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# AN ALGORITHM FOR THE RECONSTRUCTION OF THE TRUE SPECIMEN SIGNAL OF A DIFFERENTIAL SCANNING CALORIMETER

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## SUMMARY

Due to internal lag of thermal, electrical or digital nature the output signal of a measuring device only represents a distorted version of the original signal. Using a DSC-7 calorimeter as example of a measuring device, a simple algorithm is presented that allows the reconstruction of the original thermal signal by deconvolution.

## INTRODUCTION

A general problem of measuring is the distortion of the signal by the measuring instrument itself. Due to the measuring process the original signal may be changed in amplitude or temporal evolution. In particular before analyzing signals originating from a dynamic process like a chemical reaction or phase transformation a correction for these changes may be appropriate. Usually two steps are necessary:

i) to find a model function or a discreet series of values which describes as closely as possible the transient behaviour of the measuring device,
ii) to correct numerically the recorded signal with the model function developed under i) to retrieve the 'true' signal of the process.

There is no generally valid approach for the first step. Depending on the device its model function can either be determined by theoretical-analytical means /1/ or experimentally /2/, /3/. For the second step however, methods of a more general nature are known.
The correction or 'de-smearing' method applied here is based on the assumption that the recorded signal (output function) a(t) is the convolution of the 'true' signal (input function) e(t) and a function representing instrument (m(t)) /2/:

$$a(t) = \int_0^\infty e(t-\tau)\cdot m(\tau)\, d\tau \tag{1}$$

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If by a general method equation 1 is solved for e(t) then any recorded signal a(t) can be 'de-smeared' using m(t).
Although the instrument currently investigated is a calorimeter DSC-7 built by Perkin-Elmer, the method proposed is of more general nature and can be applied to various instruments. Only the individual model function of the particular device has to be determined. Since the model function used here has been tailored for the DSC-7 the way it has been determined will be described only briefly. The main point of this paper is the realisation of the 'de-smearing' procedure in the shape of a computer algorithm. Subsequently the qualities of the method will be shown using mathematical test functions as well as a calorimetric measurement.

## EXPERIMENTAL DETERMINATION OF THE DSC-7 MODEL FUNCTION

The response characteristic of an instrument can be split into the time- and the amplitude response. The latter can be evaluated from the ratio of the integral of a known input signal to that of the corresponding output signal. However, due to the rather complex internal structure of the DSC-7 the more important time response probably cannot be determined solely by theoretical analysis. This is why experiments using an approximate realisation of a thermal Dirac pulse as input were performed. Under this condition the output signal of the instrument is directly equivalent to its general time response. Principly the measured response could be used as a model function. However noise will cause the proposed algorithm not to converge, making it neccessary to smooth the measured response (i.e. by a spline interpolation). Alternatively, an analytical function, which is inherently smooth, can be fitted to the measured response. In the case of the DSC-7 a second order delay element turns out to be a very suitable approximation:

$$m(t) = \frac{1}{t_1 - t_2}\left(e^{-\frac{t}{t_1}} - e^{-\frac{t}{t_2}}\right) \tag{2}$$

The time parameters $t_1$ and $t_2$ can be determined from the experiments analyzing the distance between certain pronounced points (for details see /3/).
The variation of most of the parameters of a DSC run is reflected in a change of the time parameters $t_1$ and $t_2$ of that delay element. So the model function of the 'de-smearing' method can be varied to accommodate different measurement conditions. In addition the experiments supply results to determine the amplitude response and the dead period lag.

## THE DECONVOLUTION ALGORITHM

Due to the nature of the instrument the measured values are supplied on a discreet time basis. The model function is also easily available in discreet form, so equation 1 is transformed into a convolution sum:

$$a_n = \sum_{k=0}^{n-1} e_{n-k} \cdot m_k \qquad n=1,2,\ldots,N \tag{3}$$

Solving this equation for $e_n$ results in a recursive equation:

$$e_n = \frac{1}{m_0}\left(a_n - \sum_{k=1}^{n-1} e_{n-k} \cdot m_k\right) \qquad n=1,2,\ldots,N \tag{4}$$

The momentary 'true' element $e_n$ is calculated from the momentary measured element $a_n$. In addition the already 'de-smeared' elements $e_{(n-k)}$ weighed by the model function element $m_n$ are subtracted.
The transformation of equation 4 into an appropriate algorithm is realised using the indices k and n in two interlocked loops:

```
n: from 1 to N
    k: from 1 to n-1
        sum := Σ (m[k] * e[n-k])
    e[n] := (a[n] - sum) / m[0]
```

The discreet time basis of a(t) is determined by the measuring process. Hence care has to be taken that m(t) is used for identical time intervals as a(t). It is important that the element $m_0$ should not be zero. Thus for the start of the discrete model function an index is chosen where $m_n$ is unequal to zero.

## TESTS OF THE ALGORITHM

One test of the 'de-smearing' algorithm is the reverse approach to the one described above for determining the transient behaviour. Hence 'de-smearing' the model function m(t) with itself will produce the Dirac pulse as 'true' input signal. That this is indeed the case can be seen in figure 1.
Often the tendency to oscillate is a problem with recursive numerical methods, in particular if the measured signal carries unwanted noise in form of spikes. To

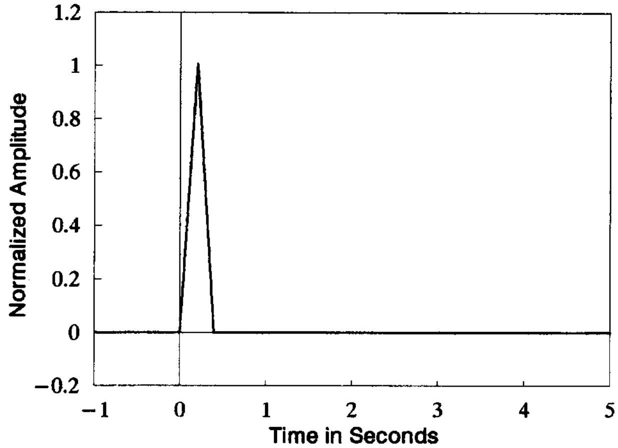


**Fig. 1:** The approximation of a Dirac pulse as the 'true' answer of the deconvolution of the model function.

check this, the Dirac pulse is used as representation of a spike and subsequently 'de-smeared'. Figure 2 demonstrates the fast decrease of the reconstructed 'true' signal e(t) without further oscillations. Extreme magnification of the final part of the relaxation curve e(t) (figure 3) shows that the numerical noise induced by the algorithm is insignificant.

