RECONSTRUCTION OF THERMOKINETICS FROM CALORIMETRIC DATA BY MEANS OF NUMERICAL INVERSE FILTERS

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A simple method for removing the distortion due to thermal lags from calorimetric curves is described and tested. The method is based upon the use of numerical inverse filters. Its results are equivalent to those of the more sophisticated deconvolution methods, using Fourier transform analysis or state function theory. The new method is easily adapted to the on-line reconstruction of calorimetric data by means of a microprocessor.

The calorimetric determination of the kinetics of fast reactions is often hindered by the distortion in the calorimetric curves which is caused by thermal lags in the instrument.

However, several methods are available to correct ("to reconstruct") the calorimetric curves:

1. a graphical method [1];
2. (automatic) analog methods [2–7];
3. numerical methods, based on Fourier transform analysis [8–9] or state function theory [10–12].

The graphical methods is simple and yields acceptable results. However, its application requires long and strenuous work which, moreover, must be accomplished after the calorimetric data have been completely collected ("off-line") [1].

Correction by analog methods can be achieved "on-line". Results are good; however, the instruments performing the reconstruction must be manually adjusted for each calorimeter and even for each new experiment. Moreover, the analog signal should be amplified when a multi-stage correction system is used, with an unavoidable increase of the noise level [2–7].

Numerical methods also yield good results. When Fourier transform analysis is used, the correction must be achieved off-line and, in the case of long experiments, a medium-sized computer (∼ 16 Kbytes for 2000 points) must be available [8–9]. The representation of the calorimetric system (calorimeter and data-acquisition line) by state functions and the resulting data reconstruction may be performed on-line [10–12]. The method requires a smaller-sized memory than the method based on Fourier transform analysis. However, both numerical methods are equally sensitive to noise in the data.

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An ideal calorimetric data-reconstruction method should be simple to use and adapted to on-line correction. The corrected data should never contain abnormal information (like overshoots, for instance) that could lead to physically meaningless interpretation. The kinetics of the phenomenon under study should be reconstructed precisely and information on heat production should be preserved accurately. The numerical reconstruction method which is described in the first part of this article has been tested with respect to these different criteria. The experimental results of the tests are presented in the second part of the article.

**Description of the reconstruction method**

The pulse response of a heat-flow calorimeter may be written [13]:

\[ h(t) = \sum_{i=1}^{\infty} a_i e^{-t/\tau_i} \quad \text{with} \quad \sum_{i=1}^{\infty} a_i = 0. \]

The step response, defined as:

\[ u(t) = \int_{0}^{\infty} h(t) \, dt, \]

may therefore be written:

\[ u(t) = \sum_{i=1}^{\infty} a_i \tau_i e^{-t/\tau_i} + K. \]  \hspace{1cm} (1)

Since the following boundary conditions must be obeyed:

\[
\begin{align*}
t & \to \infty \quad & u(t) &= K \\
t & = 0 \quad & u(t) &= 0
\end{align*}
\]

it follows that \( \sum a_i \tau_i = -K \), and Eq. (1) becomes:

\[ u(t) = \sum_{i=1}^{\infty} a_i \tau_i (1 - e^{-t/\tau_i}). \]  \hspace{1cm} (2)

Let us suppose that the calorimeter may be represented by a 1st-order system. Then:

\[ h(t) = ae^{-t/\tau} \]

and

\[ u(t) = A(1 - e^{-t/\tau}) \quad \text{with} \quad A = a\tau. \]

The transfer function \( H(p) \) of the (linear) system, defined in Laplace coordinates by \( S(p) = H(p) \cdot E(p) \), \( S(p) \) and \( E(p) \) being the Laplace transforms of respectively the calorimeter output and input functions, is identical to the pulse response of the system:

\[ H(p) = \frac{a}{p + 1/\tau}. \]