Thermochimica Acta, 187 (1991) 269–274
Elsevier Science Publishers B.V., Amsterdam

The deconvolution of DSC-curves in the experimental time domain

H.J.Flammersheim[a], N.Eckardt[a], W.Kunze[b]

[a]Friedrich-Schiller-University of Jena, Faculty of Chemistry
Lessingstr. 10, O-6900 Jena

[b]W.Kunze, Bodenseewerk Perkin-Elmer GmbH,
W-7770 Überlingen

Abstract

The kinetic evaluation of very fast reaction curves is impossible without previous deconvolution. A valid point-spread function must include both the influence of the device and the individual sample properties. The results of the deconvolution in the time domain and in the frequency domain are completely comparable.

1. INTRODUCTION

As a rule, each experimental DSC-curve is an imperfect reflection of reality. The original record h(t) requires a series of corrections until the real signal is available. Noise and signal broadening are the major sources of degradation of the original curve.
The deconvolution is the estimation of the true undistorted signal, g(t), from the observed curve, h(t). The only condition is the reliable knowledge of the point-spread function, f(t). The deconvolution is important, if the response times of the DSC apparatus and the signal have the same order of magnitude, and if the real time is important for the planned evaluations. Typical cases are the phase transformations of high-purity materials, very fast thermally activated reactions, and above all light-activated reactions.

2. THE DECONVOLUTION ALGORITHM

The usual procedure of signal restoration requires Fourier transformation of the signal and point-spread function, simple operations in the new domain and thereafter the reverse transformation to obtain the "desmeared" curve. There are a number of requirements which sometimes make these operations more difficult. The deconvolution in the original time domain is looked at as a much more complicated procedure [1]. Contrary to this the aim of this paper is to show that such calculations are well possible, too. The deconvolution of light-activated reactions yields the same results in both cases. The algorithm is very simple, the time requirement is small.

0040-6031/91/$03.50

The usual convolution integral,

$$h(t) = \int_{-\infty}^{\infty} g(t') \cdot f(t-t') \cdot dt'$$

describes the response of the apparatus to superimposed impulses if a linear relationship between impulse intensity and signal height exists. If the experimental curve is shifted in such a way that all function values before the start of the reaction disappear, the integral may be developed into the modified, finite series

$$h(t) = \sum_{i=1}^{n} g(t_i) \cdot f(t-t_i) \cdot \Delta t_i$$

where $h(t)$ = measured signal, $g(t)$ = true signal
$f(t)$ = point-spread function, Δt_i = point distance

The algorithm for the "desmearing" of the experimental curve is then the reverse procedure, the subsequent calculation of the "true" heat flux curve according to the following scheme:

$$g(0) = h(0) / f(0)$$
$$g(1) = (h(1) - g(0) \cdot f(1)) / f(0)$$
$$g(2) = (h(2) - g(1) \cdot f(1) - g(0) \cdot f(2)) / f(0)$$

and so on. Preliminary results and the basic ideas of this procedure have already been published by us [2].

3. EXPERIMENTAL

All measurements were taken using the power-compensated Perkin-Elmer DSC 2C and DSC 7 calorimeters. We used a self-made device with a light-flux stabilized mercury lamp and the DPA 7 double beam photocalorimetric accessory (Perkin-Elmer) as light sources. The samples were investigated in special pans, covered by thin quartz windows to allow entry of UV radiation. The highest possible data sampling rates were used (point distances of 0.6 s and 0.2 s, respectively). A complete experiment includes the following steps:

- Recording the light-induced polymerization curve yields the net heat flux from the calorimeter into the specimen.
- After the end of the reaction a second run is started with the reacted sample, using the same experimental conditions. The subtraction of both curves removes the influence of a possible, minor imperfect beam splitting into the sample and the reference and/or the influence of the light absoption effects.
- Estimation of the individual point-spread function, using the response to a short light flash (50-200 ms) or to a change in the steady state (light on/off or vice versa).
- Deconvolution

4. THE POINT-SPREAD FUNCTION

Figure 1 depicts the responses of the DSC 7 to a 50 ms light impulse for the empty sample holder (curve 1), for a graphite disk of 1.9 mm depth (curve 3) and for a polymer specimen (curve 2). It is obvious that the individual properties of the specimen (thermal conductivity, capacity and coupling to the sample holder) are essential and that they may not be neglected. Our experimental procedure takes this fact into account; the point-spread function actually represents the complex response behavior of the investigated sample. If the step response is used, the primary data set must be differentiated to obtain the normalized point-spread function. A disadvantage is the higher noise level compared to the flash-technique. A very important requirement is the exact orientation of the sample in the light beam; a light bypass directly to the sample holder should be avoided.