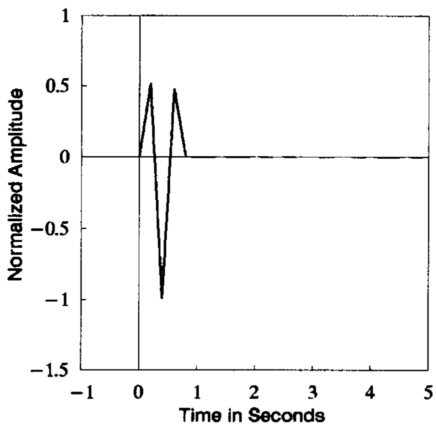


**Fig. 2:** Deconvolution of the spike shown in figure 1.

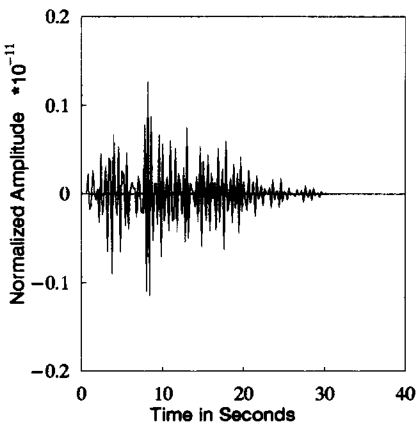


**Fig. 3:** Extreme magnification of figure 2 showing the noise on top of the deconvoluted signal induced by the algorithm.

Both tests confirm that the algorithm works as required and will produce negligible numerical noise on top of the reconstructed signal. However noise already present in the measured signal will reappear in the 'de-smeared' signal as noise of similar amplitude. Hence it may be necessary to smooth the input signal of the algorithm.

Finally a real calorimetric measurement will be 'de-smeared' to demonstrate the usefulness of the method. For this purpose a specimen is prepared where a small amount of indium is located inside an otherwise solid copper cylinder. Due to its specific heat as well as its heat conductivity the copper cylinder will distort the DSC peak when the indium melts. Using an appropriate model function the measured trace is 'de-smeared' and the melt peak of the indium inside the copper cylinder can be compared with the melt peak of an indium sample of similar weight on its own (figure 4). Thus the influence of this 'sample container' can be eliminated to a large extent from the measurement result.

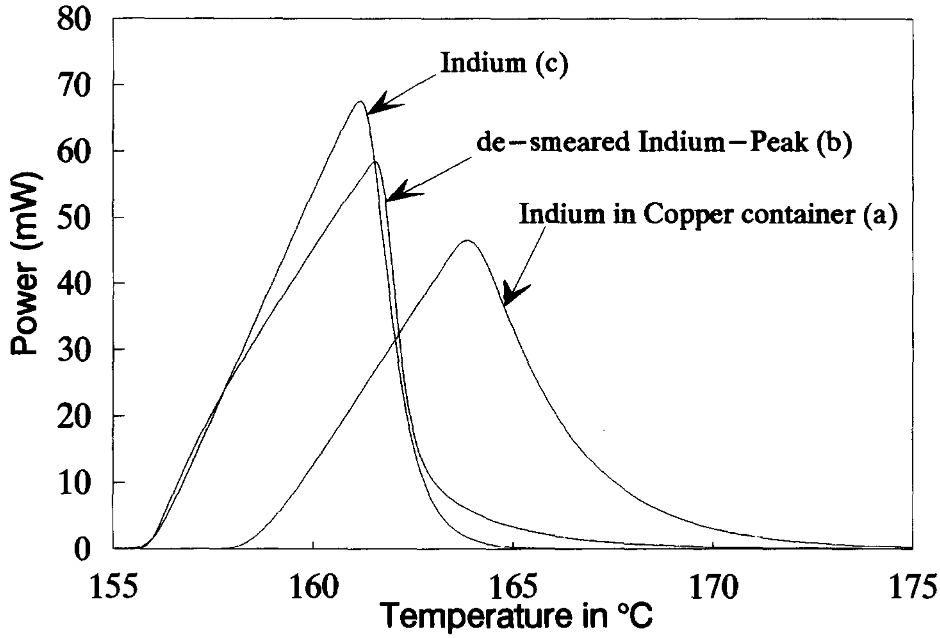


**Fig. 4:** Measured heat flow curve for Indium in copper container (a), de-smeared Indium signal (b) reconstructed from (a), and for comparison, measured heat flow curve of Indium calibration specimen (c).

## CONCLUSIONS

- The ability of the presented simple computer algorithm to deconvolute the output signal of a measuring device has been shown.
- This deconvolution does not produce significant noise on top of the deconvoluted signal.
- Though demonstrated for the deconvolution of DSC signals the method can be adapted for other measurements as well.
- For a different instrument only the new instrument function m(t) has to be determined.
- Variations of the measuring conditions (i.e. specimen weight, heating rate, temperature range) can easily be allowed for in the parameters of an analytical representation of the instrument function.

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