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Note

SMOOTHING AND DIFFERENTIATION OF THERMOGRAVIMETRIC DATA BY DIGITAL FILTERS

R.N. WHITTEM, W.I. STUART and J.H. LEVY

CSIRO, Division of Energy Chemistry, Private Mail Bag 7, Sutherland, NSW 2232 (Australia)

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Bromba and Zeigler [1] have presented simple, elegant algorithms for smoothing equispaced data by means of a recursive digital filter. Employment of these algorithms gives results identical to those obtained by the methods of Savitzky and Golay [2], but with much greater efficiency, so that computational requirements are reduced by several orders of magnitude.

In this paper we describe a modification of the Bromba–Zeigler technique which gives even greater efficiency and which can be usefully applied in thermal analysis to provide, inter alia, smoothed TG and DTG plots. As an illustration, we have used the modified procedure to obtain smoothed thermoanalytical data for the following dehydration reactions

$$\mathrm{CuSO_4 \cdot 5\,H_2O(c) \rightarrow CuSO_4 \cdot H_2O(c) + 4\,H_2O(g)} \tag{1}$$

$$\mathrm{Li_2SO_4 \cdot H_2O(c) \rightarrow Li_2SO_4(c) + H_2O(g)} \tag{2}$$

$$\mathrm{Li_2SO_4 \cdot D_2O(c) \rightarrow Li_2SO_4(c) + D_2O(g)} \tag{3}$$

MODIFIED DIGITAL FILTER TECHNIQUE FOR POLYNOMIAL SMOOTHING

The general equation for a digital filter is

$$D\mathrm{f}[\mathrm{k}] = \sum_{n=-\infty}^{\infty} \mathrm{a}[n]\mathrm{f}[k-n] \tag{4}$$

where D is the linear filter operator, $\mathrm{f}[k]$ is the kth signal point, and $\mathrm{a}[n]$ is the nth point of the filter function.

Paraphrasing Bromba and Zeigler [1], we have for the filter of degree 2 (quadratic filter) and half-width N

$$D_2\mathrm{f}[k] = E_2\mathrm{f}[k]/d_2 \tag{5}$$

where

$$d_2 = (2N-1)(2N+1)(2N+3)/3 \tag{6}$$

and

$$E_2 f[k] = E_2 f[k-3] - 3(E_2 f[k-2] - E_2 f[k-1])$$
$$- (2N-1)(N-1)(f[k-N] - f[k-N-3])$$
$$+ (2N+3)(2N-1)(f[k+N-1] - f[k-N-2])$$
$$- (2N+3)(N+2)(f[k+N+2] - f[k-N-1]) \qquad (7)$$

However, even greater computational efficiency can be obtained by modifying the method of Bromba and Zeigler in order to calculate the smoothed first derivative, as the following argument shows

$$D'_2 f[k] = E'_2 f[k]/d'_2 \qquad (8)$$

where the superscript prime refers to the first derivative with respect to k

$$d'_2 = N(N+1)(2N+1)/3 \qquad (9)$$

and

$$E'_2 f[k] = 2E'_2 f[k-1] - E'_2 f[k-2]$$
$$+ N(f[k+N] - f[k-N-2])$$
$$+ (N+1)(f[k-N-1] - f[k+N-1]) \qquad (10)$$

The smoothed integral can then be obtained from

$$D_2 f[k] = D_2 f[k_0] + \Sigma D'_2 f[i] \qquad (11)$$

where $f[k_0]$ represents the first digital signal value.

On comparing eqns. (6) and (7) with eqns. (9) and (10), it can be seen that the modification affords a significant reduction in the number of multiplications and additions. Moreover, the sizes of coefficients in the recursive calculation are in the order of N rather than N^2; this leads to the practical advantage that data obtained via a 12-bit analogue–digital converter can, in general, be handled by 16-bit integer arithmetic (using FORTRAN, for example) without the need for multiple-precision assembly language routines. The calculations of eqns. (9) and (11) do not affect any recursive calculation, and are simply performed using floating-point arithmetic.