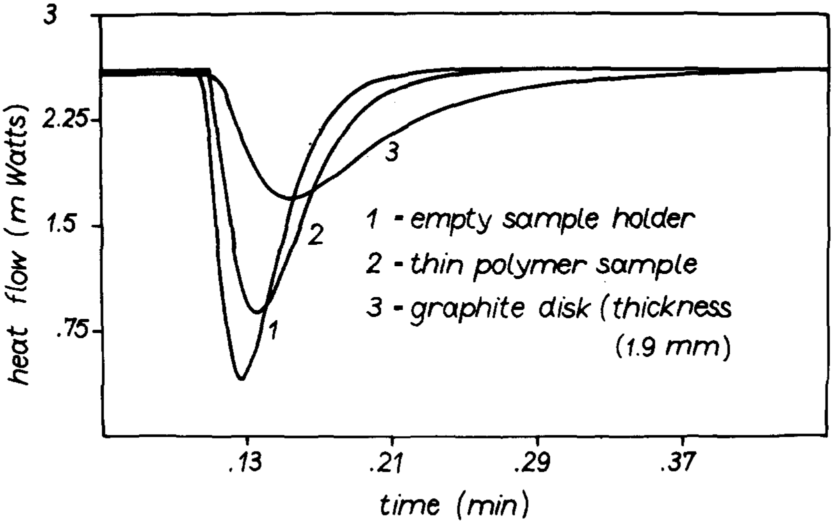

Figure 1. The influence of special sample properties on the point-spread function.

It is not necessary to know the analytical form of the function f(t). The only condition is the existence of one data point of the point-spread function for each one of the experimental curve. In other words, measured curve and point spread function should have the same point distances. This is not a severe restriction, however, because good results require the highest possible sampling rate. The results generated by the computer program, which calculates the deconvolution, are free from excessive noise and oscillations if one ignores the first 2-3 points on the leading edge of the normalized point-spread function.

4.1 Results

Figure 2 shows the fast light-induced polymerization of a multifunctional acrylate, using an ordinary photoinitiator (curve 1). The radiant intensity of the mercury lamp without monochromator was 20 mW/cm^2. Curve 3 was obtained by deconvolution in the frequency domain, using Fourier transformation. Curve 2 is the result of our algorithm in the original time domain. The results are comparable in every respect.

The result of the re-convolution of the "desmeared" curve with the point-spread function is identical to the original curve. The corresponding curve is not shown because there are no detectable differences, using the scale of Figure 2. This is an important fact, because in computing the re-convolution all data points of the point-spread function are taken into account. Hence ignoring the first data points mentioned above has almost no influence on the results of the deconvolution of normal light-induced reactions. Figure 3 shows the step responses of a graphite disk with 1.9 mm depth (curve 1) if the illumination mode is changed. The deconvoluted curve 2 is actually almost the theoretical step response. The point-spread function was obtained as response to a 50 ms impulse on the same specimen. If the deconvoluted curve is re-convoluted (curve 3), the result is nearly identical with the experimental curve.

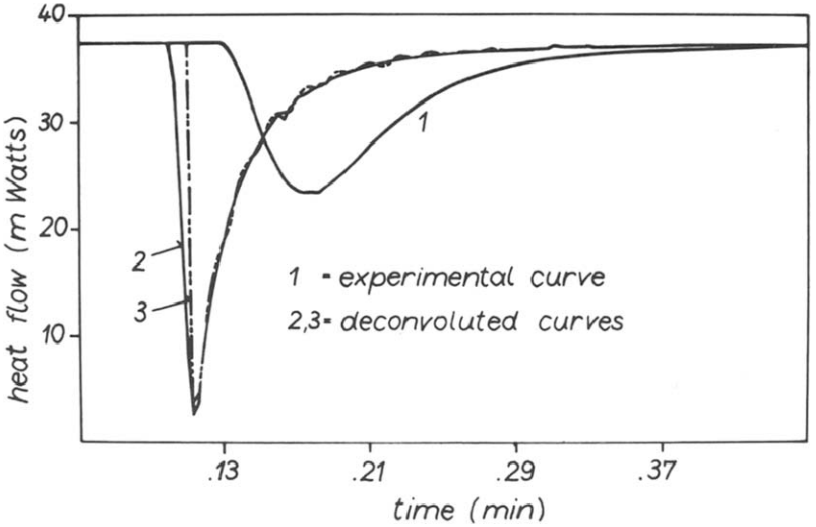

Figure 2. Comparison of the deconvolution in the original time domain (curve 2) and in the frequency domain (curve 3) for a light activated reaction.

