of the orthonormality condition of the set of functions $\{TDN_j\}$ can thus be writen as follows:

$$(S^{-\frac{1}{2}})^T \cdot S \cdot S^{-\frac{1}{2}} = 1 \tag{8}$$

where 1 denotes the unit matrix.

Having the set of functions $\{TDN_j\}$, we expand the thermal curve T on the basis of these functions:

$$T(i) = \sum_{j=1}^{M} cN_j \cdot TDN_j(i) . \tag{9}$$

The fact that it is an orthogonal set makes it easy to find the expansion coefficient:

$$cN_j = \sum_{k=1}^{N} T(i) \cdot TDN_j(i) \cdot d, \quad j = 1, \ldots, M \tag{10}$$

Incidentally, the orthogonalization was needed in order to make it possible to use this chance of expressing the coefficients as overlap integrals of the thermal curve with the functions of the basic set.

Equations (1) and (9) are analogous since they both represent a decomposition of the thermal curve into basic sets of known functions, the difference being that in Eq. (9) they are orthogonal over the interval of time covered by the curve. The coefficients c of Eq. (1) are still required, whereas the coefficients cN of Eq. (9) are already calculated in Eq. (10). However, since we know the expansion of functions TDN_j into functions TD_j from Eq. (7), it is easy to find the coefficients

c too, namely:

$$c_j = \sum_{k=1}^{M} cN_k \cdot (S^{-\frac{1}{2}})_{jk} \quad j = 1, \ldots, M. \tag{11}$$

The coefficients c give us an approximation of the profile of the thermal effect formed in the calorimeter.

Numerical example

For verification of the proposed method, use was made of calorimetric data of very good quality produced by a Spanish group for the calorimetric competition organized for comparison of the quality of different, thermal pulse identification methods, which took place in Cadarache in 1979 [4]. Both the curve of the unit rectangular pulse with the width of the sampling period (d = 1.88364 s) and that of the verifying pulse contained 45 points. The verifying pulse consisted of three rectangular pulses of increasing length (2d, 4d and 8d) and decreasing amplitude (100 : 10 : 1), and together with the intervals between these pulses it lasted 28d seconds. Thus, the set of 40 functions $\{TD_j\}$ which was used for the curve of the verifying pulse. In the first step of the procedure a new set $\{TDN_j\}$ was obtained through Löwdin's orthogonalization. No difficulties were encountered in diagonalizing the matrix S, in spite of a considerable overlap of the functions $\{TD_j\}$. Figure 1 shows the curve of the first three functions of the basic set $\{TDN_j\}$ and

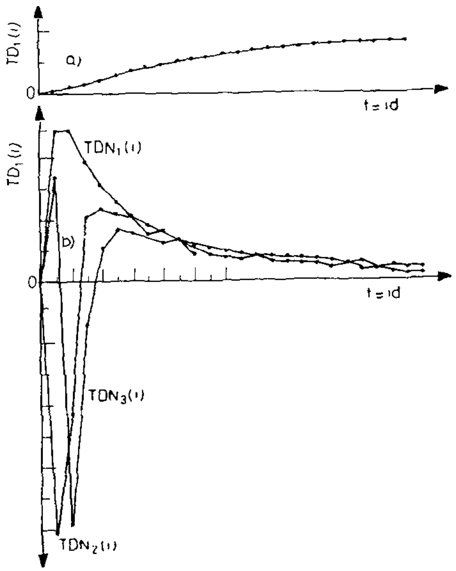

Fig. 1. The shape of thermogram TD_1 of the unit rectangular puls (part a) and three first orthogonalized thermograms $TDN_1 \cdot TDN_2$ and TDN_3 (part b)

the first of the set $\{TD_j\}$. It can be seen that forcing orthogonality considerably deforms functions $\{TD\}$.

Next, as a verification of the method, calculations were carried out on TD_{12}, as the curve to be analyzed, i.e. the curve of a unit rectangular pulse of width d, formed in the calorimeter at the moment $12d$. As regards the value at each point up to the eighth significant figure, the results obtained were in full agreement with the shape of the pulse whose curve was TD_{12}.

A calculation was then performed for the curve of the series of rectangular pulses mentioned above. This calculation is a very strong test for the method.

