

## **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:

$$E \cong \sum_{j=1}^M c_j \cdot EI_j \quad (1)$$

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.:

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