An apparent disadvantage of the modified method is that the baseline is not preserved in the calculations, so in principle $D_2 f[k_0]$ of eqn. (11) must be estimated by the user. However, this is of no practical consequence in thermogravimetry where weight change is usually expressed as % of initial sample weight and $f[k_0]$ is therefore zero. All values preceding the first signal value $f[k_0]$ (i.e. all $f[k]$ for $k < k_0$) are set at zero so that the recursion process does not introduce instabilities, and $D_2 f[k_0]$ is zero.

Second derivative (DDTG) plots can be obtained from the smoothed first derivative by a simple difference procedure.

EXPERIMENTAL

Thermogravimetric data were obtained with a Cahn RG recording balance. Temperature was measured with a chromel–alumel thermocouple placed about 2 mm below the sample pan. Analogue outputs from balance and thermocouple were amplified and connected to an LSI-11 computer via a 12-bit, eight-channel A/D converter. Other hardware included dual flexible disk drives for data storage and an X–Y plotter.

The hydrates of $CuSO_4$ and Li_2SO_4 were heated linearly in flowing N_2, $N_2 + H_2O$ or $N_2 + D_2O$, with partial pressure of H_2O or D_2O maintained at 1.07 kPa.

$Li_2SO_4 \cdot H_2O$ offers several advantages for studying isotopic effects on dehydration: rehydration of Li_2SO_4 is accomplished at ambient temperature over a period of about 8 h; and conversion of the protohydrate to its deuterium analogue occurs readily by exchange with D_2O vapour. For the first three cycles of dehydration–hydration there is a progressive decrease in DTG peak temperature but subsequent cycles give reproducible DTG and TG data, and a single sample can then be used conveniently to demonstrate the extent of isotope effects on dehydration.

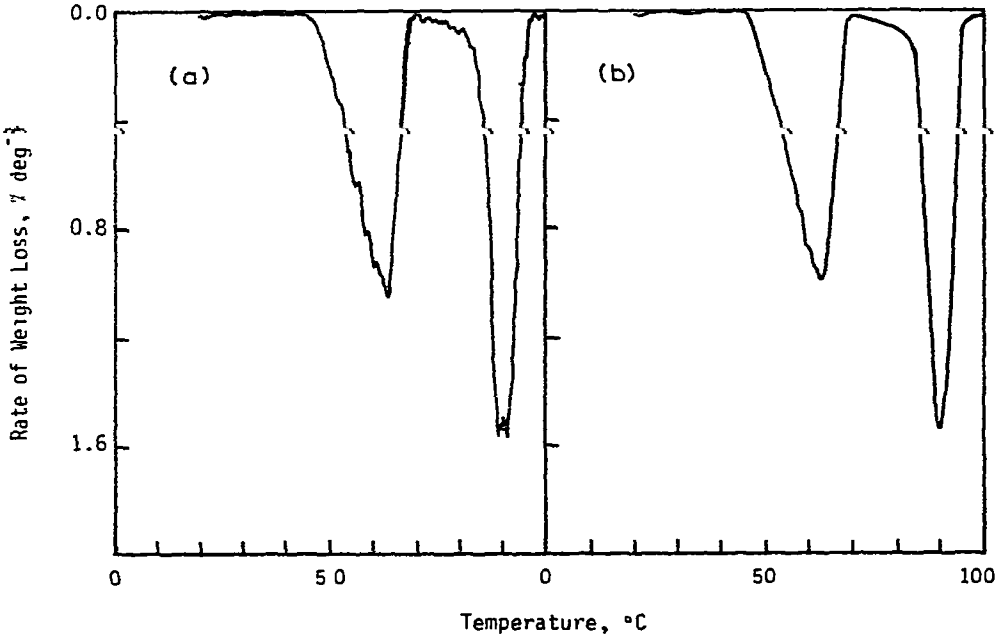

Fig. 1. DTG plots for the reaction $CuSO_4 \cdot 5\ H_2O \rightarrow CuSO_4 \cdot H_2O + 4\ H_2O$. Heating rate: 1°C min^{-1} in N_2. (a) Five-point quadratic smoothing ($N=2$); (b) nine-point quadratic smoothing ($N=4$).