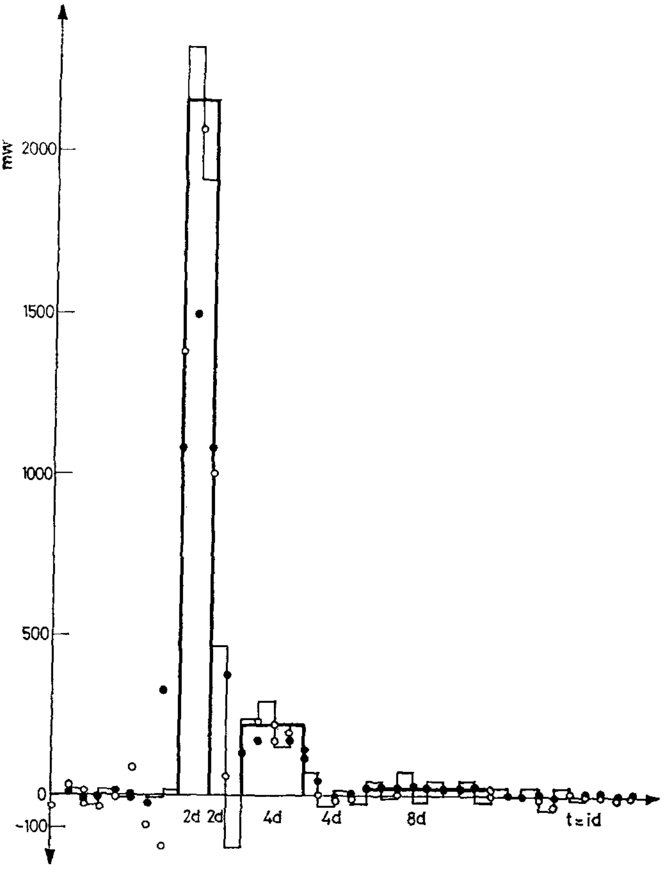

Fig. 2. Thermal puls reconstruction consisted of three rectangular pulses of the duration 2d, 4d and 8d and of decreasing amplitude (of the ratio 100 : 10 : 1) shown by the fat line in the picture. The following notation has been used to illustrate the results of the different methods: ○ for the optimization method; ● for harmonic method; and the fine line for the present method. The results of the optimization and harmonic method as well as calorimetric data have been kindly made available to me by the author of Ref. 4

The results of the calculations are shown in Fig. 2, together with a comparison with the results of the optimization method and the method of harmonic analysis. The quality of the results in all three methods is similar.

Conclusion

Accordingly, the method proposed in this paper for the analysis of a thermal curve by its spectral decomposition into curves of rectangular unit pulses gives similar results to those obtained by the two most effective methods used in calorimetry at present. Although the proposed method is based on the same approximation as the optimization method, it avoids the cumbersome process of optimization. What is more, it does not require so many points in the curve as does the method of harmonic analysis. The time of calculating the example quoted in this paper was only a few seconds on the CDC6600 computer. Limitations of applicability of the method presented here could arise in the stage of diagonalization; experience in quantum physics calculations could be very helpful here.

References

1. E. Utzig, doctor thesis, Warsaw, 1976; J. Gutenbaum, E. Utzig, J. Wisniewski and W. Zielenkiewicz, Bull. Acad. Polon. Sci. Ser. Chim., 24 (1976 193.
2. J. Navarro, V. Torra and E. Rojas, Annales de Fisica, 67 (1971) 367.
3. P. O. Löwdin, J. Chem. Phys., 18 (1950) 365.
4. E. Cesari, P. C. Gravelle, J. Gutenbaum, J. Hatt, J. Navarro, J. L. Petit, R. Point, V. Torra, E. Utzig and W. Zielenkiewicz, J. Thermal Anal., 20 (1981) 47.

ZUSAMMENFASSUNG — Eine neue numerische Methode zur Bestimmung von Thermokinetika wird vorgeschlagen. Sie beruht auf der spektralen Auflösung einer thermischen Kurve in die Grundfolge von Einheiten rechteckiger Pulskurven, welche durch eine Löwdins Transformation orthogonalisiert worden sind. Ein numerisches Beispiel zeigt, dass diese Methode bei experimentellen Kurven mit Erfolg eingesetzt werden kann.

Резюме — Предложен новый численный метод определения термокинетических параметров Метод основан на спектральном разделении термической кривой на основные группы кривых с прямоугольным биением и прямоугольность которых была осуществлена с помощью Лёвдин-преобразования. Численные примеры показали, что метод может быть успешно применен к экспериментальным кривым.