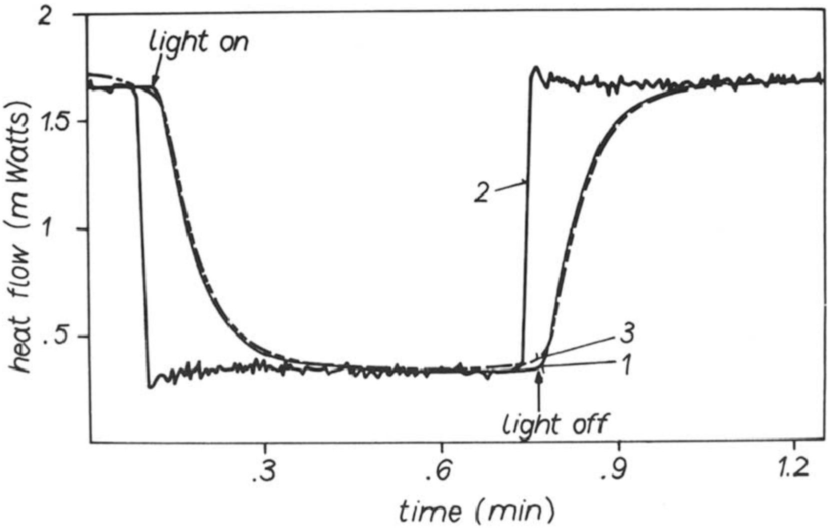

Figure 3. Deconvolution (curve 2) and re-convolution (curve 3, broken line) of step responses.

The limits of the method are demonstrated in Figure 4. The result of the deconvolution of a light impulse, using the same light impulse as point-spread function, too, should be the Dirac δ-function. The "weight" of the latter should be the product of the duration of the flash and the radiant intensity. It is clearly obvious that our algorithm functions well in this extreme situation, too. But the height of the "desmeared" impulse should be four times higher, and the pulse width should accordingly be smaller. The deconvolution in the frequency domain is restricted to the same limits. We think that a distinct improvement is possible if higher data sampling rates are used (more than 5 points/s). For the investigation of very fast chemical reactions, started by a high-energy laser instead of UV-radiation, this is an absolute requirement. It should be mentioned that the "desmeared" curve should be smoothed. The undesired effect of most smoothing procedures is a distortion of the peak, sometimes in filtering techniques also the risk of a unidirectional distortion of the peak position. We use a simple modification of the moving average respectively of the polynominal smoothing technique as smoothing algorithm [3], which is very straightforward and free of any noticeable peak distortions. The signal curve is smoothed to the best degree, independent of the special shape of the curve within an interval calculated from the n^{th} multiple (e.g. n=3; n determines the degree of smoothing) of the standard deviation of the signal noise.

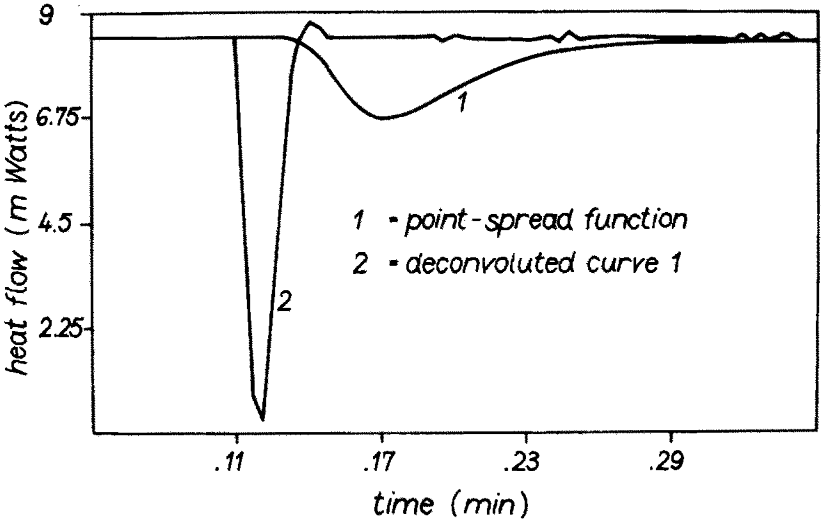

Figure 4. The current limits of our deconvovolution procedure - the deconvolution of a point-spread function by itself.

References

1 B.G.M. Vandeginste and L.Kaufmann (eds.), Chemometrics: a textbook, Elsevier, Amsterdam-Oxford-New York-Tokyo 1988.
2 H.J.Flammersheim, N.Eckardt and G.Rudakoff, Wiss. Beitr. FSU Jena, Therm. Analysenverf. in Ind. u. Forsch., 4 (1990) 62.
3 H.J.Flammersheim and N.Eckardt, J.Therm.Anal., 37 (1990) in press.