RESULTS AND DISCUSSION

The effect of different degrees of smoothing can be seen in Fig. 1 for the two-stage conversion of $CuSO_4 \cdot 5\ H_2O$ to $CuSO_4 \cdot H_2O$. By increasing the half-width from $N = 2$ (five-point quadratic smoothing) to $N = 4$ (9-point quadratic smoothing) a clear improvement in noise: signal ratio is effected without distortion.

Measurements of thermodynamic properties and IR spectra of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ have shown [3] that the deuterohydrate is the more thermally stable. This is confirmed by thermal analysis as shown in Fig. 2. Conversion of the protohydrate to its deuterium analogue gives a displacement of TG, DTG and DDTG curves to higher temperatures. DTG peak temperatures determined from the DDTG plots of Fig. 2 are 88.9°C for

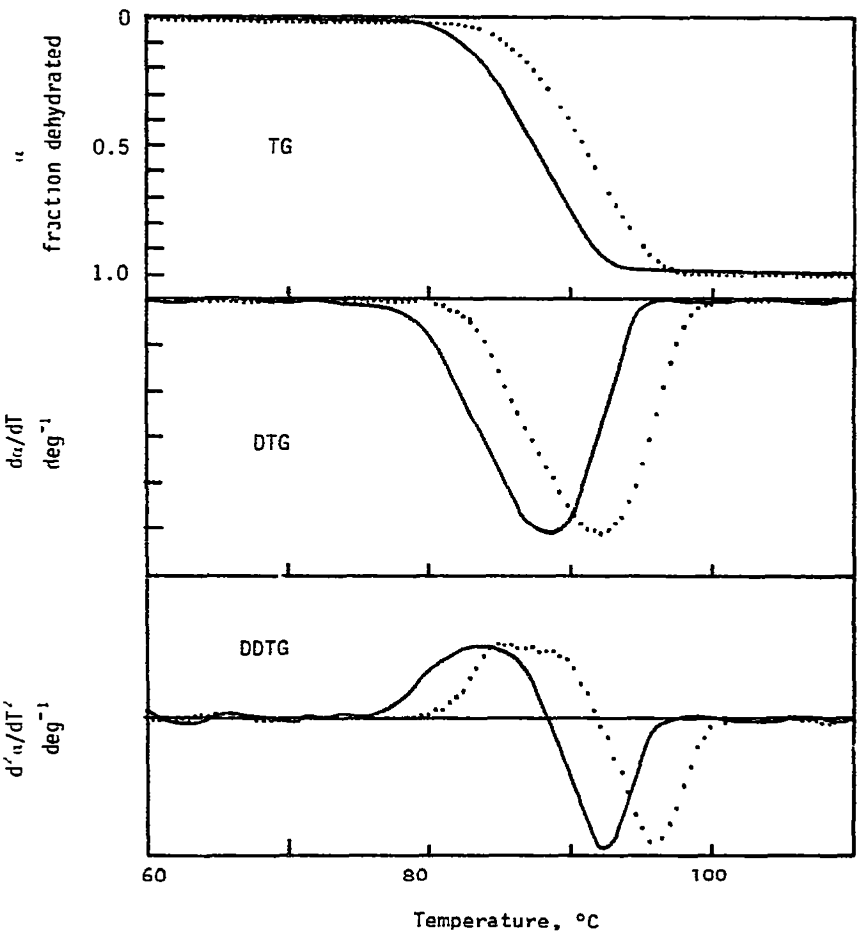

Fig. 2. TG, DTG and DDTG plots for the dehydration of lithium sulphate hydrate in $N_2 + H_2O$ or $N_2 + D_2O$. ———, $Li_2SO_4 \cdot H_2O$; ······, $Li_2SO_4 \cdot D_2O$. Heating rate: 1°C min^{-1}. Partial pressure of D_2O and H_2O: 1.07 kPa.

$Li_2SO_4 \cdot H_2O$ and 91.8°C for $Li_2SO_4 \cdot D_2O$.

The modified smoothing technique described here offers some clear advantages in thermogravimetry; TG, DTG and DDTG curves are computed simultaneously and in real time if necessary; and peak temperatures can be located precisely from DDTG curves. The technique can be equally well applied in DTA measurements.

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